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HYDROGEOCHEMICAL AND ISOTOPIC
CHARACTERIZATION OF GROUND WATERS IN THE
MYRA-PRICE HILLSIDES AND THELWOOD VALLEY,
MYRA FALLS MINING CAMP, VANCOUVER ISLAND,
BRITISH COLUMBIA CANADA

by

Graham Charles Phipps

A thesis submitted to the School of Graduate Studies and
Research in partial fulfillment of the requirements for the degree
of

Ph.D. in Earth Sciences

OTTAWA-CARLETON GEOSCIENCE CENTRE

AND

UNIVERSITY OF OTTAWA

OTTAWA, CANADA

1998

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Approved by _____

Chairperson of the Examining Committee

Chairman of the Department _____

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Abstract

Chemical and isotope characteristics of surface and ground waters were investigated within portions of the Myra Falls (Zn-Cu-Pb) mining camp, Vancouver Island (49° 35' N, 125° 34' W). This site was selected to characterize ground waters, investigate metal mobility, develop ground water exploration methods, and to elucidate ground water circulation in mountainous terrain with high rainfall.

A broad spectrum of water characteristics were found and have been subdivided into water facies which correspond to hydrologic regimes within the mining camp:

- local precipitation and surface runoff have Ca^{2+} - HCO_3^- composition.
- Ca^{2+} - HCO_3^- shallow ground waters are of recent meteoric origin, contain tritium, have low total dissolved solids (TDS) (< 200 ppm), and are nearly saturated with respect to dissolved oxygen (DO). These ground waters are mainly limited to the fractured rock carapace of the Myra-Price ridge, and shallow zones within Thelwood Valley. Many of these waters contact sulphide mineralization but have near neutral pH and SO_4^{2-} remains subordinate to HCO_3^- . Sulphur-34 in dissolved sulphate ($0 \pm 8\%$ CDT) is similar to local sulphide minerals. The mechanism largely responsible for the oxidation of sulphides, based on $\delta^{18}\text{O}_{\text{SO}_4}$, is oxidation by ferric iron. Carbon-13 in dissolved inorganic carbon (DIC) is variable ($\sim -8\%$ to -14% VPDB). Depleted $\delta^{13}\text{C}_{\text{DIC}}$ values, around -13% VPDB, coincide with higher HCO_3^- concentrations (~ 140 ppm) and are recharged through soil zones; whereas, ground waters with lower dissolved inorganic carbon and higher $\delta^{13}\text{C}_{\text{DIC}}$ have likely been at least partially recharged or influenced by recharge through fractures and faults devoid of organic carbon.
- Ca^{2+} - Na^+ - HCO_3^- and Na^+ - Ca^{2+} - HCO_3^- are meteoric waters occurring within the central core of the Myra-Price ridge. They have gained Na^+ by cation exchange in rocks previously saturated with Na^+ - Ca^{2+} - Cl^- water. These ground waters have TDS similar to Ca^{2+} - HCO_3^- ground waters.
- Na^+ - Ca^{2+} - Cl^- saline ground waters (TDS > 30,000 ppm) were discovered in areas undisturbed by mining operations. These waters are reducing, have alkaline pH, contain very low HCO_3^- , are most likely ^{14}C -free, and contain a high volume of helium. Similar I^-/Cl^- and Br^-/Cl^- ratios infer a common source of Cl^- in all ground waters. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are progressively enriched with increasing Cl^- concentration forming a trend similar to sedimentary basinal brines. Sulphate in saline waters have distinct average $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$, which are approximately $17.5 \pm 2.5\%$ CDT and $10.5 \pm 0.5\%$ VSMOW,

respectively. Ground waters undergoing sulphate reduction have enriched $\delta^{34}\text{S}_{\text{SO}_4}$, and depleted $\delta^{13}\text{C}_{\text{DIC}}$, resulting from the oxidation of vegetable (canola) oil used as a biodegradable drilling additive. Saline waters unaffected by sulphate reduction have $\delta^{13}\text{C}_{\text{DIC}}$ approximately -9‰ VPDB. The unique chemical and isotope character of the Cl^- waters imply they are exotic to this setting and are believed to originate from dewatering of underplated sediments (and oceanic crust?) beneath Vancouver Island.

- $\text{Na}^+ - \text{Ca}^{2+} - \text{SO}_4^{2-}$ and $\text{Ca}^{2+} - \text{SO}_4^{2-}$ ground waters, of meteoric origin, occur at intermediate depth in areas underlying previously mined areas and in areas where dissolution of anhydrite has dominated the anion chemistry. Sodium is acquired through exchange processes. In deeper workings of the HW mine, $\text{Na}^+ - \text{Ca}^{2+} - \text{SO}_4^{2-}$ and $\text{Na}^+ - \text{SO}_4^{2-}$ ground waters (with variable Cl^-) occur. These waters have TDS, DO and redox values intermediate between HCO_3^- and Cl^- dominated ground waters. They also invariably contain some mixture of either $\text{Ca}^{2+} - \text{HCO}_3^-$ meteoric water, or $\text{Na}^+ - \text{Ca}^{2+} - \text{Cl}^-$ saline water. The sulphate has $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ similar to the saline water indicating a common source in these waters, which is not the result of sulphide oxidation.

- $\text{Mg}^{2+} - \text{SO}_4^{2-}$ runoff waters result from intense weathering of mined waste-rock.

Ground water recharge, circulation and mixing processes are traced by chemistry and isotopes including $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Recently recharged ground waters preserve the $\delta^{18}\text{O}$ elevation variation recorded in precipitation (-0.15‰ per 100 m rise). Variation of $\delta^{18}\text{O}$ in ground waters through the Myra-Price ridge suggests a strong vertical to subvertical flow through the fractured rock with the exception of large continuous faults which may have channeled flow. Non-saline ground waters are largely recharged during the wetter fall and winter period from isotopically depleted precipitation.

Thelwood Valley is unaffected by mine development. Ground waters in this area exhibit a narrow mixing interface between modern $\text{Ca}^{2+} - \text{HCO}_3^-$ and saline waters, and have little cation exchange. This indicates that equilibrium has developed between exchange sites and cations within the water. Saline water has been displaced from rocks within the Myra-Price ridge and is currently being displaced in areas of new mine development. The elution of Na^+ lags behind Cl^- flushing and is expected to continue as the first few pore volumes of meteoric water move through the rock. The presence of saline water at shallow depth in Thelwood Valley and the current Na^+ elution process in and below the Myra-Price ridge attest to the stability of the local hydrology until it is perturbed by mining development. However, once mine development commences, highly

permeable fault and fracture systems can quickly circulate meteoric waters into the mine openings.

The pH of ground waters related to the Myra Falls mineral deposits is generally near neutral, and acidic ground waters with high metal loads are extremely rare. Amorphous oxy-hydroxides are common and comparisons from filtrate concentrations (non-filtered, 0.45, 0.22, 0.10, and 0.05 μm) indicate that the majority of suspended particles are greater than 0.45 μm . These particles are composed of Fe oxy-hydroxides but also include Mn and Al. The presence of these particles greatly affects the mobility of Zn, Cu, Pb, and Cd in ground waters. The sorption of Pb is greater than Zn and Cu and is affected little by the solution matrix. In HCO_3^- waters, the order of sorbed metals to suspended particles is $\text{Pb} > \text{Cu} > \text{Cd} \sim \text{Zn}$; which follows the order of first hydrolyses for these metals. In SO_4^{2-} waters the order is $\text{Pb} > \text{Cu} > \text{Zn}$; while, in Cl^- waters the order is $\text{Pb} > \text{Zn} > \text{Cu}$. The order of element mobility has implications toward understanding of the natural in situ metal attenuation and metal transport of pathfinder metals used in hydrogeochemical prospecting.

Zinc displays the strongest and most reliable anomaly contrasts for hydrogeochemical exploration in the dominantly bicarbonate and sulphate ground waters associated with the Zn-Cu-Pb mineralization of the Price ore-deposit. Threshold values, depending on the willingness to accept uncertainty (confidence), between the two sub-populations of Zn are 20, 25, and 38 ppb for thresholds that include 10, 5, and 1% of the lower concentration sub-population, respectively. Hydrogeochemical anomalies can be further enhanced with a suite of pathfinder elements associated with primary mineralization and hydrothermal alteration including: Cu, Pb, Cd, Mn, As, Sb, and U. Effective discrimination between anomalies in ground waters associated with massive sulphide mineralization and ground waters associated with an extensive ore-clast breccia (OCB) mineralization can be made through the use of elements associated with primary mineralization and hydrothermal alteration such as K, Rb, B, Ba, Cd, Sb, and U which are elevated in ground waters associated with massive sulphide mineralization but not those associated with the OCB.

Résumé

Les caractéristiques chimiques et isotopiques de plusieurs eaux de surface et souterraines ont été déterminées dans des régions du camp minier de Myra Falls (Zn-Cu-Pb) sur l'île de Vancouver (49° 35' N, 125° 34' W). Ce site a été choisi pour but de classer les eaux souterraines, déterminer la mobilité des métaux, développer des méthodes d'exploration d'eau souterraine et de démarquer la circulation des eaux souterraines dans une région montagneuse comprenant un taux élevé de précipitation sous forme de pluie.

Les eaux souterraines démontrent un large éventail de caractéristiques, celles-ci étant subdivisées en faciès qui correspondent à des régimes hydrologiques auprès du camp minier:

- la précipitation locale et les écoulements de surface sont composés de Ca^{2+} et de HCO_3^- .

- les eaux souterraines composées de Ca^{2+} et de HCO_3^- sont d'une origine météorique récente, contiennent du tritium (^3H), ont tous un niveau peu élevé de matières solides dissoutes (<200 ppm) et sont presque saturées par rapport à l'oxygène dissout. De plus, ces eaux souterraines sont principalement limitées dans la zone fracturée de la carapace du "ridge" Myra-Price et dans des régions peu profondes de la vallée Thelwood. Plusieurs de ces eaux sont en contact avec du soufre minéralisé, mais le pH demeure presque neutre et le SO_4^{2-} demeure subordonné au HCO_3^- . Le soufre-34 dans le sulfate dissout ($0 \pm 8\text{‰}$ CDT) est semblable au minéraux de soufre local. En principe, le mécanisme responsable pour l'oxydation des sulfides, basé sur $\delta^{18}\text{O}_{\text{SO}_4}$, est l'oxydation par le Fe^{2+} . Le carbone-13 dans le carbone inorganique dissout est variable ($\sim -8\text{‰}$ à -14‰ VPDB). Les valeurs de $\delta^{13}\text{C}_{\text{DIC}}$ sont aux alentours de -13‰ VPDB et coïncident avec des concentrations plus élevées de HCO_3^- (~ 140 ppm). De plus, les données de carbone-13 démontrent une recharge à travers le profil terrestre, tandis que les eaux souterraines, démontrant un taux plus bas de carbone inorganique dissout et des valeurs plus élevées en $\delta^{13}\text{C}_{\text{DIC}}$, ont probablement été influencées par une recharge à travers des fractures et des failles absentes de carbone organique.

- Il existe des eaux météoriques composées de $\text{Ca}^{2+}\text{-Na}^+\text{-HCO}_3^-$ et de $\text{Na}^+\text{-Ca}^{2+}\text{-HCO}_3^-$ dans le coeur du "ridge" Myra-Price. Celles-ci ont gagné leur Na par l'échange de cations dans des roches auparavant saturées avec du Na^+ , du Ca^{2+} et du Cl^- . Ces eaux

souterraines ont des taux de matières solides dissoutes semblables aux eaux souterraines de composition Ca^{2+} - HCO_3^- .

- Les eaux souterraines salines de composition Na^+ - Ca^{2+} - Cl^- (TDS > 30,000 ppm) ont été découvertes dans des régions in affectées par les opérations minières locales. Ces eaux sont chimiquement réductrices, ont un pH alcalin, contiennent des concentrations très basses en HCO_3^- , ont pratiquement pas de ^{14}C et sont enrichies d'hélium. Des rapports presque identiques de I^-/Cl^- et de Br^-/Cl^- indiquent que le Cl^- provient d'une source commune pour toutes les eaux souterraines. Les valeurs de $\delta^{18}\text{O}$ et de $\delta^2\text{H}$ démontrent un enrichissement progressif avec des concentrations de Cl^- croissantes formant ainsi une signature semblable à des "brines" de bassins sédimentaires. Le sulfate dans les eaux salines a une distinction typique dans la moyenne du $\delta^{34}\text{S}$ et du $\delta^{18}\text{O}_{\text{SO}_4}$, étant de $17,5 \pm 2,5\text{‰}$ CDT et de $10,5 \pm 0,5\text{‰}$ VSMOW, respectivement. Les eaux souterraines qui subissent la réduction par le sulfate démontrent un enrichissement des valeurs $\delta^{34}\text{S}_{\text{SO}_4}$ et un appauvrissement dans les taux de $\delta^{13}\text{C}_{\text{DIC}}$. Ceci est le résultat de l'oxydation d'huile végétal (canola) utilisé en tant que solution biodégradable durant les opérations de forage. Les eaux salines, n'étant pas affectées par la réduction de la sulfate, ont des valeurs de $\delta^{13}\text{C}_{\text{DIC}}$ d'environ -9‰ VPDB. Le caractère unique, du côté chimique et isotopique, des eaux Cl^- implique une présence exotique par rapport à ce milieu. D'ailleurs, elles découlent probablement d'un processus de "dewatering" de sédiments enfouis sous les plaques tectoniques de l'île de Vancouver.

- Les eaux souterraines composées de Na^+ - Ca^{2+} - SO_4^{2-} et de Ca^{2+} - SO_4^{2-} , et d'origine météorique, sont présentes à des niveaux intermédiaires dans des zones auparavant exploités et dans des régions où la dissolution d'anhydrite domine la chimie anionique. Le sodium lui, est acquis par des processus d'échange. Plus profondément dans la mine HW, les eaux souterraines composées de Na^+ - Ca^{2+} - SO_4^{2-} et de Na^+ - SO_4^{2-} (avec un taux variable de Cl^-) s'y trouvent. Ces eaux ont des valeurs de matières solides dissoutes, d'oxygène dissout et de rédox intermédiaires se trouvant entre les eaux HCO_3^- et les eaux souterraines dominées par du Cl^- . Invariablement, elles contiennent un mélange quelconque de soit, une eau météorique de type Ca^{2+} - HCO_3^- ou soit, une eau saline de type Na^+ - Ca^{2+} - Cl^- . Le sulfate a des taux de $\delta^{34}\text{S}_{\text{SO}_4}$ et de $\delta^{18}\text{O}_{\text{SO}_4}$ semblables à l'eau saline, lequel n'est pas le résultat de l'oxydation d'un sulfide. Par contre, ces valeurs, presque identiques, indiquent une source commune.

- Les eaux d'écoulement de surface composées de Mg^{2+} - SO_4^{2-} sont le résultat d'une érosion intense de restants de roches minées.

La recharge, la circulation et les processus de mélange des eaux souterraines ont été étudiés à partir de résultats chimiques et isotopiques, incluant le $\delta^{18}\text{O}$ et le $\delta^2\text{H}$. Les eaux souterraines, rechargées dans un temps plus récent, préservent la variation en altitude dans le $\delta^{18}\text{O}$ enregistré par la pluie (-0,15‰ pour chaque 100 m en élévation). La variation du $\delta^{18}\text{O}$ dans les eaux souterraines à travers la zone "ridge" Myra-Price suggère un écoulement vertical à subvertical très prononcé passant par la roche fracturée. L'exception serait dans les zones où on retrouve des failles continues produisant ainsi un écoulement dirigé. Les eaux souterraines de type non-salée sont rechargées pendant l'automne et l'hiver par une précipitation isotopiquement moins enrichie.

La vallée Thelwood n'est pas affectée par le développement de la mine. Les eaux souterraines dans cette région proviennent d'une interface de mélange étroite entre des eaux moderne de type Ca^{2+} - HCO_3^- et des eaux salines. De plus, le processus d'échange entre cations n'existe pratiquement pas. Ceci indique qu'un équilibre s'est développé entre les sites d'échanges et les cations dans l'eau. Les eaux salines ont été déplacées de roches faisant parties de la zone "ridge" Myra-Price et sont présentement entrain de s'écouler dans des nouveaux sites d'activité minière. À mesure que le Cl^- passe à travers la roche, le Na^+ y demeure un peu plus longtemps. Ce processus de retard est supposé de continuer pendant que les premiers volumes d'eau météorique passent à travers les pores de la roche. La présence d'eau saline à des niveaux peu profonds dans la vallée Thelwood et le processus de retard du Na^+ à travers et sous la zone "ridge" Myra-Price atteste à la stabilité de l'hydrologie local jusqu'au point où il y a une perturbation par le développement minier. Par contre, une fois que les opérations minières débutent, un réseau de failles et de fractures très perméables peut assurer une circulation d'eau météorique très rapide dans les ouvertures de la mine.

Le pH des eaux souterraines provenant des gisements minéralogiques de Myra Falls est généralement neutre et des eaux souterraines acides avec un taux élevé de métaux son extrêmement rare. Des oxy-hydroxides amorphes sont communs et des comparaisons entre les concentrations de filtrats (non-filtré, 0.45, 0.22, 0.10 et 0.05 μm) indiquent que la majorité des particules suspendues sont plus gros que 0.45 μm . Ces particules sont composées d'oxy-hydroxides de fer, mais inclu aussi de la manganèse (Mn) et de l'aluminium (Al). La présence de ces particules affecte grandement la mobilité

du zinc (Zn), du cuivre (Cu), du plomb (Pb) et du cadmium (Cd) dans les eaux souterraines. L'adsorption du Pb est supérieure au Zn et au Cu, et est affectée très peu par la matrice de la solution. Dans les eaux composées de HCO_3^- , l'ordre des métaux adsorbés par rapport aux particules suspendues est $\text{Pb} > \text{Cu} > \text{Cd} \sim \text{Zn}$, ce qui suit l'ordre de l'hydrolyse premier pour ces métaux. Dans les eaux composées de SO_4^{2-} , l'ordre est $\text{Pb} > \text{Cu} > \text{Zn}$, tandis que dans les eaux composées de Cl^- , l'ordre est $\text{Pb} > \text{Zn} > \text{Cu}$. L'ordre de la mobilité des éléments a des implications envers la compréhension de l'atténuation des métaux in-situ et le transport de métaux "pathfinder" utilisé dans la prospection hydrogéochimique.

Le zinc démontre l'anomalie contrastante la plus grande et la plus fiable pour l'exploration hydrogéochimique dans des eaux souterraines associées avec la minéralisation Zn-Cu-Pb du gisement Price. Les valeurs premières entre deux sous-populations de Zn sont 20, 25 et 38 ppb pour des valeurs premières qui incluent 10, 5 et 1% de la concentration la moins élevée de la sous-population, respectivement. Des anomalies hydrogéochimiques peuvent être davantage dérivées par une gamme d'éléments "pathfinder" associés avec la minéralisation primaire et l'altération hydrothermal incluant le Cu, Pb, Cd, Mn, As (arsenic), Sb (antimoine) et U (uranium). Une discrimination effective entre des anomalies dans des eaux souterraines alliées avec la minéralisation massive du soufre et des eaux souterraines associées avec une minéralisation «ore-clast» bréchifiée extensive peut se faire à partir de l'usage d'éléments liés à la minéralisation primaire et l'altération hydrothermale. Le potassium (K), le rubidium (Rb), le bore (B), le barium (Ba), le cadmium, l'antimoine et l'uranium sont des exemples d'éléments qui sont élevés dans des eaux souterraines unies avec la minéralisation massive du soufre, mais pas nécessairement associé avec la minéralisation «ore-clast» bréchifiée.

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Foreword

The research contained in this thesis grew out of a project envisioned by Dan Boyle (Geological Survey of Canada; GSC), and organized by Dan Boyle and Harlan Meade (Westmin Resources) during the spring of 1993. High topographic relief and the sensitive geographic location of the Myra Falls Mining complex (operated by Westmin Resources within Strathcona Provincial Park) has limited the amount of surface exploration drilling which can be conducted at this location. Most exploration on the Westmin property is conducted from underground drilling stations, which prompted a desire to investigate non-traditional methods of geochemical exploration that could utilize ground waters accessed from both existing and new bore holes within the mine property. In addition, studies of hydrology and hydrogeochemistry in mountainous areas are uncommon, and Westmin Resources were able to provide a suitable study area to pursue these topics. The study of hydrogeochemistry in this setting is important in ascertaining the nature of the chemistry of ground waters within the mine and surroundings, and developing an understanding of the main mechanisms controlling the ground water chemistry.

I was informed of an advertisement for graduate studies posted on the bulletin board of the Ore Gangue lounge (U. of Sask. Geology Dept.) and managed to send a resume to Dan Boyle at the GSC. The project description met my desire to do research on trace metal chemistry in a natural setting. The added bonus of an isotopic study was also very appealing. Soon after sending my application I received a call from Dan, who enthusiastically summed up the program in a few minutes. That short project description has now grown into a greater than four year project, and has finally born fruition.

Three summers were devoted to fieldwork (1993, 1994, and 1995), in which an excess of 1600 water samples were collected. This number includes quality control samples, temporal monitoring samples, and extra, curiosity-type samples. A numerical scheme of numbering the samples was followed to differentiate the year of sampling. Sample designations are 1001 to <2000 for 1993 sample series, 2001 to <3000 for the 1994 sample series, and the 1995 series begins at 3001. One hundred and ten precipitates and gouge material were sampled as part of this program (same numbering format as

waters except with an S prefix). Additionally, hundreds of waters were collected for isotopic analyses, although financial constraints limited the number of analyses. In total two-hundred and seventy four analyses of $^{18}\text{O}_{\text{H}_2\text{O}}$ were completed, 143 deuterium analyses, 41 analyses of $^{13}\text{C}_{\text{DIC}}$, 20 analyses of ^{34}S , 8 of $^{18}\text{O}_{\text{SO}_4}$, 24 analyses of tritium, 4 analyses of ^{14}C , 3 analyses of $^{87}\text{Sr}/^{86}\text{Sr}$, 3 analyses of ^3He , ^4He , and $^{20/21/22}\text{Ne}$, and 6 analyses of ^{37}Cl were completed.

The underground areas emphasized in this study (Myra mine and Price deposit) were chosen because most drill holes in the Price and Myra mines were left open or plugged with easily removable rock bolts (Price 4 and 5 levels), or in certain cases with margot plugs, as was the case in Price 9 level and areas of Price 13 level. Current drilling practice is to immediately cement-up drill holes after completion; although recent drilling at the end of drifts on HW 20 and 21 levels were left open due to labour relation problems in 1993 and have been sampled in this study. The Price and Myra mines are readily accessible and do not require a hoist-operator and cage tender for access. These areas are also not currently being operated which allows safe unfettered sampling and observation of the area. These areas can be seen in relationship to the entire mine layout in the area plan map in the back pocket of this theses.

Other complementary research programs were carried out at Myra Falls as part of the Industrial Partners Project (IPP) between the Geological Survey of Canada (GSC) and Westmin Resources Ltd.. A physical hydrology research program accompanied the hydrogeochemical component with Martin Stapinsky (Ottawa-Carleton Geoscience Centre (OCGC)) beginning field research in 1994. The areas of emphasis of the physical hydrology program are the ground waters flowing within the Price and Myra drifts and Price hillside. A bore hole geophysics project, supervised by J. Mwenifumbo (GSC), was conducted on the property during 1994. Several bore holes were geophysically logged on the lower Price hillside and Thelwood Valley. As part of the hydrogeochemical research program several drill holes were sampled with a portable inflatable-packer system; many of the zones sampled were based on results of the geophysical logging project.

The following list of publications, presentations, posters, and reports have been prepared/ presented during this graduate program:

Publications

G.C. Phipps, D.R. Boyle and I.D. Clark, Groundwater Hydrogeochemical methods of exploration for volcanogenic massive-sulphide deposits, in the Buttle Lake Paleozoic Inlier, Vancouver Island, British Columbia. [submitted to *J. Geochem. Expl.*]

I.D. Clark, W.T. Bajjali and G.C. Phipps, 1996. Constraining ^{14}C ages in sulphate reducing groundwaters: Two Case Studies from Arid Regions. *In* *Isotopes in Water Resources Management*, I.A.E.A. S.M-336/10 Volume 1: 43-56

Oral Presentation

G.C. Phipps, I.D. Clark and D.R. Boyle, The Impact of Mine Openings on Groundwater Circulation in Crystalline Rock: An Analogue for a Radioactive Repository *in* *Hydrogeochemistry: Noble Gases, Stable Isotopes and Radioelements* Reading U.K. April 2-3 1996

Poster Presentations

G.C. Phipps, I.D. Clark and D.R. Boyle, Hydrogeochemistry of the Paleozoic Buttle Lake uplift, Vancouver Island, British Columbia. presented at Geological Association of Canada / Mineralogical Association of Canada joint meeting Ottawa On. May 19, 1997

G.C. Phipps, D.R. Boyle and I.D. Clark, Element mobility and groundwater hydrogeochemical exploration in the volcanogenic massive sulphide deposit, Buttle Lake Paleozoic inlier, British Columbia. presented at the Geological Association of Canada / Mineralogical Association of Canada joint meeting Ottawa On. May 19, 1997

D.R. Boyle, G.C. Phipps, I.D. Clark, Ground water geochemical exploration for volcanogenic massive sulfide deposits on Vancouver Island, British Columbia. Cordilleran Round-Up, Vancouver, B.C., Feb., 1996

D.R. Boyle, G.C. Phipps, I.D. Clark, Ground water geochemical exploration for volcanogenic massive sulfide deposits on Vancouver Island, British Columbia. Geological Survey of Canada Colloquium, Ottawa On. Jan. 22-24, 1996

D.R. Boyle, J. Desbarats, C.J. Mwenifumbo, G.C. Phipps, M.J. Stapinsky, I.D. Clark, M.J.L. Robin, J. Hamilton, D.C. Gregoire, Etudes hydrogeologiques et hydrogeochimique du complexe minier a metaux communs de l'exploitation de la Westmin, en Colombie-Britannique, Congres annuel de l'Association professionnelle des geologues et des geophysiciens du Quebec, Laval P.Q. April 19-21, 1995

D.R. Boyle, J. Desbarats, C.J. Mwenifumbo, G.C. Phipps, M.J. Stapinsky, I.D. Clark, M.J.L. Robin, J. Hamilton, D.C. Gregoire, Hydrogeological and hydrogeochemical studies of a base metal mining complex, Westmin Myra Falls Operation, British Columbia. Cordilleran Round-Up, Vancouver, B.C., Feb., 1995

D.R. Boyle, J. Desbarats, C.J. Mwenifumbo, G.C. Phipps, M.J. Stapinsky, I.D. Clark, M.J.L. Robin, J. Hamilton, D.C. Gregoire, Hydrogeological and hydrogeochemical studies of a base metal mining complex, Westmin Myra Falls Operation, British Columbia. Geological Survey of Canada Forum, Ottawa On. Jan. 16-18, 1995

D.R. Boyle, G.C. Phipps, I.D. Clark, M.J.L. Robin, C.D. Gregoire, The Myra Falls Hydrogeochemical Project, Vancouver Island, British Columbia - a GSC/Westmin Resources Industrial Partners Project. Cordilleran Round-Up, Vancouver, B.C., Feb. , 1994

D.R. Boyle, G.C. Phipps, I.D. Clark, M.J.L. Robin, C.D. Gregoire, The Myra Falls Hydrogeochemical Project, Vancouver Island, British Columbia - a GSC/Westmin Resources Industrial Partners Project. Geological Survey of Canada Minerals Colloquium, Ottawa On. Jan. 17-19, 1994

Internal Publications

G.C. Phipps, D.R. Boyle and I.D. Clark, 1996. Myra Falls Groundwater Geoscience Project: Hydrogeochemical database with sampling protocol and QA/QC. Internal Report Geological Survey of Canada and Westmin Resources Ltd. 123 pp. [Internal Company and Government Report]

G.C. Phipps, D.R. Boyle and I.D. Clark, 1995. Hydrogeochemical Applications *in* Geological Survey of Canada/Westmin Resources Ltd. Industrial Partners Project; Interim Report to March 1995, D. R. Boyle (ed.). pp. 12-26 [Internal Company and Government Report]

Acknowledgments

Funding for this project was jointly provided by Westmin Resources Ltd. and the Geological Survey of Canada under an Industrial Partners Project (IPP). Additional funding for isotopic analyses was provided by an NSERC grant to Ian Clark. Monetary support was provided to myself by Westmin Resources (summers of 1993 and 1994), the government of Ontario (Ontario Graduate Scholarship, fall of 1994 to 1997), the University of Ottawa (Excellence Scholarship, fall of 1994 to 1997), and Ian Clark (Research Assistantship Fall of 1997).

Much of what is found in Chapter 7 - Ground Water Hydrogeochemical Exploration Methods has been submitted for publication and much of the editing of multiple versions of this chapter was conducted by Dan Boyle.

I would like to thank my supervisors Ian Clark and Dan Boyle for providing the opportunity to conduct this research. Their insights into various hydrochemical and isotope processes, and their kind but thorough editing has all been greatly appreciated.

The diverse nature of this study and the abundance of analyses limited the number and type of analyses that I was able to conduct, and therefore many individuals in various labs were responsible for chemical analyses. Chemical analyses (water, whole-rock, and precipitate) were conducted at the GSC Analytical Chemistry Section laboratory under the watchful eyes of Conrad Gregoire and Peter Belanger. Arsenic analyses by hydride generation method and alkalinity titration (1994 and 1995) were performed by Gille Gauthier at the Analytical Development Section, Mineral Resources Division (GSC). X-ray diffraction on precipitate samples was conducted at the GSC by Robert Delabio (1994 and 1995) and Andrew Roberts (1996). Many of the pieces of the field equipment were fabricated at the GSC instrument development shop by Romio Forconi, Ken Lalonde, and Sean Going, under the supervision of Steve Belanszki. Strontium isotope analyses was provided by Jan Veizer and Ajaz Karim (OCGC). Helium and neon analyses were conducted by Tom Kotzer at the Environmental Research Branch, Atomic Energy of Canada Ltd., Chalk River. Tom also clarified the methods and uses of He. I would like to thank Natalie Morisset, Wendy Abdi, and Gilles St. Jean at the G.G. Hatch Isotope

Laboratory (U. of Ottawa) for demonstrating techniques and helping with stable isotope extraction and analyses.

I would also like to acknowledge the helpful geology staff at Myra Falls, namely, Cliff Pearson, Steve Juras, and Finley Baker for providing access to company reports, and geological drawings, providing insight into the mine geology, and giving guided tours of areas of the HW mine (HW 18, 20, and 21 levels; S.J.) and various levels of HW (1995 GAC/MAC mine tour; S.J. and F.B.). Structural elements of the mine were patiently explained and or examples shown by Steve Juras, Jack Hamilton, and Rolle Reid (U of Indiana; aspects of structure on HW 18 level). Able-bodied field assistance was provided by Richard Pearson (1993) and Gavin Dirom III (1994 and 1995). Lithogeochemical sampling, summarized within this theses, was carried out by Jack Hamilton during the summer and fall of 1994, while employed by the GSC/Westmin IPP and by Westmin Resources Ltd.

I apologize to anyone, who I have through oversight, not included in these acknowledgments.

I would like to especially thank Brenda and Allison who have always been there for me; providing moral support, encouragement, patience, love and understanding.

1. Introduction

1.1 Objectives

The primary objectives of this study are to:

1. Characterize ground water geochemical facies and determine the geochemical and isotopic evolution of waters, the spatial variations of ground waters, and mean residence times of ground waters within a fractured flow system located in a mountainous region with high precipitation.
2. Obtain an understanding of the hydrochemical processes that control concentrations and mobility of metals in this setting.
3. Develop ground water hydrogeochemical exploration methods that can be used for discovering new mineralization, and/or extensions to existing ore-bodies within the Myra Falls mining camp.
4. Create a quality controlled database of ground and surface water chemistry that can be used in future environmental investigations in this area.

The duality of the objectives into environmental studies and mineral exploration originally suggest an unseemly combination. Yet, the understanding of flow systems in a mountainous setting and the mobility of metals in ground waters related to poly-metallic massive sulphide mineralization is important in assessing the use of these elements in hydrochemical exploration programs, and also in mitigating the environmental consequence of mining these deposits.

1.2 Location

The Westmin Resources' Myra Falls mining operation, located in the centre of Vancouver Island, British Columbia, Canada (49° 35' N, 125° 34' W) is hosted within the Buttle Lake Paleozoic inlier, one of the major Paleozoic uplifts on Vancouver Island (Figure 1-1). The Myra Falls region is located within the central Vancouver Island mountain ranges.

The study area is largely confined to the Myra - Price ridge, and to Thelwood Valley (Figure 1-2). Some water sampling, especially preliminary and temporal, sampling was also conducted on the Phillips ridge side (northwest) of Myra Valley, within the part of HW mine that extends below Myra Valley, and within Myra Valley itself (see map in back pocket for orientation).

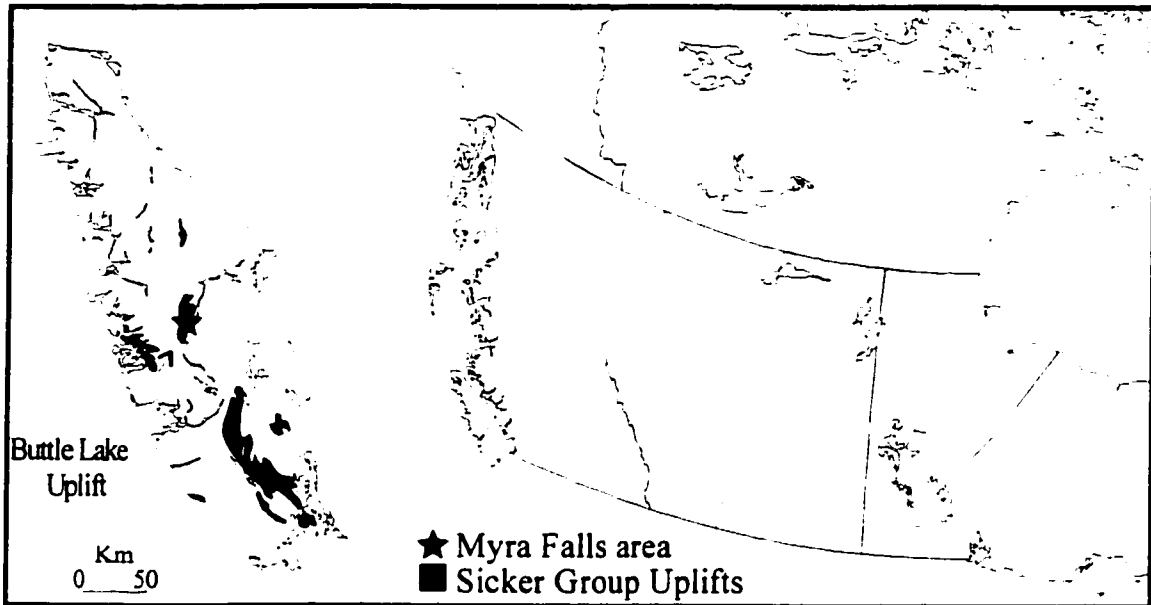


Figure 1-1. Location map of Myra Falls study area Vancouver Island, British Columbia.

1.3 Mine Development History

The Westmin mining claim lies within the Strathcona Park and is designated as Strathcona-Westmin Class B Park, and therefore, all mining activities, and the eventual reclamation and rehabilitation of the site, take place under a park use permit. Indeed the presence of the mine has aided in accessibility and enjoyment of the park, initially through the construction of a 40 km access road on the eastern shores of Buttle Lake, and later by the construction of a foot path up Phillip's ridge (initiated by mine personnel), and also by providing surface mine tours to interested tourists.

Variations exist on the history of the original mineral claims held in Strathcona Park. The information related here comes from Pearson (1993), the Westmin Resources surface tour information material, and Aquamin (1996). The more common history states

that the Lynx and Price showings were originally staked in 1917, some six years after the formation of Strathcona Park, British Columbia's first provincial park. The Myra mine, formally known as Paramount after the Paramount Mining Co., who held the claim, received some development work between 1919 and 1925, but no mining activity. All the claims were consolidated in 1959 and sold to Western Mines Ltd. (precursor to Westmin Resources) in 1961. Production from the Lynx open-pit mine started in 1967, after the construction of the mill (concentrator) and surface facilities, and remained active until 1975. The Lynx underground mine was in production from 1976 until 1993. Myra mine development commenced in 1970, and mining came on line in 1972 and continued until 1985 when reserves were exhausted. Exploration was increased as ore reserves began to dwindle in the late 1970's. The Price deposit received little serious attention until drifting and drilling activity on Price hillside, which ran from 1979 to 1981. However, further development of the Price deposit was relinquished with the discovery of the much larger HW deposit. The HW ore-body was discovered in 1979 and commissioned in 1985.

The Westmin Resources mining complex is within an environmentally sensitive area located in a mountainous area dissected by streams draining into Buttle Lake, which forms the headwater of a river system important to recreational, and commercial fish habitat, as well as a drinking water reservoir. Regulatory compliance of effluent has been a problem in the past but to a large extent has been rectified by the diversion of surface water around the major waste dump areas and completion of the 'super-pond' water treatment facility (Aquamin, 1996). Metal levels in Buttle Lake as of 1996 are within compliance of the B.C. water quality standards for the protection of aquatic life with the exception of Cu (compliance concentration = 5 ppb), which may be the result of natural sources (Aquamin, 1996).

1.4 Mine Plans

The following section is meant to acquaint the reader with the mine site and various mine levels which were sampled as part of this research program. The plan map of Westmin Resources claim and surrounding area (see map in back pocket) includes infrastructure (roads and buildings), elevation contours, waterways, plan of ore zones, surface drill hole collars (Thelwood Valley and Price hillside), and mining development.

Mine co-ordinates are laid out with the ore bodies trending mine east and west. Mine north is oriented $\sim 45^\circ$ E of true N. Location co-ordinates are in metres (m) (or feet depending on development date) and expressed relative to a 100 m (or 100') grid. For example 15+00 mE, 14+40 mN is 1500 m east and 1440 m north of the arbitrary origin (0,0 co-ordinate), which is located off the mine property.

The ruggedness of the area becomes more apparent on the aerial photograph (Figure 1-2) taken July, 1962, prior to mine development. Superimposed on the photo are 200 m contours. Also shown on the diagram is the close proximity to environmentally sensitive areas such as Buttle Lake, the trail to the Lynx showing is apparent in Myra Valley as well as logging operations in Thelwood Valley, and perennial snow cover on Mount Myra.

The Price deposit (Price 4 and 5 levels) is accessed on foot via an abandoned road on the Price hillside. Price 9 level is easily accessed mainly by vehicle. Price 13 level is accessed by an adit in Thelwood Valley, by Myra 13 level via the HW shaft (man-way or cage), by the Myra decline ramp, and Myra 13, by the escape man-way from HW 20 level. The Myra mine, Myra 10 level, and 9 level via 10 level (Myra 9 level adit has collapsed) is accessed on the Myra Valley hillside; Myra decline ramp and Myra 11, 12, 12.5, and 13 which join it, are accessed via Myra Valley. The lower levels in the HW mine are accessed by the HW shaft and cage.

Elevations of levels are outlined in Table 1-1, to orient the reader on the approximate elevation of each level sampled. Elevations are for adits where drifts intersect the surface, or indicate the drift elevation at the HW shaft, or in the Myra mine (M- 11, 12, and 13) where the levels intersect the Myra decline ramp. Levels are generally separated by about 46 metres or 150 feet. The abbreviations for drill hole and site locations that will be used throughout this manuscript are as follows: Pr = Price mine, M = Myra mine, HW = HW mine, PR = Thelwood Valley and Price hillside surface drill holes, W = Myra Valley surface drill holes; underground drift orientations are: de = drift east, dw = drift west. xcn and xcs are cross-cut north and cross-cut south, respectively.

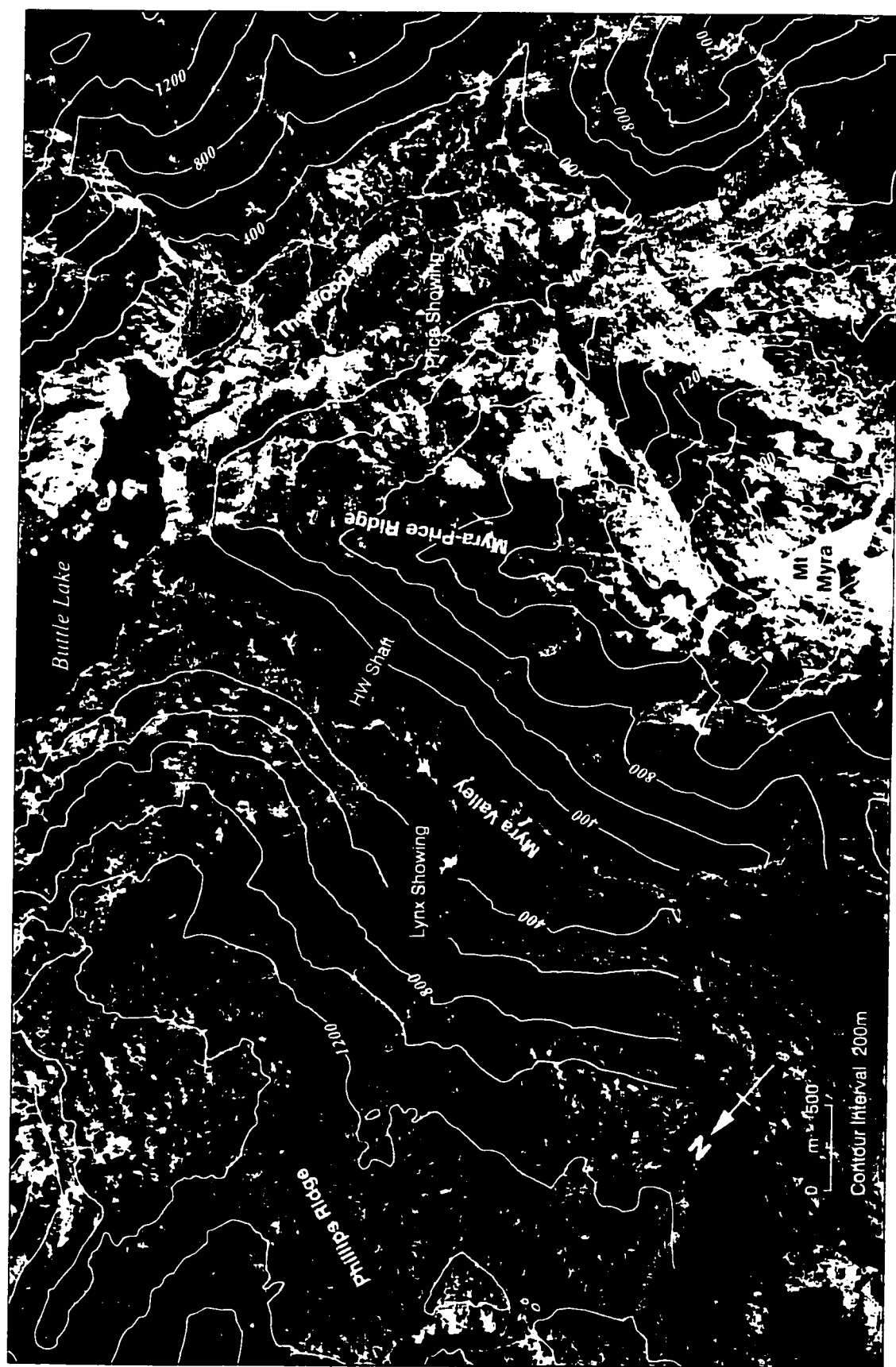


Figure 1-2 Aerial photograph of Mt. Myra, and Myra-Price ridge extending towards Buttle Lake. Myra Creek and trail to Lynx showing are apparent in Myra Valley and logging roads show clearly in Thelwood Valley.

Table 1-1. Level elevations (metres with respect to sea level).

Mine	Level	Elevation (m)
Price	4	626.4
Price	5	579.7
Price	9	416.1
Price	13	238.0
Myra	9	413.6
Myra	10	367.0
Myra	11	325.2
Myra	12	281.9
Myra	13	241.4
Lynx	5	570.5
Lynx	6 N	548.6
Lynx	8	453.0
Lynx	10	381.0
HW	18	6.7
HW	20	-85.4
HW	21	-129.8

1.5 Topography and Physiography

The topography is mountainous with steep rugged slopes dissected by stream gulches, some of which are steeply incised. The Myra - Price ridge is bounded on the northwest (mine west) by Myra Valley and on the southeast (mine east) by Thelwood Valley, and extends from Mount Myra (1814 m) on the southwest to Buttle Lake (221±m), on the northeast. The mountain sides are generally quite steep with abundant outcrops and little overburden (Figure 1-2 and Figure 1-3). The major valleys are glacial/fluvial formed and sediment-filled (colluvial, fluvial, and glacial sediments) (Walker, 1992).

Douglas fir, hemlock and western red cedar, some of which are 'old growth' forest within Myra Valley, are the dominant climax vegetative species. Various deciduous species, along with sapling conifers occur as thick re-growth in cleared and burned areas.

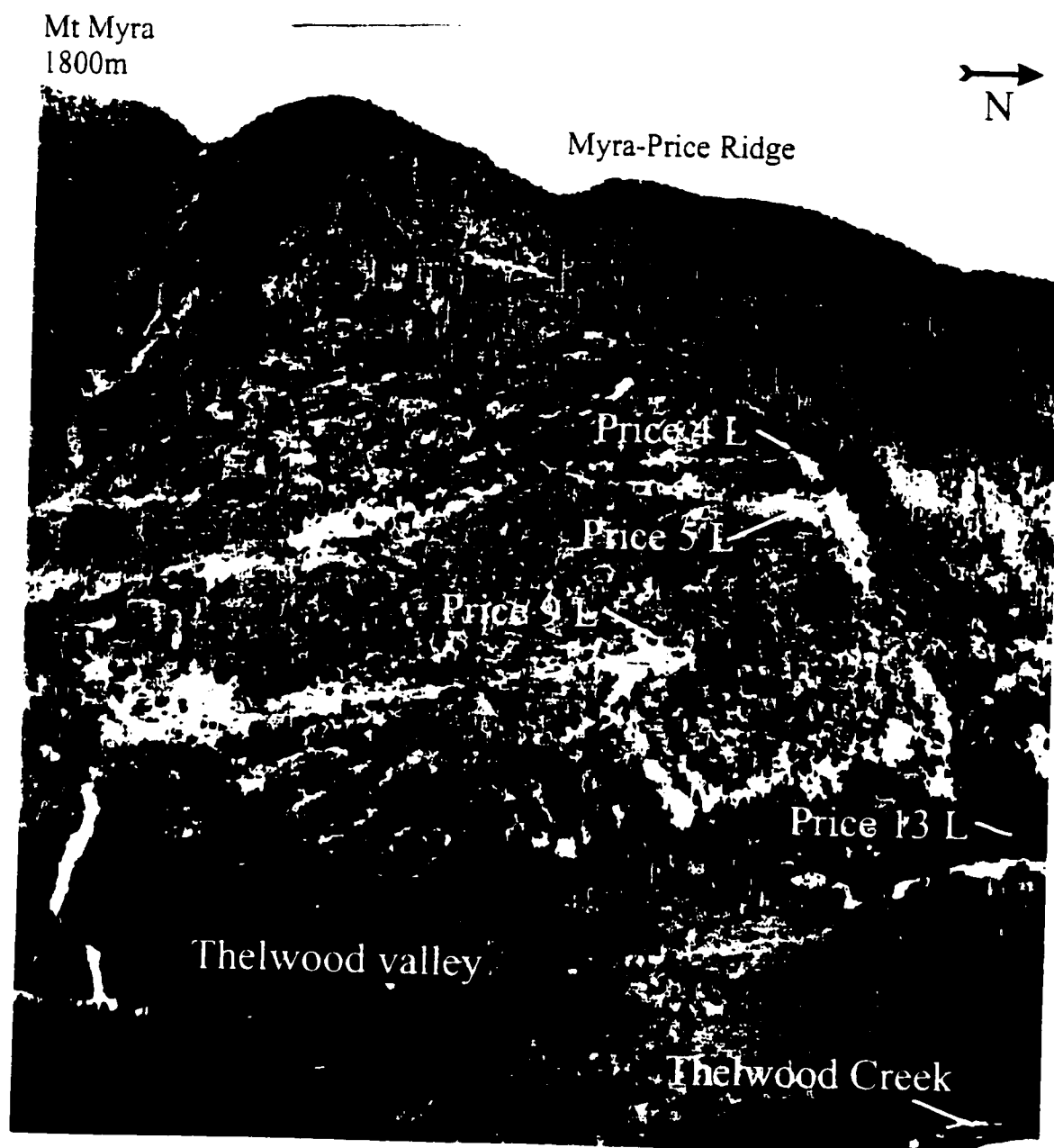


Figure 1-3 Photo of Price hillside outlining Price adits and Thelwood Creek. Mt. Myra is in the background.

1.6 Climate

Mean annual precipitation at Myra Falls exceeds 2,500 mm, most of which falls during the autumn and winter months (Figure 1-4); much of the winter precipitation at higher elevations falls in the form of snow. Over 4 metres of snow may fall at higher elevations over the winter, and rainfall in the valley, even during late spring and early fall, may be accompanied by snow on the mountains. July and August are dry with high evapo-transpiration. Within Myra Valley (360 m elevation), daily temperatures ranges from -12°C to 27°C with a mean value of 8.7°C (Environment Canada data).

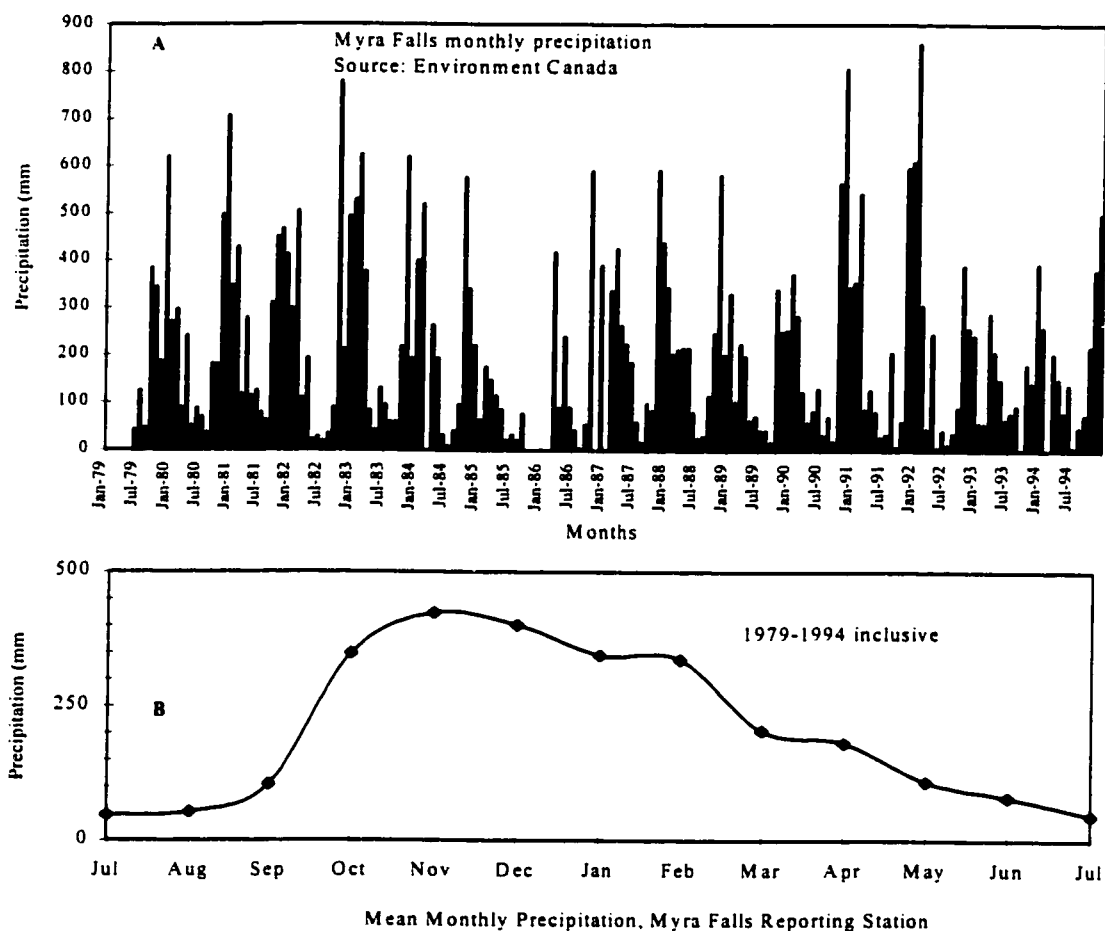


Figure 1-4 Monthly precipitation recorded at Environment Canada reporting station Myra Valley (a) and average monthly precipitation (b).

1.7 Geology

1.7.1 Stratigraphy

The Buttle Lake Camp ore deposits consist of many individual massive sulphide lenses within the lower two of three felsic volcanic intervals in the Paleozoic Sicker Group. The Sicker Group, exposed locally in the fault bounded Buttle Lake uplift (Figure 1-5), are the oldest rocks on Vancouver Island and represent the known base of the allochthonous Wrangellia terrane (Jones et al., 1977). The Sicker Group is exposed in three major fault-bounded structural uplifts (Buttle Lake, Cowichan - Horne Lake, and Nanoose) on Vancouver Island and several unnamed uplifts (Figure 1-1). In addition to the Buttle Lake Uplift, mining has take place intermittently in the Sicker Group near Duncan B.C. (Pearson, 1993).

The lower three formations of the Sicker Group, the Price, Myra, and Thelwood Formations, are accessed by surface drill holes, within the mine workings, and from drill holes originating within the mining complex. The Myra and Thelwood Formations are also exposed in outcrops within the area. The Flower Ridge Formation is the youngest formation of the Sicker Group and lower portions of it are exposed on Westmin Resources property. Working (mine) terminology for the Price, Myra, and Thelwood Formations, are the footwall HW andesite, the mine sequence, and the sharp(ly) banded tuff, respectively.

A comprehensive account of the mine stratigraphy is detailed in Juras (1987). The following stratigraphic summary is largely based on his work along with works of Walker (1985), Juras and Pearson. (1990), and Pearson. (1993).

The Price Formation (footwall HW andesite) is the oldest and lowermost unit exposed in the Buttle Lake uplift, and consists of a thick sequence of massive to pillowed basaltic andesite flows, flow breccias and volcanoclastics. Flow members consist of alternating 30 to 150 m thick sequences containing variably amygdaloidal, feldspar-phyrlic, and pyroxene porphyritic. This formation is greater than 400 m thick and the base of the formation has not been delineated. It has been intersected by drilling throughout the property. Moderate to strong alteration to chlorite + epidote + albite $\pm$ actinolite is characteristic of the Price Formation.

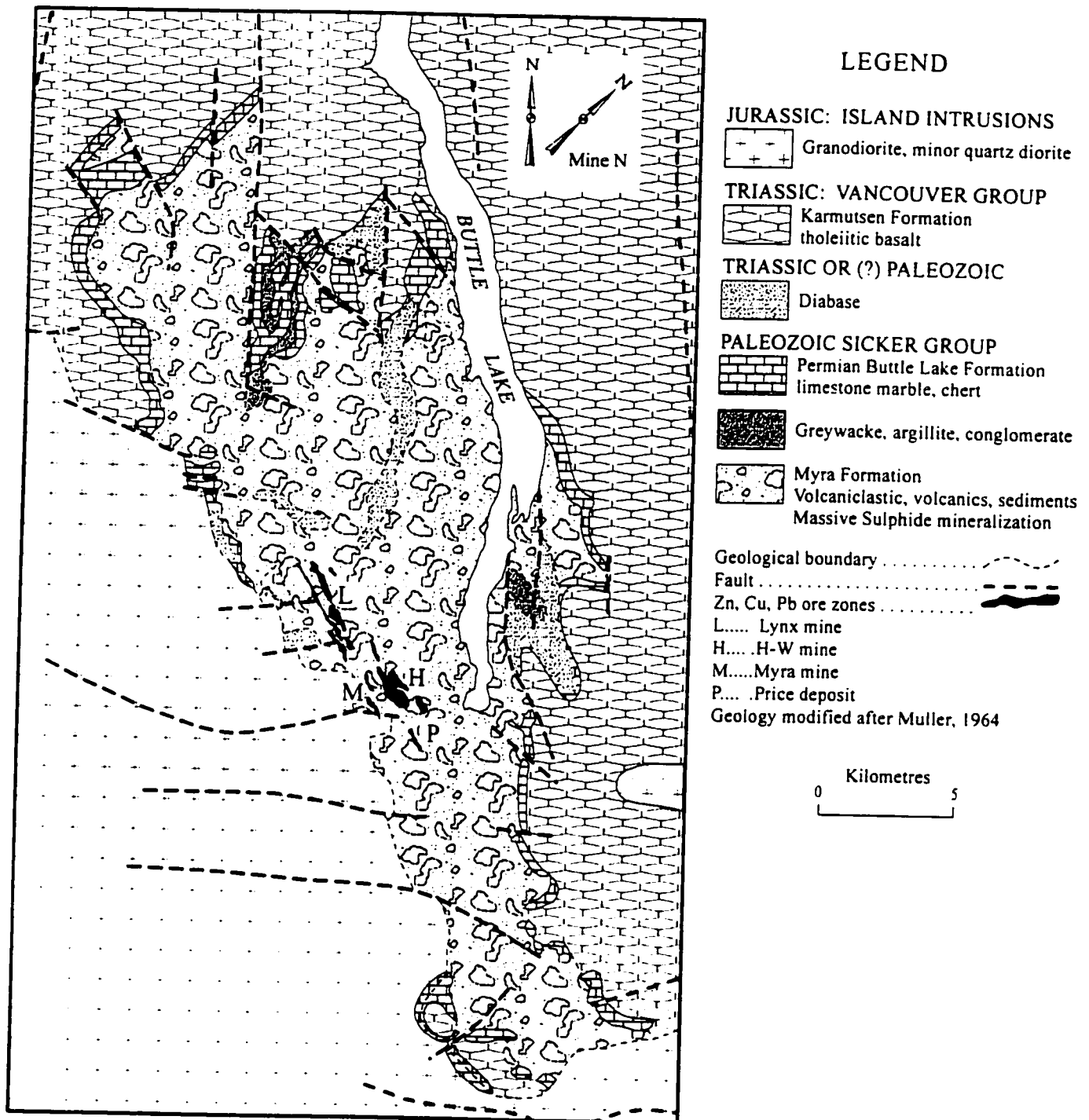


Figure 1-5. Regional geology of the Butte Lake uplift with ore-deposits outlined. Location of area outlined is shown in Figure 1-1

The Myra Formation (mine sequence) hosts all known occurrences of sulphide mineralization, is up to 450 m thick, and is characterized by rapid lateral (mine north - south) facies changes. Least facies variations trend mine East-West along strike of a rift basin development and are linearly continuous for >7 km. The mine sequence has been subdivided into 10 lithostratigraphic units by Juras (1987). These are, in decreasing relative age: HW horizon [DCm1], hanging wall HW andesite [DCm2], ore-clast breccia [DCm3], lower mixed volcanoclastics [DCm4], upper dacite / SE andesite / north dacite [DCm5], Lynx-Myra-Price horizon [DCm6], G-flow unit [DCm7], upper mixed volcanoclastics [DCm8], upper rhyolite unit [DCm9], and upper mafic unit [DCm10] (Figure 1-6). The unit designations correspond to whole rock geochemistry sampled by J.V. Hamilton during contract field work for lithological and structural mapping of the Price hillside and Thelwood Valley (Hamilton, 1994) and is summarized in Table 1-3. A generalized schematic cross-section (Figure 1-6) through the major features of the Buttle Lake camp illustrates the relationship of various units.

The base of the mine sequence is marked by the HW horizon [DCm1] which is predominantly rhyolite-dacite and ranges in approximate thickness from 15 to 200 m. This horizon can be subdivided into five separate lithologies which consist of felsic tuffs and flows, subordinate argillites, mafic flows, volcanoclastics, and massive sulphides. The felsic flow member can be subdivided into: a quartz feldspar porphyritic (QFP) rhyolite [DCm1q], an aphyric to feldspar porphyritic rhyolite [DCm1f], and a feldspar porphyritic dacite [DCm1d]. The dacite flows thicken in the Price area. No alkali feldspar phenocrysts were observed in the QFP, although the groundmass contains albite and potassium feldspars. Accessory minerals in the QFP and FP are apatite, zircon, and opaque oxides (magnetite or hematite).

The argillite [DCm1a] is 1.5 to 45 m thick and is more or less continuous. It is often in beds made up of varying amounts of argillite and tuff. The argillites are composed of quartz, feldspar, minor chlorite, carbonaceous matter (graphitic?), and ubiquitous but minor thin laminae or lenses of pyrite, or sometimes pyrrhotite. Bedded sequences are normally graded and display A-E or A-B-E Bouma sequence.

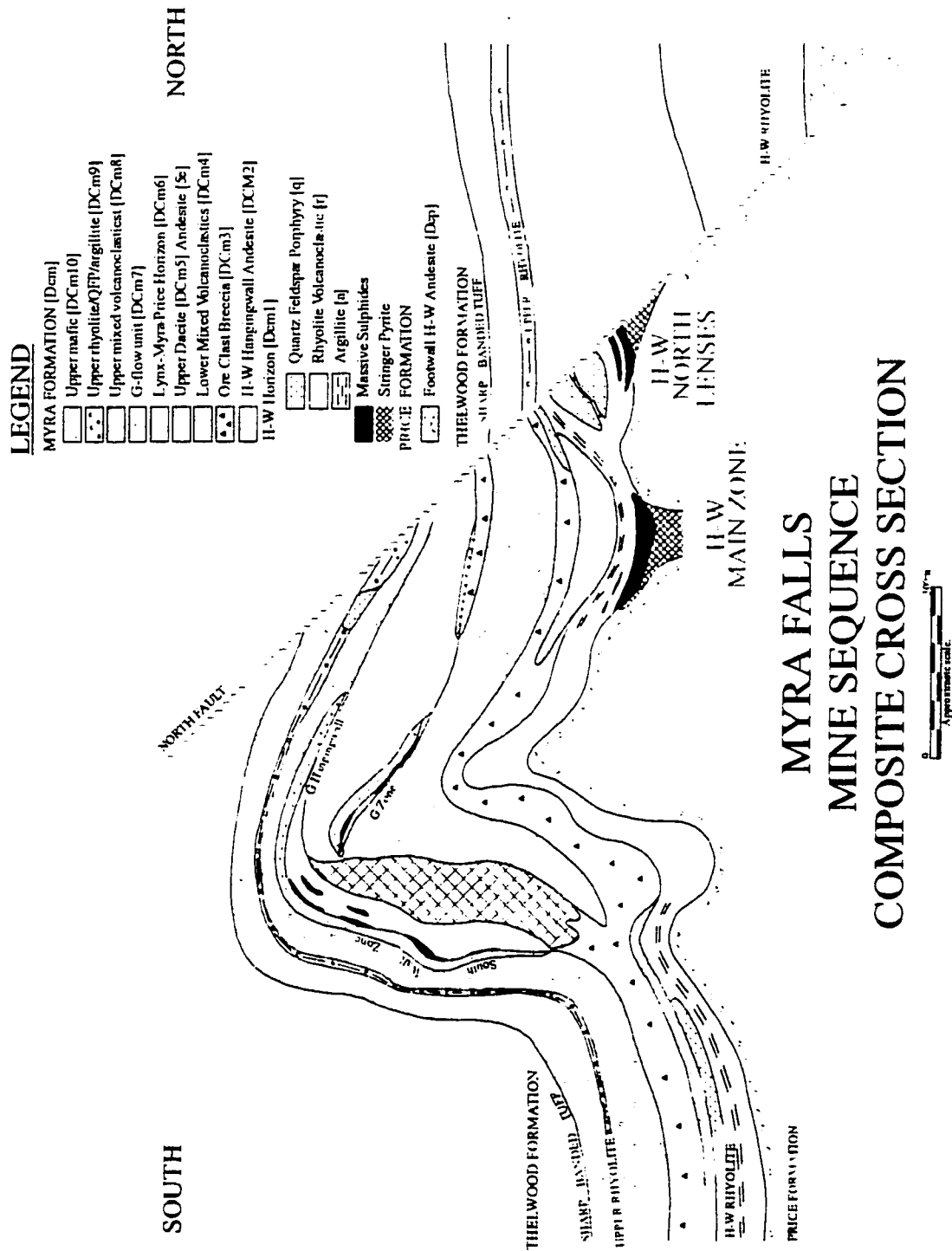


Figure 1-6. Schematic cross section through the Myra Formation (mine sequence) with unit designations of Juras (1987), after Pearson (1993).

The HW horizon, in the central region of the camp, is mostly pyroclastic and volcanoclastic [DCm1r] consisting of quartz feldspar lapilli and tuff deposits containing trace apatite accessory grains and a small percentage of argillic and massive sulphide (pyrite, sphalerite, pyrrhotite) clasts.

The mafic flow member [DCm1m] of the HW horizon consists of pyroxene-phyric high Mg basaltic flows and hyaloclastics. It generally occurs within or above the argillite member. The flow contains up to 5 percent clinopyroxene phenocrysts in a fine groundmass containing feldspar, actinolite, and minor calcite and epidote. The hyaloclastics may contain clasts of felsic tuffs, feldspar and quartz, and occasionally massive sulphide fragments.

Overlying the HW horizon is the hanging wall andesite [DCm2]. It is up to 100 m thick. It consisting of basaltic andesite to andesite flows and breccias. Basaltic andesite to andesite flows consist of approximately 20 percent plagioclase glomerophenocrysts, and up to one percent pyroxene phenocrysts, with trace amounts of apatite or opaque oxides. Amygdales are filled with chlorite and epidote $\pm$ quartz. The hanging wall andesite is thickest over the HW main lens and is moderately to strongly altered; in the brecciated portions some fragments have been completely altered to epidote.

The ore-clast breccia (OCB) [DCm3] as the name suggests is a breccia, likely of submarine debris flow origin, containing sulphide clasts and olistoliths of mineralized rhyolite tuff to lapilli tuffs. The unit is found throughout the mine-area and is thickest in the central and Price areas where it is up 90 m thick. The breccia matrix can be either rhyolite rich or poor. Clast composition span a wide range of lithologies and include: chert, argillite, rhyolite, dacite, andesite, and mafic clasts, and also massive-sulphide clasts of dominantly pyrite composition. Rhyolite olistoliths are usually mineralized with disseminated pyrite with some lenses containing massive sulphide, barite, and quartz pods. Clasts are generally supported in a fine-grained to aphanitic epidote, and minor quartz and feldspar matrix. Phyllosilicate minerals are rare. Clast size is highly variable ranging from 1 to 150 cm; while rhyolite olistoliths may reach dimensions of 50 m long by 15 m wide. The coarsest clasts and largest olistoliths occur in the Price area. An upper and lower breccia are separated by an interzone rhyolite up to 20 m thick.

The lower mixed volcanoclastic unit [DCm4] is dominantly andesitic composition ranging from fine tuffs to breccia. Bedded clasts are composed of chloritized relict andesite fragments which are aphyric to plagioclase-phyric. Bedded clastic sequences are contained in a matrix of fine-grained epidote, chlorite, and feldspar. Coarse clastic deposits are made up of andesite to dacite clasts in a groundmass that is strongly altered to epidote and leucoxene. The lower mixed volcanoclastics occur throughout the property and are thinnest in the Lynx mine area, thickest in the Price to Myra / HW area, reaching a maximum thickness of 300 m. In the northern mine area the lower mixed volcanoclastics may directly overly the HW hanging wall andesite. This unit does not contain rhyolite or massive sulphide components and may have formed as a subaqueous debris flow.

The upper dacite [DCm5], 5E andesite [DCm5e] and north dacite [DCm5n] units represent three non-overlapping, nearly concurrent yet different eruptive events. The upper dacite is present in the Price area where it consists of bedded deposits of dacite to rhyolite hyaloclastite, flow breccia, and subaqueous pyroclastic deposits. The lower upper dacite contains feldspar porphyritic flow clasts and aphyric altered vitric clasts with trace apatite and magnetite(?) microphenocrysts. The matrix is fine-grained and contains relict vitric textures and intergrowths of feldspar and sericite. Chlorite, quartz, Fe-Ti oxides, and epidote may also be present in clast matrix or groundmass. The upper member of the upper dacite is strongly feldspar porphyritic (25%), and contains apatite and opaque oxide (magnetite?) accessories. The groundmass is comprised of fine-grained chlorite, feldspar, and minor epidote. The north dacite is a feldspar porphyritic felsic flow unit only present along the northern margin of the camp. The 5E andesite is not present in the hydrogeochemical study area.

The Lynx-Myra-Price (L-M-P) [DCm6] (Figure 1-6) is the second felsic horizon within the Myra Formation, and varies from 10 to 150 m thickness. Two spatially distinct units, the G-zone [DCm6] and the G-zone hanging-wall member [DCm6h], are separated by 10 to 60 m by units of the upper dacite member in the Price mine area. The separation increases moving towards the Lynx mine. Both zones are laterally extensive throughout the mine property, and vary in thickness from 1 to 45 m with the G-zone generally the thicker of the two. Both the G-zone and the G-hanging wall zone consist of massive to

bedded, fine to coarse quartz - feldspar crystal vitric rhyolite tuffs and lapilli tuffs. Massive sulphide mineralization and hydrothermal alteration are also present. The rhyolite tuffs are comprised of up to 10 to 25 percent broken plagioclase crystals, 5 to 15 percent quartz crystals, and 5 percent disseminated pyrite, and accessory apatite. The matrix is composed of sericite and quartz; while, plagioclase is usually altered to quartz or sericite. The massive sulphide deposits generally occur on or near the uppermost contact of their respective rhyolites. A chert horizon exists in the central regions of the Price and HW - Myra sections and attains a thickness of 1 to 3 m. It is composed of thin to medium laminated beds of white to light green chert, jasper, and rarely, a black argillaceous chert.

The hanging wall to many of the L-M-P ore bodies is the G-flow unit [DCm7]. It consists of several 2 to 15 m thick basaltic to komatiitic flows, flow breccias, and hyaloclastic deposits. This unit is thickest in the (mine) west and thins towards Price. In the Price region it consists of pyroxene phyric, amygdaloidal, massive to pillowed flows with subordinate lapilli-tuff and coarse tuff zones. In the HW and Myra areas these units are moderately to intensely altered by carbonate and hematite. The least altered flows contain augite, trace chromite, and trace olivine(?) phenocrysts in a groundmass of fine-grained felted actinolite, subordinate chlorite, minor plagioclase, and relict clinopyroxene. The flows are always amygdaloidal, with amygdaloes containing chlorite, epidote and calcite. Pillowed flows contain magnetite-rich relict selvages in the Price area with jasper in pillow interstices.

The upper mixed volcanoclastics [DCm8] is up to 50 m thick, and consists of mafic to intermediate, bedded, fine to coarse, tuff and lapilli-tuff sequences, and massive lapilli-tuff to tuff-breccia deposits. Bedded sequences are thinly to medium bedded, normally graded intermediate to mafic tuffs, and contain feldspar crystals (25 to 40%). Massive lapilli-tuffs and tuff breccias contain 5 to 15% plagioclase, trace pyroxene, and a wide variety of vitric and flow clasts. The matrix is fine-grained epidote, albite, and chlorite. Clastic fragments include plagioclase porphyritic mafics, intermediate volcanics, felsics, pyroxene porphyritic basalt, strongly epidotized feldspar $\pm$ pyroxene porphyritic andesite, and minor rip-up clasts of tuffaceous siltstone, mudstone and black chert. Upper

mixed volcanoclastic rocks are moderately altered to chlorite, epidote, sericite, albite, and hematite.

The stratigraphically highest rhyolite in the mine sequence is the upper rhyolite unit [DCm9]. It is composed of two members, a thin lower argillite - chert member and an upper thick pyroclastic rich member. The lower member (1 to 15 m thick) consists of thin to medium laminated siliceous grey to black argillite, pale green chert, rhyolite fine-tuff, and minor jasper. In the Price area thin layers of semi-massive pyrite are intercalated between the siliceous argillite and fine tuff. In most areas the argillite - chert member is overlain by a thick (up to 50 m) pyroclastic unit consisting of moderately well sorted fine to coarse tuff, tuff-breccia, and tuffaceous breccia. Non-rhyolitic components consist of lapilli-sized clasts of andesite or dacite, chert, jasper, sulphide mineralized tuff containing pyrite-sphalerite-chalcopryrite, or pyrite and argillite. Pervasive hematite alteration lends a purple or maroon hue to these rocks. Jasper is common in the hematite fine tuffs. The coarse tuff to lapilli-tuff contains plagioclase, minor quartz, trace amphibole, and accessory zircon and apatite.

The uppermost stratigraphic unit in the mine sequence is the upper mafic unit [DCm10]. It can be >200 m in thickness, thinning to approximately 5 to 20 m in the northeast and sometimes it can be very thin or missing entirely in areas since the contact between the Myra Formation and the overlying Thelwood Formation likely represents an unconformity. The upper mafic unit is dominantly basaltic in composition, occurring as hydroclastic and pyroclastic deposits; flow breccias and pyroclastic units are less common. Hydroclastic and pyroclastic deposits are tuff, lapilli-tuff, and tuff-breccia. Main clasts are composed of pyroxene and feldspar porphyritic basalt. Jasper $\pm$ magnetite, chert, mafic fine tuff, and epidote-rich mudstone is also present. Flow and flow breccias may occur in the middle and upper parts of the unit where the rock is pyroxene and plagioclase porphyritic with calcite and chlorite amygdales and up to 7 percent epidote veinlets. In the southern part of the mining complex the hyaloclastites in the uppermost parts of the unit are strongly hematite, calcite $\pm$ sericite altered. In the middle and lower part of the unit, sediments ranging in thickness from 2 to 7 m thick are composed of thin bedded to massive cherty-tuff, chert and epidote-rich mudstone.

The Thelwood Formation (sharp banded tuff) unconformably(?) overlies the mine sequence and is present throughout the mine property. It is from 270 to 500 m thick and consists of a repetitive sequence of thick bedded siliceous tuffaceous sediments, subaqueous pyroclastic flows, and penecontemporaneous mafic sills (Muller, 1980; Juras, 1987). The tuffaceous sediments, range from 5 to 30 m in thickness, and consist of massive to thinly bedded tuffaceous mudstone, and siltstone, mudstone, and vitric $\pm$ fine tuff. Minor chert layers are also present. Pyroclastic units, 4 to 25 m thick, are intermediate in composition and consist of vitric-lithic, lapilli-tuff to coarse tuffs interbedded with tuffaceous deposits. Mafic sills are 1 to 90 m thick and are generally massive basaltic to basaltic andesite in composition.

At least four intrusive phases are present in the mine area; these are: Paleozoic or Triassic dikes, Triassic basaltic sills and dikes related to the Karmutsen Formation, Jurassic feldspar porphyry and quartz porphyry dikes related to the Island Intrusions (Bedwell Batholith) and Jurassic or younger quartz porphyritic rhyolite and hornblende gabbro dikes. The oldest dikes are usually narrow (<1 m) dark brown aphyric and always carbonate altered. Dikes related to the Karmutsen Formation are thick, up to 300 m, coarse to very coarse grained, and contain relatively unaltered pyroxene and plagioclase crystals. The most abundant dikes are those related to the Jurassic Island Intrusions. They are up to 25 m wide and are intermediate in composition. The quartz and feldspar porphyritic rhyolite dikes are the rarest of the last intrusive series. These along with the gabbro dikes crosscut all other rocks of the Sicker Group as well as most faults.

Overburden resources, as a source of clean fill for mining infrastructure, have been the subject of an internal Westmin report (Walker, 1992). Overburden deposits range from non-existent on steep slopes to a thin to moderate veneer on hillsides, to greater than 60 m thick in valley bottoms. These sediments were deposited as: basal and washed till, end-moraine, colluvium, alluvium, and alluvial fan deposits. The desire for clean fill for construction of the tailings-pond berm led to geochemical sampling of the fine components of the B and C soil horizons. Each overburden type had similar log normal metal distributions even though the proportion of fine material varied between sediment types. Within the C horizon, median and maximum concentrations of metals in the less than 40 mesh fraction are 18 ppm and 38 ppm for Pb, 74 and 140 ppm for Zn, and

97 and 265 ppm for Cu. The oxidized B soil horizon has median and maximum concentrations in the <80 mesh of 30 and 39 ppm for Pb, 93 and 145 ppm for Zn, and 108 and 230 ppm for Cu. Interestingly, the oxidized B horizon has similar element concentrations and probability distributions as the underlying supposedly less oxidized C horizon; although, different sized fractions are compared. On average, sand and gravel combined makeup over 80 percent of the sediments.

1.7.2 Mineralization and Alteration

The Price and Myra Formations represent volcanism and volcanogenic sedimentation in an northwest-southeast trending basin developed in an intra-arc rift environment within a mature oceanic island arc system (Juras, 1987). This depositional environment has left a linear distribution of lithologies including the massive sulphide mineralization.

Delineated ore bodies within the Myra Falls camp (Figure 1-5) range in size from 10,000 tonne zinc-rich poly-metallic lenses to 10,000,000 tonne zoned massive sulphide lenses. Sulphide minerals, in decreasing abundance are: pyrite, sphalerite, chalcopyrite, galena, tennantite, and bornite. Minor amounts of electrum, stromeyerite, chalcocite, and argentite are also present. Quartz, sericite, and barite constitute non-sulphide gangue minerals (Pearson, 1993).

The massive sulphide-bearing member in the HW horizon contains of a number of massive sulphide deposits including the HW main lens, HW north lenses, and Trumpeter, Ridge and Battle zones. These lenses are mainly pyritic with sphalerite, chalcopyrite, galena, barite, and minor tennantite and bornite. Trace native gold and arsenopyrite are also present (Walker, 1985; Juras, 1987; Pearson, 1993). The Upper lenses and Gap zone are smaller baritic, precious-metal-rich polymetallic ores located higher in the stratigraphy of the HW horizon. The Hangingwall zone is located at the top of the HW horizon on the western Ridge zone (Pearson, 1993). Pre-mining inventory grades of the various zones within the Myra Falls camp are presented in Table 1-2.

Massive sulphides of the Lynx-Myra-Price Horizon commonly consist of banded sphalerite, chalcopyrite, pyrite, galena, and minor tennantite. Barite, quartz and sericite are common non-sulphides. These deposits have a smaller percentage of pyrite compared

to the HW deposits (Juras and Pearson, 1990). Ore reserves of the Price deposit are around 180,000 tonnes (Pearson, 1993) with 1.23 g Au/t, 53.1 g Ag/t, 1.10% Cu, 1.07% Pb, and 8.31% Zn (Juras, 1987).

Table 1-2. Pre-Mining Geological Reserves of the various ore deposits within the Myra Falls camp (from McKinley et al., 1997).

Massive Sulphide Deposit	Tonnes (X10 ⁶)	Au (g/t)	Ag (g/t)	Cu (%)	Pb (%)	Zn (%)
HW Main Lens	12.7	2.2	32.9	2.4	0.3	4.2
HW North Lens	4.4	2.5	32.1	1.9	0.2	4.3
Battle Zone	3.3	1.1	26.1	2.1	0.5	11.2
Gopher Zone	0.9	1.2	29.4	2.3	0.5	14.3
Lynx-Myra-Price	6.7	3.3	130.6	2.0	1.4	10.2

Trace metal contents in several sulphide samples from HW ores were examined by Wilson (1993) using electron microprobe and proton microprobe methods. Wilson (1993) reported that the main sulphides (dominantly pyrite) contain less than 500 ppm As. Cadmium is present in sphalerite (0.33 wt %) and in tennantite (0.1 to 1.2 wt %). Chalcopyrite contains up to a few tens of ppm of Se and In, and up to 500 ppm Te. Pyrite and chalcopyrite contain tens of ppm Mo.

Hydrothermal alteration coeval with massive sulphide mineralization exists both as discrete crosscutting zones in the footwall and as haloes around the ore-bodies (Juras, 1987). An extensive feeder/stringer pyrite zone is present beneath the main HW and the Lynx-Myra deposits. Pyrite is coarser grained in the stringer zone than overlying massive sulphides. Smaller feeder zones are associated with the HW north lenses, the Price deposit, and the Battle and Gap zones. Feeder zones, typically are developed in the footwall andesites where assemblages of quartz, sericite, pyrite ± chlorite have completely replaced the preexisting rock. These zones may contain up to 30% pyrite, and non-economic chalcopyrite and sphalerite. Chlorite-bearing rocks appear on the less intensely altered fringes. Additionally HW main lens feeder has a flanking albite, quartz and/or sericite assemblage which surrounds the quartz-sericite-pyrite core. This assemblage also occurs irregularly within the upper units of the Price Formation (Walker,

1985; Juras and Pearson, 1990; Pearson, 1993). In the G-zone, hydrothermal fluids may have traveled along strike and the alteration of the Myra and Price rhyolites is variable but may be intense (Juras, 1987).

The footwall rocks of the Price formation beneath massive sulphide mineralization are pervasively quartz-sericite-pyrite altered. The hydrothermal fluids responsible for the formation of the deposit were apparently K/Mg rich, which produced extensive sericite rather than chlorite alteration (Barrett and Sherlock, 1996).

The Price, Myra, and Thelwood Formations have undergone greenschist metamorphism, are mildly to moderately deformed, and have moderate to strong hydrothermal alteration. Epidote and chlorite are common metamorphic alteration minerals (Pearson, 1993; Juras, 1987).

The metamorphic facies of the mine rocks is lower greenschist; which may have occurred at a temperature of over 400 °C and at depth of >10 km (Walker 1985). Large scale folding likely resulted during metamorphism which was followed by exhumation, large scale block faulting, and more brittle deformation (see 1.6.5 Structural Geology for additional information).

1.7.3 Formation Ages

Juras, (1987) dated several of the lithologies within the stratigraphic pile. A rhyolite unit in the upper part of the Myra Formation was dated as Late Devonian (370±18/-6 Ma) using the U-Pb method. The age of the HW horizon and hanging wall HW andesite using Rb-Sr are also Late Devonian (365 Ma), while other samples may have been partially reset during later metamorphism and/or intrusion. The K-Ar ages range from 138 to 168 Ma, which may reflect the emplacement of the Jurassic Bonanza-Island Intrusions (Bedwell batholith) and the beginning of subsequent uplift (Juras, 1987). Barrett and Sherlock (1996) report an age of 365±4 Ma for the lower Myra felsic sequence directly overlying the HW deposit. The Thelwood formation (sediment sill unit of Muller) overlying the Myra formation contains radiolaria of Early Mississippian age (Muller, 1980). These ages constrain the Myra formation between Late Devonian to Early Mississippian age. Hamilton (1993) reports that the Bedwell batholith has been recently dated at 187 ±7 Ma (Middle Jurassic) using the U-Pb method in zircon by (R.L.)

Armstrong of U.B.C. The Bonanza Island (Intrusive) Group is correlated with Bowen Island Group metavolcanic rock which has been dated at $185 \pm 8/-3$ Ma (Friedman and Armstrong, 1995).

1.7.4 Lithogeochemistry

Whole rock lithogeochemical sampling was conducted by J.V. Hamilton during the summer of 1994 while working under contract for the GSC/Westmin IPP and later while employed by Westmin resources (fall 1994). Whole-rock geochemistry, although not as desirable as mineral separate chemistry, since different minerals will not weather equally, may be used to ascertain the source lithology(s) of various constituents in ground water. Median rock concentrations are summarized in Table 1-3 for lithologies using the mine stratigraphy developed by Juras (1987), and correspond to units designations in the schematic mine section in Figure 1-6. Included Table 1-3 are analyses for the Thelwood and Price formations from Juras (1987), which were not sampled by Hamilton. Sampling was conducted on Price hillside (Juras) and within Price 4 and 9 levels and drill holes from those drifts, as well as drill holes located in Thelwood Valley (Hamilton; analyses summarized in Table 1-3). Sampling lithologic units can be confounded by alteration, which in many cases obliterates the original texture and composition of the rock.

Oxidized ground waters traversing the stratigraphy will mobilize elements related to the individual units. Ground water will likely assume a complex chemical history as fracture controlled flow will move water along permeable zones throughout the strata often irregardless of lithology. Assuming solutes remain in solution, the dissolution of minerals as the water traverses heterogeneous mineralogy will result in a combined chemical history of the fluid. The sources of trace elements in the ground waters, if they remain in solution, may be discerned from the host lithologies. For example mafic units may contribute elements such as Ni, Cr, Co, V, Mg, and Mn. Ground waters associated with zones of intense alteration may be enriched in K. Uranium is enriched within the ore, and also within discrete fault zones (J. Mwenifumbo, personal communication). Dissolution of ore zones will enrich the ground water in sulphate and may also mobilize trace elements related to the ore deposit such as Zn, Cd, Cu, and Pb. Boron is enriched in L-M-P unit. Arsenic is enriched in ore and in argillic units.

Table 1-3 Median concentrations for rock samples from Myra Falls mining complex. Rocks are from the Price area and Thelwood valley. Analyses was done at GSC lab (Si-U) and XRAL Laboratories (B-Th, all in ppm)

Description	Price Fm* basaltic- andesite	Massive Sulphide (H-W)	H-W rhyo- dacite	H-W DCm1r	H-W mafic	H-W argillite	H-W QFP	H-W hanging- wall andesite	Diss Min DCm1DC m2	Ore-Clast Breccia (OCB)	P-P faults	Lower mixed volcano- clastics	N Dacite	Upper Dacite	Upper Dacite FPD
Unit				DCm1a	DCm1m	DCm1a	DCm1q	DCm2		DCm3		DCm4	DCm5n	DCm5u	DCm5u
No. of analyses	5	8	17	12	3	2	22	wt %	5	43	8	10	4	20	4
SiO2	54.3	1.4	68.3	55.4	78.5	69.8	50.2	51.7	58.1	55.9	55.6	55.6	68.2	58.0	70.4
Al2O3	16.7	0.3	14.2	17.6	5.8	13.2	16.7	12.3	14.7	16.1	16.1	16.5	14.3	16.3	14.1
Fe2O3	10.2	54.6	5.1	8.2	3.4	3.0	9.9	6.4	6.7	7.5	8.3	8.3	3.2	7.2	2.7
MnO	0.16	0.01	0.04	0.13	0.03	0.06	0.16	0.03	0.11	0.13	0.12	0.12	0.06	0.12	0.03
MgO	6.12	0.06	1.48	3.33	1.53	1.14	4.77	1.33	2.67	2.53	3.56	3.56	0.79	3.11	0.44
CaO	7.12	0.19	2.89	5.26	2.33	3.66	7.94	3.39	5.19	7.09	5.26	5.26	2.85	4.56	1.81
Na2O	4.34	0.08	0.9	1.9	0.3	3.0	2.55	0.6	2.1	1.3	2.5	4.55	3.85	4.75	
K2O	0.18	0.05	3.0	2.73	1.42	2.02	0.43	3.18	1.34	1.81	1.99	2.44	1.04	3.29	
CO2	--	0.4	1.8	1.05	3	2.75	2.35	2.3	1.9	5.05	3.65	2.1	2.2	1.5	
P2O5	0.28	0.02	0.1	0.29	0.1	0.09	0.16	0.1	0.15	0.17	0.29	0.10	0.2	0.10	
S	--	46.1	0.09	0.04	0.37	0.06	0.02	4.93	0.35	0.77	0.37	0.03	0.02	0.02	0.01
Ba	164	3650	1700	855	1500	1200	335	5100	940	945	665	630	590	760	
Be	--	0.25	1.0	0.70	0.50	1.15	0.38	0.90	0.60	0.75	1.25	1.45	0.80	1.20	
Co	--	2.5	2.5	15.0	2.5	3.8	23.0	2.5	13.0	19.0	14.5	5.0	11.0	2.5	
Cr	95.0	5.0	5.0	8.0	40.0	7.5	38.0	5.0	12.0	12.5	30.5	8.5	8.0	5.0	
Cu	68	69000	33	59	42	30	47	2600	60	96	54	17	22	5	
Ni	35	29	5.0	5.0	55	5.0	16	5.0	5.0	5.0	5.0	5.0	5.0	5.0	
Sc	--	2.7	8.9	24.5	6.1	8.0	30.0	7.2	22.0	23.5	22.0	8.1	24.0	7.6	
Sr	424	29	150	385	61	195	370	76	250	205	205	185	370	175	
Zn	100	7000	82	93	240	74	86	27000	200	260	92	51	95	28	
Ag	--	88	0.1	0.1	0.6	0.25	0.1	22	0.5	0.7	0.2	0.1	0.1	0.08	
Bi	--	205	0.5	0.5	0.5	0.5	0.5	2	0.5	0.5	0.5	0.5	0.5	0.5	
Cd	--	--	--	--	--	--	--	--	--	--	--	--	--	--	
Cs	--	0.04	0.76	0.73	0.39	0.47	0.24	0.72	0.46	0.95	0.63	0.44	0.42	0.38	
Mo	--	155	1.6	0.8	13.0	0.35	0.5	9.2	1.6	1.65	0.9	6.8	0.55	0.35	
Pb	--	240	13.0	5.5	21.0	29.0	4.0	1100	30.0	28.5	7.5	5.0	5.5	5.5	
Rb	4	0.9	53.0	50.0	29.0	35.0	7.2	58.0	21.0	27.0	40.5	39.0	18.5	43.5	
U	--	14	1.3	0.8	3.9	1.2	0.4	3.1	1.1	1.4	1.1	1.1	1.1	1.8	
No. of analyses	8	6	5	3	2	2	8	5	13	0	3	2	6	4	
B	--	10	18	<10	15	14	<10	36	<10	--	13	<10	<10	<10	
As	--	245	16	6.0	150	6.0	3.5	60	20	--	9.0	<2	<2	<2	
Se	--	17	<5	<5	<5	<5	<5	<5	<5	--	<5	<5	<5	<5	
Br	--	<1	<1	<1	<1	<1	<1	<1	<1	--	<1	<1	<1	<1	
Sb	--	180	0.75	1.5	1.7	0.9	1.05	7.5	3.0	--	0.6	0.4	1.0	0.2	
Th	--	0.7	3.1	2.0	1.5	4.1	1.3	2.8	2.0	--	3.2	5.1	2.9	5.1	

* from Juras (1987)

Table 1-3 continued

Description	L-M-P (rhyolite- sericite- schist)	Massive Sulphide (Price)	L-M-P hanging- wall	G-flow unit	G-flow? mafic	Upper mixed volcano- clastics	Upper Mafic Unit	Pr4 faults	Pr4 alteration	OCB with minor sulphides	Cherts	Thelwood Fm* pyroclastic deposits	Thelwood Fm* mafic sill basaltic
Unit	DCm6	DCm6h	DCm7	DCm7(?)	DCm8	DCm10							
No. of analyses	5	7	12	2	6	15	7	13	18	7	8	3	4
	wt %												
SiO ₂	60.4	12.2	60.6	43.8	50.3	53.4	49.1	57.3	60.1	55.4	81.4	68.6	53.8
Al ₂ O ₃	16.2	3.3	14.6	12.1	15.1	16.6	15.2	15.2	15.3	16.3	5.9	12.9	14.8
Fe ₂ O ₃	6.1	43.3	5.9	9.5	8.7	8.0	10.0	5.6	5.4	8.9	2.6	7.5	14.0
MnO	0.04	0.02	0.08	0.20	0.16	0.10	0.20	0.16	0.10	0.11	0.04	0.16	0.26
MgO	1.05	0.5	2.12	12.2	5.31	3.12	3.35	2.36	2.05	3.44	0.91	2.15	4.68
CaO	2.69	0.8	4.6	10.4	8.54	5.9	6.81	9.6	3.58	6.02	2.34	3.82	6.59
Na ₂ O	0.37	0.145	2.7	1.5	2.3	3.4	0.8	0.3	0.7	2.9	0.95	2.68	3.8
K ₂ O	3.96	0.87	1.6	0.05	0.57	1.14	1.69	1.95	3.13	0.76	0.51	1.29	0.06
CO ₂	2.1	1.4	2.6	4.7	4.3	1.9	2.0	3.2	2.8	1.0	1.55	--	--
P ₂ O ₅	0.21	0.02	0.14	0.16	0.18	0.22	0.12	0.17	0.19	0.17	0.06	0.19	0.38
S	3.36	37.1	0.01	0.01	0.01	0.04	0.01	0.04	2.31	0.60	0.03	--	--
	ppm												
Ba	1700	8600	820	270	400	730	700	1300	1350	700	310	620	69
Be	0.90	0.25	0.80	0.25	0.70	0.70	0.50	1.10	0.90	0.70	0.25	--	--
Co	9.0	10.0	9.5	43.5	30.0	14.0	28.0	9.0	12.5	19.0	3.8	--	--
Cr	17.0	5.0	19.5	1300	650	23.0	140	79.0	12.0	10.0	8.0	21.0	19.0
Cu	26	27000	5	83	31	54	30	5.0	39	240	22	15	24
Ni	5.0	32	30	275	190	13	61	26	5.0	5.0	10	15	18
Sc	19.0	4.3	20.0	39.0	34.5	27.0	39.0	20.0	16.5	25.0	5.2	--	--
Sr	86	71	380	210	360	320	180	350	150	320	75	338	198
Zn	160	6200	74	82	110	110	98	110	140	540	46	100	98
Ag	0.8	23	0.05	0.175	0.05	0.1	0.1	0.1	0.3	1.2	0.1	--	--
Bi	0.5	57	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.6	0.5	--	--
Cd	--	23.0	--	--	--	--	--	--	1.60	2.35	--	--	--
Cs	1.1	0.13	0.57	0.14	0.48	0.36	0.58	3.6	0.61	0.19	0.15	--	--
Mo	2.3	64.0	0.35	0.3	0.3	0.65	0.3	0.5	2.2	2.5	0.5	--	--
Pb	37.0	520	4.0	2.5	5.5	6.0	5.0	7.0	38.5	46.0	10.0	--	--
Rb	60.0	12.0	37.0	0.8	12.6	20.0	41.0	44.0	45.5	11.0	12.3	17.0	<4
U	1.3	4.7	1.0	0.4	1.0	1.3	0.3	1.1	1.4	0.9	1.3	--	--
No. of analyses	4	2	6	2	3	7	4	0	0	2	0	--	--
B	30	13	<10	<10	<10	<10	<10	--	--	<10	--	--	--
As	20	350	<2	3.0	3.5	3.0	4.0	--	--	1009	--	--	--
Se	<5	30	<5	<5	<5	<5	<5	--	--	20	--	--	--
Br	<1	<1	<1	<1	<1	<1	1.0	--	--	<1	--	--	--
Sb	3.4	28.0	0.65	0.55	0.9	0.7	0.7	--	--	15.6	--	--	--
Th	3.05	2.6	1.95	0.9	1.25	2.4	1.8	--	--	1.7	--	--	--

* from Juras (1987)

1.7.5 Structural Geology and Structural History

The regional structure of northern Vancouver Island during the Mesozoic and Tertiary has been discussed by Nixon et al. (1994), who proposed three phases of deformation. Phase 1 occurred during the mid to late Jurassic and is characterized by NE compression and NW striking thrusts, and NW trending folds (including the Buttle Lake uplift). Phase 2 is characterized by N compression and NW striking oblique dextral faults during the Late Cretaceous. During the Tertiary (phase 3) NW-NNW extension, and NE-ENE striking normal faults, and reactivation of wrench faults took place. [Orientations in this and the next section are relative to map co-ordinates, not mine co-ordinates unless specified; mine north is approximately 45° E of map north.]

Several studies (i.e., Juras, 1987; Reid, 1992; and Berry, 1995) have addressed structural geology within localized areas of the mining complex. These studies were intended to address specific problems generally related to the massive sulphides and host lithologies within the mine complex, and in so generally did not address how these structural elements relate to the tectonic history of the Buttle Lake uplift and surrounding terrane. As part of the hydrology component of the GSC/Westmin IPP program J.V. Hamilton was employed as a consulting geologist to map the structures (and lithologies) of Price 4 and 9 levels. Results of that work are presented in Hamilton (1993).

Structural elements began with initial and resurgent rifting during the emplacement of the ore deposits and surrounding volcanic sequences approximately 370+ Ma (Devonian) in a rifting volcanic arc / back arc basin. During Carboniferous and Permian time, erosion leveled the volcanoes to form a shallow submarine plain on which crinoids, brachiopods, and bryozoa flourished forming limestone of the Buttle Lake Formation (Yorath and Nasmith, 1995). Rifting, resumed again in the late Triassic resulted in basaltic volcanism of the Karmutson Formation which is characterized by pillow lavas in the lower sequence and lava flows in the upper parts (Yorath and Nasmith, 1995). Juras (1987) recognized a pre-Island Intrusive deformation made up of sub-vertical NW striking faults.

The Jurassic was a busy time for the terranes making up Vancouver Island. The Bonanza Group volcanics including the Island Intrusion Suite and local metamorphism

occurred during this period (Yorath and Nasmith, 1995). Wrangellia, Alexandria, and the (Alaska) Peninsula terranes, including the western Coast Belt, if correlations are correct, were unified by the time of the major magmatism of the Bonanza-Island arc (circa 200-165 Ma) (Friedman and Armstrong, 1995). Even if the western Coast Belt (mainland B.C.) was not amalgamated to the Insular Super terrane during the earliest Jurassic it had accreted to the Wrangellia terrane prior to docking with the North American plate (Friedman and Armstrong, 1995). The intrusion of the Bedwell batholith likely marked the onset of initial uplift of this area.

During the mid-Cretaceous, approximately 100 Ma ago, Wrangellia (Insular super-terrane) accreted to N. America (Jones, et al., 1982, Yorath and Nasmith, 1995). The collision resulted in intense deformation and metamorphism and was followed by uplifting of the terranes to the east. Relatively undeformed Tertiary granites in the eastern terranes indicate that accretion of Wrangellia to the North American craton was complete by the Tertiary (Jones, et al., 1982). Sediments forming the Nanaimo Group were shed into low basins with shallow swampy margins (ca. 85 Ma) (Yorath and Nasmith, 1995). During accretion, Wrangellia was compressed forming the Cowichan and Buttle Lake Anticlinoria.

Not surprisingly, with the tectonic events occurring to the terranes making-up Vancouver Island during the Mesozoic, the predominant deformational event(s) in the Myra Falls camp is Mesozoic in age and affects all pre-Mesozoic stratigraphy in the area (Juras, 1987). Structural geology of the mine site is dominated by a period of NE-SW compression resulting in ductile and brittle deformation during the Mesozoic (Pearson, 1993). This was followed by a period of relaxation that was accompanied by extensional faulting.

During the Tertiary period, the Pacific Rim and Leech River complexes (~55 Ma), and the Crescent Terrane (~42 Ma) were accreted to Vancouver Island. These later collisions resulted in the uplift of the western and southern margins of Wrangellia. As much as 10 km of erosion may have been shed from central and southern Vancouver Island during and after the uplift (Yorath and Nasmith, 1995). Compression from the Tertiary accretions was translated to the eastern side of Vancouver Island resulting in the folding and faulting of the Nanaimo Group forming the Gulf Islands.

At least three glaciations occurred on Vancouver Island during the Pleistocene; although evidence of previous glaciations have been mostly eradicated by the latest, the Fraser glaciation (Yorath and Nasmith, 1995). The Fraser alpine glaciation began around 29 Ka years ago, climaxed approximately 15 Ka years ago. The glacier ice likely covered mountains on Vancouver Island up to the present 1200 to 1500 m contour at the 49th latitude (Mathews et al, 1970). Ice depth thinned towards the south and likely exceeded 1500 m (above modern sea level) in central Vancouver Island (Clague, et al., 1982). The mountain glaciers coalesced to fill the valleys and the coastal depression, and ocean straights. Accumulation of ice during the glacial maximum was greatest in the Strait of Georgia, due to confluence of alpine glaciation, which resulted in the east coast of Vancouver Island being depressed by 150 to 300 m (Mathews et al., 1970; Yorath and Nasmith, 1995).

Uplift in the region of Myra Falls within the Vancouver Island Mountain Ranges has been estimated to be $2 \cdot 10^3$ m in the last 10 Ma years (Parrish, 1983; Monger, 1991; Monger and Journeay, 1992). The greatest uplift on Vancouver Island has occurred through the central portion of the island which is coincident with the Nootka fault zone and is likely due to crustal tilting (and uplift) from the geometry of accommodating the Explorer and Juan de Fuca plates during subduction (Dragert, 1987). The area is still quite tectonically active and epicentres of at least two major on-shore earthquakes have been recorded on Vancouver Island this century (Holdahl et al., 1989). The 1946 earthquake may be responsible for a landslide above the HW mine shaft. Contemporary vertical uplift in the Myra Falls region is around $1\text{-}2 \text{ mm yr}^{-1}$ (Holdahl et al., 1989).

1.7.6 Faulting

Numerous high angle normal faults, some with strike slip, occur on the mine property (Juras, 1987). Many of the faults are associated with schistose zones and are gouge and/or breccia filled. The majority of the faults are probably post-Mesozoic having formed during uplift in the Late Cretaceous (Yorath et al, 1985), or during a local(?) extensional regime during the Tertiary (Muller, 1980).

The interpretation of faulting within the mine is generally consistent with that occurring in a regional context with the exception that early faults have been reactivated

during the Cretaceous instead of the dextral movement on NW striking faults as seen in northern Vancouver Island (Berry, 1995).

Fracture filled veining within the camp is dominantly quartz-chlorite-calcite (Pearson, 1993; Juras, 1987). Except for the early quartz-chlorite-carbonate-hematite veins that are clearly overprinted by the early shear structures, most of the quartz veins and veinlets in the Price area are relatively late (Hamilton, 1995).

Berry (1995) notes that veining in the upper Myra formation associated with pre-Jurassic deformation tends to be calcite rich and with minor epidote. Deformation during this stage was ductile, likely occurring during peak metamorphism. Shearing occurs in steep NE dipping (left lateral?) strike-slip zones striking NW. Late Mesozoic deformation includes ductile and brittle textures (discrete faults surrounded by narrow cleavage zones). Quartz-carbonate veining is associated with this phase of deformation. Tertiary faults tend to accommodate normal movement and may be gouge filled. Extension is towards the NE and may possibly correlate with the formation of the Queen Charlotte basin. Hamilton (1993) also noted that late normal faulting tends to be gouge filled (e.g. North fault).

Sub-vertical strike-slip faults in the Price area are aligned along the ore-zone in the Lynx-Myra-Price horizon (Berry, 1995) and strike-slip movement in the Price drifts was identified by Hamilton (1993) as being one of the earliest deformational features. Hamilton (1993) also identified late stage reactivation of early fault systems in the sense of dip-slip or steeply-oblique movement on various early surfaces.

Within the area of study the major faults are the Myra-Price fault, the North fault, and many faults accommodating extension in the Thelwood Valley (Figure 1-7). The surface trace of the Myra-Price fault runs from near the top of Myra Peak, across Price hillside and enters the floor of Thelwood Valley at 180+00E, 147+00N (Plan map in back pocket). It is a major structure in the Myra-Price ridge, which offsets stratigraphy both left-laterally and down-dip. The fault trends between 040° and 050° and has a moderate to steep dip to the N (Hamilton, 1993). Price 4 and 5 levels do not intersect the Myra-Price fault; however, the projection of the fault takes it over the top of the west end of 4 level. Drill holes in the north wall near the end of 4 level appear to cut wide sections of disturbed ground which undoubtedly represents the Myra-Price fault (Hamilton, 1993).

The Myra-Price fault cuts Myra 13 level at ~40+40 m E, and Myra 10 at ~41+00 m E, is intersected by drill holes at the southern end of HW20-371 xcs (mine co-ordinates), and is intersected by drill holes in Thelwood Valley. Several (mine) E-W trending, moderately to steeply north dipping faults cut across Price hillside. These faults are generally gouge- and fault breccia-filled appearing in parallel sets and/or merging faults (Hamilton, 1993). The faults downdrop stratigraphy to the north. These faults may be localized along earlier E-W (mine co-ordinates) trending shear zones or zones of weakness associated with an earlier compressional phase of deformation. The North fault and the (mine) E-W oriented, late faults in the hanging wall of Price 4 Level are examples of this generation of major extensional faulting. The is intersected by drill holes in Thelwood Valley, and by HW 20-415 xcn and HW 21-316 xcn drifts.

Faults orientated 070° (mine co-ordinates) in the Price area, and the E-W trending strike slip faults may represent late faulting equivalent to phase 3 of Berry (1995). The 070° faults are not as dramatic as faults of other orientations, and although these faults are relatively short and narrow they control stream patterns in the area of Price 4 Level (Hamilton, 1993).

The structural geology is complicated with many faults at several predominant orientations. Tracing even major faults within the property can be difficult and the interpretations of structural geology of the property is under continual revision as additional information is unearthed. Fractures, faults, and alteration zones act as conduits for ground-water flow. Difficulty often exists in trying to isolate individual interconnected fault networks and therefore also individual (discrete) flow paths within each fault system.

~57+50m E

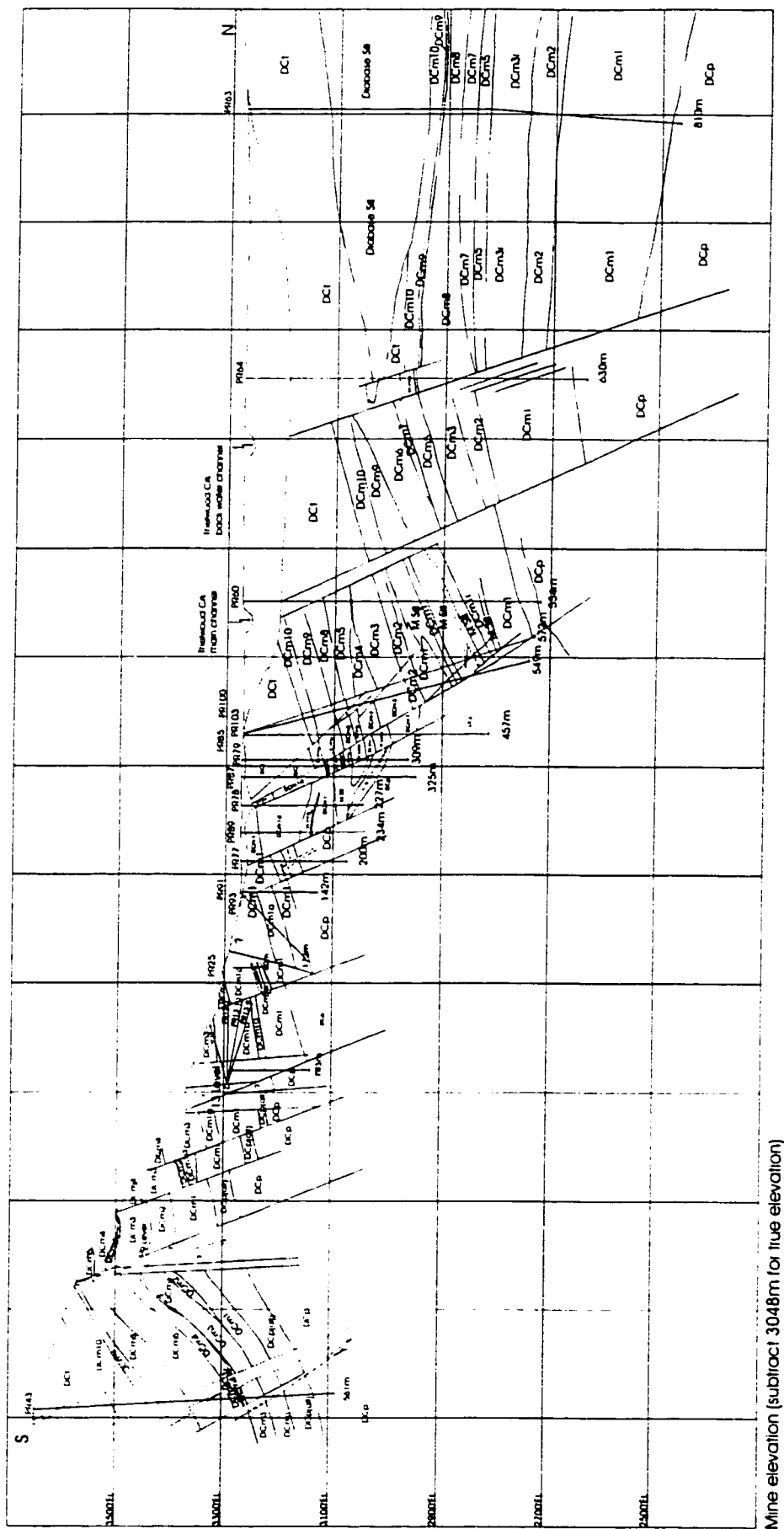


Figure 1-7. Section approximately through 57+50m E from lower Price hillside into Thelwood valley illustrating the complex structure with successive extensional faults down-dropping the mine sequence towards the North. . Unit designations are those of Juras (1987). Section drawn by J. V. Hamilton (unpublished).

1.8 Hydrology

A concurrent study of the physical hydrology within the Myra-Price Ridge (Myra and Price mines) is conducted being by Martin Stapinsky (thesis in progress) at the Ottawa-Carleton Geoscience Centre. A comprehensive discussion of the hydrology of this area can be obtained by consulting that body of work.

Permeability in fractured material will be dominated by the interconnected fracture network and to a much lesser extent by rock matrix porosity. Diffusion into and out of the rock matrix, dead-end pores, and immobile fluid zones within the uneven surface of fracture openings will influence solute transport (Neretnieks, 1980, Raven et al, 1988). Faults may act as barriers to ground-water flow in high permeability material, but they may also represent migration pathways in low permeability crystalline rocks. Gouge-filled faults may be accompanied by an outer damaged or fractured zone with higher permeability than the surrounding rock which will allow greater ground-water flow, if mineral precipitates do not reduce the porosity (Smith et al., 1990). The hydrology of fractures and shear zones is generally difficult to study, especially on a scale greater than 10's of metres. Fracture dominated hydrology in crystalline rock is of particular interest lately, especially in the context of establishing long-term safe repositories for spent nuclear fuel. Ground-water flow in fractured crystalline rock has been studied for example, at Aspo (Sweden) by Banwart et al. (1994), and Smellie et al. (1995), Stripa (Sweden) by Abelin et al. (1991).

Mine openings will undoubtedly have an effect on the pre-mining local hydrology. Such effects have been studied on the local hydrology due to various types of underground mining activities such as mine openings (i.e., Stoner, 1983; Vincent et al., 1991), shaft excavations (Yanagizawa et al., 1995), and tunnels (Shimajima et al., 1993). The effects of mining on local hydrology is also a foci of this thesis, especially in terms of altering pre-mining hydrochemistry and also of thesis of Martin Stapinsky (OCGC).

Surface drainage consists of permanent and intermittent streams that tend to follow zones of structural weakness. Late-stage faults have the longest lengths and may be the most permeable component within the Price area. The majority of recharge within the mountain core is likely contributed from these late extensional faults that control stream positions overlying the Price ore body (Hamilton, 1994). Many of the streams appear to be 'losing' streams; this is especially apparent at lower elevations where streams flow over coarser colluvium/alluvial material. Streams have intermittent flow and many are waterless during

arid periods A stream overlying Price 4 level was never observed to be dry in its channel proximal to the adit, yet this stream was never observed to be flowing at the road in Thelwood Valley (late spring and summer observation period). Likewise, a second stream north of Price 4 would cease to run or flow at very low volumes at the Thelwood Valley road, while some flow would inevitably be encountered when tracing the stream bed up the hill. Since streams are likely the greatest component of recharge to the mountain, stream water chemistry should well represent the input or recharge water chemistry to the core of the mountain.

Underground drill holes instrumented with pressure sensing transducers within the Price hillside indicate that response to precipitation events is rapid with a sharp recession after recharge events (Stapinsky et al., 1997). This response is characteristic of bi-modal permeability; rapid response to precipitation is characteristic of fracture flow, while base flow is typical of the influence of matrix porosity. The base flow response observed in this setting was attributed to smaller scale fracture sets. An apparent bulk hydraulic conductivity of the rock surrounding the Price 4 level drift was calculated as ranging between $5 \cdot 10^{-9}$ to $5 \cdot 10^{-8}$ ms^{-1} , similar to fractured granitic rocks.

Inflows into the mine are not excessive and generally decrease with depth and towards the central core of the mountain (Myra-Price ridge ground water divide). The first 100 or so metres into drifts accessed from the hillside on the mountain (within the fractured rock carapace) tend to be wet. In the remainder of the drifts the majority of water inflows are from fractures and faults, and open drill holes that channel water into the drifts from intersected permeable structures. Wet areas in the drift itself are generally composed of several or many small scale fractures within an area that combine to form drips and wet surfaces. These are then separated by dry areas of rock. Flow volumes from drill holes within the drifts may range from a low of a drip every minutes (lowest recorded flow was $4 \cdot 10^{-7} \text{L min}^{-1}$, site 2352) to greater than 30 L min^{-1} (for margot plugged holes on Price 9 level). The vast majority of ground water samples collected in the mine drifts are from flowing drill holes. Occasionally, the drift walls are damp without any other source of structurally controlled water nearby, possibly indicating matrix flow (i.e., precipitate sample S1003), or condensation on the cool wall from moisture laden ventilation air.

2. Environmental Isotopes

2.1 Introduction

Environmental isotopes form an important contribution to hydrogeologic studies by acting as natural tracers of recharge processes, provenance, solute source, and identifying mechanisms of incorporation (dissolution) of solutes, hydrogeochemical evolution, water-rock interaction, and mixing of ground waters from different reservoirs. Isotopes have played useful roles in identifying modifications to hydrogeologic regimes due to manmade perturbations such as tunnel and shaft openings (Nordstrom, et al., 1992, Banwart et al., 1994; Smellie et al, 1995); which have implications towards mine dewatering and water quality, and as analogues of waste repositories.

Recent reviews on the utility of environmental isotopes in hydrological studies can be found in Clark and Fritz (1997) and Mazor (1997).

The following sections 2.2 to 2.9 present observations and characterizations of isotopes in Myra Falls waters, mechanisms of solute incorporation, and processes. Discussion of the effects of mining on ground water circulation and further discussion on saline water is presented in Chapter 6

2.2 ^{18}O and ^2H - Stable Isotopes of Water

2.2.1 Introduction

Stable isotopes of oxygen and hydrogen act as useful tracers in hydrological studies of mountainous areas, such as: identifying variation of isotopic signature as a function of elevation and applying that information to identifying recharge elevation of waters in underground openings; and developing an understanding the hydrogeologic character and flow paths within crystalline rock aquifers. Much of this research has taken place in the Alps (Switzerland, Italy, and France) (Fontes et al., 1980), (Siegenthaler and Oeschger, 1980), (Schmassmann, 1990). Stable isotopes of O and H have also been important in assessing water-rock interaction in geothermal, volcanic, and convergent plate margin settings (Blattner, 1984; Giggenbach, 1992; Nesbitt and Muelenbachs, 1995). Analytical results, and materials and methods for ^{18}O and ^2H in Myra Falls waters are presented in Appendix B (Isotope Data).

2.2.2 Rainfall (LMWL)

Monthly rainfall was collected (August, 1993 to July, 1995) at the Environment Canada Meteorological station (360 m elevation) located within the mine site in Myra Valley. Only rarely does snow fall during the winter months at the meteorological station in Myra valley as opposed to high snowfall on the mountains during this same time period. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic values of weighted mean rainfall based on 19 monthly aliquots of precipitation are $\delta^{18}\text{O} = -12.0\text{‰}$, and $\delta^2\text{H} = -87.2\text{‰}$ VSMOW, which lie on the global meteoric water line (GMWL) as defined by Rozanski et al. (1993).

There is seasonal variation in the rainfall. The winter MWL plots above the line for summer rains. The local meteoric water line (LMWL) for the high precipitation winter period from October to March (see Section 1.6 Climate) is:

Equation 2-1

$$\delta^2\text{H} = 8.49 \pm 1.47\text{‰} \cdot \delta^{18}\text{O} + 15.1\text{‰}; \text{ with a deuterium excess} = 9.1\text{‰};$$

and for the dryer summer period from April to September, the LMWL is:

Equation 2-2

$$\delta^2\text{H} = 8.39 \pm 0.97\text{‰} \cdot \delta^{18}\text{O} + 7.79\text{‰}; \text{ with a deuterium excess} = 3.1\text{‰}.$$

The summer LMWL at Myra Falls has a similar slope to the summer MWL recorded at Victoria, B.C. (Fritz et al., 1987), while both water lines from Myra Falls lie above those for Victoria precipitation which are:

$$\text{winter} - \delta^2\text{H} = 7.5\text{‰} \cdot \delta^{18}\text{O} - 1.6\text{‰}; \text{ with a deuterium excess} = 3.9\text{‰}.$$

$$\text{summer} - \delta^2\text{H} = 8.3\text{‰} \cdot \delta^{18}\text{O} + 3.9\text{‰}; \text{ with a deuterium excess} = 1.6\text{‰}.$$

The deuterium excess (d ; $d = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$, largely a measure of the relative humidity in the source area, is greater at Myra Falls than at Victoria. The deuterium will be greater under less humid conditions due to kinetic fractionation (Rozanski et al., 1979).

The Myra valley precipitation data has wide variations between individual months within summer and winter periods. Some summer rains are as depleted as winter precipitation. This variation is also seen in the Victoria rainfall (Figure 2-3); where there are some summer months with precipitation having values as low as the depleted winter precipitation (e.g. Victoria June 1980; and June, July and August, 1994 at Myra Falls).

The winter precipitation at Myra Falls has high deuterium excess, which may be due to lower relative humidity in the vapour source region in winter or the effect of a high proportion of snow fall from the vapour mass. The higher deuterium excess from stations dominated by winter precipitation was noted by Rozanski et al. (1993) from the IAEA global isotope monitoring network (GNIP - Global Network for Isotopes in Precipitation).

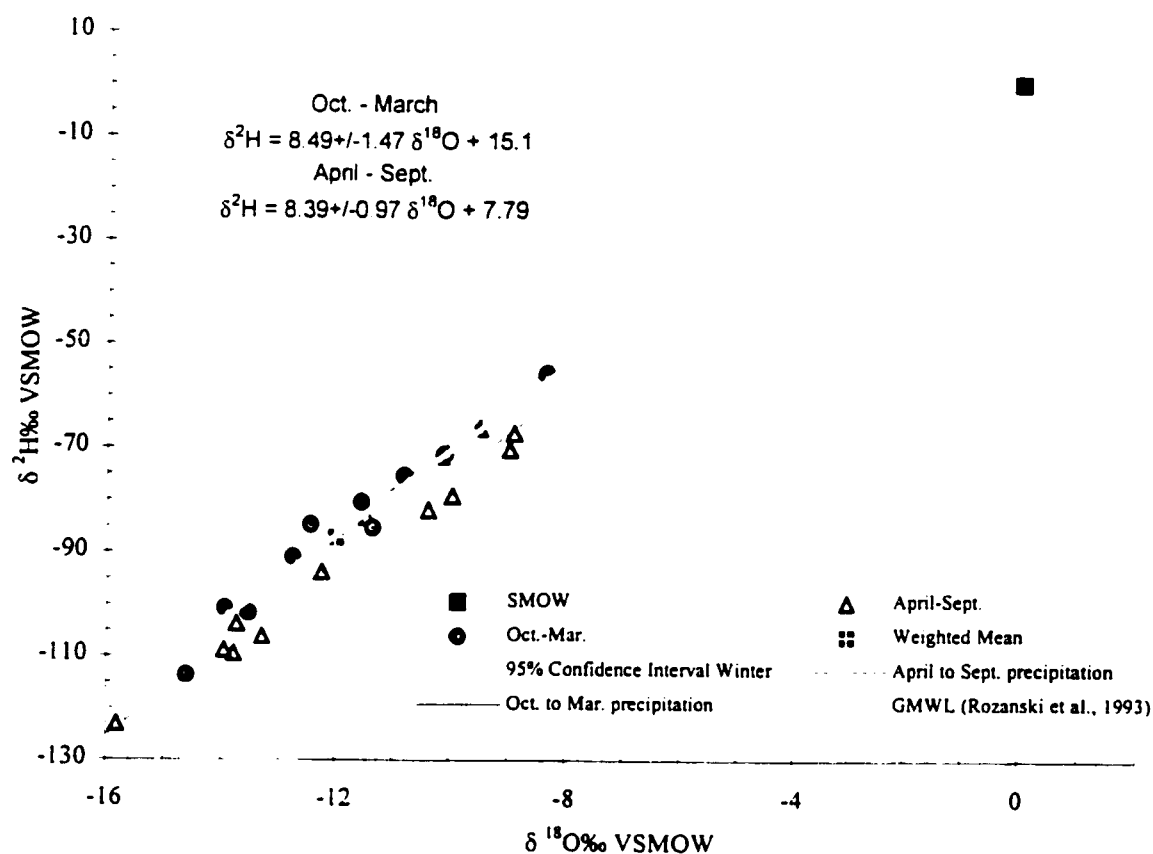


Figure 2-1 Deuterium - ^{18}O of summer, winter, and amount-weighted precipitation. Winter, summer, and global precipitation lines are shown, as well as confidence interval for the winter precipitation which includes the world meteoric line within its boundary.

2.2.3 ^{18}O - ^2H : Stable Isotope Temporal Monitoring

An intermittent monitoring record exists for a number of sites from July 1993 to September 1995. The location and pertinent data of sites is listed in Table 2-1. Several of the original monitoring sites were discontinued due to their inaccessibility during the winter months (Lynx 5 and 6 portal, and S1) and the extra sampling burden placed upon the

Westmin staff who were collecting the waters. Other sites were added to the monitoring program in 1994 due to the shift in emphasis from a property wide study to one focusing primarily on the ground waters of Myra and Price mines, and Thelwood Valley. The sampling periodicity in these samples is too irregular to make much more than general statements about temporal variations within the sites which were being monitored.

One year of continuous monthly composite rainfall (October 1993 to September 1994) and intermittent monthly sampling show a general decrease in $\delta^{18}\text{O}$ during the winter months (Figure 2-2), which is similar to the trend, although with less range, for precipitation in Victoria B.C. (Figure 2-3).

All monitoring sites, with the exception of U2 (HW20-832), plot below the mean weighted rainfall $\delta^{18}\text{O}$ value of -12.0‰, implying that winter precipitation, and precipitation falling at high elevations are large contributors to these waters. Surface waters have different trends than ground waters. Sites S1 and Arnica are both located on the Phillips ridge side of Myra Valley, and the few data point from these two sites appear to behave in a similar fashion. Variations in isotopes in rainfall are greater in stream S2, which has several tributaries draining areas of steep relief on Price hillside below the drainage divide on Mount Myra.

The most obvious observation from the data is the attenuation of the variation in input from rainfall to surface waters and finally to ground waters. Surface waters show a slight sinusoidal pattern which is attenuated in ground waters; although, a similar but less pronounced pattern exists between surface and ground waters (i.e., N fault 20 level- U1: 13 level - U3). This implies there is an advection dominated piston flow through faults and the fault damaged zones and fractures and only limited dispersion. The fact that there is greater than 600 m of rock overlying the N fault intersection on HW20 level, and greater than 200 m of rock overlying U3 on Price 13 level portrays the strong advective flow in highly permeable zones within these crystalline rocks.

The monitoring of a flowing saline water source on HW 20 level (U2) illustrates the lower variability of $\delta^{18}\text{O}$ with increasing Cl^- in saline ground water at depth (mean = $-6.41 \pm 0.16\text{‰}$ (1σ)) and reflect a uniform source of saline water (see Section 2.2.7).

Table 2-1 Temporal monitoring site stable isotope information.

Site	Type	Location	Easting (m)	Northing (m)	Elevation (m asl)	Duration of monitoring	Number of analyses $\delta^{18}\text{O}$	Mean $\delta^{18}\text{O}\text{‰}$ VSMOW	$\delta^{18}\text{O}$ Std. Dev.	Number of analyses $\delta^2\text{H}$	Mean $\delta^2\text{H}\text{‰}$ VSMOW	$\delta^2\text{H}$ Std. Dev.
Rainfall	precipitation weighted mean	Myra Valley	20+10	30+18	360	09/93-07/95	19	-11.8 -12.0	1.9	19	-86.8	16
M1	Myra Creek	upstream of powerhouse	18+90	15+25	345	07/93-09/95	7	-12.8	0.78	6	-87.2	4.8
M2	Myra Creek	before Myra Falls	38+31	51+45	293	07/93-08/94	7	-12.5	0.40	7	-90.0	3.4
L5	portal effluent	Lynx 5 level Lynx open pit	17+18	34+91	549	07/93-08/94	5	-12.9	0.19	5	-91.7	0.8
L6	portal effluent	Lynx 6 level Lynx open pit	16+95	33+54	571	07/93-08/94	5	-12.7	0.10	5	-91.2	1.3
A1	Amica Creek	Phillips ridge hillside	15+94	29+97	1200	07/93-08/94	7	-13.2	0.38	5	-92.3	2.9
T	Tennant Lake	Tennant powerhouse penstock at lake	19+00	15+35	1007	07/93-09/95	8	-12.7	0.44	2	-94.6	2.5
S1	spring	Phillips ridge hillside	16+15	26+50	410	07/93-08/94	6	-12.83	0.44	6	-89.5	1.8
S2	stream	Price hillside	63+70	28+20	320	08/93-09/95	8	-12.7	0.77	6	-88.3	5.4
S3	stream	beside Myra 10 level portal	31+64	31+71	1400	08/93-09/95	3	-13.6	0.61	1	-94.4	-
S4	stream	Price hillside near 13 portal	58+58	38+23	1300	05/94-09/95	5	-13.1	0.67	3	-95.12	5.6
U1	underground	North Fault HW2 level	41+49	40+02	-50	07/93-09/95	12	-12.7	0.10	3	-90.3	1.2
U2	underground	HW20-832	44+34	39+85	-50	07/93-09/95	12	-6.41	0.16	6	-56.1	2.1
U3	underground	M13-229	33+59	32+15	244	08/93-09/95	9	-12.5	0.19	8	-89.1	1.9

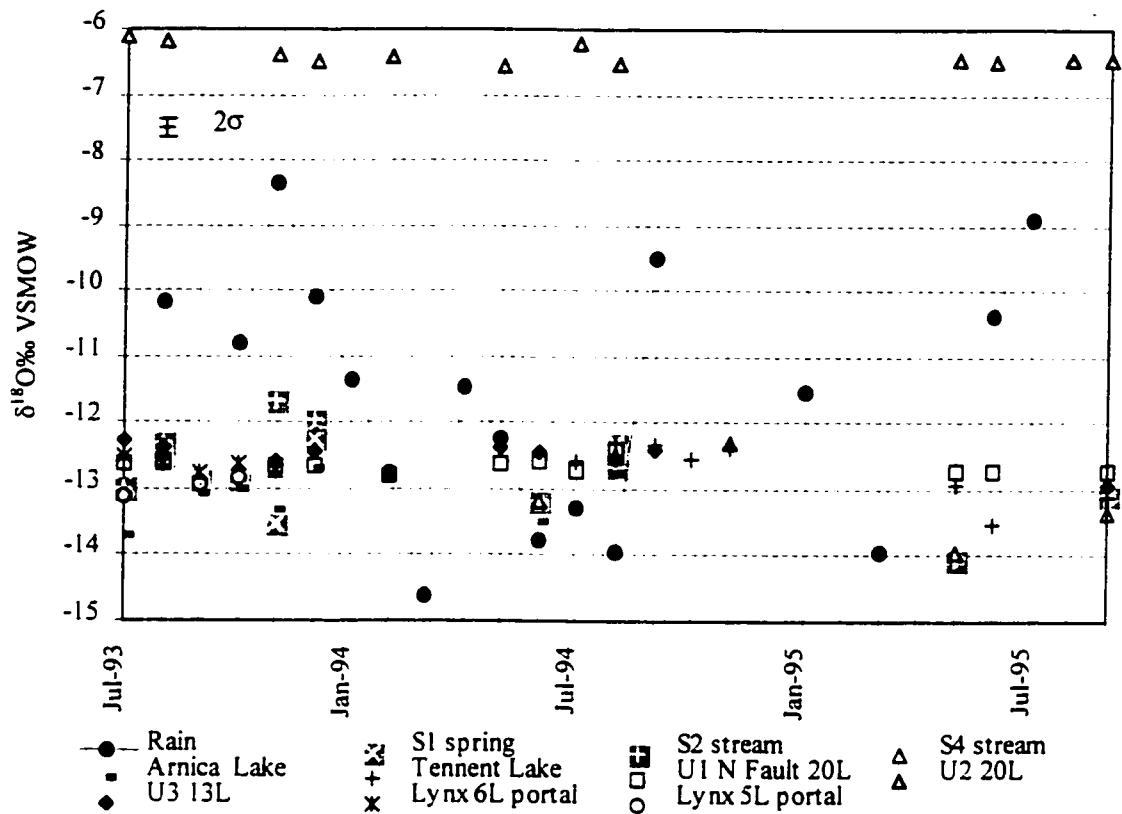


Figure 2-2 $\delta^{18}\text{O}$ for temporal monitoring sites which include: rainfall (Myra Valley MET station), surface waters (Myra and Thelwood Valleys), and ground waters (Lynx, Myra, Price and HW mine areas).

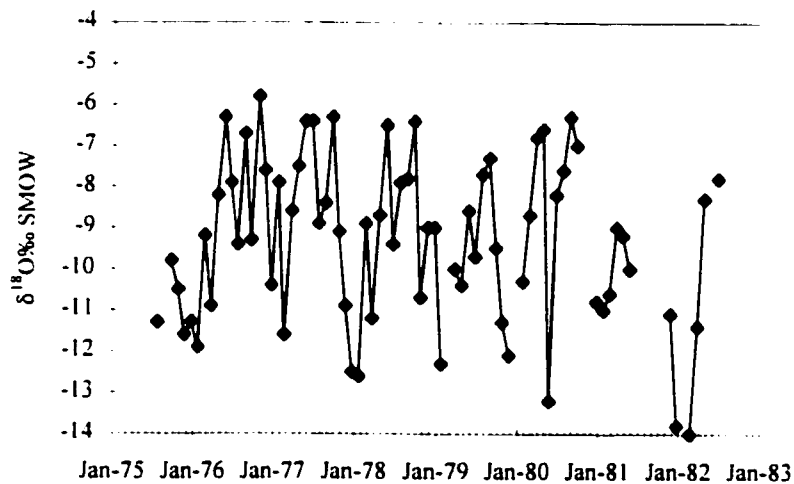


Figure 2-3 $\delta^{18}\text{O}$ of rainfall from Victoria B.C. (data from IAEA GNIP).

2.2.4 Elevation Effect

The study area has high topographic relief and defining the local elevation effect is useful in distinguishing the approximate elevation of recharge to the subsurface waters..

Several surface water sources, (precipitation, lakes, and streams) have been used to calculate the altitude effect. Stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) indicate that lakes used in this calculation have not suffered noticeable evaporation effects. Sites were chosen because they have a limited variation in elevation over their drainage basin. These sites ranged in elevation from 360 m, for the MET station in Myra valley to 1360 m for a small lake on Mount Myra, which is mainly fed from melting snow in a small basin on the northwest side of the mountain.

The calculated $\delta^{18}\text{O}$ gradient is -0.15‰ $\delta^{18}\text{O}$ per 100 m rise in elevation in the Myra Falls area (substituting the non-amount-weighted precipitation for the amount-weighted value results in a gradient of -0.18‰ per 100 m rise; using mountain drainage basin data only results in little change; -0.16‰ per 100 m rise, $R^2=0.64$), and is near the lower end of the range for the elevation effect (-0.10‰ to -0.31‰ $\delta^{18}\text{O}$ per 100 metre rise in elevation; Bortolami, 1979; Clark et al., 1982; Clark, 1987).

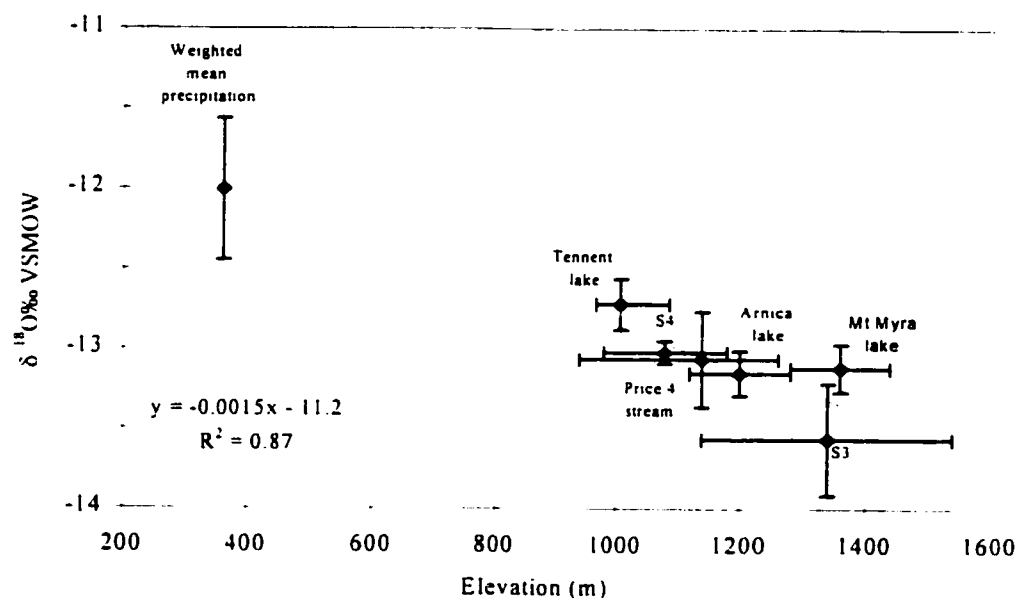


Figure 2-4 The effect of elevation on the $\delta^{18}\text{O}$ composition of precipitation. Vertical error bars represent 1σ for monitoring sites except Mt. Myra lake which is displayed with analytical precision. Horizontal error bars are the approximate range of elevation for catchments.

2.2.5 Myra-Price Ridge - Ground Water Transect

The variation of $\delta^{18}\text{O}$ with elevation can be seen in a transect through the Myra-Price (M-P) hillside via 13 level and Myra 10 level. Ground waters from the hill periphery have an enriched $\delta^{18}\text{O}$ compared to those from the central core of the ridge (Figure 2-5). The $\delta^{18}\text{O}$ values become gradually depleted moving towards the central part of the transect indicating an increasing elevation of recharge towards the centre of the M-P ridge. The paucity of data between 42+00 m and 47+00 m likely represents the ground water divide within the Myra-Price mountain ridge. Depleted $\delta^{18}\text{O}$ values indicate higher recharge elevations for these ground waters (Figure 2-4) as compared to the more enriched $\delta^{18}\text{O}$ values more common towards the hillsides.

The $\delta^{18}\text{O}$ values for ground waters accessed from Myra 10 level (367 m) are quite similar to those from the underlying 13 level (241 m) on the west side of the ridge (Figure 2-5). This pattern implies a strong vertical or subvertical gradient of the ground-water flow through fractures in the crystalline rock between these two levels.

Ground waters from the major fault system through this area of the M-P ridge, the Myra-Price fault, do not follow the same vertical gradient between the two levels as flow through smaller scale fractures, and possibly smaller faults. Although the two waters from the M-P fault were collected from the drift floor, neither appear to experience evaporation effects, as both plot along the winter LMWL. The variation between two waters collected along the same fault system implies that flow along this major (continuous) fault is not uniform. This may be due to low permeability gouge fill or areas with a low degree of damage around the fault, resulting in channeling water along flow lines that are less than the maximum gradient of the dip of the fault (Myra 13 level intersects the M-P fault approximately 50 m along strike from a perpendicular line down dip from Myra 10 level). The M-P fault on both levels is a wide (~10 m) brecciated zone. Fault-gouge is saturated but water is only found on the floor of the drift. There are no mine workings above Myra 10 level in the vicinity of the M-P fault. There are mine workings above 13 level but the closest would be approximately 100 or more meters to the west. An alternative explanation for the high $\delta^{18}\text{O}$ in water originating from the M-P fault on 13 level is from 'short-circuiting' ground-water flow from old mine workings. However this explanation cannot possibly account for

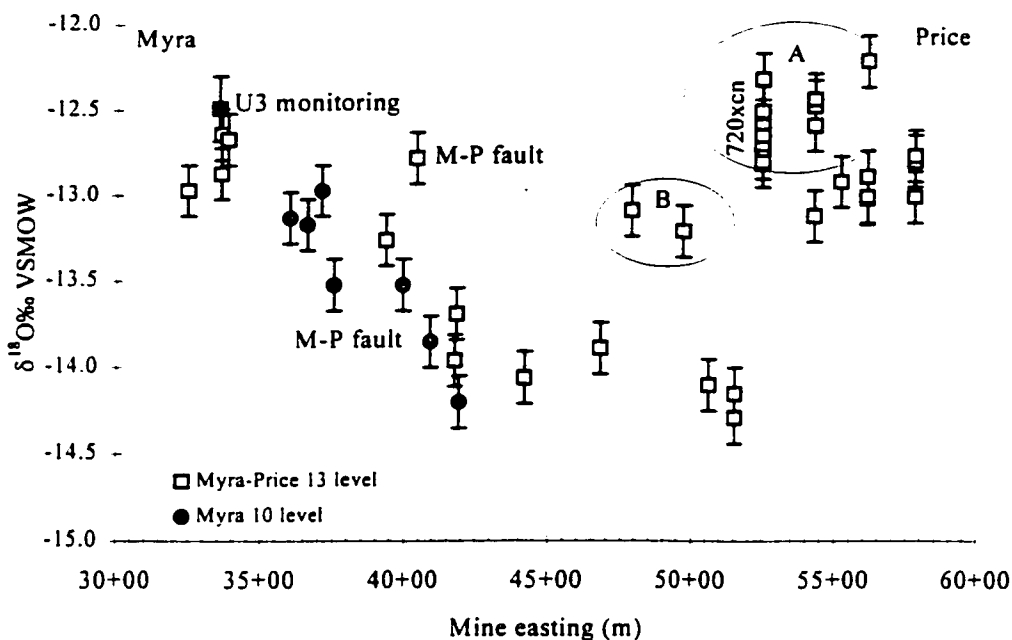


Figure 2-5 ^{18}O transect through Myra-Price ridge via Myra 10 level and Myra-Price 13 level. See text for description of fields.

the similarities between water from the M-P fault and drill holes further East (designated B in Figure 2-5) which intersect the M-P fault in an area remote to mine workings.

The $\delta^{18}\text{O}$ pattern on the east side of the M-P ridge (>47+50 m E) is less distinct and more complicated than that on the west (Myra) side. Surface elevations contours of the slope of the Price hillside do not run perpendicular to the drifts as they do on the Myra hillside, and the ground surface elevation decreases towards the adit and also towards the north. As well several streams originating at different elevations traverse the Price hillside area.

The waters collected from within the main Price 13 level drift through the hillside form a fairly smooth continuation from lower $\delta^{18}\text{O}$ values close to the ground water divide to higher values near the Price hill fringe (Figure 2-5). Another group of waters (designated A on Figure 2-5) have $\delta^{18}\text{O}$ that are enriched and lay above this first group on Figure 2-5. This second group of ground waters originates from the north trending cross cut drift (Pr13-720xcn) at 52+40 m east. This cross-cut has lower ground surface elevation above the drift towards mine north, and therefore lower recharge elevation for the permeable fractures and faults. The remainder of the points in group A (east of 720xcn on Figure 2-5) are from drill holes trending north from the main 13 level drift. These drill holes have a variety of lengths

and plunges which intercept water from rock with lower ground surface elevation overhead towards mine North. Ground waters in the group designated B in Figure 2-5 intersect the M-P fault and likely show the effect of mixing waters (possibly within the drill hole) from fractures that have gained water from various recharge elevations.

2.2.6 Surface and Low Chloride Ground Waters

The stable isotopes of surface waters plot mainly along and above the winter LMWL (Figure 2-6). It appears that the LMWL defined from a limited number of precipitation samples comes close but does not fully describe the stable isotopes of snowfall at higher altitudes from which most surface waters are derived. The surface waters that lie above the winter LMWL are still within the field of individual monthly rainfall analyses.

From the graph of surface waters (Figure 2-6) it is apparent that evaporation has little affect on the sampled surface waters. These streams and lakes originate at high altitude, where the climate is cooler during the summer period of evaporation. The lakes are all below the tree line and would be shielded from most winds thus lowering potential evaporation.

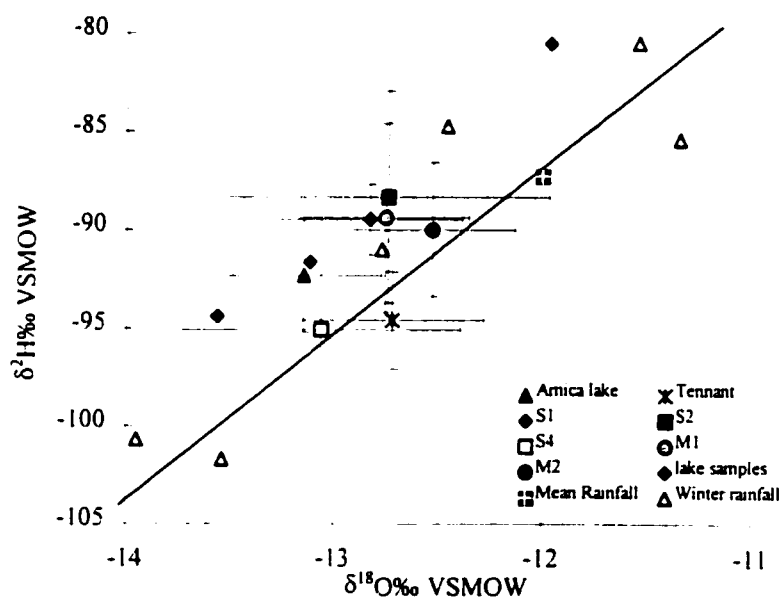


Figure 2-6 Surface water stable isotopes for monitoring sites. The winter LMWL (and 95% confidence limits) is shown for reference. Error bars are 1σ for monitoring sites. See Table 2-1 for description of monitoring sites in legend.

The contribution to surface water from precipitation at higher elevations, dominantly snow fall, is evident from the plot of surface waters which are generally depleted with respect to the average precipitation in Myra Valley (Figure 2-6).

Low chloride bearing ground waters were encountered throughout most of the upper mine workings, the rock volume making up the Myra-Price ridge, and shallow ground waters from Thelwood Valley. The $\delta^{18}\text{O}$ - $\delta^2\text{H}$ field of low chloride ground waters in Figure 2-7 is similar to the surface waters, which are depleted from the weighted mean rainfall (Figure 2-6). Although many points lie above the LMWL they fall within the range of individual monthly rainfall analyses. Ground waters with $\text{EC} > 500 \mu\text{S cm}^{-1}$ are SO_4^{2-} waters, and the $\delta^{18}\text{O}$ - $\delta^2\text{H}$ - depleted 'trail' on Figure 2-7 are from the central core of the M-P ridge under the highest recharge elevations. Again the contribution from high elevation snow melt is apparent. There is no effect on ground water stable isotopes ($\delta^{18}\text{O}$ - $\delta^2\text{H}$) by increased low temperature water rock interaction reflected in the slightly elevated EC in these ground waters. The bulk of the low EC ground waters appear to be recharged at elevations less than 1200 m, while the more depleted waters are recharged at elevations up to 1600 m (Mt. Myra is 1814 m) (based on $\delta^{18}\text{O}$ gradient of -0.15‰ per 100 m).

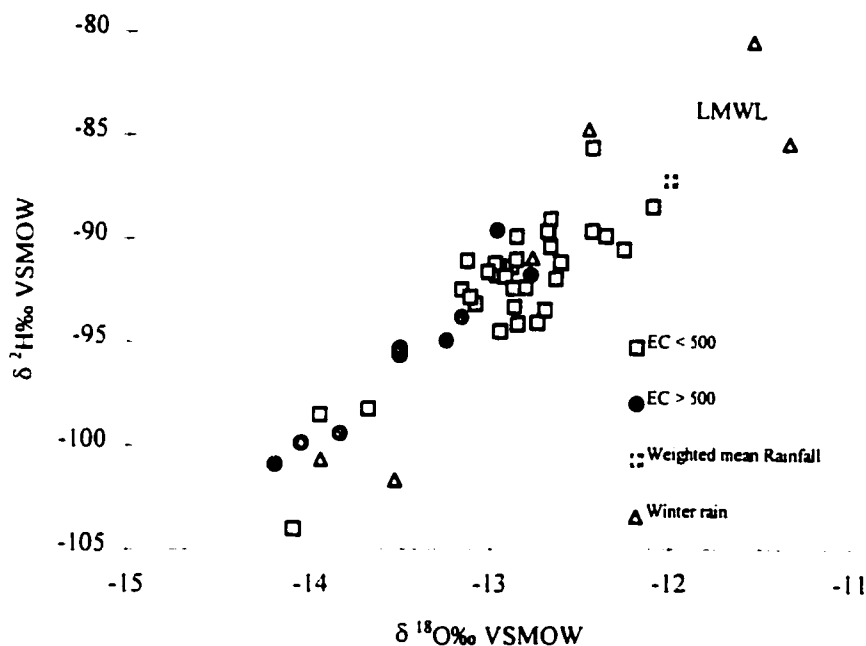


Figure 2-7 Stable isotopes ($\delta^{18}\text{O}$ - $\delta^2\text{H}$) for ground waters with $\text{Cl} < 30$ ppm. Winter LMWL with 95% confidence interval, and rainfall for reference. Ground waters are grouped by electrical conductance (EC, $\mu\text{S/cm}$).

2.2.7 Chloride Waters

Ground waters containing chloride were discovered, sometimes at shallow depth, in drill holes located in Thelwood Valley and within the HW mine. Chloride concentrations of these ground waters reach >17,000 ppm (see the Chapter 3 Chemical Characterization and Hydrochemical Evolution for further detail). Ground waters containing high Cl^- concentrations have distinctly different $\delta^2\text{H}$ and $\delta^{18}\text{O}$ signature than the local meteoric waters (Figure 2-8). The stable isotope trend for chloride waters lies below the MWL in a similar fashion to sedimentary basinal-brine trends. Ground waters with low concentrations of Cl^- plot in a similar field as local meteoric waters and then diverge away from the modern meteoric water with increasing Cl^- content, with a slope of 5.6.

The positive relationship between $\delta^{18}\text{O}$ and Cl^- concentration in ground waters can be seen in Figure 2-9(a). Both these parameters tend to increase with decreasing elevation of sampling. The scatter in Figure 2-9(b) likely results from the variability in the extent of mixing various proportions of dilute variable $\delta^{18}\text{O}$ modern meteoric waters with Cl^- dominated $\delta^{18}\text{O}$ enriched saline waters. The enriched $\delta^{18}\text{O}$ and Cl^- content in the saline waters appear to be the result of similar processes, and/or similar sources.

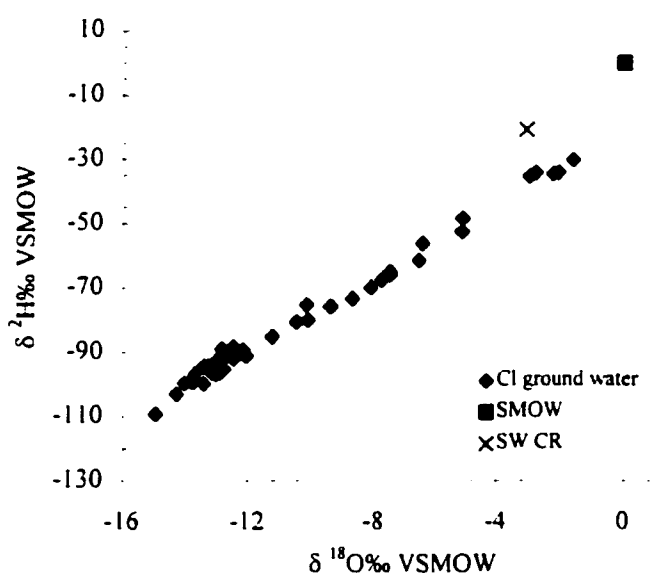


Figure 2-8 Deuterium - $\delta^{18}\text{O}$ plot of ground waters with $\text{Cl}^- > 30$ ppm. SMOW and winter LMWL for reference. SW CR is a sea water from Campbell River. Error bars lie within plotting symbols.

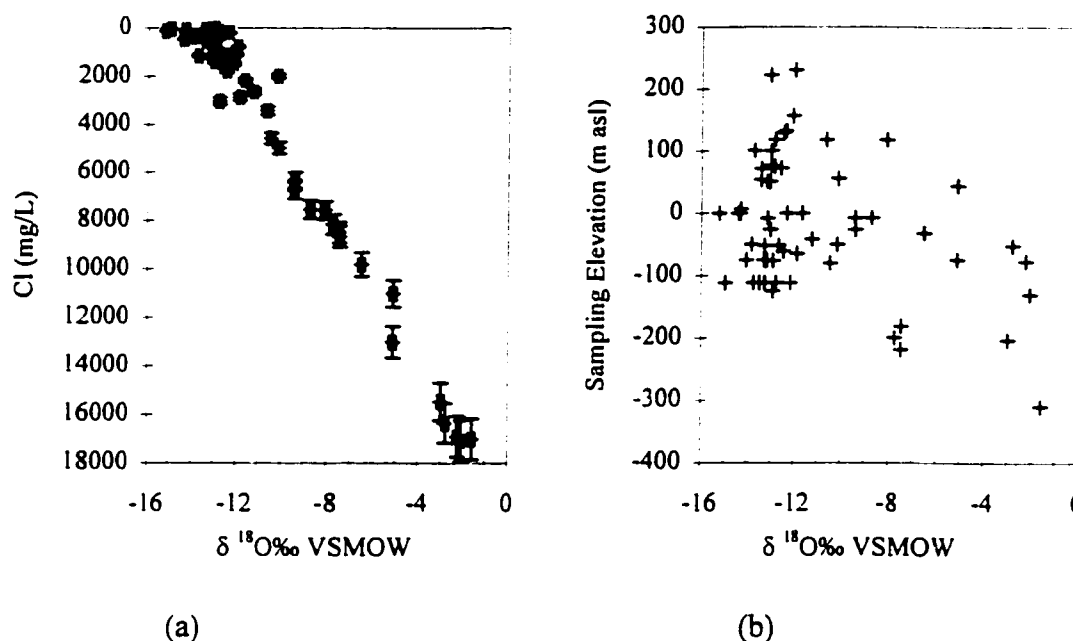


Figure 2-9 $\delta^{18}\text{O}$ variation with increasing Cl (a), and $\delta^{18}\text{O}$ variation with depth of sampling Cl ground waters (b).

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of sea water collected from the shoreline of Discovery passage, Campbell River (SW CR on Figure 2-8) indicates that ocean waters between Vancouver Island and mainland B.C. are diluted by the inflow of rivers with modern meteoric stable isotopes. A similar dilution of ocean water resulting from mixing with Fraser river water ($\delta^2\text{H} \sim -140\text{‰}$, $\delta^{18}\text{O} \sim -17.5$) was seen in Miners Bay off the east coast of Vancouver Island (Dakin, et al., 1983). At the Campbell River location sea water in Discovery passage is diluted by approximately 25% meteoric water (using $\delta^{18}\text{O}_{\text{meteoric}} = -12\text{‰}$). The saline water trend at Myra Falls lies below the diluted sea water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ on Figure 2-8.

The saline ground waters are clearly not the result of mixing modern meteoric and modern ocean waters.

2.3 ^{13}C - Dissolved Inorganic Carbon

2.3.1 Introduction

Carbon-13 is one of two stable isotopes of carbon (1.11% natural abundance); ^{12}C being the other. Carbon-13 in dissolved inorganic carbon (DIC: H_2CO_3 , HCO_3^- , and CO_3^{2-}) can be used to evaluate the evolution of DIC in ground waters, and can be used to infer processes occurring during recharge, dissolution and precipitation of carbonate-bearing minerals, and oxidation of organic carbon. All of which will add or decrease total C and ^{13}C in the system. Often, biological controls are in effect, resulting in very distinct $\delta^{13}\text{C}$ reservoirs.

Carbon-13 is useful in assessing recharge processes since the partial pressure of CO_2 (P_{CO_2} , often expressed as $\log[\text{CO}_2]$) in the soil or recharge zone is higher than in the atmosphere, and the amount of interaction between the water and the soil environment can be assessed by the content and $\delta^{13}\text{C}$ of DIC in the water. The P_{CO_2} of the atmosphere is around $10^{-3.5}$ with a $\delta^{13}\text{C} \approx -6\text{‰}$ (Friedli et al., 1986); while soil gases have a wide range of $\delta^{13}\text{C}$ depending on the prominent vegetation that is decaying in the soil zone. The $\delta^{13}\text{C}$ of soil CO_2 ranges from around -10‰ to -30‰ ; the higher values are for C_3 plants (trees) while the lower values are for C_4 plants (grains) (Smith and Epstein, 1971). Soil P_{CO_2} can vary over a wide range, but typically is around $10^{-2.5}$. Water can freely equilibrate with soil CO_2 while the system remains open. Once the water has been removed from contact with the soil atmosphere (closed system) the $\delta^{13}\text{C}_{\text{DIC}}$ and carbonate alkalinity can be altered through the addition of dissolved carbonates or oxidation of reduced forms of carbon. Waters experiencing sulphate reduction with a depleted carbon source will have their $\delta^{13}\text{C}_{\text{DIC}}$ altered as the reaction progresses. The change in $\delta^{13}\text{C}_{\text{DIC}}$ along with $\delta^{34}\text{S}_{\text{SO}_4}$ can be used to monitor the extent of the reduction (see section 2.4 ^{34}S).

2.3.2 Results

Thirty-five waters were analysed for $\delta^{13}\text{C}$ in dissolved inorganic carbon (DIC). The results are presented in Table 2-2. The DIC was analysed from a wide cross-section of available sources including surface waters, shallow non-saline ground waters, and saline ground waters. Methods and materials for $\delta^{13}\text{C}$ are given in Appendix B.

Table 2-2 ^{13}C in DIC data. P_{CO_2} and $\text{SI}_{\text{calcite}}$ are calculated using PHREEQC (Parkhurst, 1995; Appendix D) [() denotes monitoring sites].

Sample	Location	Drill Hole	Elevation (m asl)	$\delta^{13}\text{C}_{\text{‰}}$ VPDB	Alkalinity as HCO_3^- ppm	P_{CO_2} log[CO ₂]	$\text{SI}_{\text{calcite}}$
2561	Pr9-930dw	Pr9-12	416	-9.79	109	-2.44	-0.55
2569	Surf/stream	(S4)	1300	-7.24	52.3	-2.62	-1.18
2572	Surf/stream	(S3)	1400	-4.31	37.7	-2.79	-1.46
2584	HW20-415xcn	N fault (U1)	-50	-11.5	82.6	-1.89	-1.71
2587	M13-108dw	M13-230	242	-8.68	85.4	-2.25	-1.18
3078	Pr9-930dw	Pr9-12	416	-9.80	68.4	-2.91	-0.59
3186	Pr5-830dw	Pr5-40	583	-12.8	133	-2.65	-0.26
3216	Surf/ddh	PR-106	51	-7.43	56.7	-2.75	-0.06
3262	HW20-415de	HW20-832 (U2)	-50	-9.64	19.0	-3.74	-0.59
3273	Surf/ddh	PR-106	157	-13.6	109	-3.15	0.68
3274	Surf/ddh	PR-92	-52	-10.8	125	-3.88	0.62
3277	Surf/ddh	PR-92	-26	-8.54	31.5	-4.30	0.52
3286	Pr13-720xcn	Pr13-73	242	-13.2	125	-2.58	-0.35
3321	Surf/ddh	PR-101	-218	-21.4	33.0	-3.95	0.51
3345	Surf/ddh	PR-92	54	-9.11	123	-2.83	-0.91
3346	Surf/ddh	PR-73	-21	-12.6	113	-2.10	-1.66
3363	Surf/ddh	PR-101	-26	-17.3	50.2	-3.99	0.58
3365	Surf/ddh	PR-106	-130	-9.63	17.0	-2.72	-0.98
3385	Surf/ddh	PR-101	119	-11.0	123	-2.82	0.02
3394	M10-048de	M10-127	370	-12.3	115	-2.50	-0.49
3399	M10-048de	M10-17	370	-7.65	117	-2.97	-0.07
3429	Surf/ddh	PR-100	-203	-26.0	153	-2.51	0.76
3444	M10-370xcs	M10-??	373	-10.5	107	-5.93	0.34
3486	M13-108dw	M13-230	242	-9.71	89.0	-3.13	-0.21
3505	Pr13-930dw	Pr13-13	242	-12.9	151	-2.36	-0.27
3515	Pr13-930dw	Pr13-20	242	-12.3	143	-2.22	-0.46
3517	Pr13-930dw	Pr13-28	242	-12.2	145	-2.46	-0.23
3527	Surf/stream	(S2)	320	-3.68	27.5	-3.05	-1.60
3546	Pr4-680dw	Pr4-136	631	-13.5	143	-2.75	-0.05
3547	Pr4-630xcn	Pr4-87	631	-13.5	112	-3.18	0.09
3548	Pr4-680dw	Pr4-82	630	-14.1	124	-2.82	-0.13
3549	Pr4-800dw	Pr4-35	630	-12.0	138	-1.66	-1.17
3550	Pr4-800dw	Pr4-15	629	-12.3	138	-1.94	-0.94
3566	Surf/ddh	PR-84	-41	-9.56	49.9	-3.50	-0.04
3568	Surf/ddh	PR-92	-8	-9.02	59.2	-3.31	0.09

2.3.3 Discussion (Recharge Processes and Carbonate evolution)

Three surface waters had DIC analysed for $^{13}\text{C}/^{12}\text{C}$ (2569, 2572, and 3527 which are monitoring streams S4, S3, and S2, respectively; Table 2-2). The P_{CO_2} (reported as $\log[\text{CO}_2]$) of these stream waters ranges from -3.5 to -2.6 (mean of -2.8) and $\delta^{13}\text{C}$ averages -5.1‰ VPDB. The low P_{CO_2} and $\delta^{13}\text{C}$ values indicate these waters are either in equilibrium with atmospheric CO_2 , or contain a mainly atmospheric component of CO_2 ($P_{\text{CO}_2(\text{atmosphere})} \sim -3.5$; $\delta^{13}\text{C}_{\text{atmosphere}} \sim -6.5\text{‰}$ to -7‰ VPDB) and likely contain some addition of depleted $\delta^{13}\text{C}$ from the soil zone. An 'excess air' component may be incorporated by agitation and bubble incorporation during turbulent flow which may enable the stream waters to contain a P_{CO_2} greater than equilibrium solubility of an open water source with the atmosphere. Temperature dependent equilibrium fractionation between $\text{CO}_{2(\text{atmosphere})}$ and DIC at 5 °C will result in HCO_3^- enrichment of around 10‰ over $\text{CO}_{2(\text{atmosphere})}$. Degassing of an interflow component to the streams would result in an enriched $\delta^{13}\text{C}$ contribution.

Shallow ground waters from Price 4 and 5 levels have an average $\delta^{13}\text{C}$ of -13.0‰ VPDB ($\pm 0.8\text{‰}$ 1σ), and $\log P_{\text{CO}_2}$ averages -2.5. These ground waters are close to calcite saturation with one water (3547) slightly over-saturated. The average $\delta^{13}\text{C}$ decreases only slightly from this value in 13 level waters ($-12.6\text{‰} \pm 0.5$), with an average $\log P_{\text{CO}_2}$ of -2.4.

There is a very regular trend between depleted $\delta^{13}\text{C}$ and higher concentrations of HCO_3^- with sampling location throughout the M-P ridge (Figure 2-10). Waters from surface streams and recently recharged ground waters (containing tritium, DO, low Na, and where applicable, $\delta^{34}\text{S}$; i.e., ground waters that have not undergone sulphate reduction or excessive water rock interaction) were used to assess the recharge environment from a carbonate standpoint. The M-P ridge has steep, poorly vegetated slopes. It is poorly vegetated on the Price side due to a forest fire that ravaged Thelwood Valley several decades ago. Streams traversing the M-P hillsides, which are presumably the main recharge sources (see 1.8 Hydrology), lie in narrow gorges with high topographic gradients and little vegetation (i.e., no soil cover). These same streams at higher elevations, especially above Price 4 level tend to have more moderate stream bed gradients and an abundance of organic matter (tree dead fall, mosses etc.) in and around the

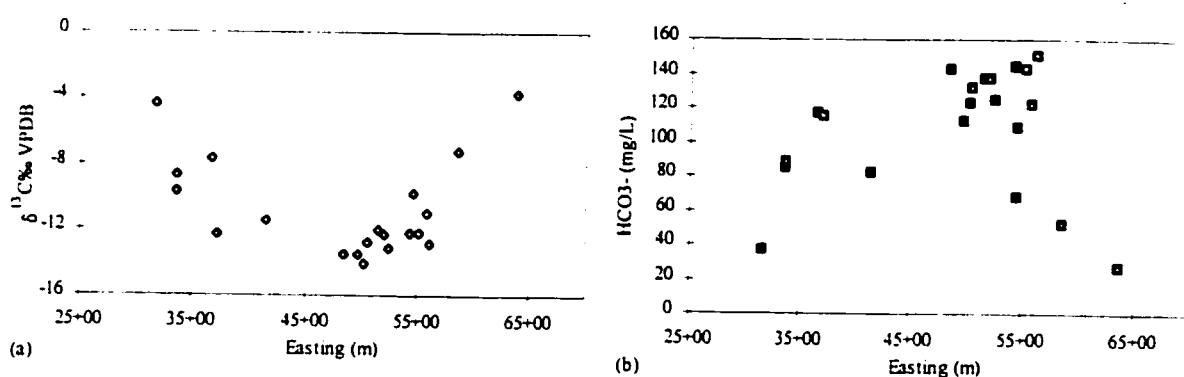


Figure 2-10 Variation of $\delta^{13}\text{C}$ (a) and bicarbonate concentration (b) with location of ground water and streams from Myra-Price ridge. The amount of vegetation on the M-P ridge varies by location, and is sparse on hill slopes. Lower topographic gradients and greater vegetation in areas overlying Price mine results in higher HCO_3^- concentrations with lower $\delta^{13}\text{C}$.

stream beds. Also, towards the north of the Price mine area the topographic gradient tends to diminish and the forest vegetation, unaffected by the fire, recovers.

As waters pass through and equilibrates with soils containing higher concentrations of CO_2 (higher recycling of organic carbon) a larger amount of DIC with a soil $\delta^{13}\text{C}$ will be incorporated into the recharging water. The result of this can be seen in the inverse relationship between $\delta^{13}\text{C}_{\text{DIC}}$ with the bicarbonate (alkalinity) concentrations in the recently recharged ground waters (Figure 2-11). Higher concentrations of HCO_3^- having lower $\delta^{13}\text{C}$ results from recharge through a soil zone. The $\delta^{13}\text{C}$ of the soil CO_2 can be estimated based on equilibrium fractionation factors for CO_2 - HCO_3^- and the ambient temperature. Using a temperature of 5°C , which should represent typical temperatures of the shallow pedosphere during recharge, the fractionation factor of Mook et al. (1974), and a $\delta^{13}\text{C}_{\text{DIC}}$ value of -13‰ gives a $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ value of -23‰ . Correcting this value for the contribution from surface streams ($\delta^{13}\text{C} = -5$ and 39 ppm HCO_3^-) gives an estimate for $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ of -26.7‰ . The range from -23‰ to -27‰ is typical for C3 plants (including trees).

The initial HCO_3^- content and $\delta^{13}\text{C}$ values prove to be extremely useful in this setting in assessing the recharge environment. Waters recharging on the hill slopes (Figure 2-10) carry a smaller component of the soil organic matter CO_2 signature and more of an atmospheric one. This can be seen in Figure 2-11 as waters with low HCO_3^- concentrations have enriched $\delta^{13}\text{C}$ values. Ground waters recharged through faults and fractures with little soil cover over or in the

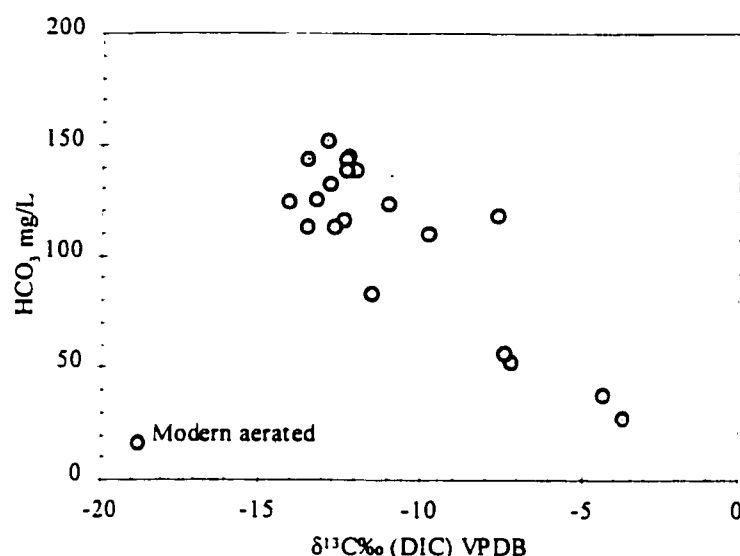


Figure 2-11 $\delta^{13}\text{C}$ variation with bicarbonate concentration of surface and recently recharged ground waters. As waters recharge through soil cover with higher P_{CO_2} the DIC concentration increases and the isotopic character of the soil gas is reflected in the HCO_3^- .

fractures or faults, or mixing surface water (with a greater component of atmospheric $\delta^{13}\text{C}$) with runoff from areas with higher organic matter content will result in intermediate $\delta^{13}\text{C}$ values (Figure 2-13). Infiltration directly from a soil zone overlying permeable fractures and faults would result in $\delta^{13}\text{C}$ values of approximately -12‰ VPDB.

As the ground waters infiltrate to further depths in the M-P ridge the $\delta^{13}\text{C}_{\text{DIC}}$ becomes only slightly depleted (Price 4 and 5 levels mean $\delta^{13}\text{C}_{\text{‰}} = -13.0 \pm 0.8\text{‰}$ ($n = 6$); Price 13 level mean $\delta^{13}\text{C}_{\text{‰}} = -12.6 \pm 0.5\text{‰}$ ($n = 4$)) while the alkalinity (as HCO_3^-) increases marginally from 131 ± 12 ppm for Price 4 and 5 levels to 141 ± 11 ppm for Price 13 level ground waters. The similarity $\delta^{13}\text{C}_{\text{DIC}}$ between these levels suggests the $\delta^{13}\text{C}$ of calcite veining is near, to slightly less than 0‰ VPDB.

No single reaction path can describe DIC evolution in Myra Falls waters. With increased depth and an increase in reducing conditions such as those measured in ground waters of Thelwood Valley several trends become apparent.

Moving into deeper horizons an increasing number of waters have reached saturation with respect to calcite (mean $\text{Si}_{\text{calcite}} = 0.3 \pm 0.7$) as compared to shallower waters. Ground waters from surface drill holes in Thelwood Valley (PR106 (-130 m), PR92, and PR84) and

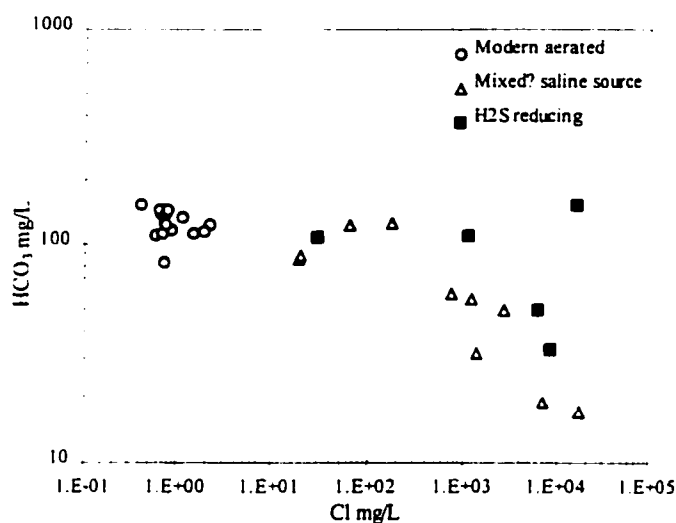


Figure 2-12 Alkalinity variation (HCO_3^-) vs. Cl^- content of ground waters with $\delta^{13}\text{C}$. Saline waters have low alkalinity, while saline waters undergoing sulphate reduction have increased alkalinity and are saturated or oversaturated with respect to calcite.

mean HCO_3^- concentration is considerably lower in saline waters than ground waters from Price drifts. Average alkalinity for the saline waters is 68 ± 42 ppm, which is intermediate between surface waters and shallow Price 4 and 5 level waters and decreases with increasing Cl^- . The most saline waters in this trend have alkalinity measurements of less than 20 ppm as HCO_3^- (Figure 2-12).

A second separate trend is apparent in highly reducing waters (Figure 2-14). The depletion in $\delta^{13}\text{C}$ results from SO_4^{2-} reduction using a depleted C source.

The use of canola oil as a drilling additive in Thelwood Valley drill holes (and other drill holes?) has lead to a depleted carbon source as an electron donor for sulphate reduction (see the next section, Sulphate Sources and Sulphate Reduction). Since canola uses the C3 photosynthetic pathway it should have $\delta^{13}\text{C}$ values in the range of -21 to -27‰ VPDB (B Ellert; Agriculture Canada, Lethbridge, personal communication). Indeed, canola seed has $\delta^{13}\text{C}$ values from around -25 to -28‰ (G. Parry, Saskatchewan Institute of Pedology, personal communication [unpublished data]), and a single sample of the processed oil (Liberty® 100% Canola oil) has a $\delta^{13}\text{C}$ value of -29.0 ± 0.01 ‰ (1σ , 3 analyses). The canola oil was likely

3262 from HW 20 level have relatively constant $\delta^{13}\text{C}_{\text{DIC}}$ values which remains constant with increasing salinity (and enriched $\delta^{18}\text{O}$) (Figure 2-14). This linear trend around -9‰ VPDB (Figure 2-14) in these ground waters results from the $\delta^{13}\text{C}$ of the saline water which occurs at shallow depth in the study area. The mean $\delta^{13}\text{C}_{\text{DIC}}$ value of these waters is -9.21 ± 0.9 ‰ VPDB (1σ). Slight variation in this source can be attributed to mixing with recent recharge or with waters undergoing SO_4^{2-} reduction (Figure 2-15). The

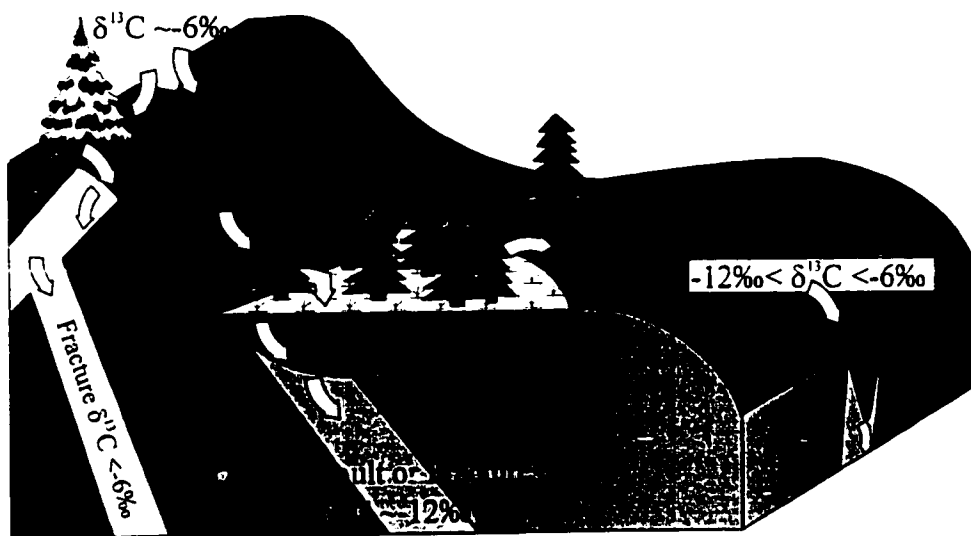


Figure 2-13 Schematic of various routes of recharge and accompanying $\delta^{13}\text{C}$ values. Water with a dominant atmospheric component will have high $\delta^{13}\text{C}$ value, recharge through faults and fractures with little organic matter will result in high $\delta^{13}\text{C}$ values ($\leq -6\text{‰}$ VPDB). Recharge through faults and fractures underlying soil zones ($\delta^{13}\text{C} \approx -26\text{‰}$ VPDB) where equilibration between water and soil CO_2 occurs results in $\delta^{13}\text{C}_{\text{DIC}}$ of $\sim -12\text{‰}$. Streams will vary between these two extremes depending on the contribution of soil derived DIC.

partitioned onto mineral surfaces during drilling (gouge and fracture fill) and was then later utilized by sulphate reducing bacteria.

An additional depleted C source may be methane, detected at low concentrations in some ground waters (Appendix A). However, the carbon source involved in SO_4^{2-} reduction contains ^{14}C which would preclude the involvement of CH_4 in this reaction.

$\delta^{13}\text{C}$ indicates that recharge to the M-P ridge is occurring in equilibrium with soil, and also directly into permeable zones with little soil contact, and variations in-between. The equilibrium with soil CO_2 is highly dependent upon location and topography of the area.

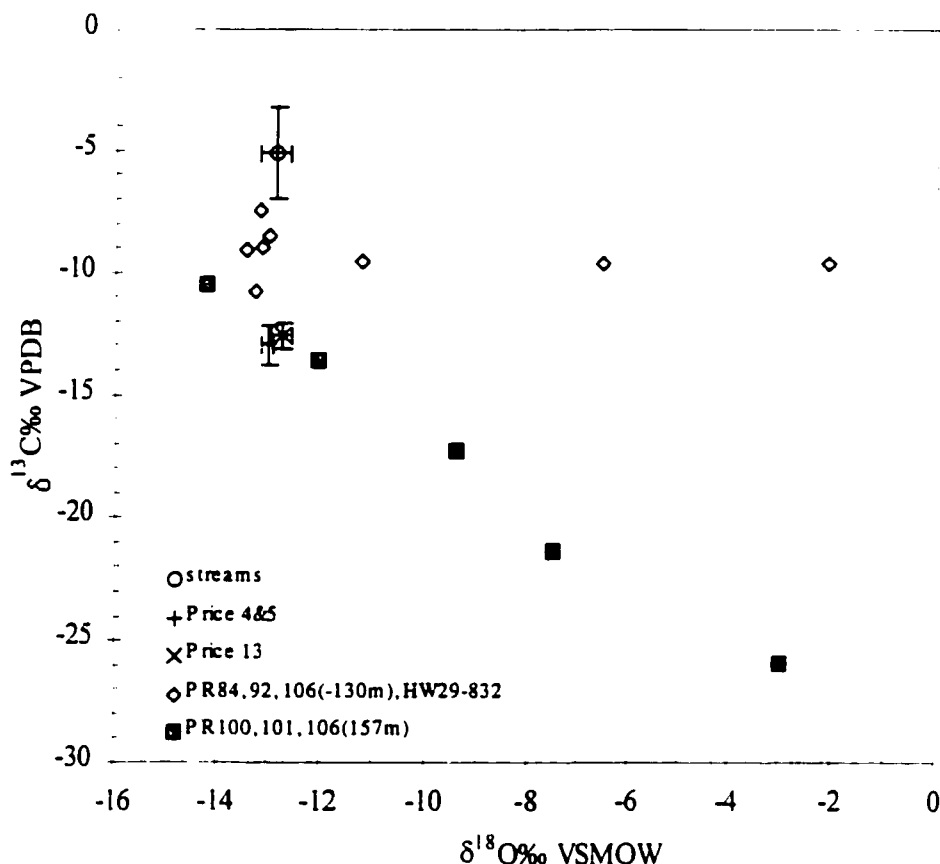


Figure 2-14 $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ shows several trends. Ground waters (diamonds) show recharge $\delta^{13}\text{C}$ values between Price 4&5 waters and streams. These waters then have a fairly consistent $\delta^{13}\text{C}$ in mixing waters (enrichment of ^{18}O). In the bottom trend a $\delta^{13}\text{C}$ depleted source of C is being added during sulphate reduction.

Saline waters have extremely low alkalinity (<20 ppm as HCO_3^-) and a $\delta^{13}\text{C}$ of approximately -10‰ VPDB. In zones of active SO_4^{2-} reduction the $\delta^{13}\text{C}$ becomes modified (depleted). The apparent linear relationship between $\delta^{13}\text{C}$ depletion in SO_4^{2-} reducing waters and increasing salinity results from the very low HCO_3^- concentrations in the saline water, which are not able to buffer the $\delta^{13}\text{C}$ additions from the oxidation of canola oil which was used as a biodegradable lubricant during drilling.

Sulphate reduction in a mixed saline water (lower salinity and higher bicarbonate) results in a depletion in $\delta^{13}\text{C}_{\text{DIC}}$ (Figure 2-15 b).

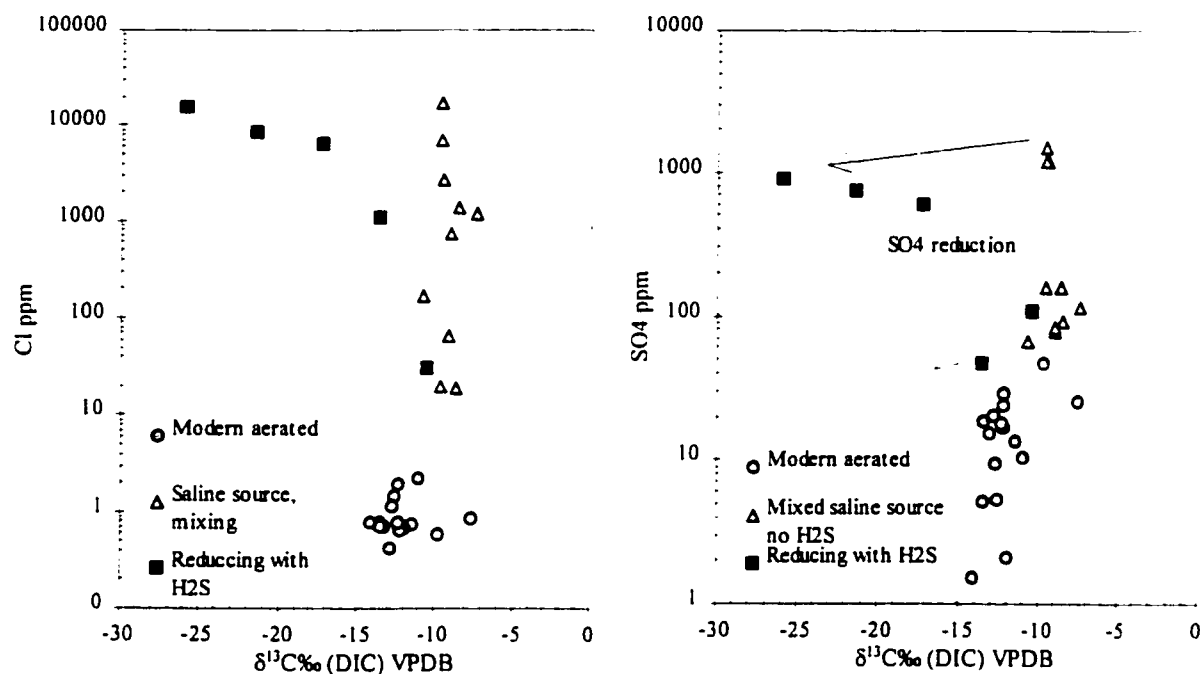


Figure 2-15 $\delta^{13}\text{C}_{\text{DIC}}$ variation with Cl^- (a) and SO_4^{2-} concentrations (b). Plotted are ground waters from recent recharge with no sulphate reduction, waters with actively reducing sulphate, and $\delta^{13}\text{C}_{\text{DIC}}$ ground waters of a predominantly saline origin which may include some degree of mixing with the other waters. Mixing between recent recharge and saline water may also be occurring. The effect of sulphate reduction on the $\delta^{13}\text{C}_{\text{DIC}}$ can be clearly seen, as well as the overlapping values of $\delta^{13}\text{C}$ between each process.

2.4 ^{34}S , $^{18}\text{O}_{(\text{SO}_4)}$ - Sulphide Oxidation, Sulphate Reduction and $^{34}\text{S}_{(\text{SO}_4)}$ Trends

2.4.1 Introduction

Sulphur has four stable isotopes with masses of 32, 33, 34, and 36. The most abundant isotopes are ^{32}S and ^{34}S and have natural abundances of 95.00% and 4.21%, respectively. Sulphur has oxidation states ranging from -2 to +6, and oxidation transitions are often accompanied by isotopic fractionation. Furthermore the $\delta^{18}\text{O}$ in the dissolved sulphate can infer mechanisms of oxidation of sulphide minerals. The use of stable isotopes of S and O in SO_4 are useful in interpreting S cycling in the ground water environment.

2.4.2 Sulphide Oxidation

2.4.2.1 Introduction (Sulphide Mineral Oxidation)

Pyrite, being the most ubiquitous sulphide mineral present in many settings, has led to a multitude of studies of the mechanisms involved in the oxidation of pyrite (see Singer and Stumm, 1970; Lawson, 1982; Wiersma and Rimstidt, 1984; McKibben and Barnes, 1986; Moses et al., 1987).

The oxidation of sulphide minerals may be an abiotic, or biotic reaction. Abiotic reactions are chemically redox controlled. Biotic (microbial) mediated oxidation may be direct (bacterially-catalyzed) through the contact of the microbe to the surface of a sulphide, or may be indirect (chemical oxidation) through the bacterially mediated oxidation of an element (i.e., Fe) that is then free to oxidize the surface of the sulphide.

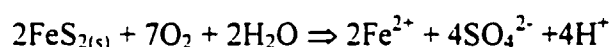
Moses and Herman, (1991) proposed an abiotic mechanism of pyrite oxidation at near neutral pH, in which Fe^{2+} is sorbed to the pyrite surface. Dissolved oxygen (DO) is responsible for oxidation of Fe^{2+} to Fe^{3+} which in turn oxidizes the pyrite surface by repetitive transfers of e^- from the surface to Fe^{3+} . Hydroxyl groups are transferred from Fe^{3+} to the pyrite surface which results in Fe^{3+} itself being reduced. The OH^- groups are transferred to a S in the pyrite structure which eventually weakens the Fe-S₂ bond. Sulphur is eventually freed as $\text{S}_2\text{O}_3^{2-}$ (or another intermediary redox S) which is, except under unusual

circumstances, oxidized rapidly and within close proximity to the pyrite surface. Under acidic conditions, where dissolved Fe^{3+} is stable, the proposed mechanism involves direct attack by hydrated Fe^{3+} with no requirement for Fe sorption to the pyrite surface (Moses et al., 1987). The oxidation of pyrite by Fe^{3+} can occur under aerobic and anaerobic conditions (Moses et al., 1987). The formation of intermediary redox sulphur complexes should be short lived in natural environments with the possible exception of alkaline solutions or where high flow across the sulphide surface may remove these complexes before full oxidation of S has taken place (Moses et al., 1987). The rate limiting step in the above mechanisms remains the oxidation of Fe^{2+} to Fe^{3+} as shown by Singer and Stumm (1970). However, microbial aided oxidation may not follow the steps outlined by the abiotic experiments of Moses and Herman (1991).

Oxidation of the pyrite surface directly by DO was investigated by Moses et al. (1987), Goldhaber (1983), and reviewed by Lawson (1982). Goldhaber (1983) described the rate limiting step as the adsorption of O_2 to the pyrite surface, and will as such be pH dependent. The most rapid rise in pyrite oxidation by DO was found to be near pH 7 which is approximately equivalent to the zero point charge of the surface, and increases with higher pH.

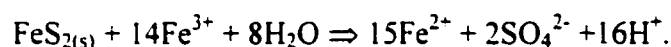
Where denitrification is not involved, the pyrite oxidation reactions involving O_2 and Fe^{3+} can be summed up as written below (Moses et al., 1987; Lawson, 1982; Moses and Herman, 1991). The first reaction is oxidation of pyrite by dissolved oxygen.

Equation 2-3



Where, $7/8$ of the oxygen in SO_4^{2-} is derived from atmospheric oxygen originally incorporated during recharge. The second mechanism of pyrite oxidation involves oxidation by ferric iron and is written as:

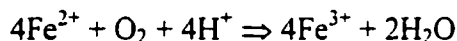
Equation 2-4



In this reaction all the SO_4^{2-} -O is derived from the water. Reaction Equation 2-4 is much faster than Equation 2-3, but only becomes significant when the ferric to ferrous iron ratio is greater than 2 (Kleinmann and Crerar, 1979). Both reactions are acid producing. The first

reaction (Equation 2-3) can be abiotic or by direct microbe attack (Leduc, 1997). Whereas, the second reaction (Equation 2-4) is solely an inorganic oxidation mechanism, and is limited by the availability of Fe^{3+} , and therefore the rate of reaction is limited by the oxidation of ferrous iron (Singer and Stumm, 1970):

Equation 2-5



which may be bacterially mediated or may occur abiotically .

Above a pH of approximately 4.5 the rate of abiotic Fe^{2+} oxidation is pH dependent and is second order with respect to $[\text{OH}^-]$; below a pH of 3.5 the rate is pH independent but remains first order with respect to $[\text{Fe}^{2+}]$ and $[\text{O}_2]$ (Singer and Stumm, 1970). At low pH the dominant role of O_2 is in the oxidation of Fe^{2+} and consequently sulphate oxygen is obtained mainly from the water (Taylor et al, 1984(a)). At extremely low pH such as in highly acidic mine drainage exchange between SO_4^{2-} and H_2O will result (Hoering and Kennedy, 1956) and therefore the usefulness of $\delta^{18}\text{O}_{\text{SO}_4}$ in distinguishing sulphide mineral oxidation mechanisms may be limited in these environments.

Overall, within the pH range of 2 to 9, abiotic pyrite oxidation by Fe^{3+} occurs more favourably than abiotic O_2 oxidation; although the difference decreases with increasing pH. At a pH of 9, oxidation by Fe^{3+} is at least an order of magnitude greater than oxidation in a saturated DO solution (Moses, 1987).

The rate of Fe^{2+} oxidation by O_2 in an aerobic environment at intermediate pH is high and pH limitations are broken when microbes such as *Thiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, and *Ferrobacillus ferrooxidans* are involved. These bacteria will greatly accelerate this process under acidic conditions (Taylor et al., 1984(b); Ehrlich, 1995; and Figure 2-16). The rate of microbial mediated oxidation of Fe^{2+} may be a factor of 10^6 greater than abiotic oxidation (Singer and Stumm, 1970). The oxidation of Fe^{2+} by bacteria is an indirect interaction: whereas, in direct interaction the microbes directly oxidize a sulphide mineral producing a soluble sulphate salt (Ehrlich, 1995). Organisms such as: *Thiobacillus thiooxidans* *Thiobacillus ferrooxidans*, *Acidianus brierleyi* and *Sulfolobus acidocaldarius* will catalyse the oxidation of sulphide minerals. All are aerobic and acidophilic. Direct oxidation of pyrite by *Thiobacillus ferrooxidans* is only about $1/7$ as fast as indirect oxidation

(Walsh, 1978 in Kleinmann and Crerar, 1979) and therefore is not a significant contributor to acid mine drainage. *Thiobacillus ferrooxidans* and *T. thiooxidans* are acididophilic, (thrive in acidic environments) and are mesophilic (optimal temperature range of growth is approximately 15 to 50°C) (Leduc, 1997) (see Figure 2-16).

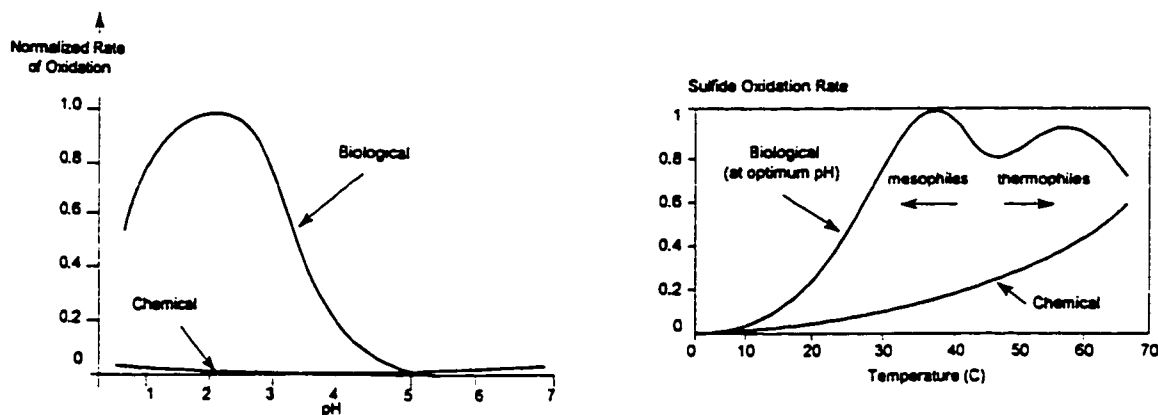


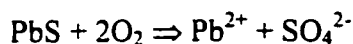
Figure 2-16 Kinetics of sulphide oxidation and acid generation (from Lawrence, 1996).

Experiments on the low temperature oxidation mechanisms for base metal sulphides have been primarily of interest to metallurgists for ore recovery processing techniques. McIntosh et al. (1997) provide a recent review of probable reactions for oxidation of common ore-forming minerals. Other studies include the in-situ and laboratory oxidation of sulphides by Sato (1960a and 1960b), chalcopyrite and pyrrhotite by Steger and Desjardins (1978), and one experimental run of sphalerite by Moses et al. (1987). None of these experiments investigated sulphur isotope fractionation during sulphide mineral oxidation. Both chemical and bacterial catalysed oxidation processes are known to occur for the most common sulphide minerals (McIntosh et al., 1997).

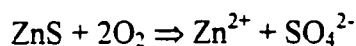
The oxidation of some sulphide minerals does not have to include oxygen derived from water. These include *Thiobacillus ferrooxidans* direct oxidation of chalcopyrite (CuFeS_2), and chalcocite (Cu_2S), and the oxidation of Cu^+ , using only molecular oxygen (Nielson and Beck, 1972; Shrihari et al., 1991; McIntosh et al., 1997). Direct oxidation of chalcopyrite by *T. ferrooxidans* can be written as:

Equation 2-6

(Shrihari et al., 1991); and galena as:

Equation 2-7

(Silver et al., 1986); and sphalerite as:

Equation 2-8

(Torma, 1971). Although H_2O may be a product in the initial sulphide oxidation (sulphide to elemental S), it later becomes a reactant in the final oxidation process (S^0 to SO_4^{2-}) resulting in no net H_2O additions in the overall stoichiometry. Note that the last three equations are acid neutral.

Direct oxidation by microbes utilizing only DO may play a role in the oxidation of sulphide minerals at Myra Falls (since most waters are pH ~ neutral), although the extent of this is not known. Nonetheless, oxidation of ubiquitous pyrite will likely be the prevailing mechanism in the formation of dissolved sulphates and risk of acid mine drainage. However, even though pyrite is the most common sulphide mineral present (Pearson, 1993), the oxidation mechanisms and dissolution of sulphides other than pyrite is of importance since minerals such as: sphalerite (ZnS , a simple mono-sulphide), chalcopyrite (CuFeS_2), and tennantite - tetrahedrite ($((\text{Cu,Fe})_{12}(\text{As,Sb})_4\text{S}_{13})$) are present in the Price hillside and the deeper strata.

In addition to SO_4^{2-} from the oxidation of sulphide minerals dissolution of some SO_4^{2-} minerals such as massive and disseminated barite and anhydrite may occur, adding SO_4^{2-} to the water.

Once SO_4^{2-} has been formed the rate of exchange of oxygen between SO_4^{2-} and water is extremely slow (Lloyd, 1967 and references therein) except at very low pH, where the bisulphate ion is protonated and water molecules are exchanged with $\text{SO}_{3(\text{aq})}$ in equilibrium with non-dissociated sulphuric acid (Hoering and Kennedy, 1957). Therefore under most pH conditions at Myra Falls the SO_4^{2-} will carry the $\delta^{18}\text{O}_{\text{SO}_4}$ signature of the oxygen sources involved in the sulphide oxidation.

Oxygen isotope ratios of SO_4^{2-} are useful in assessing the mechanisms of oxidation (Fe^{3+} vs. O_2 ; Equation 2-3 and Equation 2-4; Taylor and Wheeler, 1982; Wheeler and Taylor, 1982; Everdingen and Krouse, 1985), although it may not be instructive in determining the involvement of bacteria in the O_2 oxidation mechanism.

The fractionation of ^{34}S during sulphide mineral oxidation will depend upon the presence of intermediate redox S species, and upon the kinetic isotope effects of the bacterial oxidation (Kaplan and Rafter, 1958, Nakai and Jensen, 1964; Krouse, 1980; Fry et al., 1988). Kinetic isotope effects, however, are not always uniform, at times produce conflicting results, and interpretations are often complicated (Chambers and Trudinger, 1979).

The presence of sulphur species of intermediary redox (between S^{2-} and S^{6+}) has been documented during experimental abiotic sulphide oxidation (Moses, 1982; Goldhaber, 1983) and fractionation would only be expected between the different oxidation species if they are transported away from the sulphide surface before complete oxidation has occurred. Fractionation would not be likely at pH values less than 8 and normal ground water gradients.

Studies of the fractionation of ^{34}S during oxidation dissolution of sulphide minerals have lead to varied results. Experimental results indicate that ^{34}S fractionation is minimal during sulphide mineral oxidation, as compared to reduction. Nakai and Jensen (1964) found an enrichment $[1000(\alpha_{\text{pyrite-SO}_4}-1)]$ of -1.0 to -1.7‰ CDT using non-pure microbe cultures during aerated pyrite oxidation where pH was allowed to drift. Oxidation of S^0 to SO_4^{2-} by *Thiobacillus thiooxidans* results in no fractionation of ^{34}S (Jones and Starkey, 1957; in Kaplan and Rafter, 1958). Kaplan and Rafter (1958) found only very slight enrichments of ^{34}S when *Thiobacillus concretivorus* oxidized S^0 (-0.5 to 1.6‰ CDT). $\delta^{34}\text{S}$ of sulphate in contaminated ground waters due to mine drainage from Mississippi Valley type mineralization could not be explained by dilution of sulphates or sulphate reduction. For this case Toran (1987) suggested that neutrophilic microbe strains were responsible for a $\delta^{34}\text{S}_{\text{SO}_4}$ depletion of approximately 2 to 8‰ CDT during oxidation of the sulphide mineral source. In another study of acid mine drainage (Taylor et al., 1984(a)) sulphide oxidation must have occurred completely and at the mineral surface since there was little or no fractionation during sulphide mineral oxidation. Generally these studies indicate that no more than a $\pm 1\%$ difference ($\delta^{34}\text{S}_{\text{pyrite}}-\delta^{34}\text{S}_{\text{SO}_4}$) should be expected during pyrite oxidation.

2.4.2.2 Results

Twenty-four dissolved sulphates were analysed for $\delta^{34}\text{S}$, three of these waters were analysed for coexisting $\delta^{34}\text{S}$ in H_2S , and nine SO_4^{2-} were analysed for $\delta^{18}\text{O}_{\text{SO}_4}$. Methods and analytical technique are outlined in Appendix B. Results are presented in Table 2-3 and represent ground waters from various regions underground, and ground waters accessed from Thelwood Valley exploration drillholes. The $\delta^{34}\text{S}$ in SO_4^{2-} has a range greater than 40‰ (from -8.1‰ to +32.5‰; Table 2-3 and Figure 2-17) in ground waters from this study. This range is over 200 times the routine analytical precision in ^{34}S determinations.

Table 2-3 $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ and $\delta^{18}\text{O}$ data for selected ground waters.

Sample	Location	Drillhole/ Site	Elev. (m asl)	pH	Eh (V)	DO (mg/L)	SO ₄ (ppm)	H ₂ S Odour ^a	$\delta^{34}\text{S}\text{‰}$ SO ₄ CDT	$\delta^{34}\text{S}\text{‰}$ H ₂ S CDT	$\delta^{18}\text{O}\text{‰}$ SO ₄ ²⁻ VSMOW	$\delta^{18}\text{O}\text{‰}$ H ₂ O VSMOW
2561	Pr9-930dw	Pr9-12	416	7.4	0.35	8.0	47	no	-8.1		-7.8	-12.7
3505	Pr13-930dw	Pr13-13	242	7.4	0.41	2.9	20	no	-2.5			-12.9
2584	HW20-415xcn	N fault	-50	6.8	0.32	8.2	13	no	0.0		-1.7	-12.4
3385	Surf/ddh	PR-101	119	7.9	0.18	0.4	10	no	0.8			-12.9
3270	HW20-371xcs	HW20- 653	-75	7.5	0.32	8.7	773	no	3.1		10.3	-13.2
3399	M10-048de	M10-17	371	7.9	0.31	3.9	26	no	3.7			-13.2
2583	M13-108dw	M13-229	244	7.0	0.27	3.7	36	no	4.1			-12.4
3193	Pr5-830dw	Pr5-39	583	7.4	0.41	10.5	10	no	5.8			-12.9 ^b
3486	M13-108dw	M13-230	242	8.0	0.20	0.5	157	no	6.1			-12.9
3345	Surf/ddh	PR-92	54	7.8	-0.03	4.8	84	?	12.5			-13.4
3566	Surf/ddh	PR-84	-41	7.9	0.04	0.3	1200	no	12.6			-11.2
2416	M13-370xc	M13-225	244	9.3	0.38	9.6	278	no	12.7			-14.1
3274	Surf/ddh	PR-92	-52	8.8	0.21	0.9	68	no	13.5		8.5	-13.3
2585	HW20-415de	HW20- 832	-50	6.8	0.31	3.4	1420	yes, from drift floor ^c	15.6		11.3	-6.6
3216	Surf/ddh	PR-106	51	7.4	0.02	1.0	117	v v sl	18.3			-13.2
3277	Surf/ddh	PR-92	-26	8.6	0.08	1.4	92	?	18.6			-13.0
3363	Surf/ddh	PR-101	-26	8.2	-0.13	0.0	593	sl	20.7	-13.6	12.0	-9.4
3321	Surf/ddh	PR-101	-218	8.1	-0.08	0.0	741	yes	20.8	-10.6	11.6	-7.5
3267	HW20-371xcs	HW20- 650	-75	8.6	0.04	2.6	548	?	21.3			-11.9
3083	Surf/ddh	PR-106	-32	8.7	0.13	0.0	613	v v sl	24.0			-6.5
2611	Surf/ddh	PR-110	-310	7.1	0.08	0.0	1070	v v sl	24.5			-1.6
3273	Surf/ddh	PR-106	157	8.0	0.33	3.6	47	?	26.3			-12.1
3429	Surf/ddh	PR-100	-203	7.4	-0.17	0.0	900	str	28.3	-9.6	14.0	-3.0
3444	M10-370xcs	M10-??	373	10.1	-0.22	1.3	108	yes, black mud on drift floor	32.5		11.1	-14.2

^a sl. = slight, str. = strong, v. = very, no = none detected^b ^{18}O from Pr5-40 (+35‰N) drill hole located immediately below Pr5-39 (+45‰N)Routine error for ^{34}S is $\pm 0.20\text{‰}$ 2σ , these samples are likely higher due to impurities, largely Fe-hydroxidesPooled variance from 6 duplicate analyses of $^{18}\text{O}_{\text{SO}_4}$ is 0.26‰ VSMOW

2.4.2.3 Discussion of Sulphide Oxidation Mechanisms and Sulphate Sources

Mineral sulphide $\delta^{34}\text{S}$ in the Myra Falls mining camp vary over a wide range, and values ranging from -7.9‰ to +4‰ have been measured from sulphide minerals in the Battle zone (n=1 bornite, n=1 sphalerite, n=1 chalcopyrite, and n=11 pyrite) (B. Sinclair, University of Tasmania, personal communication). Pyrite varies over the entire range. The mean $\delta^{34}\text{S}$ is 0.9‰ CDT. This range is similar to that found in other base metal deposits (Rye and Ohmoto, 1974, Ohmoto and Rye, 1979). For example in Kuroko style massive sulphide deposits pyrite may vary over a wide array, approximately from -8‰ to +8‰ and will depend if the pyrite is early or late stage in the development of the deposit. Where order of genesis is apparent sulphide minerals evolve from heavy to light sulphur, from early to late stage deposition, and galena is depleted as compared to sphalerite due to equilibrium fractionation factors. Barite in sulphide deposits will be enriched over sulphide minerals by 20‰ or more.

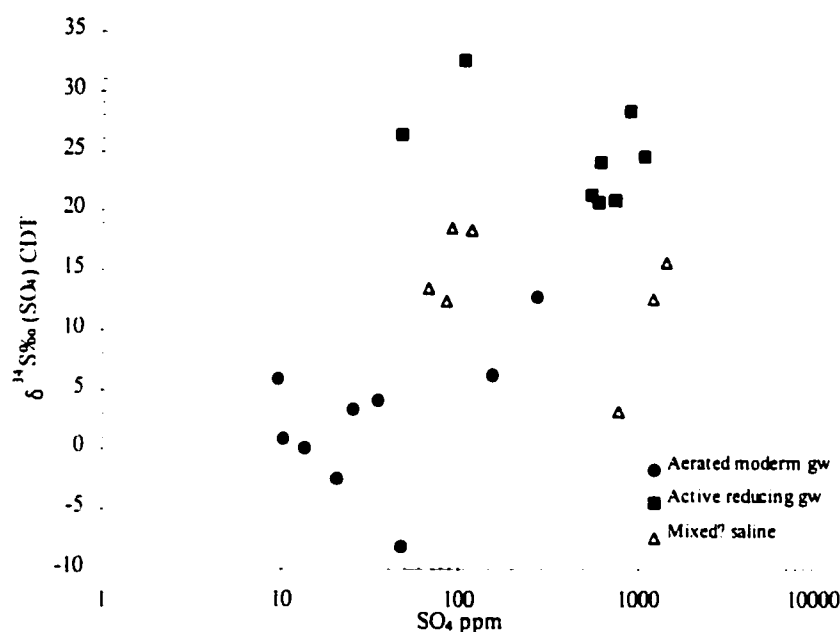


Figure 2-17 $\delta^{34}\text{S}$ vs. dissolved sulphate concentration. Unaltered dissolved sulphates (aerated modern) have $\delta^{34}\text{S}$ similar to sulphide minerals (some mixing is apparent in 2 samples). Reducing saline ground waters that have detectable H_2S have enriched residual $\delta^{34}\text{S}_{\text{SO}_4}$. Waters plotting in between these two groups appear to have a mixed source of SO_4^{2-} . High SO_4^{2-} concentration in the mixed(?) saline waters are likely have the least altered $\delta^{34}\text{S}$ due to mixing or reduction, but may include either or both of those components.

Several possibilities are explored to determine the reasons for the variation in $\delta^{34}\text{S}_{\text{SO}_4}$. Barite is present within and proximal to mineralization. Idealized contributions towards $\delta^{34}\text{S}_{\text{total}}$ were calculated based on the concentrations of Ba and SO_4^{2-} in these waters. Using an excessively high $\delta^{34}\text{S}_{\text{barite}}$ value of +40‰ and no fractionation during dissolution, would at most, result in a +0.6‰ enrichment in the resulting $\delta^{34}\text{S}_{\text{total}}$ based on the Ba and SO_4^{2-} ground water concentrations. Even with dissolution-recrystallization of barite along the flow path it would be difficult to attribute the wide range and high $\delta^{34}\text{S}_{\text{total}}$ to a barite source.

The wide range of $\delta^{34}\text{S}_{\text{SO}_4}$ values (Table 2-3 and Figure 2-17) in highly oxidized waters likely reflects variability in the S source. Variation in ^{34}S of coexisting sulphide and sulphate minerals is the norm in ore deposits. Also variation exists between early and late stage sulphide mineralization. A varying proportion of any of these components or variability between the rate of oxidation of these minerals would result in varying $\delta^{34}\text{S}_{\text{SO}_4}$. This would be expected in the Myra Falls mining camp especially when considering the changes in geology involved over the various sampling locations. There may also be a slight variation in

fractionation factors during sulphide mineral oxygenation due to different oxidation mechanism.

A positive shift of $\delta^{34}\text{S}_{\text{SO}_4}$ values in strongly reducing waters is most probably due to residual SO_4^{2-} being enriched since ^{32}S is preferential reduced during sulphate reduction.

An enriched $\delta^{34}\text{S}$ sulphate in the saline ground waters should be considered as a source of elevated $\delta^{34}\text{S}_{\text{SO}_4}$ values in some of the waters. There is a corresponding increase in enriched $\delta^{34}\text{S}$ in ground waters with increasing chloride concentration (Figure 2-18). Active SO_4^{2-} -reducing ground

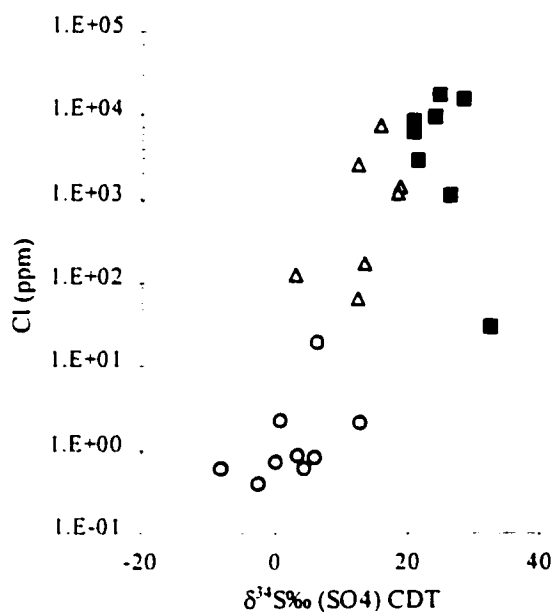


Figure 2-18 $\delta^{34}\text{S}$ increase with increasing Cl^- concentration. Legend is the same as in Figure 2-17

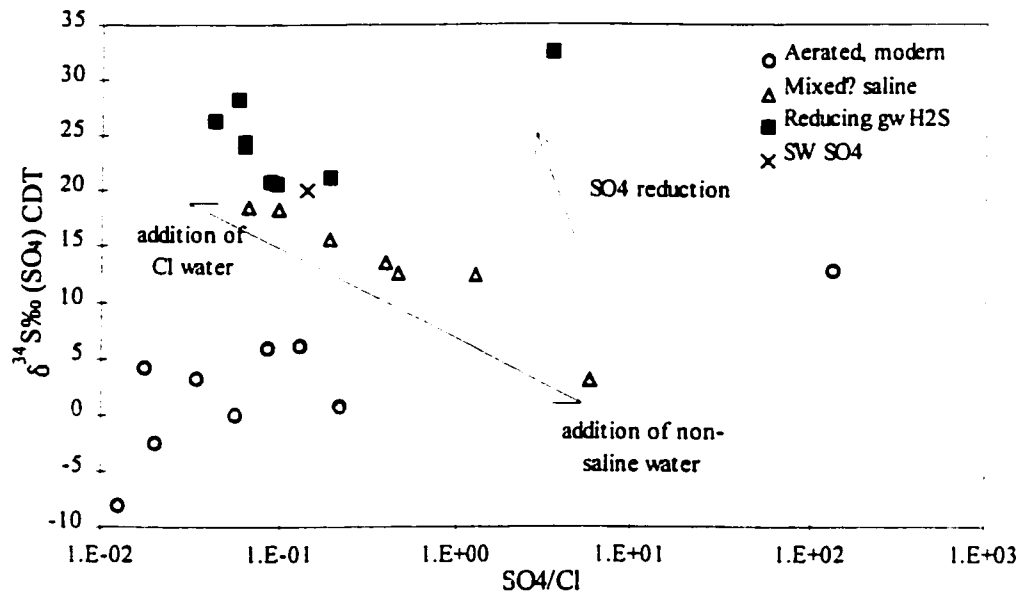


Figure 2-19 $\delta^{34}\text{S}$ vs. $\text{SO}_4^{2-}/\text{Cl}^-$ (mass ratio) discrimination diagram showing aerated unaltered SO_4^{2-} , reduced SO_4^{2-} , and the mixed saline source SO_4^{2-} which do not appear to be currently undergoing sulphate reduction, yet mainly have enriched $\delta^{34}\text{S}$. The one tipped arrow shows the approximate trend expected during SO_4^{2-} reduction. The line along the mixed source SO_4^{2-} shows the effects of mixing non-saline and saline waters. Modern sea water (SW) is plotted for reference.

waters have $\delta^{34}\text{S}_{\text{SO}_4}$ values greater than 20‰. Reasonably clear distinctions can be made between a recently oxidized sulphide source, actively reducing sulphate ground waters, and an intermediate varying-salinity component that shows little or no current sulphate reduction. The $\delta^{34}\text{S}$ in the latter group tends to have enriched values with increasing Cl contribution (lower $\text{SO}_4^{2-}/\text{Cl}^-$) (Figure 2-19), suggesting an enriched $\delta^{34}\text{S}$ of the SO_4^{2-} in the saline waters.

The isotopically distinct sources of O, water (variable, but all $<0\text{‰}$ VSMOW) and DO ($\delta^{18}\text{O} \approx +23.5\text{‰}$ V-SMOW) (Craig, 1972; Horibe et al., 1973), involved in oxidation reactions (Equation 2-3 and Equation 2-4) allows the monitoring of the resulting $\delta^{18}\text{O}_{\text{SO}_4}$ and establishing the contribution from each mechanism in sulphide mineral (pyrite) oxidation. However, this process is not always straight forward and will be complicated by any barite dissolved which will carry its own $\delta^{18}\text{O}_{\text{SO}_4}$ signature. The addition of SO_4^{2-} from the dissolution of sulphides will result in over-saturation with respect to barite in a water already in equilibrium with barite due to the common ion. This may then precipitate barite out of

solution; which will add a second complication to $\delta^{18}\text{O}_{\text{SO}_4}$, if fractionation results during barite precipitation. A further complication of this application will result where SO_4^{2-} reduction is occurring. The $\delta^{18}\text{O}_{\text{SO}_4}$ will be enriched as sulphate reducing bacteria such as *Desulfovibrio desulfuricans* preferentially reduce SO_4^{2-} containing light isotopes (^{16}O and ^{32}S) (Lloyd, 1967; Krouse, 1987). The last and probably the greatest complication is SO_4^{2-} in the saline water carrying an independent signature, mixing with SO_4^{2-} oxidized locally.

If the $\delta^{18}\text{O}_{\text{SO}_4}$ of barite reflects Devonian sea water ($\approx +16\text{‰}$; Claypool et al., 1980) from which it was precipitated then this source would be intermediate between $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{atmosphere}}$ and this contribution would be difficult to distinguish from other sources. However, the contribution of barite sulphate to the total $\delta^{18}\text{O}_{\text{SO}_4}$ would be expected to be quite minimal. Molar ratios of Ba/SO_4 in $\delta^{18}\text{O}_{\text{SO}_4}$ sampled waters ranges from $1.6 \cdot 10^{-5}$ to $1.1 \cdot 10^{-3}$. The contribution from such a small proportion of $\delta^{18}\text{O}_{\text{barite}}$ would be insignificant in the final $\delta^{18}\text{O}_{\text{SO}_4}$. Any precipitation of barite, or equilibrium exchange with barite along the flow path through dissolution-recrystallization processes will influence the ^{34}S and ^{18}O , leaving the residual SO_4^{2-} depleted in both constituents (Krouse, 1987). Once again, the ratio of barite / dissolved sulphate that would take part in these processes would be quite low and would likely impart a minimal if any noticeable shift in $\delta^{18}\text{O}_{\text{SO}_4}$.

The graphical representation of the contributions of Equation 2-3 and Equation 2-4 are shown on Figure 2-20. The relationship between $\delta^{18}\text{O}$ of the SO_4^{2-} ($\delta^{18}\text{O}_s$) and that of the water ($\delta^{18}\text{O}_w$) of the dissolved sulphate and co-existing water is shown. Control lines indicating the degree of oxidation by reactions Equation 2-3 and Equation 2-4 were generated using the isotope balance equation:

Equation 2-9

$$\delta^{18}\text{O}_s = R(\delta^{18}\text{O}_w + \epsilon_w) + (1 - R)[\frac{7}{8}(\delta^{18}\text{O}_a + \epsilon_a) + \frac{1}{8}(\delta^{18}\text{O}_w + \epsilon_w)]$$

Where R is the fraction of SO_4^{2-} oxidation produced from Equation 2-3; $\delta^{18}\text{O}_w$, $\delta^{18}\text{O}_s$, and $\delta^{18}\text{O}_a$ are the $\delta^{18}\text{O}$ values for the water, SO_4^{2-} , and air, respectively ($\delta^{18}\text{O}_a = 23.5 \text{‰}$; Craig, 1972; Faure, 1986). Enrichment factors, of the water (ϵ_w) and air (ϵ_a) are $+4.1\text{‰}$ (Taylor et al., 1984) and -8.7‰ (Lloyd, 1967), respectively. Taylor et al. (1984a) measured an ϵ_a value of -4.6‰ in a submersed abiotic pyrite oxidation experiment, and -11.2‰ for *T. ferrooxidans* mediated oxidation. The value of Lloyd (1967) was used in spite of the fact that

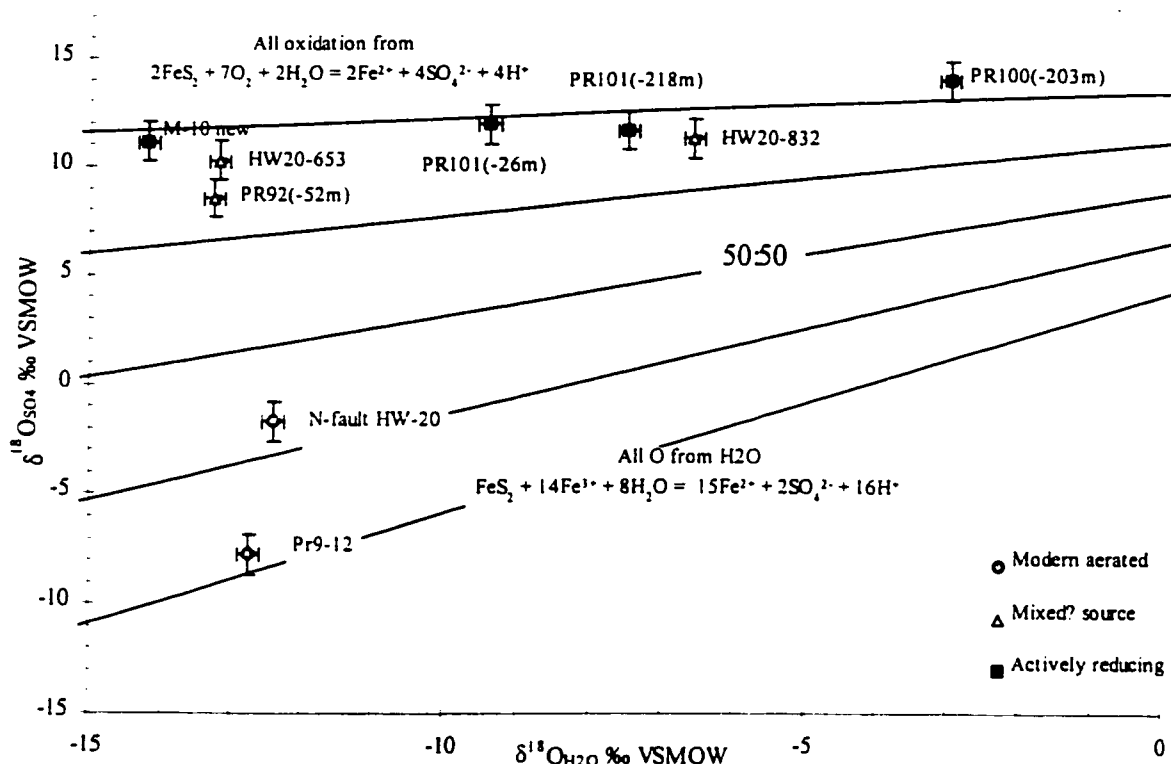


Figure 2-20 Relationship between $\delta^{18}\text{O}$ of SO_4^{2-} and $\delta^{18}\text{O}$ of ground water used to determine the oxidation mechanisms for sulphide mineral oxidation. The top line is for oxidation from only DO, while the bottom line signifies all oxidation from Fe^{3+} . Lines are spaced at 25% increments. Refer to text for the description of the control lines. Error bars are 2σ .

his experiments used oxidation of Na_2S instead of pyrite since it was conducted abiotically; which may be more representative of the circum-neutral pH of the ground waters involved in this study and more intermediate to the range of values reported by Taylor. Using an ϵ_a value of -11.2‰ simply has the effect of lowering the control lines that contain an atmospheric oxygen component. Taylor's ϵ_w is the lower value he measured in abiotic submersed pyrite oxidation experiments; although, it is slightly greater than the 2.6‰ used by van Everdingen et al. (1985) which they determined from the lowest possible ϵ_w from acidic mine drainage reported by Taylor et al. (1984(a)).

From Figure 2-20, it would appear that for the majority of samples, oxidation from DO is prevalent, contributing 75% percent or more toward the SO_4^{2-} . None of these ground waters are acidic and therefore sulphate - water exchange at low pH (Hoering and Kennedy, 1956) after sulphide oxidation can be ruled out as an explanation of the two lower $\delta^{18}\text{O}_{\text{SO}_4}$

values. However, as previously mentioned, the $\delta^{34}\text{S}$ of waters containing Cl^- tends to be enriched. A distinct source of SO_4^{2-} would be expected to bring along with it a distinct $\delta^{18}\text{O}_{\text{SO}_4}$ as well.

Figure 2-21 shows the $\delta^{18}\text{O}_{\text{SO}_4}$ variation with Cl^- concentration. The two waters where the SO_4^{2-} is attributed to recent oxidation of sulphide minerals plot with distinctly lower $\delta^{18}\text{O}_{\text{SO}_4}$ values on Figure 2-21 as they did on the oxidation mechanism diagram (Figure 2-20). From these two diagrams along with Figure 2-18 and Figure 2-19 it is apparent that the SO_4^{2-} related to the saline water has a unique SO_4^{2-} isotopic signature. This SO_4^{2-} isotopic signature has been altered to varying degrees by mixing with locally derived SO_4^{2-} and by processes such as SO_4^{2-} reduction. The $\delta^{18}\text{O}_{\text{SO}_4}$ of the saline SO_4^{2-} of the Cl^- bearing waters in Figure 2-21 is approximately +10‰ VSMOW.

Ground water from HW20-653 (Table 2-3) is the result of mixing recent meteoric (tritium bearing) waters with an older residual saline ground water (see Chapter 6 Ground Water Circulation). From Figure 2-20 it can be seen that the saline water contributes much of the $\delta^{18}\text{O}_{\text{SO}_4}$ (10.3‰ VSMOW), yet this water has a low $\delta^{34}\text{S}_{\text{SO}_4}$ (3.1‰ CDT). The SO_4^{2-} concentration of the saline water must be high enough that contributions from this source, which may possibly include secondary SO_4^{2-} minerals now being leached by meteoric water, are easily able to overwhelm the isotope ratios from sulphide oxidation in recent circulating waters. Sulphate concentrations in saline water from HW20-832 drill hole is up to 1400 ppm. An alternative explanation of the high $\delta^{18}\text{O}_{\text{SO}_4}$ and relatively low $\delta^{34}\text{S}_{\text{SO}_4}$ involves SO_4^{2-} produced from the oxidation of HS^- by oxygen within circulating meteoric waters mixing with a more saline member. This would result in a depleted $\delta^{34}\text{S}_{\text{SO}_4}$ with a $\delta^{18}\text{O}_{\text{SO}_4}$ partially derived from atmospheric O_2 . Indeed, metals have low concentrations in this water and any HS^- generated in the system may persist until oxidized by mixing meteoric water.

The two ground waters from the modern aerated group (Pr9-12 and the N-fault; Table 2-3) plot with distinctly low $\delta^{18}\text{O}_{\text{SO}_4}$ on Figure 2-20 and Figure 2-21. These same two waters are the only two waters on Figure 2-20 that are mainly the result of oxidation of sulphide minerals by Fe^{3+} (Equation 2-4). The Fe/SO_4 molar ratios are the highest in these two waters ($1.8 \cdot 10^{-3}$ and $4.6 \cdot 10^{-3}$). Pr9-12 and the N-fault waters are also very well aerated which would allow for rapid oxidation of Fe^{2+} which may then oxidize sulphide minerals such as pyrite.

Acidic mine runoff waters are infrequent and highly acidic ground waters are only encountered under previous mine workings in effluent draining Myra 12 level. Sulphate production in these ground waters is reasonably low (1,100 to 1,800 ppm), as compared to sulphate effluent in other mining districts (i.e., Shasta California, up to 11,500 ppm; Wheeler and Taylor, 1982). The prevalence of reaction Equation 2-4 with some contribution from DO (Equation 2-5) is similar to acidic and non-acidic mine effluent studies of Taylor et al. (1984) and van Everdingen et al. (1985). Taylor et al. (1984) indicate an increasing contribution from direct DO oxidation (Equation 2-3) in aerated environments and neutral low SO_4^{2-} waters from West Shasta where oxidation has an approximately 75% contribution by oxidation from Fe^{2+} (Equation 2-4). The circum-neutral to alkaline nature of the majority of Myra Falls ground waters is likely severely limiting the growth of acidophilic microbes thereby minimizing the rates of sulphide oxidation (Figure 2-16). Rapid precipitation of Fe^{3+} - hydroxides after iron oxidation (see Chapter 4 Physical Speciation (Filtration Studies)) would limit the availability of Fe, thereby limiting the further oxidation of sulphide minerals. Coating of sulphide surfaces would also slow the oxidation process; in this regard. Precipitating oxy-hydroxides may be a plausible mechanism in coating and limiting the

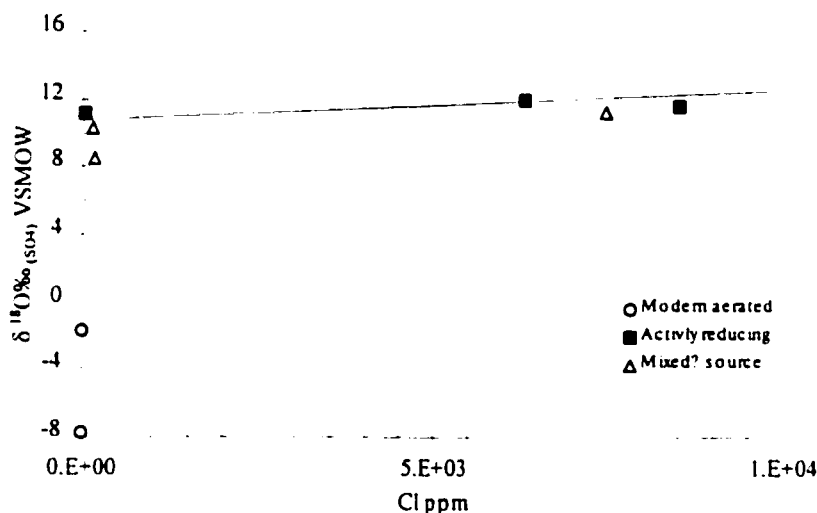


Figure 2-21 Plot of Cl vs. $\delta^{18}\text{O}_{\text{SO}_4}$ in ground waters. The Cl waters appear to have a $\delta^{18}\text{O}_{\text{SO}_4}$ of around 10‰. Sulphate reduction will then enrich ^{18}O further. However there is a general agreement between increasing Cl and increasing $\delta^{18}\text{O}_{\text{SO}_4}$ which may reflect the source SO_4^{2-} . Plotting symbols are the same as previous diagrams.

oxidation of pyrite. This limitation is generally overcome in oxidation experiments by stirring.

Core samples from the Price area have been exposed to the atmosphere more than 15 years and visual inspection of mineral surfaces of old core does not indicate if Fe coating took place before or after drilling.

From the above discussion it is apparent that three general groups of ground waters can be categorized based on the S and C isotopes, and water chemistry. The recently oxidized sulphate minerals have $\delta^{34}\text{S}$ values ranging from approximately -8 to +6‰ with a mean value of 1.2‰ CDT. The mean value is nearly equivalent to the mean $\delta^{34}\text{S}$ for sulphide minerals from the Battle zone (mean $\delta^{34}\text{S}$ is 0.9‰ CDT) (B. Sinclair, personal communication). A saline end-member SO_4^{2-} has a fairly constant $\delta^{18}\text{O}_{\text{SO}_4}$ value of $\approx +10$ ‰ VSMOW, and a $\delta^{34}\text{S}$ value of $\approx +15$ ‰ to +20‰ CDT. These isotopic values can then be enriched by SO_4^{2-} reduction. There is also water intermediate between these two types mentioned above, the result of mixing. The most saline component of the mixed water is likely not currently experiencing SO_4^{2-} reduction. Nevertheless it may include a component of the actively reducing water through mixing.

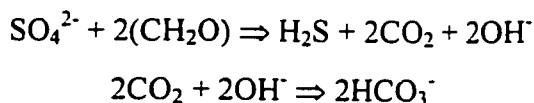
2.4.3 Sulphate Reduction

2.4.3.1 Introduction

Dissimilatory sulphate reduction can be catalysed by heterotrophic (organisms requiring one or more organic nutrients for energy and growth), autotrophic (organisms capable of growth totally at the expense of inorganic nutrients (i.e., H_2)), mixotrophy (organisms which simultaneously use organic and inorganic carbon sources and/or inorganic or organic energy sources) (Ehrlich, 1995); or, sulphate can be reduced by chemical reduction by Fe^{2+} . The latter reduction reaction mechanism occurs during deep sea water circulation in submarine basalts $\geq 250^\circ\text{C}$ (Styrud et al., 1981). In experiments conducted by Shanks et al. (1981), H_2S was not detected in sulphate reduction experiments using a fayalite iron source at 200°C and 500 bars, but mass balance equations showed that some pyrite was produced over the >200 day period. Sulphate reduction using ferrous iron would be expected to be kinetically slow at near surface temperatures.

Bacterial mediated sulphate reduction using organic carbon (represented as CH₂O) as an energy source will oxidize the carbon in the source and will incorporate $\delta^{13}\text{C}$ derived from the organic carbon into the DIC pool. These reactions can be written as:

Equation 2-10



This leads to a depleted $\delta^{13}\text{C}_{\text{DIC}}$ since most organic carbon sources are depleted. Likewise, sulphate reduction would affect the $\delta^{34}\text{S}$ of the remaining sulphate. This results in an enrichment in the residual $\delta^{34}\text{S}_{\text{SO}_4}$, as well as the $\delta^{18}\text{O}_{\text{SO}_4}$. Bacterially mediated sulphate reduction will have an enrichment ($\epsilon^{34}\text{S}_{\text{SO}_4\text{-HS}^-}$) between approximately 20‰ and 40‰ (Krouse et al., 1970).

Sulphate reducing bacteria such as *Desulfovibrio desulfuricans* will preferentially reduce SO_4^{2-} containing light isotopes (^{32}S and ^{16}O) (Lloyd, 1967). Lloyd (1967, 1968) found the enrichment for oxygen ($\epsilon^{18}\text{O}_{\text{SO}_4} \approx 1000(\alpha - 1)$) in the fraction remaining to be -4.6‰. Although, ^{18}O enrichment during enzymatic sulphate reduction may be dependent upon $^{18}\text{O}_{\text{H}_2\text{O}}$, as found by Mizutani and Rafter (1973) using an unspecified bacterial species cultured from natural sediments. Possibly there are two pathways where $^{18}\text{O}_{\text{H}_2\text{O}}$ can be exchanged; 1) in the SO_4^{2-} - enzyme complex, or 2) with the intermediate product, reduced SO_3^{2-} . Mizutani and Rafter (1973) fractionation varied with the composition of the solution and decreased with decreasing $\delta^{18}\text{O}_{\text{H}_2\text{O}}$. Their fractionation factor (α (residual sulphate / water)) ranged from 0.9988 to 1.025 and at $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ in the range of Myra Falls ground waters included the value of Lloyd (1967, 1968). Strebel et al. (1990) also determined that $\epsilon^{18}\text{O}$ range (-4.7 to -7.0‰) during sulphate reduction which included the value of Lloyd. Fritz et al. (1989) recognized in their experiments and those of Mizutani and Rafter (1973) that the $\delta^{18}\text{O}_{(\text{SO}_4)}$ tends to flatten out as the reaction proceeds and the maximum enrichment factor approaches an equilibrium (temperature dependent) enrichment factor; however, this would only be expected to occur with extensive SO_4^{2-} reduction (where the fraction remaining (f) is $\sim < 0.5$).

In a SO_4^{2-} closed system (i.e., barring a continual supply of SO_4^{2-}) the evolution of the residual $\delta^{34}\text{S}$ during sulphate reduction can be described by Rayleigh fractionation:

Equation 2-11

$$\delta\text{Isotope}_{\text{remaining}} - \delta\text{Isotope}_{\text{original}} = 1000(\alpha - 1) \ln f$$

where α is the fractionation factor and f is the fraction remaining.

Sulphate adsorption may also be another mechanism that enriches residual $\delta^{34}\text{S}_{\text{SO}_4}$, but would leave the $\delta^{13}\text{C}_{\text{DIC}}$ unaltered. Even though Fe-hydroxides are plentiful in these ground waters (see Chapter 4 Physical Speciation (Filtration Studies)), anion adsorption would not be expected at the neutral to the alkaline pH (Ali and Dzombak, 1996; Drever, 1997) of the Myra Falls waters. The results of experiments by Ali and Dzombak (1996) showed no loss of sulphate using goethite at pH 8.0. At a pH of 7.0 these same experiments showed losses of sulphate to adsorption were not appreciable at concentrations as low as 0.25 mmol L^{-1} SO_4^{2-} , but increased to approximately 30% at 0.025 mmol. On natural aquifer material the loss of SO_4^{2-} was less than 20 $\mu\text{g g}^{-1}$ aquifer material at circum-neutral pH during artificial recharge experiments of Wood (1978). However, no sulphur isotopes were measured during these experiments. Sulphate adsorption may leave the residual sulphate enriched in $\delta^{34}\text{S}$; however, fractionation has been shown to be highly variable and Krouse (1987) suggests that physical adsorption may not be the only factor involved in fractionation. Enrichment of $\delta^{34}\text{S}_{\text{SO}_4}$ does not occur until concentrations are ≥ 50 ppm and a pH 8.0. Adsorption of sulphate on Fe-hydroxides would be extremely minimal at the conditions in the Myra Falls ground waters. As well, the H_2S odour in the Myra Falls ground waters experiencing $\delta^{34}\text{S}$ enrichment is further evidence that sulphate reduction is taking place and therefore adsorption can be largely ruled out as a mechanism in $\delta^{34}\text{S}_{\text{SO}_4}$ enrichment.

2.4.3.2 Discussion

Kinetic isotopic effects during the reduction of SO_4^{2-} will result in an enrichment of $\delta^{34}\text{S}$ in the remaining fraction of sulphate. The average enrichment ($\epsilon_{\text{SO}_4\text{-H}_2\text{S}}$) of 34.5‰ ($n=3$) in the Myra Falls ground waters would likely represent an instantaneous fractionation factor as HS^- would likely not build-up in the water since it should be quickly removed from the ground water through the precipitation of sparsely soluble sulphide minerals.

The enrichment factor of 34.5‰ clearly points to bacterial mediated reduction, which generally has an $\epsilon_{(\text{SO}_4\text{-H}_2\text{S})}$ between 20 and 40‰ (Krouse, 1970), as opposed to a thermodynamic equilibrium source (i.e., geothermal or mantle) which at 15°C (using the equation for the equilibrium fractionation factor of Sakai, 1968) would have a $\epsilon_{(\text{SO}_4\text{-H}_2\text{S})}$ of 76‰.

Kaplan and Rittenberg (1964) found an inverse relationship between fractionation and rate of reduction during sulphate reduction using *Desulfovibrio desulfuricans*. They attributed this to the activity of the microbes, which have greater isotope discrimination during slower rates of reduction. This rate effect was also noted by Krouse et al. (1970). The average $\delta^{34}\text{S}$ difference ($\Delta^{34}\text{S}_{\text{SO}_4\text{-H}_2\text{S}}$) for the three Thelwood Valley ground waters that have coexisting $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ is $34.5 \pm 3.3\text{‰}$ (1σ). According to Kaplan and Rittenberg, 1964) this enrichment would suggest that moderately low rates of sulphate reduction is occurring; approximately equivalent to $\leq 1 \cdot 10^{-15} \text{ g S cell}^{-1} \text{ hr}^{-1}$. A $\Delta^{34}\text{S}_{\text{SO}_4\text{-H}_2\text{S}}$ within the range measured at Myra Falls was attributed to reduction by two species in natural (hot spring) settings (Krouse et al., 1970). The first organism was believed to reduce SO_4^{2-} to an intermediate redox state, and a second strain completed the reduction - producing S^{2-} . The high $\Delta^{34}\text{S}_{\text{SO}_4\text{-H}_2\text{S}}$ could not be duplicated in the lab and the small isotopic fractionation was attributed to the fast rate of reduction in the lab experiments.

Three separate groups of waters (see previous section 2.4 for discussion of groupings) are plotted on Figure 2-22 from which it is apparent that two groups are $\delta^{34}\text{S}_{\text{SO}_4}$ enriched as compared to SO_4^{2-} derived from recent oxidation of sulphide minerals. Ground waters not affected by sulphate reduction plot in the $\delta^{34}\text{S}$ range of approximately $0\text{‰} \pm 8\text{‰}$ CDT and $\delta^{13}\text{C}_{\text{DIC}}$ of approximately $10\text{‰} \pm 3.5\text{‰}$ VPDB. A strong H_2S odour was evident in the three ground waters with depleted $\delta^{13}\text{C}_{\text{DIC}}$, the same three sites where coexisting $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ was precipitated and analysed. These three ground waters plot with enriched $\delta^{34}\text{S}$ and depleted $\delta^{13}\text{C}_{\text{DIC}}$ compared to the non-affected ground waters, typical of sulphate reduction from a depleted carbon source. In this case sulphate reducing bacteria are using organic carbon (canola oil - used as a drilling additive) as an energy source; which will incorporate enriched modern organic carbon ($\delta^{13}\text{C}$ and ^{14}C) into the DIC pool. Other ground waters that have only slight or no detectable H_2S odour, or the H_2S may have been released from muddy (usually

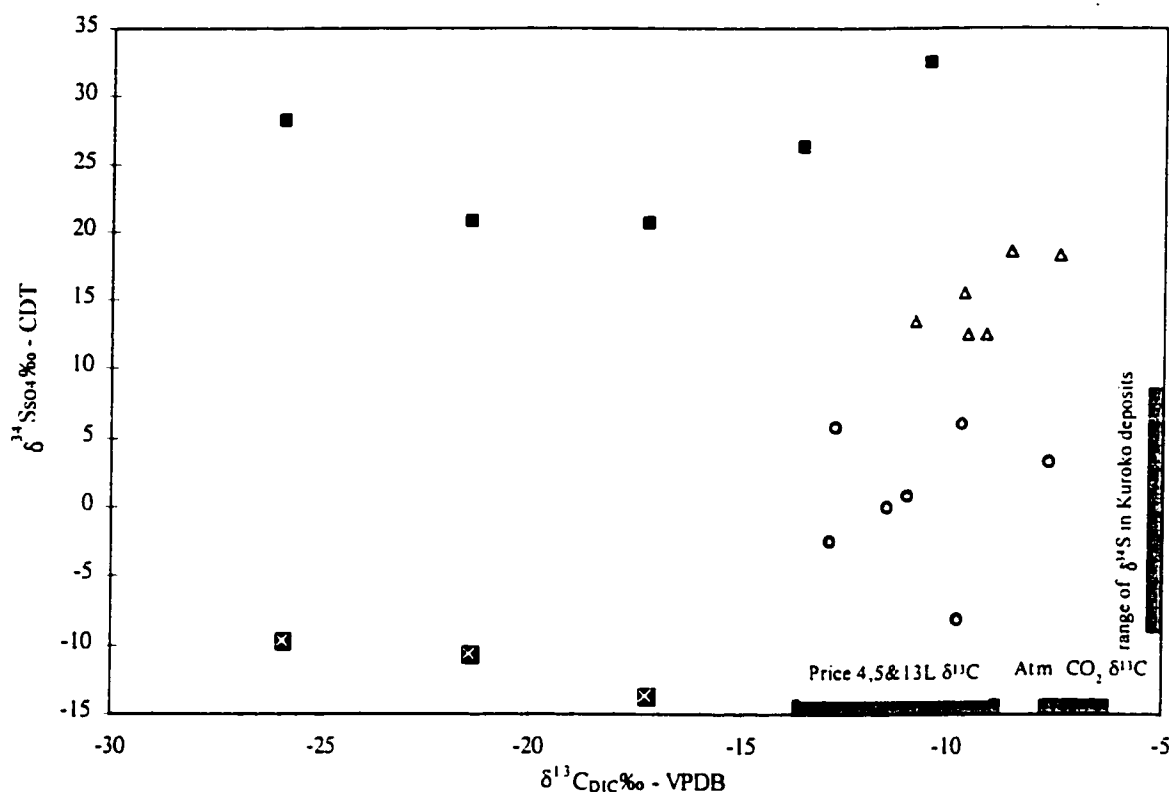


Figure 2-22 $\delta^{34}\text{S}_{\text{SO}_4}$ - $\delta^{13}\text{C}_{\text{DIC}}$ plot of ground waters. Plotting symbols are similar to Figure 2-20 except sulphide (squares with white x) analyses is added. Dashed tie-lines join coexisting sulphide and sulphate in ground waters. Sulphate derived from a mainly saline (mixed) source have enriched $\delta^{34}\text{S}$ values as compared to sulphate derived from modern oxidation of sulphide minerals. Error (2σ) is within the plotting symbols.

black coloured) sediments on the drift floor (i.e., #3444 M10-new), have enriched $\delta^{34}\text{S}$ (although no CdS or ZnS would precipitate from solution, and possibly other odours were mistaken for H_2S) but plot with similar values of $\delta^{13}\text{C}_{\text{DIC}}$ to the ground waters not affected by sulphate reduction (Table 2-3).

There will be a significant and noticeable effect on $\delta^{34}\text{S}$ with an increasing fraction of the amount of sulphate reduction. The estimate of the fraction remaining can be garnered from the shift in $\delta^{34}\text{S}_{\text{SO}_4}$. Ideally the combination of $^{18}\text{O}_{\text{SO}_4}$ and $^{34}\text{S}_{\text{SO}_4}$ would be used in determining the extent of sulphate reduction; the paucity $^{18}\text{O}_{\text{SO}_4}$, and variation due to mixing (Figure 2-23) does not allow a good estimate of the initial value of $^{18}\text{O}_{\text{SO}_4}$. For SO_4^{2-} formed from the reaction involving DO oxidation of sulphide minerals (Equation 2-3), the $^{18}\text{O}_{\text{SO}_4}$

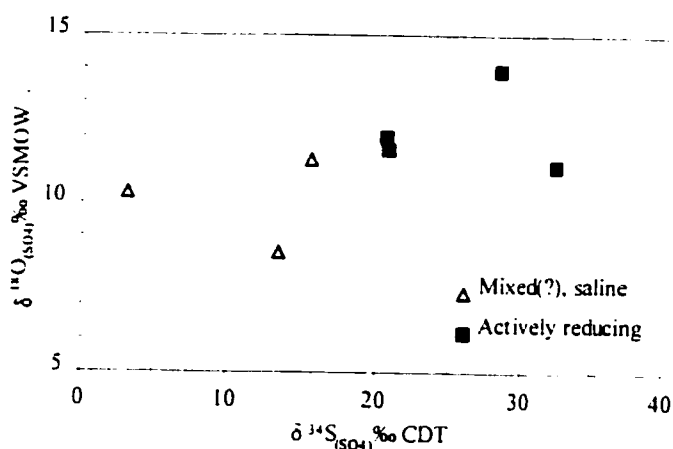


Figure 2-23 $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ of SO_4^{2-} reducing ground waters and saline waters. Variation in the saline non-reduced waters may be due to mixing of different sources.

could also be variable due to the variable $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ in ground waters throughout the property (i.e., possibly #3270; Table 2-3).

Using $\Delta^{34}\text{S}_{\text{SO}_4\text{-H}_2\text{S}}$ equal to 34.5‰ and an original $\delta^{34}\text{S}$ values of 15, 17.5 and 20‰ CDT (which is the approximate range of the $\delta^{34}\text{S}$ of the saline water SO_4^{2-})

a fraction remaining can be

calculated by rearranging Equation 2-11. The fraction remaining (f) of the original sulphate is as low as 0.62 in ground water from Thelwood Valley, and as low as 0.54 for ground water #3444 from Myra 10 level (Table 2-4). Using the lower two $\delta^{34}\text{S}$ original values also results in the allocation of some portion of the saline mixed group of SO_4^{2-} waters having been reduced. If this is true, this low amount can easily be explained by mixing between the saline water with a reduced SO_4^{2-} water component. There is likely a full range of mixing between a modern oxidizing water with low SO_4^{2-} and Cl^- concentration and the saline water, which may include some reduced SO_4^{2-} component (Figure 2-24).

Table 2-4 Estimate of original SO_4^{2-} fraction remaining (f) after SO_4^{2-} reduction for waters designated as mixed source and reducing, and estimates of the original $\delta^{18}\text{O}_{\text{SO}_4}$ before reduction for each scenario. $\delta^{34}\text{S}$ referenced to CDT; $\delta^{18}\text{O}$ from SO_4^{2-} referenced to VSMOW.

Sample	$\delta^{34}\text{S}\text{‰}$ measured	$\delta^{18}\text{O}\text{‰}$ measured	f $\delta^{34}\text{S} =$ 15‰	$\delta^{18}\text{O}_{\text{orig}}\text{‰}$ $\delta^{34}\text{S} =$ 15‰	f $\delta^{34}\text{S} =$ 17.5‰	$\delta^{18}\text{O}_{\text{orig}}\text{‰}$ $\delta^{34}\text{S} =$ 17.5‰	f $\delta^{34}\text{S} =$ 20‰	$\delta^{18}\text{O}_{\text{orig}}\text{‰}$ $\delta^{34}\text{S} =$ 20‰
3345	12.5		1.00		1.00		1.00	
3270	3.1	10.3	1.00	10.3	1.00	10.3	1.00	10.3
3274	13.5	8.5	1.00	8.5	1.00	8.5	1.00	8.5
2585	15.6	11.3	0.98	11.2	1.00	11.3	1.00	11.3
3566	12.6		1.00		1.00		1.00	
3277	18.6		0.88		0.96		1.00	
3216	18.3		0.89		0.97		1.00	
3267	21.3		0.80		0.87		0.95	
2611	24.5		0.71		0.78		0.85	
3273	26.3		0.67		0.73		0.80	
3083	24.0		0.73		0.79		0.87	
3321	20.8	11.6	0.81	10.6	0.89	11.0	0.97	11.5
3363	20.7	12.0	0.82	11.0	0.89	11.4	0.98	11.8
3429	28.3	14.0	0.62	11.6	0.68	12.0	0.74	12.5
3444	32.5	11.1	0.54	8.0	0.59	8.5	0.64	8.9
SO4/Cl estimate of original			0.14		0.12		0.10	

The fraction remaining can then be used to calculate the $\delta^{18}\text{O}_{\text{original}}$ (before reduction) of the saline water that is currently undergoing SO_4^{2-} reduction. The results will be sensitive to input parameters and will include a greater amount of uncertainty. The enrichment from Lloyd [(1967, 1968; -5‰ for oxygen, $\epsilon^{18}\text{O} \approx 1000(\alpha - 1)$)] is used for this calculation. Three scenarios are presented in Table 2-4 based on the fractions (f) calculated using $\delta^{34}\text{S}$ values of 15‰, 17.5‰, and 20‰ CDT in the original saline SO_4^{2-} . Using the lower $\delta^{34}\text{S}_{\text{original}}$ results in calculated original $\delta^{18}\text{O}_{\text{SO}_4}$ values in the 10 to 11‰ range, similar to those for $\delta^{18}\text{O}_{\text{SO}_4}$ of SO_4^{2-} from waters that do not appear to be undergoing active sulphate reduction (higher Eh,

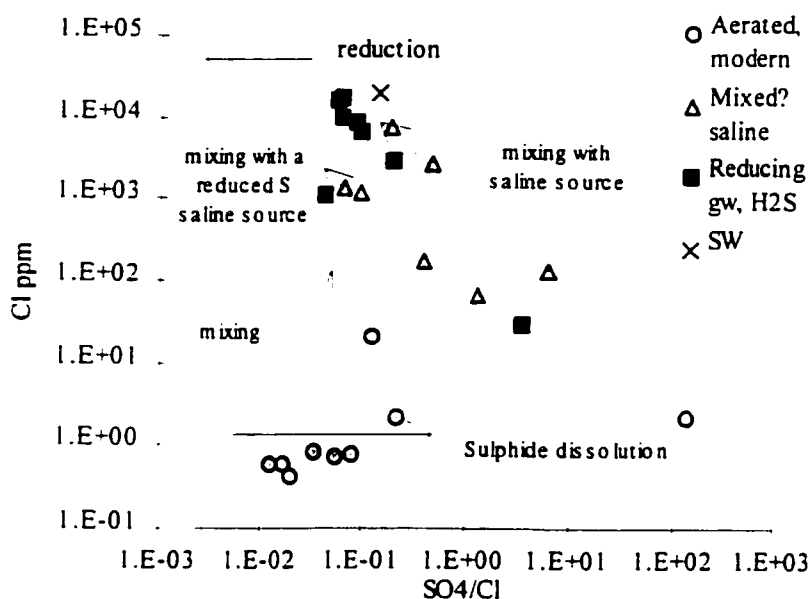


Figure 2-24 Cl vs. SO_4/Cl plot exploring sources of SO_4^{2-} and processes affected SO_4^{2-} using Cl as a conservative tracer. Mixing with a Cl water will plot as a straight line. Sulphate reduction will remove SO_4^{2-} at a constant Cl concentration. Sea water (SW) plotted for reference.

and contain some DO) (site 3274, Table 2-4 likely contains a mixing contribution from recently oxidized SO_4^{2-} reflected in its' low $\delta^{18}\text{O}_{\text{SO}_4}$).

The fraction reduced agrees fairly well with concentrations of SO_4^{2-} in these ground waters. For example water #3429 (Table 2-3, Table 2-4) from PR-100 has 900 ppm SO_4^{2-} ; which is 0.63 of 1420 ppm (the highest concentration of SO_4^{2-} from a saline non-reducing water; #2585). The estimated fraction remaining using $\delta^{34}\text{S}_{\text{original}}=15\text{‰}$ is 0.62.

2.4.4 Summary (Sulphide Oxidation and SO_4^{2-} Reduction)

The rate of biological and abiotic reactions are temperature dependent, and the rate of reactions tend to double for every 10°C increase (McIntosh et al., 1997, and references therein). Sulphide oxidation is an exothermic reaction, nevertheless the temperature surrounding the area of sulphide dissolution can be highly buffered, or regulated by the degree of water circulation past the oxidation zone (McIntosh et al., 1997). Ground waters from drill holes in the M-P ridge (Price 4&5 levels) are generally $6-7^\circ\text{C}$ (Table 3-1). This low temperature would moderate reactions and is not as conducive to the growth of most strains of the primary sulphide oxidizer *Thiobacillus ferrooxidans*, which is mesophilic (ability to grow (divide) within the approximate temperature range of 15 to 50°C). *Thiobacillus ferrooxidans* is also acidophilic, and thrives at a pH of less than two. Flushing of ground water by fresh recharge water, although supplying a continuous reserve of oxygen, may inhibit bacterial growth by maintaining a cool temperature and by buffering the pH, both of which inhibit bacterial growth. As mentioned previously, at low pH the dominant role of O_2 is in the oxidation of Fe^{2+} and consequently sulphate oxygen is obtained mainly from the water (Taylor et al, 1984(a)). The two waters with measured $\delta^{18}\text{O}_{\text{SO}_4}$ that the majority of their sulphate attributed to recent oxidation of sulphide minerals have a large contribution ($>70\%$) from oxidation of sulphide minerals by Fe^{3+} (Figure 2-20). The primary role of O_2 in these waters is in the oxidation of Fe^{2+} . The rapid removal of Fe^{3+} by the formation of Fe-oxyhydroxides (Chapter 4) may also play a prominent role in the lack of acidic waters in the Myra-Price ridge. The removal of Fe^{3+} will limit the amount of sulphide minerals that can be oxidized by Equation 2-3 which is predominant oxidation mechanism of sulphide minerals and the formation of sulfuric acid waters.

Several distinctive components of SO_4^{2-} can be seen in the Myra Falls ground waters:

1. the first SO_4^{2-} component is from the oxidation of sulphide minerals by recent meteoric waters. This component has low SO_4^{2-} , and $\delta^{34}\text{S}$ of around $0 \pm 8\text{‰}$ CDT. The Cl^- concentrations are low and the SO_4/Cl ratios are variable.
2. a saline water with SO_4^{2-} concentration approaching 1500 ppm. These waters are close to saturation with respect to

gypsum. The Cl^- concentrations are high and the SO_4/Cl mass ratio is around 0.06. The $\delta^{34}\text{S}$ of the saline end-member is estimated to be approximately $17\text{‰} \pm \text{CDT}$, and $\delta^{18}\text{O}_{\text{SO}_4}$ is approximately 10‰ VSMOW. 3. A distinct component with high $\delta^{34}\text{S}$ in the residual SO_4^{2-} results from actively reducing SO_4^{2-} . These waters have H_2S associated with them.

A full array of mixing is apparent between these different end-members, especially between the recently oxidized SO_4^{2-} (from sulphide) and the saline water SO_4^{2-} , which results in lower SO_4^{2-} concentrations, and variable SO_4/Cl (which increases with decreasing Cl^- concentration; Figure 2-24).

All but one of the actively SO_4^{2-} reducing sites is located in Thelwood Valley, and canola oil, used as a drilling adjunct (lubricant), is implicated as an energy source in bacterially mediated reduction. Zones which were sampled with the straddle packer system were chosen based on geophysical logging. Low density indicating fractures or faults and fluctuations in temperature gradient indicating water flow were the primary conditions used to select a sampling interval. Active flow in these zones should flush any free canola from the water. These zones were also developed until physical parameters stabilized. This implies that the canola oil used as an energy source by SO_4^{2-} reducing bacteria was likely partitioned onto solid phases from where it was later slowly released and utilized by bacteria.

The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ of the saline water SO_4^{2-} is estimated at around $17.5 \pm 2.5\text{‰}$ CDT, and approximately 10 to 11‰ VSMOW for $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$, respectively. If this SO_4^{2-} is from a sea water (or from gypsum precipitated from sea water) that has retained its SO_4^{2-} isotope signature, a Jurassic to Early Cretaceous oceanic SO_4^{2-} source based on the sea water $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ curves of Claypool et al. (1980). However, if the $\delta^{18}\text{O}_{\text{SO}_4}$ relationship vs. Cl^- is valid and the more saline waters have a $\delta^{18}\text{O}_{\text{SO}_4}$ closer to 14‰ VSMOW then a much broader overlap occurs on the sea water curve including Devonian to early Permian and Triassic to Late Cretaceous.

2.5 Strontium: $^{87}\text{Sr}/^{86}\text{Sr}$

2.5.1 Introduction

In ground water studies, strontium isotopes act as a tracer of not only Sr but also Ca, since these two elements have very similar geochemical character. Rubidium-87 decays to ^{87}Sr through emission of a negative β particle. Chemically, Rb is more similar to K. The $^{87}\text{Sr}/^{86}\text{Sr}$ can be indicative to the source of the Sr (and Ca) in brines, and in ground water mixing (McNutt, 1987, McNutt et al, 1989; Lyons, et al., 1995). The study of Sr isotopes may reveal information on the origin of Ca in these ground waters.

2.5.2 Results

Strontium isotopes were measured in three ground waters from Myra Falls, which span almost the full range of Sr concentrations, and include low to high salinity ground waters. These three ground waters comprise a high elevation, low TDS water from 5 level Price (#3186), a brackish mine water (HW20-832; #2585), and a Thelwood Valley saline water from PR106 (#3365). Water 2585 (HW20-832 U2) comes from an open hole that is completed into the Price andesite (HW footwall andesite); whereas 3365 was sampled by a single packer isolating the bottom of the hole in which the major water inflows determined by geophysical logging, are located in the lower mine sequence. Strontium concentration varies from 1.3 to 67 ppm. The $^{87}\text{Sr}/^{86}\text{Sr}$ results are fairly uniform (Table 2-5), varying over a narrow range of 0.705005 to 0.705588 $^{86}\text{Sr} / ^{87}\text{Sr}$.

Table 2-5 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope measurements in select ground waters.

Sample	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$	Ca ppm	Rb ug/L	Cl ppm
3186	1.3	0.705097	42	<0.2	1.13
2585	27.0	0.705588	1020	6.00	7467
3365	67.0	0.705005	3270	34.0	16338

2.5.3 Discussion

Strontium isotope ratios in sea water are approximately 0.7092 (Veizer, 1989) and have had a complex history in oceans over geologic time. Maximum variations of sea water from the Devonian to present are from approximately 0.7067 to 0.7091 (Burke et al., 1982; Veizer, 1989); considerably higher than the Myra Falls ground waters.

Juras (1987) analysed twelve whole-rock samples of flow unit rocks for strontium and found a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70433 to 0.71091). He attributed the variation to alteration of the original rocks, possibly by sea water soon after emplacement (Devonian sea water $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7078$ to 0.7088; Burke et al., 1982), or by a later fluid related to regional metamorphism or intrusion. Rubidium is associated with hydrothermal alteration and the Rb/Sr ratios of the rock increase with increasing $^{87}\text{Sr} / ^{86}\text{Sr}$ in the rocks that are the most altered. Rocks with higher $^{87}\text{Sr} / ^{86}\text{Sr}$ have lower Sr concentrations and high Rb/Sr which approach 0.90, a considerable increase from less than 0.01 for least altered high Sr rock. The calculated initial Sr ratio for the Myra Falls rocks is 0.7023 to 0.7047 (Juras, 1987) which indicates dominantly a mantle source for the rocks.

The Sr ratio of the low EC water plots between the saline waters, and for these three samples no trend is apparent with increasing chloride content (salinity) or Sr content (Table 2-5). There is no relationship between 1/Sr concentration vs. Sr isotopes, the variation indicating the $^{86}\text{Sr} / ^{87}\text{Sr}$ variation in these three waters is not the result of binary mixing.

The source of Sr is similar in saline and non-saline waters as compared to the ranges of strontium ratios in the mine sequence rocks. The ground water $^{86}\text{Sr} / ^{87}\text{Sr}$ ratios approximately reflect the modern ratios in rocks with higher Sr and lower Rb concentrations. Dissolution of Sr containing phases in the more altered rocks will lead to slightly higher $^{86}\text{Sr} / ^{87}\text{Sr}$ ratios, but the Sr ratio of this low Sr content source would be masked by the high Sr concentrations of the rocks with $^{86}\text{Sr} / ^{87}\text{Sr}$ closer to 0.7045 to 0.7050.

In summary the Sr ratios of the water reflect equilibration with the current $^{86}\text{Sr}/^{87}\text{Sr}$ within the higher concentration whole-rock Sr basaltic flows of the mine sequence rocks and footwall andesites. The $^{86}\text{Sr}/^{87}\text{Sr}$ reflects a dominantly mantle source, which these rocks are derived.

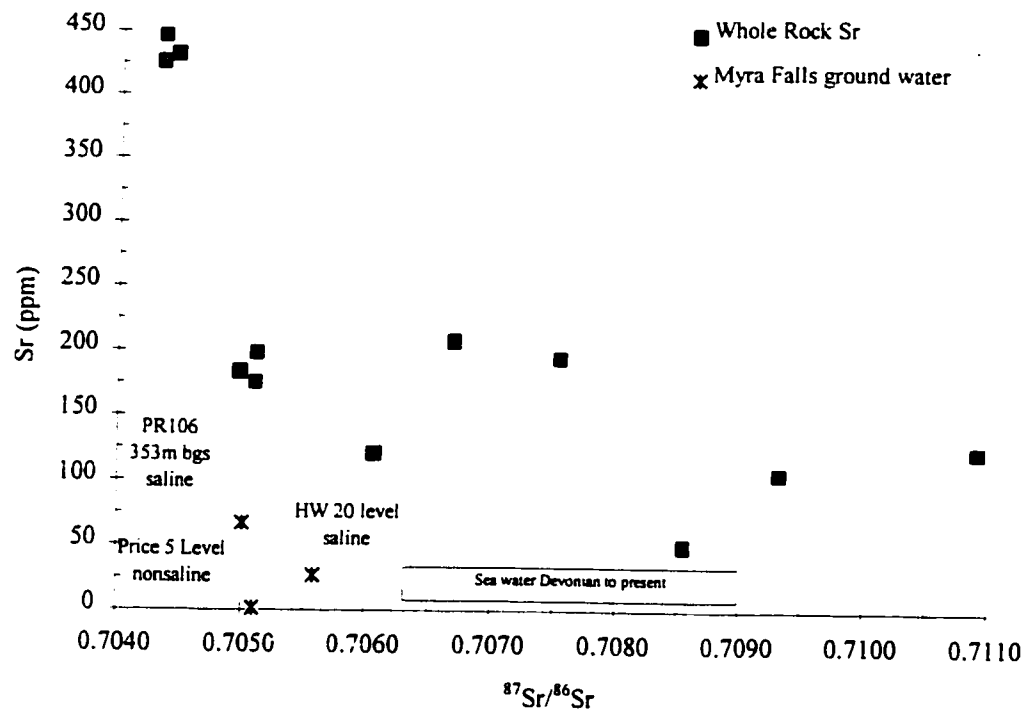


Figure 2-25 Strontium isotopes from Myra Falls ground water and whole-rock samples (whole-rock strontium (ppm) from Juras, 1987).

2.6 $^{37}\text{Cl}/^{35}\text{Cl}$: Stable Chloride

2.6.1 Introduction

Chlorine-37 is one of two stable isotopes of chloride; ^{35}Cl being the other. Natural abundances of ^{35}Cl is 75.53%, and ^{37}Cl is 24.47%. Chlorine-37 is reported in the delta notation referenced to Standard Mean Ocean Chloride (SMOC). The small mass difference to average mass between these two isotopes leads to less fractionation as compared to the lower molecular weight elements. This results in a low range of chloride isotope ratios in the surface and near surface environments. Because chlorine exists in nature as monovalent chloride ion, there is no large oxidation or reduction fractionation effect as seen in nuclides like ^{13}C and ^{34}S . Until fairly recently the ^{37}Cl variations had not exceeded the precision of the measurement, but with increasing precision of mass spectrometers and extraction methods small variations can be determined (Owen and Schaeffer, 1954; Hoering and Parker, 1961; Kaufmann et al., 1984). Fractionation, diffusion, and filtration, are the likely mechanisms for chlorine isotope variations seen in nature (Kaufmann, 1988). Our knowledge of the processes that affect chlorine isotopic systematics is still in its infancy and its utility in identifying distinct Cl reservoirs (with the exception of the modern ocean) is only beginning to be assessed; although, local lithological sources may have distinct, narrow ranges (Long et al., 1993).

The range of $\delta^{37}\text{Cl}$ compositions of natural waters is generally less than $0 \pm 2\text{‰}$ SMOC (Long et al., 1993), and the range of most $\delta^{37}\text{Cl}$ in chloride minerals does not vary more than $\pm 1\text{‰}$ SMOC; although some recent work by Ransom et al. (1995) and Magenheimer et al. (1995) extend the range of natural waters to $\sim -8\text{‰}$ and hydrous silicate minerals up to $+8\text{‰}$. However, there has been criticism on the validity of early thermal ionization measurements used in some of this work (Long et al., 1993).

Evaporite minerals, secondary sedimentary minerals, and magmatic minerals all have little $\delta^{37}\text{Cl}$ variation (Eggenkamp and Schuiling, 1995). The low variation in magmatic minerals is probably due to low fractionation at high temperatures, and in the evaporitic and secondary minerals is due to restricted fractionation during precipitation (Hoering and Parker,

1961; Eggenkamp and Schuiling, 1995). Kaufmann, et al. (1984) measured $\delta^{37}\text{Cl}$ values between +0.40‰ and +0.45‰ for three hydrothermal waters from California, New Zealand, and Mexico. They also suggest that the salt deposits they measured tend to be slightly enriched over sea water; although this is dependent upon the extent of sea water evaporation (Eggenkamp and Schuiling, 1995). Biotite tends to be enriched in ^{37}Cl with respect to hydrothermal fluids from which it forms (Eastoe and Guilbert, 1992). Fumarolic minerals (PbCl and NH_4Cl) from Vesuvius and Etna volcanoes have low $\delta^{37}\text{Cl}$ values, -0.46‰ and -4.88‰, respectively and are deposited from a depleted vapour phase (Eggenkamp and Schuiling, 1995). Chloride has low fractionation at low temperature, excluding possible diffusion related processes.

High $\delta^{37}\text{Cl}$ values have been analysed from oxidation zone minerals and chlorides within oxidizing base metal environments ($\delta^{37}\text{Cl}$ up to 5.96‰; Eggenkamp and Schuiling, 1995). Eggenkamp and Schuiling (1995) suggest that elevated $\delta^{37}\text{Cl}$ in ground waters draining base metal deposits may function as an exploration tool. The explanation for the enriched values was suggested as isotopically depleted gaseous HCl loss during base metal oxidation (with low pH) with residual Cl forming Cu , Ag , and Pb secondary minerals. Experimental verification of this process showed that an enriched Cl would remain, but approximately 75% of the chloride would have to be lost from the system to enrich the residual Cl by 0.5‰ SMOC. However, Eastoe and Guilbert, (1992) during Cl extraction of minerals felt the partial pressure (fugacity) of $\text{HCl}_{(\text{gas})}$ at pH of 1 ($\log f = -7.2$) is so small that the loss of Cl would be minimal, which puts in doubt the explanation of Eggenkamp and Schuiling (1995) for the enriched $\delta^{37}\text{Cl}$ in minerals associated with base metals.

A wide range of $\delta^{37}\text{Cl}$ has also been reported from Canadian shield brines (from -0.45‰ to +0.77‰; Kaufmann et al. 1987; Kaufmann et al. 1992 Kaufmann et al., 1993), with most values >0.40‰.

Preliminary investigations of pore waters from subducting sediments in convergent margins show low $\delta^{37}\text{Cl}$, which range between -1.97‰ to -7.71‰ (Ransom et al., 1995).

Several processes will fractionate stable Cl isotopes. Fractionation can be caused by: a). precipitation or dissolution of Cl -bearing minerals that are at least partially covalently bonded (Magenheim et al., 1995); b). diffusion may also fractionate Cl isotopes where the

effects of diffusion is greater than advection since ^{35}Cl will diffuse faster than ^{37}Cl (Desaulniers et al., 1986; Eggenkamp, et al., 1994); c). membrane filtration will enrich the effluent in ^{37}Cl , as the lighter isotope will be more effectively repelled by the negative surface charge of clay minerals (Phillips, and Bentley, 1987); and d). vapours resulting from steam separation will be enriched in the light isotope (Eggenkamp and Schuiling, 1995).

Since Cl^- is a major component of the saline waters in Myra Falls possibly ^{37}C may reveal some of the processes involved in regard to this element.

2.6.2 Results

Six waters spanning the full range of chloride concentration at Myra Falls, a wide range of pH, and almost the full range of sampling elevation were analysed for $\delta^{37}\text{Cl}$ (Table 2-6). The $\delta^{37}\text{Cl}$ ranges from -0.07‰ to +0.64‰ for individual measurements which is about 6 times the precision of the analytical method.

Water sample #3505, the only water with tritium above detection, represents modern recharge and has a Cl^- concentration similar to that observed in local rainfall.

Table 2-6 Chlorine-37 results for select waters. Analyses completed at U. of Waterloo.

Sample	Site Location	Elevation (m)	Cl (ppm)	$\delta^{37}\text{Cl}$ ‰ SMOC
2585	HW20-415de-832	-50	7470	0.34
3274	PR-92	-52	172	0.19
3321	PR101	-218	8490	-0.07
3429	PR-100	-203	15500	0.18
				0.27
3444	M10-370xcs	373	30.2	0.55
				0.64
3505	Pr13-930dw-13	242	0.41	0.14
precision 1.96 σ (pooled variance of 2 duplicate samples)				± 0.12

2.6.3 Discussion

All of these waters are undersaturated with respect to common secondary chloride minerals, including AgCl (as calculated with PHREEQC; Parkhurst, 1996), and therefore it is unlikely that precipitating Cl bearing phases are influencing the $\delta^{37}\text{Cl}$.

Average chloride content in rainfall measured at the Myra Falls Environment Canada monitoring station is $1.14 \text{ ppm} \pm 2.24 \text{ ppm}$ (1σ) and would be expected to originate as marine aerosols with a $\delta^{37}\text{Cl}$ similar to SMOC ($\sim -0.00\text{‰}$). The lowest Cl^- concentration of waters sampled for ^{37}Cl is 0.41 ppm (#3505) and has a $\delta^{37}\text{Cl}$ of $0.14 \pm 0.12\text{‰}$, similar to Pacific Ocean $\delta^{37}\text{Cl}$ (ocean waters have been measured at $0.00 \pm 0.05\text{‰}$, 1σ ($n=8$; Kaufmann et al., 1984), and $0.0 \pm 0.15\text{‰}$ (Magenheim et al, 1994)). Therefore, modern tritium bearing recharge water (#3505) carries an oceanic ^{37}Cl signature. The remainder of the ground waters contain Cl^- in excess of rainfall (excluding contributions from atmospheric dry fall out), and therefore derive their Cl^- from sources other than rain.

The most enriched ^{37}Cl from water 3444 ($\delta^{37}\text{Cl} = 0.60 \pm 0.12\text{‰}$ SMOC mean of 2 samples $\pm 1.96\sigma$); is within the range of Cl from several sources such as oxidation zone minerals from metal deposits, hydrothermal fluids, alteration minerals (Eggenkamp and Schuiling, 1995), and salt deposits (Kaufmann et al., 1984), and is approaching the upper-end reported for ground waters ($+0.8\text{‰}$) analysed by Long et al. (1993). The pH of water #3444 is 10.12. The high isotopic value in this water cannot be attributed to fractionation of Cl during gaseous HCl loss due to the high pH of the water. The Cl concentration (30 ppm) in #3444 water is added insitu, and may be the result of a combination of: leaching grain-boundary salts, weathering Cl-containing minerals, diffusion of a remnant Cl^- water from the rock matrix or dead-end pore space, or leaching of fluid inclusions (H_2O rich primary inclusions contain up to 8 equivalent weight % NaCl (Barrett and Sherlock, 1996)).

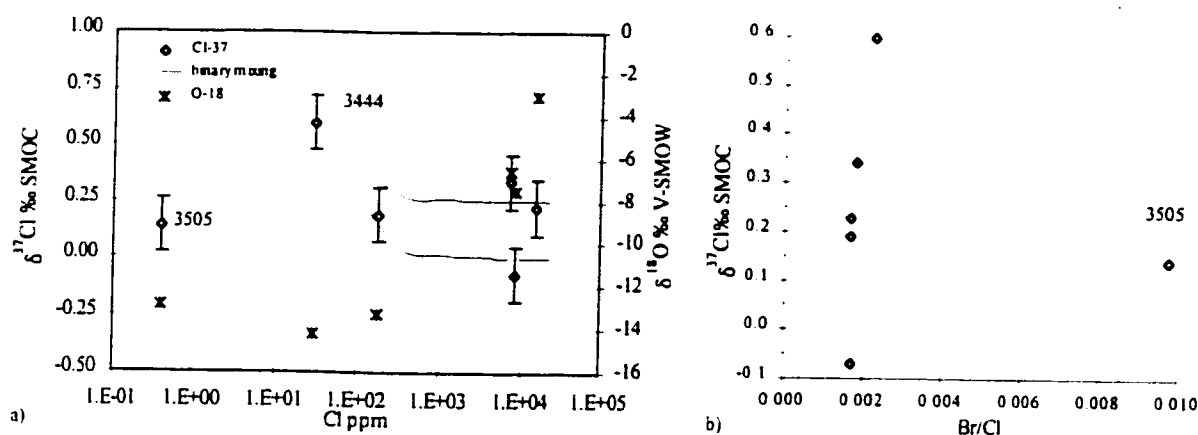


Figure 2-26 ^{37}Cl vs. Cl concentration (a) with ^{18}O for comparison and the trajectory line of binary mixing between water similar to #3444 and waters with $\delta^{37}\text{Cl}$ equal to 0‰ and 0.25‰. ^{37}Cl vs. Br/Cl (b) shows the similarity between all samples except 3505. Either genetic similarities exist or processes have affected Cl and Br in a similar manner in these waters.

There is a poor relationship between $\delta^{37}\text{Cl}$ and Cl concentration or $\delta^{18}\text{O}$ of the water (Figure 2-26); although, there tends to be a depletion of $\delta^{37}\text{Cl}$ with decreasing sampling depth (excluding 3505) (Figure 2-27). Mixing waters similar to 3444 with a high concentration chloride reservoir with a fixed $\delta^{37}\text{Cl}$ (0.25‰ and 0.0‰) would result in mixing lines similar to that calculated and displayed on Figure 2-26a. The variation in $\delta^{37}\text{Cl}$ does not appear as a straight forward binary mixing with a single $\delta^{37}\text{Cl}$ source on Figure 2-26a as is seen in $\delta^{18}\text{O}$ vs. Cl relation (Figure 2-9a). Processes other than advective mixing may be responsible for this variation. Although similar processes seem to be affecting the Br^- and Cl^- in these waters with the exception of #3305.

Diffusion in the mixing environment may be expected, if a concentration gradient exists and advection is very low (Eggenkamp et al., 1994). Diffusion would enrich ^{37}Cl in the residual fluid since the lighter isotope has higher diffusivity (Eggenkamp et al., 1994). The lack of relationship between $\delta^{37}\text{Cl}$ and Cl concentration suggests that if diffusional or filtration processes are affecting the $\delta^{37}\text{Cl}$, then these processes are not operating uniformly, which would likely be due to heterogeneity of the host rocks. Upward diffusion of Cl from waters would enrich ^{37}Cl in the residual chloride and would result in a $\delta^{37}\text{Cl}$ enrichment as compared to the $\delta^{18}\text{O}$ and residual Cl^- concentration. Water 2585 is from a drill hole that has been artesian since it was drilled. The piezometric pressure from the zone that water was

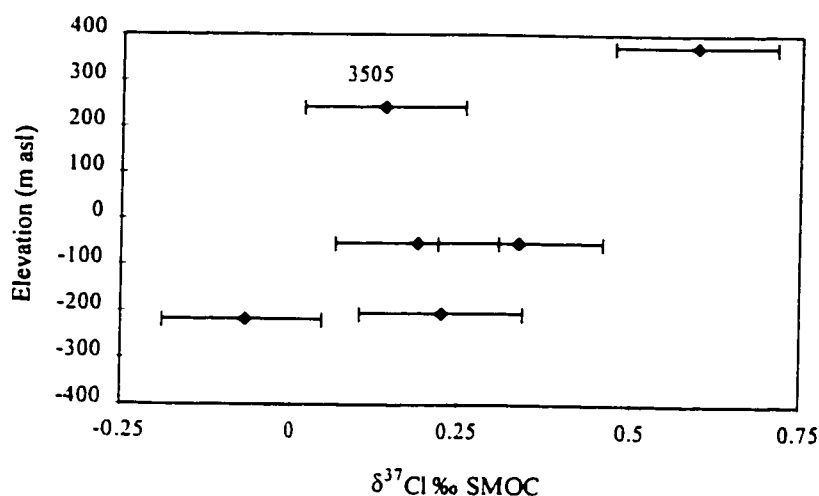


Figure 2-27 Elevation of sampling vs. ^{37}Cl . Chloride in ground water 3505 is likely derived from marine aerosols in rain; all other ground waters have Cl^- in excess of rainfall concentration.

sampled for 3429 is unknown since the packer string with the pressure transducer equipment was lost down a hole prior to developing this zone. Diffusion of Cl^- from these two zones may result in enriched $\delta^{37}\text{Cl}$ in the residual water. However this would require some isolation from the underlying saline waters in order to develop a distinct $\delta^{37}\text{Cl}$ values.

Waters 3321 and 3274 were both from zones which developed rather quickly, suggesting reasonable permeability, and #3321 was artesian in early development; thus, advective flow should dominate over diffusion.

Water 3444 has high Cl^- concentration for its location in upper M-P ridge. The displacement of a saline water from the ridge over an extended period of time during uplift may have resulted in some residual water remaining in dead-end pore spaces and within the rock matrix. Diffusion of Cl^- in these waters over an extended period of time may have enriched $\delta^{37}\text{Cl}$ values. Indeed Br/Cl mass ratios in 3444 is similar to other waters (with the exception of 3505) suggesting a similar origin for salinity in all the waters. Diffusional processes during the flushing of saline waters (aquifer freshening) in the upper ground waters may be responsible for the enriched $\delta^{37}\text{Cl}$ with elevation.

The few data presented here represent an introductory look at Cl isotopes in this setting and definitive conclusions based on $\delta^{37}\text{Cl}$ are not feasible.

2.7 Helium (^3He , ^4He) and Neon (^{20}Ne , ^{21}Ne , and ^{22}Ne)

2.7.1 Introduction and Applications

Helium and neon are both noble (inert) gases and therefore are not involved in chemical reactions. In the case of $^3\text{He}/^4\text{He}$, ratios can be used to determine the contributing source of the He in the ground water. The use of He and Ne, often in conjunction with other gases, noble and otherwise, have been used for variety of applications including: estimating ground water ages, temperature conditions during recharge, and interactions between ground water and the rock matrix.

Helium-4 is the product of α decay of U and Th. The volume of ^4He increases with ground water residence, and can be used to yield a semi-qualitative age for ground water, to assess ground water velocities in low permeability environments, and to interpret ground water mixing regimes (Marine, 1979; Heaton and Vogel, 1981; Bottomley, 1984; Andrews, 1985; Andrews et al., 1989). Helium-3 can be used along with ^3H in determining ages of young waters independently of the initial ^3H content. Helium ratios between different reservoirs are distinct (see Table 2-7) and can be used in determining sources of helium in ground waters, and ground water circulation characteristics (Gregory and Durrance, 1987). Helium fluxes have been used in determining heat transport and convection patterns in the mantle (O'Nions and Oxburgh, 1983) since the upper mantle has a fairly uniform $^3\text{He}/^4\text{He}$ ratio of $\sim 3 \cdot 10^{-5}$. Since helium ratios are so distinct between different mantle and crustal reservoirs, Poreda and Craig (1989) have used He to determine the relative contribution of crustal and mantle materials in circum-Pacific volcanism.

Helium ratios (R) are often reported normalized (R/R_a) to the atmospheric equilibrated He ratio ($^3\text{He}/^4\text{He} = 1.384 \cdot 10^{-6} = R_a$)

2.7.2 Sources of He and Ne

The atmosphere contains a well mixed reservoir of noble gases at known concentrations and isotopic ratios. Water infiltrating the ground will carry noble gases at concentrations in equilibrium with the atmosphere (at the base of the unsaturated zone) which will be dependent upon ambient temperature, pressure (altitude), and salinity, and will often

contain an 'excess air' component containing noble gases in the same proportions as the atmosphere (Heaton and Vogel, 1981). The 'excess air' originates as tiny air bubbles entrapped in water as it moves through the unsaturated zone and will eventually become dissolved with increasing hydrostatic pressure. Helium in excess of that incorporated during recharge will be derived from non-atmospheric sources (i.e., from the rocks).

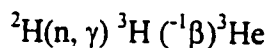
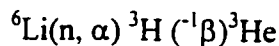
Helium-4 concentration in the atmosphere is 5.24 ppmv and the atmospheric $^3\text{He}/^4\text{He}$ (R_a) is $1.384 \cdot 10^{-6}$ (Mamyrin and Tolstikhin, 1984). The water equilibrated solubility is temperature, pressure, and salinity dependent, but at one atmosphere and 5°C is $4.8 \cdot 10^{-8} \text{ cm}^3$ He per cm^3 water. Neon has an atmospheric concentration of 1.818 ppmv (Mazor, 1997), and has a solubility at 5°C of $2.12 \cdot 10^{-7} \text{ cm}^3$ Ne per cm^3 water.

Helium from a radiogenic source is calculated to have a production ratio of $^3\text{He}/^4\text{He}$ (R_{He}) of $1 \pm 0.5 \cdot 10^{-8}$ in crustal and mantle sources, and values within this range are typically found in areas of old continental crust. In typical crustal rocks the $^3\text{He}/^4\text{He}$ ratios are expected to be 10^{-7} or less (O'Nions and Oxburgh, 1983) reflecting the accumulation radiogenic origin of ^4He , but can vary considerably. The R/R_a in ground waters from old crustal areas is typically around or less than 0.02 (Poreda and Craig, 1989), but may range from 0.01 to 0.05. but even within old crust R/R_a from shallower waters may range up to 1 (O'Nions and Oxburgh, 1983) due to mixing with recent meteoric water. Regions of extensional tectonics may incorporate a sizable mantle fraction of He, and have R values reflecting a contribution from the mantle ($^3\text{He}/^4\text{He} \sim 10^{-5}$; O'Nions and Oxburgh, 1983). Upper mantle R/R_a is around 8 while the He ratio related to the deep mantle (hot-spot volcanism) is much higher, with an R/R_a as high as 30 (Poreda and Craig, 1989). Mantle helium can be added along plate margins directly from the mantle reservoir and from diffusion from rocks produced from the mantle. Mantle derived He degassing at spreading centres and from quenched glass has high He ratios ($6 < R/R_a < 10$; upper mantle; O'Nions and Oxburgh, 1983), while unaltered glass in MORBs have a mantle $^3\text{He}/^4\text{He}$ ratio of $\sim 1.4 \cdot 10^{-5}$ (Craig and Lupton, 1976). Hydrothermal alteration of oceanic crust near spreading ridges alters the $^3\text{He}/^4\text{He}$ ratio and R/R_a is generally < 2 (Poreda and Craig, 1989) due to the removal of He present prior to alteration. The hydrothermal alteration will alter He within the oceanic crust to depths up to 5 km.

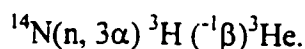
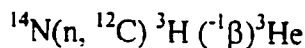
Helium-4 increases with ground water residence, and is added to the ground water through α decay of natural U and Th in the aquifer. Since the rate of radioactive decay is a

first-order reaction, the accumulation of ^4He will be directly related to the residence time the water is in contact with the U and Th bearing aquifer (if there is no diffusion into or out of the aquifer).

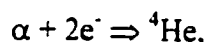
Helium-3 is produced by radiogenic processes as summarized in the reactions:



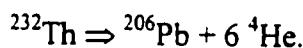
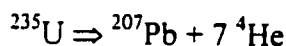
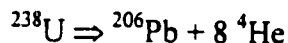
(Hill, 1941; Morrison and Pine, 1955) and it is also produced in the atmosphere by:



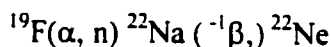
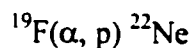
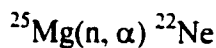
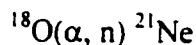
Helium-4 is also produced within rocks from α emission in the above reactions:



and by the decay of U and Th through α and β decay:



Neon is largely primordial in origin and has a concentration of 18.18 ppmv in the atmosphere. The natural abundances of neon are 90.5% ^{20}Ne , 0.268% ^{21}Ne , and 9.23% ^{22}Ne . The most abundant isotope, ^{20}Ne , has only a slight radiogenic subsurface source ($^{17}\text{O}(\alpha, n) ^{20}\text{Ne}$; which will be low since ^{17}O has 0.4% natural abundance), and in ground waters is incorporated during recharge from the atmosphere. Neon-21 and ^{22}Ne , in addition to equilibration with the atmosphere, can be added to ground waters through subsurface production. Subsurface production is the result of the interaction α particles from U and Th decay and light elements (primarily ^{25}Mg and ^{18}O) (Bottomley, et al., 1978; Gascoyne and Kotzer, 1995) such as:



and excess ^{21}Ne and ^{22}Ne may also be a useful indicator of ground water age (Bottomley et al., 1984). Neon is also used to check for excess air, recharge or contamination, since Ne is

only slightly soluble in water, any incorporation of atmospheric air (18.18 ppmv Ne) will swamp the dissolved Ne concentration.

2.7.3 Sample Degassing

Waters are at high risk of degassing due to the method (N_2 lift from the packer isolated zone) involved in gas collection from isolated fracture zones at considerable depth. Alternative sampling (i.e., bail type approach) to sampling in an open drill hole will not isolate waters from individual fractures. Applying back pressure above the copper sampling tube at the ground surface would be necessary to minimize gas stripping. Andrews et al. (1989) suggest that when sampling deep (>50 m) ground waters pressure comparable to the hydrostatic pressure of the sampling zone should be applied to the copper tube. This procedure was not possible using the packer equipment as the pressure rating of return tubing (poly-ethylene) is low, and bursting of the return line would result if excess back-pressure were applied. Back-pressure equivalent to hydrostatic pressure would be required to simulate pressures at depth of sampling which would require excess pressure on the N_2 drive inlet. During sampling, the outboard and well-side refrigerator clamps on the copper sample tubing were alternately tightened, with greater tightening being applied to the outboard clamp which was tightened to ensure it was the first to form a cold weld. This procedure would gently create a back-pressure on the sample, but does not guarantee sample integrity.

Although excess gases are common in inert gas studies of ground waters (Heaton and Vogel, 1981), only one of the three waters (3321) has a Ne concentration near equilibration with the atmosphere. The other two samples are below Ne solubility and indicate that considerable degassing took place during(?) sampling, or even possibly within the open drill hole prior to developing. The low Ne concentrations, besides indicating degassing, also confirms the integrity of the cold weld seals (and the Cu tubing itself) on the copper sampling tubes as Ne would have diffused into the samples had the cold weld been inadequate (leaky).

Corrections for degassing rely upon knowledge the concentrations of dissolved and exsolved gases in a water and the flow rate of the water that carried the exsolved gases (Andrews, 1987; Andrews and Wilson, 1987; Youngman, 1989). Unfortunately, rigorous degassing corrections cannot be performed on the He samples from Myra Falls with the

known information (M. Youngman, National Radiological Protection Board, Chilton, Didcot, Oxon., United Kingdom; written communication).

2.7.4 Results

Four samples were collected for noble gas He and Ne analyses (Table 2-7). See Appendix B for sampling, extraction, and analytical methods.

The ^{21}Ne was close to background voltage in the faraday cup during analyses of ^{21}Ne in the degassed waters (3365, 3566); and therefore, the reliability of the analyses is questionable.

Table 2-7 He and Ne analyses of selected ground waters, and isotopic values of different reservoirs.

Site	Drill hole and depth	^4He ($10^{-6} \text{ cm}^3/\text{g}$)	$^3\text{He}/^4\text{He}$	R/R_s	Ne total (cm^3/g)	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$
3321	PR100 442 m	1.12	$2.47\text{e-}7$	0.18	$2.02\text{e-}7$	9.980	0.0330
3365	PR106 353 m	55.9	$1.94\text{e-}7$	0.14	$3.95\text{e-}8$	9.731	0.0465
3429 ^a	PR100 425 m	--	--	--	--	--	--
3566	PR84 266 m	1.19	$2.28\text{e-}7$	0.17	$3.32\text{e-}8$	9.546	0.0487
<u>Sources</u>	<u>Reactions</u>						
Primordial ^c	nucleosynthesis		$3\text{e-}4$			12 - 13	0.03
Upper Mantle	primordial and crustal		$\sim 3\text{e-}5$	~ 8			
Lower Mantle	primordial		$\sim 1\text{e-}4$	~ 30			
Radiogenic ^c	α decay (U, Th)		$\sim 1\text{e-}8^c$				0.3 - 1.0
Spallegenic ^c	cosmic ray		$2\text{e-}1$			0.9	0.95
Atmosphere ^b		5.24ppm	$1.384\text{e-}6$ $\pm 0.013^c$		18.18	9.89 - 9.90	0.030
Equilibrium	Solubility @ $5\text{C}^{d,e,f}$	$4.8\text{e-}8$	$1.36\text{e-}6$	1	$2.12\text{e-}7$	9.89	0.029

^a poor crimp seal, sample leaked

Values from ^b O'Nions and Oxburgh, 1983; ^c Mamyrin and Tolstikhin, 1984; ^d Bottomley et al., 1984; ^e Poreda and Craig, 1989; ^f Mazor, 1997;

2.7.5 Discussion

The insitu production ratio of $^3\text{He}/^4\text{He}$ cannot be calculated with certainty for rocks making up the mine sequence since the Li concentrations of the rocks is not known. Andrews (1985, 1987) showed that the $^3\text{He}/^4\text{He}$ ratio produced within a rock is, for the most part determined by the Li content of the rock and to a much lesser extent by the Th content, and is independent of the U content. The average $^3\text{He}/^4\text{He}$ value of $2.2 \cdot 10^{-7}$ for the 3 samples analysed is one to two orders of magnitude too great to have been produced insitu from typical Li concentrations for a wide range of rocks. Ratios of He isotopes in this range are not unique, and have been reported by Andrews (1985) for He in natural gas wells, which had He ratios ranging from $0.5 \cdot 10^{-7}$ to $5.0 \cdot 10^{-7}$, and Mamyrin and Tolstikhin, (1984) show plots of waters with similar He ratios as found at Myra Falls ($>10^{-7}$).

If He resulted from a local source (i.e. He produced insitu - within the mine sequence, underlying andesites, and possibly the nearby granodiorite) mixing with a deeper source containing a high $^3\text{He}/^4\text{He}$ (closer to mantle), then a change in volume should be reflected by a change in He ratio. This is not seen in the Myra Falls ground waters. Figure 2-28 shows the

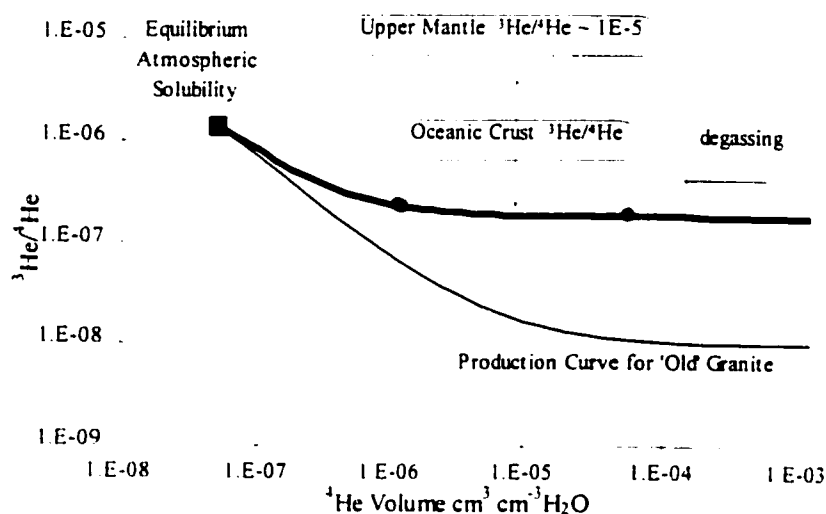


Figure 2-28 Helium ratios vs. helium volume showing equilibrium atmospheric solubility and expected production curve for old granites ($^3\text{He}/^4\text{He} = 10^{-8}$). Sample degassing has shifted volumes to the left. Mixing between waters originating from two sources (e.g. mantle and crustal) should plot with $^3\text{He}/^4\text{He}$ variation as waters mix between sources with different ratios (slope will be largely dependent upon volumes of sources for each source). The He ratios in Myra Falls waters can be explained as being produced by rock having a low initial primordial He through loss due to hydrothermal alteration, and possibly a lower $^3\text{He}/^4\text{He}$ initial ratio (crustal contamination of mantle material).

relationship between He ratios and non-corrected He volume. If the He seen in the Myra Falls ground waters was the result of mixing of a oceanic crustal and local source, a mixing line with a steep slope would be expected (the slope of the line would be dependent upon the volumes of He related to each source).

The $^3\text{He}/^4\text{He}$ ratios seen in the Myra Falls ground waters can be explained by the removal of initial (primordial) He from the submarine andesites (largely mantle derived, but may contain some crustal material) by hydrothermal convection leaving a low initial R/R_a value. Craig et al. (1978), and Poreda and Craig (1989) suggest that hydrothermal circulation of oceanic crust would result in an R/R_a of ~ 2 or less, and that 'little if any primordial ^3He would be retained'. Loss of volatiles during eruption and strong hydrothermal alteration after the emplacement of the Myra Falls rocks would be expected to strip a large amount of any volatiles present. The He production curve fitting the Myra Falls waters can be generated, as suggested by Poreda and Craig by reducing the initial primordial He to extremely low amounts ($\sim 2\%$ remaining) before radiogenic production and mixing with meteoric surface waters.

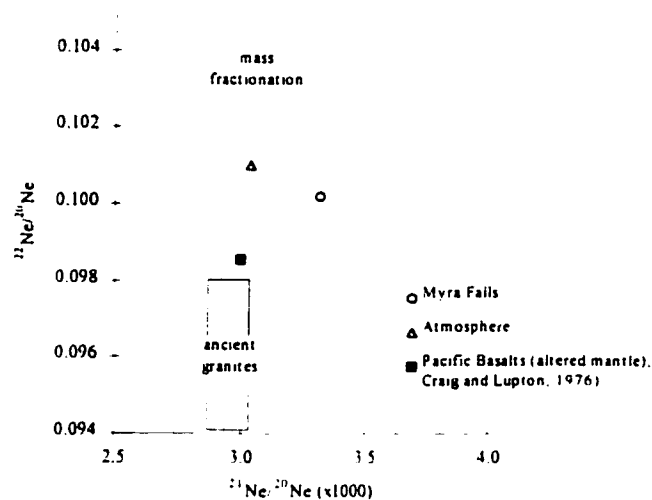


Figure 2-29 Ne isotopes of Myra Falls. Field of 'ancient granites' and the mass fractionation line is from Bottomley et al., (1984). The Myra Falls Ne intersects the mass fractionation line at higher $^{22}\text{Ne}/^{20}\text{Ne}$ and $^{21}\text{Ne}/^{20}\text{Ne}$ than Pacific ocean basalts.

The $^{22}\text{Ne}/^{20}\text{Ne}$ and $^{21}\text{Ne}/^{20}\text{Ne}$ ratio values in Myra Falls ground water with the highest Ne concentration plots above and to the right of the value for Pacific basalts. This may confirm that the initial ^{20}Ne (higher initial $^{22}\text{Ne}/^{20}\text{Ne}$ and $^{21}\text{Ne}/^{20}\text{Ne}$) was largely removed from the rock.

The helium volumes, at least in 3365 (the least de-gassed sample), suggest that ground waters sampled for He are old. The $^3\text{He}/^4\text{He}$ ratios are around $2 \cdot 10^{-7}$ which is higher than crustal ratios but well below a mantle ratio. The He ratios seen in the Myra Falls ground waters, are not unique among natural He from other settings (e.g.(Mamyrin and Tolstikhin, 1984; Aldrich and Nier, 1948; $^3\text{He}/^4\text{He} = 0.5 \cdot 10^{-7}$ to $5.0 \cdot 10^{-7}$ from natural gases).

2.8 Tritium

2.8.1 Introduction

Tritium (^3H) is the heavy unstable isotope of hydrogen. It has a half life ($t_{1/2}$) of 12.43 years, decaying via the emission of β^- particles to form ^3He . Tritium is formed naturally in the stratosphere by cosmic ray neutrons interacting with ^{14}N ($^{14}\text{N} + n \Rightarrow ^{12}\text{C} + ^3\text{H}$). Large concentrations of ^3H were also added to the upper atmospheric reservoir by above-ground nuclear bomb testing, dominantly from 1952 to 1963. This resulted in waters recharged during this period exhibiting 'bomb-peak' tritium concentrations. Tritium concentrations are expressed in terms of tritium units (TU), where: $1 \text{ TU} = ^3\text{H} \cdot 10^{-18} \text{ H atoms}$. The decay of tritium is a first order rate equation, as are all decay reactions, and is written as:

Equation 2-12

$$^3\text{H}_t = ^3\text{H}_0 \cdot e^{-\lambda t};$$

where $^3\text{H}_0$ is the initial tritium activity, $^3\text{H}_t$ is the tritium activity after time t , and λ is the decay constant which is equal to $(\ln 2)/t_{1/2}$.

Natural background levels of ^3H are generally low, somewhere between 5 and 10 TU depending on location. Coastal areas that have high oceanic dilution and limited atmospheric mixing of vapour masses tend to have lower ^3H than rainfall from continental locations (see tritium for Victoria, B.C. as compared to Ottawa On., Figure 2-30).

Tritium is a useful indicator of young ground waters and the designation of 'modern' ground waters is given to those waters that contain measurable ^3H . Tritium can be used as a ground water dating technique if the original concentration of ^3H in the recharge is known.

2.8.2 Results

The result for 24 tritium analyses from Myra Falls are presented in Table 2-8. The analyses were conducted in three batches: November and December of 1995, and May of 1996 (all analyses <D.L. from May 1996). No corrections for decay between sampling and analyses are necessary to the tritium values between November and December batches because one month decay would result in a ratio of 0.995 between similar tritium concentrations analysed one month apart.

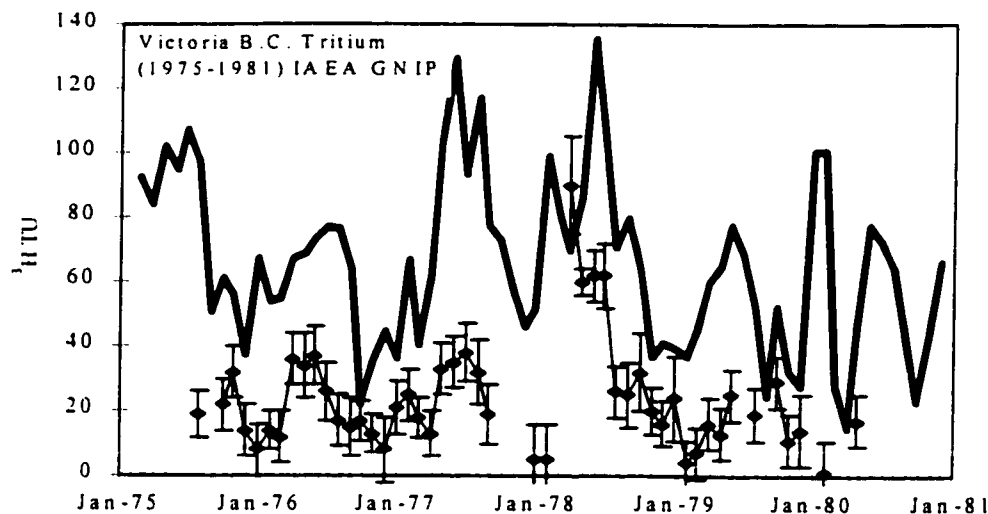


Figure 2-30 Tritium in precipitation from Victoria, B.C.(thin dark line; near ocean location), and tritium from Ottawa (thick line; continental location) during the same time period showing the lower ^3H from a coastal reporting station.

2.8.3 Discussion

The tritium concentrations are quite low with modern tritium likely represented by the Tennant lake sample (2.7 ± 0.4 TU) recharged largely from seasonal snow melt. The highest measured ^3H concentration is 5.1 ± 0.5 TU from an underground drill hole on Price 13 level. No ground waters had tritium values representative of recharge during 'bomb-peak' years which would be expected to contain in the order of 25 TU or greater.

Generally, ground waters containing significant Cl^- , such as ground waters sampled at depth from HW mine and Thelwood, had no detectable ^3H . There are two reasons for this. Firstly, the time period to accumulate significant concentration of Cl^- in ground waters of meteoric origin would be expected to be greater than the time for initial tritium to decay to less than detection values (e.g. 30 ppm Cl^- , as in ground water from a recently driven drift and exploration drill hole at the end of Myra 10 level, near the central core of the M-P ridge; refer to Section 2.6). Secondly, ground waters with high Cl^- concentrations would have the initial ^3H signal of the meteoric water diluted during mixing with the tritium-free high chloride waters.

Table 2-8 Tritium data for surface and ground waters.

Sample	Date	Easting (m)	Northing (m)	Type of sample	Sampling method	Location	Drill hole I.D.	Elevation (m)	Tritium (TU)	Error (TU)
2561	8/18/94	54+56	33+13	Drillhole	Margot plug	Pr9-930dw	Pr9-12	416	3.8 ±0.5	
2584	8/24/94	41+50	40+02	Fault	Fast drips	HW20-	N fault (U1)	-50	4.2 ±0.5	
2585	8/24/94	44+35	39+85	Drillhole	Flowing hole	HW20-415de	HW20-832 (U2)	-50	<0.8 ±0.3	
3019	5/24/95	33+59	32+14	Drillhole	Margot plug	M13-108dw	M13-229 (U3)	244	3.2 ±0.6	
3083	6/9/95	60+15	42+44	Drillhole	Packer	Thelwood	PR-106	-32	<0.8 ±0.5	
3178	6/24/95	19+00	15+35	Lake	Powerhouse tail	Tennant Lake		1007	2.7 ±0.4	
3184	6/26/95	60+15	42+44	Drillhole	Packer	Thelwood	PR-106	-52	<0.8 ±0.6	
3186	6/27/95	50+45	33+48	Drillhole	Flowing open	Pr5-830dw	Pr5-40	583	2.1 ±0.5	
3216	6/27/95	60+15	42+44	Drillhole	Packer	Thelwood	PR-106	51	<0.8 ±0.5	
3257	6/28/95	60+15	42+44	Drillhole	Packer	Thelwood	PR-106	71	<0.8 ±0.5	
3267	6/30/95	37+30	31+97	Drillhole	Flowing hole	HW20-	HW20-650	-75	<0.8 ±0.3	
3270	6/30/95	37+30	32+00	Drillhole	Fast drips	HW20-	HW20-653	-75	1.2 ±0.4	
3273	7/3/95	60+15	42+44	Drillhole	Packer	Thelwood	PR-106	157	<0.8 ±0.5	
3274	7/3/95	55+56	44+07	Drillhole	Packer	Thelwood	PR-92	-52	<0.8 ±0.5	
3277	7/4/95	55+56	44+07	Drillhole	Packer	Thelwood	PR-92	-26	<0.8 ±0.5	
3286	7/5/95	52+43	39+53	Drillhole	Margot plug	Pr13-720xcn	Pr13-73	245	2.9 ±0.5	
3292	7/5/95	52+43	39+53	Drillhole	Margot plug	Pr13-720xcn	Pr13-70	245	4.1 ±0.5	
3309	7/5/95	50+60	35+80	Drillhole	Margot plug	Pr13-930dw	Pr13-32	245	5.1 ±0.5	
3321	7/7/95	55+75	43+64	Drillhole	Packer	Thelwood	PR-101	-218	<0.8 ±0.5	
3385	8/26/95	55+75	43+64	Drillhole	Packer	Thelwood	PR-101	119	3.1 ±0.5	
3444	8/28/95	41+91	29+90	Drillhole	Flowing	M10-370xcs	M10-new	373	<0.8 ±0.3	
3505	9/3/95	56+08	35+88	Drillhole	Margot plug	Pr13-930dw	Pr13-13	241	3.1 ±0.5	
3517	9/3/95	54+26	35+80	Drillhole	Margot plug	Pr13-930dw	Pr13-28	242	3.2 ±0.5	
3568	7/5/95	55+56	44+07	Drillhole	Packer	Thelwood	PR-92	-8	<0.8 ±0.3	

Modern, tritium containing ground waters, have penetrated to all areas sampled along 13 level, which dissects the M-P ridge (~240 m). These waters have traversed a variable thickness of overlying rock (up to approximately 400 m vertical) (Figure 6-6 and Figure 6-7). These results indicate that recharge is very rapid into mine workings located above the valley level.

Two dashed tie lines in Figure 2-31 connect tritium-free and tritium-bearing waters that are in close proximity (N fault and HW20-832; and drill holes HW20-650 and 653). In both examples the tritium-bearing ground waters are emanating from above the drifts, while the tritium free water flow from drill holes oriented below the drifts. This results from modern waters being drawn down to working levels within the mine. The only water from Thelwood Valley drill holes with measurable tritium is from a single fracture in PR101 at 105 metres depth that delivers modern meteoric water (4.1 ± 0.5 TU) to the drill hole.

Results from mixing ground waters on HW20 level (Chapter 6) indicate that the major component of ground-water flowing from drillhole HW20-653 is young. Various

scenarios are presented in Table 2-9 to estimate the flow velocity for modern water to reach the depths of HW20 level. The modern tritium, corrected for mixing, is less than 2 TU and could not have been recharged during years of high anthropogenic contribution of ^3H . Nor could it have recharged prior to bomb input (assuming similar background tritium to today), as this would result in a value below detection in the current ground water. Input used for the various scenarios presented in Table 2-9 are $^3\text{H}_0$ values between 3 and 5 TU (similar to modern), $^3\text{H}_t$ (measured) values between 1.5 and 1.7 (see Chapter 6 for details), a recharge elevation of 1000 m which is reasonable considering the location of the drill hole, and the $\delta^{18}\text{O}$ of -13.2‰ (not adjusting for mixing with a slightly enriched brackish water). Ground water is considered entering the drill hole at its furthest vertical extent (105 m asl). Scenarios A to D in Table 2-9 assume a steady state of ground water flux. Scenario E and F assume modifications to the hydrology resulted in an entirely new flow regime being initiated after the drift opening in 1990 and water flowing from the drill hole not being recharged until after drifting and drilling of the hole which resulted in modifications to the hydrology. Scenarios C and D are not likely since H_0 tritium levels 20 years before present ranged from around 10 to 20 TU in the high rainfall winter precipitation (Victoria, B.C.) which has the lowest tritium (Figure 2-30). However, tritium values lower than the 10 to 20 TU range were measured in Victoria rainfall during the winters of 1977 (6 TU), 1978 (5 TU), and 1979 (4 TU). The tritium level in rainfall from 10 to 12 years before present at Myra Falls is unknown but may have been higher than 3 TU used in scenarios A and B. Scenarios E and F may be the most probable. The water from HW20-653 is moving rapidly and estimated flow velocities from all scenarios are high, ranging from 1.3 to $5.7 \cdot 10^{-6} \text{ ms}^{-1}$.

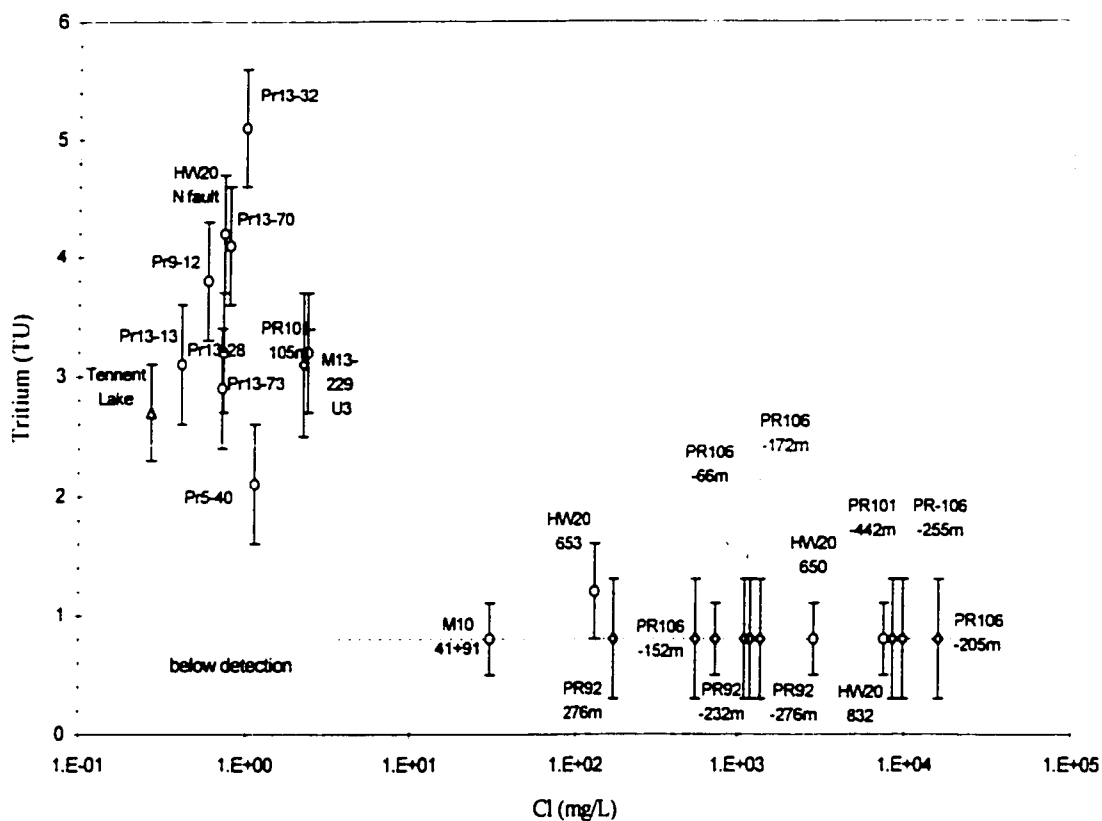


Figure 2-31 Tritium concentrations vs. chloride content of ground and surface waters. Dashed lines tie saline (tritium free) and non-saline (tritium-bearing) ground waters sampled in close proximity to one another.

Table 2-9 Estimates of ground water age and flow velocity for HW20-653

Scenario	H ₀ TU	H _t TU	Estimated age years before 1995	Vertical Velocity m/yr.	Vertical Velocity m/s
A	3	1.7	10.2	93	$3 \cdot 10^{-6}$
B	3	1.5	12.4	72	$2 \cdot 10^{-6}$
C	5	1.7	19.3	46	$1.5 \cdot 10^{-6}$
D	5	1.5	21.6	41	$1.3 \cdot 10^{-6}$
E	2.2	1.7	5	180	$5.7 \cdot 10^{-6}$
F	2.0	1.5	5	180	$5.7 \cdot 10^{-6}$

Tritium concentrations in Myra Falls surface and ground waters are low as expected for coastal regions. However, tritium in many ground waters is an important tracer in identifying and verifying the rapid descent of water entering mine workings and perturbations of the natural hydrology due to underground mine workings.

2.9 ^{14}C - Carbon-14 in Dissolved Inorganic Carbon

2.9.1 Introduction

Carbon-14 is a radioactive isotope of carbon primarily produced in the upper atmosphere by the cosmic ray neutron bombardment of nitrogen [$^{14}\text{N}(\text{n},\text{p})^{14}\text{C}$]. The prime use of ^{14}C in ground water studies is in determining the mean residence time of waters in regional flow systems; although, it is also a useful isotope to trace carbon cycling and carbons sources.

2.9.2 Results

Four waters were analysed for ^{14}C . These waters represent recently recharged water (3186), modern meteoric water drawn to great depth within the HW mine (2584), and two waters from Thelwood Valley with moderate (3274) and high salinity (3321).

The two tritium containing waters (3186 and 2584), which represent recently recharging meteoric waters, have ^{14}C activities of 40 and 53 pmC, respectively. Unfortunately, the two ground waters from Thelwood Valley have had a major component of modern carbon added to their DIC from the oxidation of a modern carbon source (canola oil; see section on ^{13}C), and have the highest activity of ^{14}C .

The activity of ^{14}C in water from drill hole Pr5-40 suggests that roughly one half of the DIC in the ground water is derived from incorporation of soil CO_2 .

Water #3321 had an air head-space above the sample prior to CO_2 extraction. The maximum contribution from the head-space atmosphere with full C exchange is calculated to be less than 2 pmC.

Table 2-10 Data for ground waters with ^{14}C measurements.

Site	Location	Elevation m asl	^{14}C pmC	$^{13}\text{C}\%$ VPDB	Alkalinity as ppm HCO_3^-	^3H TU	SO_4^{2-} $^{34}\text{S}\%$ CDT
3186	Pr5-40	583	52.50 ± 0.45	-12.8	133	2.1	5.8 ^a
2584	N fault	-50	39.95 ± 0.38	-11.5	82.6	4.2	0.0
3274	PR-92	-52	59.02 ± 0.46	-10.8	125	<0.8	13.5
3321	PR-101	-218	63.74 ± 0.50	-21.4	33.0	<0.8	20.8

^a ^{34}S from Pr5-39

2.9.3 Discussion - ^{14}C Ground Water

The estimation of mean residence time for the saline water is difficult due to the problems outlined in the previous sections; namely: the low HCO_3^- concentration of the saline waters, mixing with meteoric waters, and the addition of a modern carbon component from the oxidation of canola oil used as a drilling adjunct. Uncertainty in estimates of each of the above influences will result in compounded errors. However, spreadsheet modeling can demonstrate with reasonable certainty that the saline water occurring at depth is ^{14}C -free.

2.9.3.1 ^{14}C Mixing in Thelwood Valley Saline Water

The addition of any modern organic carbon incorporated into the DIC pool (i.e. canola oil used during drilling) will carry with it a modern ^{14}C signature. The measured ^{14}C activity will have to be corrected for this addition if a residence time can be calculated. Unlike correcting for a modern soil carbon component, the organic oil was injected into the aquifer without dilution from the dissolution of a ^{14}C free mineral component. It is suggested here that the hydrophobic oil would reside on aquifer material after injection of the drilling fluid; since organic compounds have been found to be readily sorbed to aquifer material due to hydrophobic effects (Fetter, 1993). The oil would then later be consumed during microbial growth and in conjunction with sulphate reduction.

A rigorous approach was applied to the problem of mixing waters from different sources, each with its own ^{14}C signal. A solution to this problem was applied through the use of spreadsheet modeling. Geochemical processes accounted for in this modeling process were: (A) mixing modern recharge and saline waters, using Cl^- as a conservative tracer; (B)

sulphate balance through the dissolution of anhydrite; (C) cation exchange to balance Mg^{2+} , Na^+ , and K^+ ($0.5 \cdot [\text{Ca} + \text{Mg}] \Rightarrow [\text{Na} + \text{K}]$); (D) oxidation of modern carbon source and the reduction of sulphate; and (E) precipitation of calcite. Milli-equivalent and isotopic mass-balances were used to constrain the reactions. The basis of this operation was to elaborate on the processes involved in mixing and determine the maximum ^{14}C activity of an end-member saline water. The saline end-member ground water is responsible for the Cl^- waters found at shallow depth in Thelwood Valley and in areas underlying workings in the HW mine.

An optimum hydrochemical scenario was sought that made geochemical sense and used values of the recharging waters that were within the range of known values. Different scenarios were tested to determine an optimum chemistry (which is not the only solution) and the affects and sensitivities of adjusting parameters within reasonably constrained amounts.

Chloride was used as a conservative tracer in proportioning the degree of mixing between a low Cl^- recharging water (1 ppm) and a high Cl^- (17,000 to 30,000 ppm) saline water. The initial chemistry of the mixed water was determined by using the fraction of saline water component (X) in each water and was calculated for mass per kilogram of water of $[I]$ and isotopic ratio (δI , where I is the element of interest) by:

Equation 2-13

$$[I]_m = (X \cdot [I]_s) + ((1-X) \cdot [I]_r)$$

$$\delta I_m = ((X \cdot \delta I_s [I]_s) + ((1-X) \cdot [I]_r)) / [I]_m$$

(see designation of subscripts below)

An isotope mass-balance was used to determine the contribution of modern carbon to the $\delta^{13}\text{C}_{\text{DIC}}$ pool. This is calculated as follows:

Equation 2-14

$$\delta^{13}\text{C}_A = (([\text{DIC}]_s \cdot \delta^{13}\text{C}_s) + ([\text{DIC}]_c \cdot \delta^{13}\text{C}_c) - ([\text{DIC}]_{\text{ppt}} \cdot \delta^{13}\text{C}_{\text{ppt}})) / [\text{DIC}]_A$$

$$\text{and } [\text{DIC}]_A = [\text{DIC}]_m + [\text{DIC}]_c - [\text{DIC}]_{\text{ppt}}; \text{ and } [\text{DIC}]_m = (X \cdot [\text{DIC}]_s) + ((1-X) \cdot [\text{DIC}]_r)$$

where: subscripts A = analysed, s = saline, r = recharge, m = mixing saline and recharge, c = oxidized canola, ppt = precipitating calcite, and X is the fraction of saline water based on Cl^- concentrations. Isotopic variables are outlined in Table 2-11. The fractionation factor of Mook (1980) was used for $\delta^{13}\text{C}$ of precipitating calcite. Modern carbon was assumed to have a valence of zero (C(0)) and was oxidized to C(IV) while S(VI) was reduced to S(-II).

The residual $\delta^{34}\text{S}_{(\text{SO}_4)}$ was calculated using the approximation of the Raleigh distillation equation:

Equation 2-15

$$\delta^{34}\text{S}_{\text{SO}_4(f)} \approx \delta^{34}\text{S}_{\text{SO}_4(o)} + \varepsilon^{34}\text{S}_{\text{H}_2\text{S}-\text{SO}_4} \cdot \ln f$$

where: f = the fraction remaining is $1 - ([\text{SO}_4^{2-}]_{\text{reduced}} / [\text{SO}_4^{2-}]_o)$, $o = \text{SO}_4^{2-}$ before reduction = $[\text{SO}_4^{2-}]_o = [\text{SO}_4^{2-}]_a + [\text{SO}_4^{2-}]_m$, a = adjusted for mass balance by the addition of anhydrite, and ε = isotopic enrichment. The SO_4^{2-} mass-balance is described by: $[\text{SO}_4^{2-}]_f = [\text{SO}_4^{2-}]_o - [\text{SO}_4^{2-}]_{\text{H}_2\text{S}}$. Since the addition of modern carbon is a recent phenomenon modeling the reduction of SO_4^{2-} as a single process, with the resulting sulphide removed from the system by precipitation of metal sulphides should be a reasonable assumption. The isotopic compositions of the dissolving phase used to mass-balance SO_4^{2-} and the saline water SO_4^{2-} were set to the same value ($\delta^{34}\text{S}_{\text{SO}_4} = 17.5 \pm 2.5\text{‰}$ CDT). This is justified since sulphate concentrations of HW mine waters are equal to or greater than Thelwood saline ground waters (Figure 3-18) and the isotopic values are within the estimated range of $\delta^{34}\text{S}_{\text{SO}_4}$ not affected by sulphate reduction (Section 2.4.3). Ground water within this $\delta^{34}\text{S}_{\text{SO}_4}$ range and with high SO_4^{2-} concentrations were not, or were only marginally, affected by SO_4^{2-} reduction. The same SO_4^{2-} source is implicated in these high sulphate waters.

Calcium is adjusted through the addition of anhydrite, cation exchange, and loss through calcite precipitation. The cation exchange is constrained by the difference in concentrations of Mg^{2+} , Na^+ and K^+ in the mixed water and the analyses (other sources and sinks will be minor). The mmol of precipitating CaCO_3 is constrained by the HCO_3^- concentration. The resulting modeled Ca^{2+} concentration is used along with the $\delta^{13}\text{C}$, $\delta^{34}\text{S}$, and $[\text{SO}_4^{2-}]$ as a verification of results of modeling scenarios.

An optimum recharge water chemistry similar to the chemistry of waters within recently recharging environments within Price hillside was used. The recharge and resulting modeled chemistry was inspected for charge balance to assure electro-neutrality of the waters. The modeled chemical results were within ~5% of the analysed values. An ideal saline water used in mixing was garnered from data from this chapter (isotopic values) and Chapter 3 (Chemical Characterization and Hydrochemical Evolution). The results for spreadsheet modeling for ground waters #3321 and #2584 are provided in Table 2-11.

Two additional saline end-members were used (23,000 and 30,000 ppm Cl^-) in modeling #3321 ground water because the Cl^- concentration of the true saline end-member is unknown. The saline ground water end-member has to have at least 17,000 ppm Cl^- , but may be considerably higher at greater depth. The chemistry of the saline waters was determined in the same mass proportions relative to chloride as other saline ground water from Thelwood Valley (Section 3.9). This exercise resulted in a similar modeled ^{14}C activity as the lower, 17,000 ppm Cl^- , simulation (67 to 68 pmC). This is due to the fact that an increasing amount of modern organic carbon is required to be oxidized to maintain the $\delta^{13}\text{C}$ in the final water. With a similar recharge water chemistry an increasing amount of modern carbon (1.3, 1.4, and 1.7 mmol C) must be oxidized and an increasing amount of CaSO_4 (2.6, 2.7, 2.9 mmol) must be dissolved to achieve a similar $\delta^{13}\text{C}$, $\delta^{34}\text{S}$, and $[\text{SO}_4^{2-}]$ to the analysed values (see Table 2-11).

The sensitivity of the results for #3321 to modification in various recharge inputs was checked and reported in Table 2-11. The results of the modeled ^{14}C are quite sensitive to the recharge HCO_3^- chemistry (concentration, $\delta^{13}\text{C}$, and ^{14}C) and to the $\delta^{13}\text{C}$ and ^{14}C of the organic carbon. The outcome of spreadsheet modeling using recharge water values outlined in Table 2-11 resulted in ^{14}C slightly greater than the measured ^{14}C activity in ground water #3321 (67 vs. 63.7 pmC), [Note: up to a maximum of 2 pmC of the total 63.7 pmC may have been added from atmospheric head-space in #3321 sampling container]. Iterative adjustment of the recharge ^{14}C resulted in the saline water remaining ^{14}C -free until the recharging water considered had less than approximately 30 pmC. Possibly the saline ground water could contain some modern component if the recharging water contained less than 30 pmC. This scenario is rather unlikely since the two modern recharging waters analysed for ^{14}C had 52.50 ± 0.45 pmC (ground water, 3186) and 39.95 ± 0.38 pmC (ground water, 2584; which was sampled at an elevation of -52). It is quite probable that the recharge water would have ^{14}C activity below the amount of the two analysed modern meteoric waters since a period time would be required for recharging waters to circulate down to 442 metres below ground surface: the sampling depth of ground water #3321. The period of time for recharging waters to reach this depth is likely decades (pre-bomb peak), or even a greater time period. In much shallower mixing scenarios for ground water #3274, the recharging water is tritium free (see below).

The modeling results, with the exception of the charge balance and chemical similarities with the analysed waters are quite insensitive to changes in the recharge Ca^{2+} , Mg^{2+} , Na^{+} , and K^{+} .

The fraction of dissolved sulphate reduced in the scenarios for #3321 (8 to 10%) agree with the estimate ($\sim 11\%$ using $\delta^{34}\text{S} = 17.5\%$ CDT) discussed in Section 2.4.3.2.

Of course, the results are not exclusive, and many other combinations of input parameters may be used. However, all of the input parameters are internally consistent with isotopic and chemical ranges for the Myra Falls waters. The recharge water chemistry is similar to ground waters from recharging areas (i.e. Pr-5-40, ground water #3186), and only expected reasonable geochemical processes were modeled. The results should accurately reflect the geochemical processes occurring in these waters.

The same procedure used above was also adopted for gaining insights into the ^{14}C in #3274 (Table 2-11). The amount of saline water necessary to mix with a 'fresh' meteoric water is minimal (1%) in order to match the Cl^{-} content of ground water #3274. The greater amount of recharge water means that the results are more sensitive to changes in the recharging water parameters. There is only approximately 1 mmol modern carbon necessary to balance the $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ during reduction of SO_4^{2-} in the end result. Due to the low saline water component the results are quite insensitive to changes in the saline water $\delta^{13}\text{C}$ component. Since water 3274 is tritium-free (<0.8 TU) and only $\sim 1\%$ saline water is required to mix with recharging waters, the recharging waters should also be tritium-free. The sampling depth of #3274 is 276 metres below ground surface (mbgs) and due to its chemical nature has a much more active meteoric water component and likely a shorter time period for circulating water to reach this depth. The mixing waters are sub-modern since they are tritium-free. The maximum ^{14}C value measured (52.5 pmC) was used as the value in the input for non-saline recharge waters. It is quite likely that the time frame for recharging waters to obtain this depth (3274; PR-92, 276 mbgs) is considerably less than the recharging waters involved in 3321 (PR 101, 442 mbgs). The resulting ^{14}C from the modeling process (56 pmC) is slightly less than the measured value of 59.0 ± 0.46 pmC using a ^{14}C -free saline water.

A second scenario was tested to see if the same chemistry would result from a mixture of modern meteoric water and water that has already undergone sulphate reduction (#3321).

Drill holes PR92 (3274) and PR101 (3321) are located <40 m apart, and mixing between these waters is conceivable. This second scenario (Table 2-11) requires 2% water similar to #3321 to mix with a modern meteoric recharge water. The results are very similar to mixing with a saline end-member with 17,000 ppm Cl^- with a modeled ^{14}C activity of 53 pmC.

The results of various scenarios in spreadsheet modeling illustrate that the saline ground water is ^{14}C -free. This high volume of He in the least de-gassed helium sample (Section 2.7) corroborates these findings and suggests that the saline waters could be considerably older than the period of ^{14}C usefulness in dating waters (i.e. older than ~30,000+ years).

The saline waters have been removed from the biosphere for a very long period of time. During this time period geochemical interactions have been at work to modify and mask the original composition and origin of these waters.

Table 2-11 Results of spreadsheet modeling for ground waters 3321 and 3274 with ranges of recharge parameters. Modeling of 3321 includes results for increasing salinity of the saline end-member and sensitivity of results to changes in input parameters.

	Saline water component (Cl = 17,000 ppm)	Range of Chemistry of Recharging Water	Sensitivity In Modeled #3321 Chemistry By Varying Inputs (for saline end-member = 17,000 ppm Cl)	Recharge Chemistry Used for #3321	#3321 Analysed Values	Results in modeled 3321 with variation in Saline End-Member	Recharge Water for #3274***	#3274 Analysed Values	Modeling Results for #3274	Modeling Results for #3274 missing with #3321
$\delta^{13}\text{C}$ (DIC) ‰ VPDB ^{13}C (DIC) ‰	-9.5 0	-9.5 to -1.3 30 to 50	results are -0.4 ‰ per 1‰ decrease in recharge value modeled results increase $\rightarrow$ 3 ‰ per 10 ‰ increase in recharge	-12 ‰ 40 ‰	Saline Fraction 0.5	Cl=17000 ppm -20.6 ‰ 67	-10 ‰ 53	-10.8 ‰ 59.0 $\pm$ 0.46	Cl=17000 ppm -10.9 ‰ 56	
$\delta^{34}\text{S}$ (SO ₄) ‰ CDT	17.5	-5 to 5	negligible for 3321 (moderate for 3274)	0.0	Saline Fraction 20.8	20.3	0 (4)	13.5	13.4	13.3
$\delta^{34}\text{S}$ (H ₂ S-SO ₄) ‰		-30 to -40	minimal effect on ^{34}S ($\pm$ 0.3 ‰ CDT) of modeled results recharging water would have to have low TU ($<$ 1.6) dependent upon elevation of recharge	-34.5 < 0.8 -1.3		-34.5 < 0.8 -7.2		< 0.8 -13.3	-34.5 < 0.8 -13.2	< 0.8 -13.2
$\delta^2\text{H}$ (TU)		< 0.8								
$\delta^{18}\text{O}$ ‰ VSMOW	$\delta^{18}\text{O}$ ‰ = 0.0007(Cl(ppm)) - 13.5									
Ca ppm	3740 (Cl*0.22)	20 to 80	negligible	35	1700	1680	45 (42)	29	28	29
Mg ppm	148 (Cl*0.0087)	1 to 8	negligible	2	64	64	2	2.3	2	
Na ppm	6800 (Cl*0.4)	1 to 50	negligible	10	3720	3720	7	150	150	150
K ppm	29 (Cl*0.0017)	0.5 to 0.8	negligible	0.5	17	17	0.5	1.1	1	1
HCO ₃ ppm	20	100 to 180	final ^{13}C $\rightarrow$ -0.7 ‰ per 20 ppm increase, final ^{13}C $\rightarrow$ -1.5 to 2 ‰ decrease per 20 ppm increase, increase HCO ₃ results in poorer modeled ^{13}C minimal effect on chemistry, resulting $^{34}\text{S}_{\text{SO}_4}$ decreases 0.3 ‰ CDT per 20 ppm increase	130	33	33	130	125.1	125	125
SO ₄ ppm	1020 (Cl*0.06)	10 to 50	...	20	741	700	25	67.9	64	67
H ₂ S*** ppm		0	increasing Cl in saline water results are slightly more sensitivity to ^{13}C of recharge, since a greater amount of recharge waters are added the modeled ^{13}C values decrease, however, keeping all other parameters equal results in low $^{34}\text{S}_{\text{SO}_4}$	0		-21	0	-1	-1.7	-1.2
Cl ppm	17000	1		1	8490	8490	1	172	174	176
Charge balance				2.3 ‰	-0.6 ‰	-0.6 ‰	-0.8 ‰	-0.8 ‰	-0.8 ‰	-1.2 ‰
Phases added to the system										
$\delta^{13}\text{C}$ ‰ VPDB of Organic C (canola oil)		-28 ‰ to -30 ‰	approximately 0.5 ‰ increase in modeled ^{13}C for each 1 ‰ increase			-29		-29		-
^{13}C of Organic C (canola oil)		100 ‰ to 120 ‰	using 100 ‰ canola resulted in ^{13}C most similar to measured, at 120 ‰ CDT modeled results were higher than measured, optimum values are recharge ^{13}C -40 ‰ CDT, Canola oil -100-110 ‰	100 to 110 pmC		100		110		-
mmol C oxidized C(IV) to C(II)		-15 ‰ to -20 ‰	modeling results are very sensitive to this factor			1.3		0.1		-
$\delta^{34}\text{S}$ ‰ CDT - CaSO ₄ mmol CaSO ₄						17.5		17.5		17.5
Fraction of sulphate reduced						2.6		0.40		0.28
						0.08		0.08		

*** negative signifies amount evolved

*** values in () used for #3274 resulting from #3321 missing with recharge

3. Chemical Characterization and Hydrochemical Evolution

3.1 Introduction

The quality of ground water is dependent upon and usually described in terms of its suitability for its intended use. Physical characteristics (i.e., temperature, turbidity, colour, and odour) and chemical content (along with bacterial and viral content for drinking standards), are generally the key considerations in quantifying water quality. Ground waters in the Myra Falls mining camp are not used as drinking water and therefore drinking water criterion is not suitable in assessing the ground water quality. Although waters issuing from sources within the mining complex will eventually be released to the environment including Buttle Lake; which is a recreational fishing area, is the head waters for fish spawning and for a drinking water source. The quality of waters issuing from underground sources is important in delineating source areas of poor quality and in the planning of mitigation of these source areas of metal pollution. Changes in water chemistry along generalized flow paths are important in assessing the evolution of water through the M-P hillside and into lower elevations.

Chemical parameters, and to a lesser extent physical parameters are used to assess the different chemical regimes and hydrogeochemical evolution trends within the study area. Together with the environmental isotopes (Chapter 2), these parameters can be used to assess physical processes occurring within the ground waters. Ground waters associated with the undisturbed Price ore-deposit can be used to determine baseline hydrogeochemical condition prior to mining this deposit. As well, these baseline concentrations can be used in assessing the impact of mining within the equivalent setting of the Myra Mine.

As ground waters traverse the saturated zone they normally increase their load of dissolved solutes and take on distinct chemical characteristics. Chebotarev (1955) observed that ground water tends to chemically evolve to the composition of sea water. The change in the dominant anionic species along regional ground-water flow tends to be:



In large sedimentary basinal flow systems this anionic evolution can be described in terms of three main zones of ground-water flow, which correlate in a general way with depth, distance, and time. Domenico (1972; in Freeze and Cherry, 1979) described these three zones as:

1. The upper zone characterized by active ground water flushing and well leached rocks. Water in this zone has HCO_3^- as the dominant anion and is low in TDS.
2. The intermediate zone characterized by a less active ground water circulation and higher TDS. The dominant anion is SO_4^{2-} .
3. The lower zone characterized by less active slower ground-water flow. Minerals with higher solubility are still present because of the lower degree of flushing. TDS and Cl^- are high in this zone.

Waters dominated by all three major anions are present in this current study; albeit, they may be present for reasons other than those for sedimentary basins. The diversity of water types in this study is quite remarkable considering the limited areal extent of the Myra Falls study.

Cation concentrations will vary by the availability of each element and by factors such as adsorption and cation exchange, and will be useful in inferring processes controlling cation concentration (i.e., mineral solubility and saturation, exchange, and adsorption).

Waters were selected so that each site sampled within the mining complex would be represented by one analysis, since bias would occur if all water analyses were used for descriptive purposes as some sites have been sampled on more than one occasion. Complete data for all chemical analyses, methods, materials, and quality control data is recorded in Appendix A.

3.2 Ground-Water Temperature

With increasing depth, ground waters will be heated by the local geothermal gradient. Ground water circulation in mountainous regions can be strongly influenced by heating from an underlying source of heat (Forster and Smith, 1990) which may result in channelized heat and fluid flow along permeable large-scale fractures (Smith and Forster, 1990). Convective ground-water flow resulting from geothermal heating is not expected at Myra Falls because there are currently no local heat sources. Quite conversely, central Vancouver Island is an

Table 3-1 Average temperature of ground waters sampled in underground drifts.

Mine	Level	Elevation (m)	Temp. °C
Price	4	626	6.6
Price	5	580	6.7
Price	9	416	7.1
Price	13	238	8.5
Myra	9	414	9.9
Myra	10	367	8.4
Myra	decline		7.9
Myra	13	241	8.1
HW	18	7	13.0
HW	20	-85	13.4
HW	21	-130	13.0

area of low geothermal gradients due to the subduction of the ocean crust made up of Juan De Fuca and Explorer plates (Lewis et al., 1986). Low geothermal gradients are typical in this setting as in other regions overlying the subduction of oceanic crust (Westbrook, 1991).

The temperature gradient of ground waters based on the mean water sample temperature is around 6.5 °C for approximately 800 m elevation. This results in a very low temperature gradient of around 8 °C per 10^3 m within and under the Myra-Price ridge. The temperature gradient of the waters between Price 13 level and HW18 level is 19 °C per 10^3 m. The upper portions of the M-P ridge have very low ground water thermal gradients.

3.3 Dissolved Oxygen (DO)

Dissolved Oxygen (DO) is important in redox reactions since it is the predominant oxidant in most shallow ground waters. It has a finite reservoir in recharge waters, which is generally determined by water equilibration with the atmospheric O₂. Dissolved oxygen should be readily consumed during the oxidation of sulphide minerals, dissolved organic carbon (DOC), nitrogen compounds, and multivalent cations (i.e., Mn, Fe, and As). Table 3-2 lists several generic reactions that will consume oxygen and the amount of product from each of those reactions if all the oxygen in the ground water was consumed.

If recharge conditions were such that a fluctuating water table allowed exposure to atmospheric oxygen alternated with saturated conditions, a much higher concentration of

SO_4^{2-} could be produced than indicated in Table 3-2. This is evident in the surface water at the base of the main waste rock dump which has a SO_4^{2-} concentration of 12,000 ppm (ground water #2579). Clearly SO_4^{2-} concentrations greater than the theoretical amount of approximately 17 ppm can be produced if water tables fluctuate enough to allow mineral contact with atmospheric O_2 , or O_2 was entrained at concentrations greater than equilibrium saturation during infiltration. Dissolved oxygen brought into the ground water system may oxidize sulphide minerals directly or indirectly through the oxidation of Fe^{2+} (see section 2.4.2 Sulphide Oxidation). However, most of the ground waters at Myra Falls, especially within the upper portions of the M-P ridge, have measurable DO and therefore none of these reactions are taken to completion. Further evidence that the sulphide oxidation reaction is not taken to completion comes from the median SO_4^{2-} concentrations in ground waters from Price 4 and 5 levels, which is 8.2 ppm.

The general sequence of redox reactions involving DOC should start with the reduction of DO, prior to the reduction of SO_4^{2-} , NO_3^- , and CO_2 (Champ et al., 1979). The persistence of DO within the ground waters indicates that only a low concentration of DOC, if any, is incorporated with recharge in most ground waters.

Curiously, anomalous concentrations of DO occur in ground waters from Price 9 level drill holes. Some drill holes on this level are fitted with margot plugs and shut-in valves. Opening valves results in a rush of gas which may last for many seconds followed by water discharging under high pressure at high flow rates containing high levels of DO. Gases discharging from the drill holes were measured with a hand-held oxygen meter (June, 1994) which registered 20% O_2 from Pr9-7 ($\text{DO} = 12.3 \text{ mgL}^{-1}$) and 19.3% from Pr9-8 ($\text{DO} = 12.2 \text{ mgL}^{-1}$). These percentages are quite similar to atmospheric proportion of O_2 (the portable O_2 meter was provided by Westmin for safety purposes and tended to register slightly low at atmospheric concentrations, ~20%). Dissolved oxygen concentrations would have been greater prior to degassing of these waters. The two ground waters with greatest DO concentrations ($>18 \text{ mgL}^{-1}$ from Pr9-13, and $>14 \text{ mgL}^{-1}$ from Pr9-15; both located at 54+56 m E) were from open drill holes oriented down-dip.

Table 3-2 Several oxygen consuming oxidation reactions are outlined below, with the amount of oxidized element expected from full consumption of O₂ (maximum product added) at equilibrium with water recharged at 5°C and 1000 m elevation (11.16 mgL⁻¹ O₂ or 3.49•10⁻⁴ molL⁻¹ O₂).

Reaction	Oxidation state Initial	Oxidation state Final	Product Added (ppm)	Byproduct Added (ppm)
$\text{CH}_4 + 2\text{O}_2 \Rightarrow \text{HCO}_3^- + \text{H}_2\text{O} + \text{H}^+$	-4(C)	+4	10.6	
$\text{NH}_3 + 2\text{O}_2 \Rightarrow \text{NO}_3^- + \text{H}^+ + \text{H}_2\text{O}$	-3(N)	+5	10.8	
$\text{CH}_2\text{O} + \text{O}_2 \Rightarrow \text{HCO}_3^- + \text{H}^+$	0(C)	+4	15.4	
$\text{FeS}_2 + 4\text{O}_2 \Rightarrow 2\text{SO}_4^{2-} + \text{Fe}^{2+}$	-2(S)	+6	16.8	4.9(Fe ²⁺)
$\text{ZnS} + 2\text{O}_2 \Rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-}$	-2(S)	+6	16.8	11.4(Zn ²⁺)
$\text{Mn}^{2+} + \text{O}_2 \Rightarrow \text{MnO}_2$	+2(Mn)	+4	19.2 (Mn ⁴⁺)	
$\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + 5/2\text{H}_2\text{O} \Rightarrow \text{Fe}(\text{OH})_3 + 2\text{H}^+$	+2(Fe)	+3	78.0 (Fe ³⁺)	

The addition of excess (atmospheric) air during the infiltration of water through the unsaturated zone is well known (Heating and Vogel, 1981; Andrews, 1987). The high concentrations of DO in the ground waters from Price 9 level may be due to a substantial amount of the infiltration resulting from alternating wet and dry periods, and/or from infiltration from heavy precipitation. Recharge of this type is responsible for air-entrapment (Freeze and Cherry, 1979) and may result in an inverted zone of saturation where the advancing wetting front traps air between itself and the water table. This may result in air pressures within fractures and regolith much greater than atmospheric. Air entrapment in the unsaturated zone during high rates of infiltration would be possible in fractured rock since narrow fracture apertures may not allow gas escape during periods of rapid water infiltration. In studies of dissolved noble gases most recharge must be corrected for an 'excess air' component presumed to result from small atmospheric gas bubbles entrained during recharge. Vigorous agitation in confined stream beds (aeration) and periods of drought following periods of high infiltration would be expected to incorporate atmospheric gases above equilibrium solubility concentrations or may trap 'pockets' of air below the recharge front. The magnitude of excess air in ground water was discussed by Andrews (1987), who felt that it was dependent upon the morphology of the flow channels (fractures) in the unsaturated zone and the frequency of recharge that together combine to permit air and air-saturated

water to alternately flow along fractures. A schematic interpretation of this recharge process is presented in Figure 3-1.

Ground waters from many localities within the mining complex were sampled from drill holes drilled up-dip (away from the drift). In drill holes with low flow the danger of re-equilibration with atmospheric oxygen is possible. This was examined in drill holes from the Price area. At most locations drill holes are arranged in a vertical fan array originating from a common drilling position. Ground waters from several drill holes at the same location allows for comparison of DO within the ground waters from drill holes with varying orientations and similar chemistries. It should be borne in mind that drill-holes with a greater vertical upright component may contain a greater concentration of DO since the water has likely traversed a lesser volume of rock as compared to drill holes originating at the same location but with more horizontal component. A lower volume of rock may limit the contact of DO with potential oxygen consuming reactions.

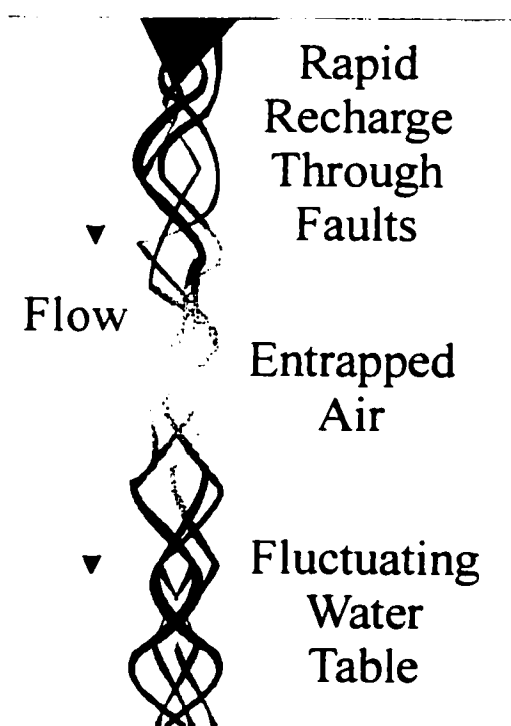


Figure 3-1 Schematic diagram of rapid infiltration in fractures trapping air above a fluctuating water table resulting in DO above saturated atmospheric-equilibrium concentration.

Figure 3-2 shows examples of DO (and measured redox; Eh) from four locations in the upper Price drifts. Possible re-equilibration with atmospheric oxygen during the waters ascent through the open drill hole appears to be occurring to varying degrees at three of the locations (48+46 mE, 52+58 mE, and 50+45 mE). Waters equilibrated with atmospheric oxygen at 7 °C and 600 m elevation will contain $11.2 \text{ mgL}^{-1} \text{ O}_2$. The top two and bottom left diagrams in Figure 3-2 shows that DO approaches that concentration with increasing drill hole angle.

Higher dissolved oxygen due to incorporation of atmospheric O_2 during ground water discharge may affect the measured Eh value which in turn will have some consequence on the results of geochemical computer code speciation of solutes in solution. The variation in results of saturation indices for these dilute waters will likely only be slight. For example, saturation indices for ground water #2160, Price 4 level (highest DO from Figure 3-2; 48+46 mE) were generated (PHREEQC; Parkhurst, 1995) using field data Eh and DO values (Eh,

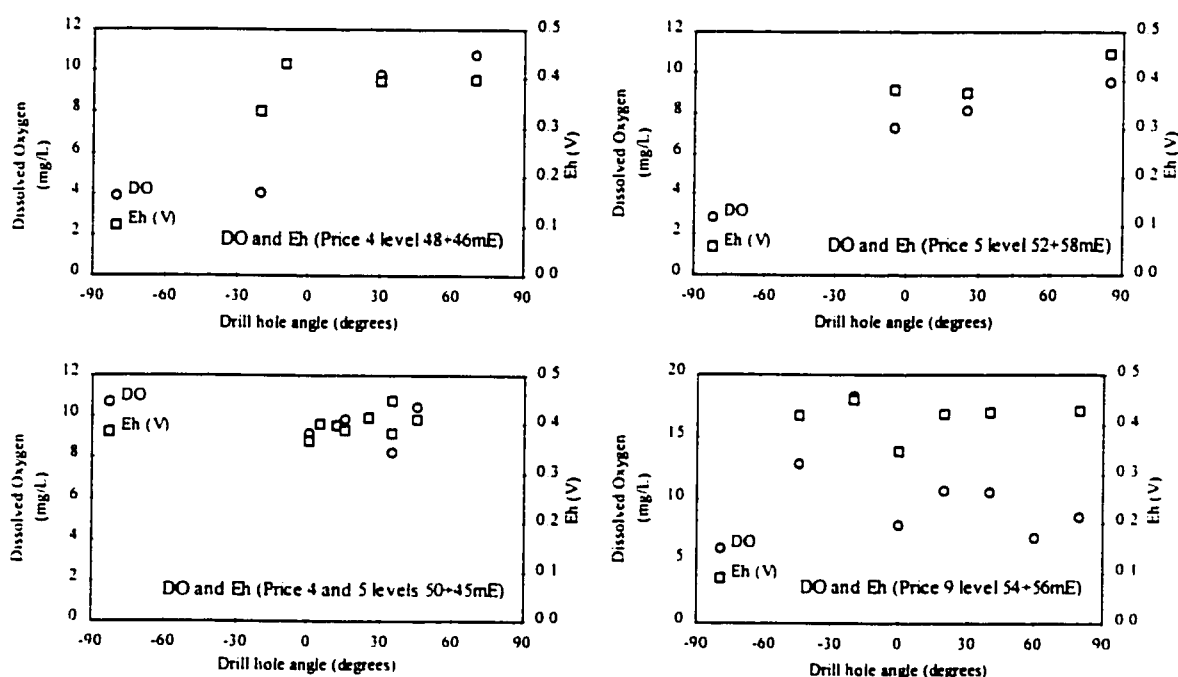


Figure 3-2 Dissolved oxygen and Eh measurements from four sections in upper Price. The top two diagrams suggest the addition of atmospheric oxygen to the waters with increasing drill hole angle. The bottom left has slight but variable increase in DO with increasing drill hole angle, while the bottom right has highly oxygenated waters from Price 9 level with decreasing DO corresponding to increasing drill hole orientation.

0.40 V; DO, 10.7 mgL⁻¹) and with Eh and DO values similar to the drill hole with the lowest values on that section (Eh, 0.29 V; DO, 2.7 mgL⁻¹). The results of this test was no noticeable change in saturation indices (SI) for common minerals. The greatest changes in SI were for oxide and hydroxide phases such as: birnessite (MnO₂), -5.5, -9.5; bixbyite (Mn₂O₃), -7.5, -11.5; Fe₃(OH)₈, -5.5, -3.6; and goethite (FeOOH), 6.23, 6.21; under high DO and high Eh, and low DO and low Eh, respectively. Although some of the above saturation indices show differences between the two models, the change in input did not result in a change of interpretation of any of the phases [undersaturated vs. oversaturated i.e., 0±0.5 which is within the expected range of error of speciation codes (Langmuir, 1997)].

Any possibility of oxygen re-equilibration could be avoided if all drill holes were fitted with margot plugs and shut-off valves; however the costs involved in this undertaking would be great, and the risks of trace element contamination from the metal parts (including brass) would be detrimental to one of the prime objectives of this research (Chapter 7 Ground Water Hydrogeochemical Exploration Methods).

Generally, not until waters with a greater dissolved solid load are encountered is the DO reduced to very low or unmeasurable concentrations, such as in ground waters from the HW mine or ground waters sampled at depth in Thelwood Valley. Summary statistics of DO for waters from various locations within the study area can be found in Table 3-4.

3.4 pH

pH is the measure of activity of the H⁺ ion (-log[H⁺]), and along with redox conditions exert strong controls on the stability, and therefore the solubility of many phases.

The pH of surface waters at Myra Falls with no or little influence from mining activities ranges from 6.0 to 9.0. The pH in surface waters that may have been influenced by mining activities ranges from 2.3 to 8.4.

The pH range in ground waters is from 2.3 to 10.1. Both extremes of pH values in ground waters are from ground waters originating in the Myra mine area. Summary statistics for pH are outlined in Table 3-4.

Unlike many sulphide mining districts, few highly acidic waters were encountered in this study. Highly acidic waters were limited to two sites. The base of the main waste rock dump had ponded waters with a pH of 2.3. While drainage from Myra 12 level, collected

from 12+00 and 12+50, levels had pH values of 2.9 and 2.3, respectively. Other highly acidic ground waters have been documented from the Myra Falls mining camp, but these have been limited to areas of the Lynx mine (Morin and Hutt, 1997; which was not included in this study).

3.5 Electrical Conductance (EC)

Electrical conductance was measured at the time of sample collection and is automatically corrected at the time of measurement to 25 °C. The electrical conductivity of the sample is the measure of the solutions' ability to pass a current, and is dependent upon and proportional to the number of dissolved ions in the water. Electrical conductivity in this study covered 4 orders of magnitude and ranged from 11 to 47000 μScm^{-1} . The relationships between EC and TDS (total dissolved solids, calculated) in waters dominated by Cl^- , SO_4^{2-} , and HCO_3^- anions are:

$$\text{Chloride (n=80)} \quad \text{TDS (ppm)} = \text{EC } (\mu\text{S cm}^{-1}) \cdot 0.67 \quad (r^2 = 0.96)$$

$$\text{Sulphate (n=55)} \quad \text{TDS (ppm)} = \text{EC } (\mu\text{S cm}^{-1}) \cdot 1.0 \quad (r^2 = 0.98)$$

$$\text{Bicarbonate (n=311)} \quad \text{TDS (ppm)} = \text{EC } (\mu\text{S cm}^{-1}) \cdot 0.84 \quad (r^2 = 0.78);$$

Hem (1989) reports the factor to convert EC to TDS for most waters is between 0.54 and 0.96 which are very similar to the factors determined in this study.

3.6 Oxidation - Reduction Potential (Redox-Eh)

The platinum electrode potential represents a bulk redox potential of the water being measured, and as such will be influenced by the redox state of redox-active constituents. Many constituents in waters have a variety of oxidation states. These include major elements (that generally occur in concentrations greater than 1 ppm) such as S, O, C, and possibly N. Many metals and trace metals are also redox-sensitive, such as Fe, Mn, As, Cr, Cu, Mo, Se, Sb, and U. The redox conditions of the water not only affects the stability of phases but it often determines the behavior, including mobility (i.e., Fe and Mn), and toxicity (i.e., As) of an element in the aqueous environment.

Other than in acidic waters, Eh reaches a maximum around 0.5 V. The greatest density of points plot with a smooth decay of O_2 coinciding with a decrease in Eh (Figure 3-

3a). The 'trail' of DO to the left of the cluster at approximately 10 mgL^{-1} DO and $\sim 0.4 \text{ V}$ may be caused by oxygen contamination and atmospheric re-equilibration during sampling. However, at several sites with low ground-water flow and a long exposure time to atmospheric O_2 , measured redox levels were low (#s 2441, 2442, 2446 from Myra 13 level). This may result from a well poised water with adequate redox buffering capacity.

The cumulative concentrations of redox-sensitive metals, such as Fe and Mn, which tend to precipitate under oxidizing conditions, and Cu which has a greater tendency to adsorb to Fe-Mn hydroxides under oxidizing conditions tend to be greatest at lower measured redox potentials (Figure 3-3 b). The exceptions to this generality are the highly acidic waters.

A more in depth discussion of redox is found in Chapter 5 Chemical Speciation: As and S.

3.7 Rainfall Chemistry

Monthly rainfall composite samples were collected at the Myra Valley meteorological station (MET) for chemical and isotopic analyses. Constituents in Myra rainfall may originate from the dissolution of atmospheric gases, marine aerosols, air-borne rock powder from milling operations or dust contamination (roads etc.).

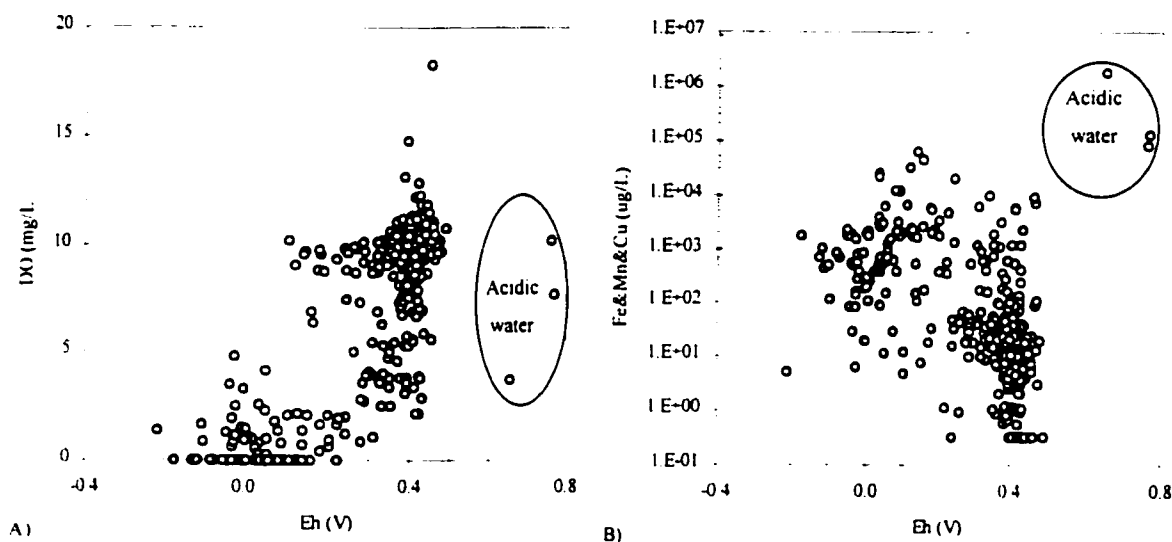


Figure 3-3 Eh (V) relationship with dissolved oxygen (DO) (all waters)(A), and with selected redox sensitive metals (Fe, Mn, and Cu) in all waters (B).

The MET station is located less than 200 m from the ore-concentrator and secondary crusher. The influence of contaminants from ore-processing operations likely influences the chemistry of some of the elements in rainfall waters (e.g. Ca, Mg, Na, K, Al, and Zn) (Table 3-3). A considerable proportion of these constituents may result from dry-fall especially from ventilation from the secondary rock crusher. The effect of the dry-fall should be attenuated at locations remote to the concentrator and MET station. For example median concentrations of Zn, Cu, and Pb in surface waters on the Price hillside are 3.8, <0.5, and <0.2 ppb, respectively (see Chapter 7 Ground Water Hydrogeochemical Exploration Methods). These values are considerably less than the 59, 12, and 0.7 ppb for Zn, Cu, and Pb, respectively in rainfall from the MET station. Sulphate concentrations, in the last row of Table 3-3 have been corrected for the oxidation of sphalerite, chalcopyrite, and galena resulting from oxidation of these minerals which contribute the observed concentrations of Zn, Cu, and Pb in the rainfall.

Concentrations of major ions from atmospheric precipitation for coastal and mountainous areas of Washington State (1996) are 0.2 to 0.8 mgL⁻¹ Cl⁻, 0.2 to 0.3 mgL⁻¹ SO₄²⁻, 46 to 180 µgL⁻¹ Na⁺, and 0.1 to 0.3 mgL⁻¹ NO₃⁻ (Langmuir, 1997). In comparison, rainfall from Myra Falls MET station has higher concentrations for all these ions.

Milling activities (crushing and milling) has added metals and major elements to precipitation from the Myra Falls meteorological station. Surface and or groundwaters in close proximity to the reporting station would require correction if used in studies such as hydrogeologic exploration in the Myra Valley as opposed to the Price hillside/Thelwood Valley area which have lower metal concentrations.

Table 3-3 Rainfall selected chemistry (non-weighted). The last row is calculated SO_4^{2-} concentration after subtracting molar balance for addition of Zn, Cu, and Pb, from sphalerite, chalcopyrite, and galena, respectively. Concentrations are in ppb except where noted.

Element	Minimum	Median	Maximum	Mean	Standard Deviation
SiO ₂ ppm	0.002	0.08	0.32	0.11	0.09
Ca ppm	0.32	1.82	11.0	2.99	3.01
Mg ppm	0.02	0.07	0.62	0.12	0.17
Na ppm	0.002	0.41	13.00	1.51	3.66
K ppm	0.05	0.36	1.08	0.42	0.31
Al	2.30	8.40	27.0	10.8	8.32
Fe	0.30	4.60	39.0	8.93	10.86
HCO ₃ ppm	1.32	5.15	18.62	7.44	5.00
SO ₄ ppm	0.33	0.81	4.55	1.17	1.22
Cl ppm	<DL	0.6	10	1.1	2.2
NO ₃ -N	17.2	26.1	101	34.1	32.9
Sr	1.10	4.40	200	21.9	56.2
Ba	21.0	44.0	93.0	46.3	20.0
Zn	19	59	209	73	48
Cu	6.2	12.0	68.0	17.8	17.2
Pb	0.2	0.7	2.2	0.9	0.7
Cd	0.5	1.7	20.0	4.1	5.4
SO ₄ ppm (calculated)	0.24	0.67	4.23	1.04	1.16

3.8 Major Element Characterization and Evolution

3.8.1 Introduction

The piper diagram (Piper, 1944) is a convenient way of displaying and classifying waters based on the proportions of major ions in solution. This allows for a graphical means of displaying waters that have similar major element characteristics and which have likely acquired their major chemistry through similar means. It is also very useful to outline mixing and evolutionary trends of major elements in waters.

Surface and ground waters from the Myra Falls mining camp have a wide variety of water facies. There is nearly full coverage of the central diamond of the piper diagram (Figure 3-4). These water facies can be broken down into water types originating from various localities within the camp as well as certain water-rock interaction and mixing processes.

Summary statistics for data are presented in Table 3-4, and complete analyses for individual waters is available in Appendix A.

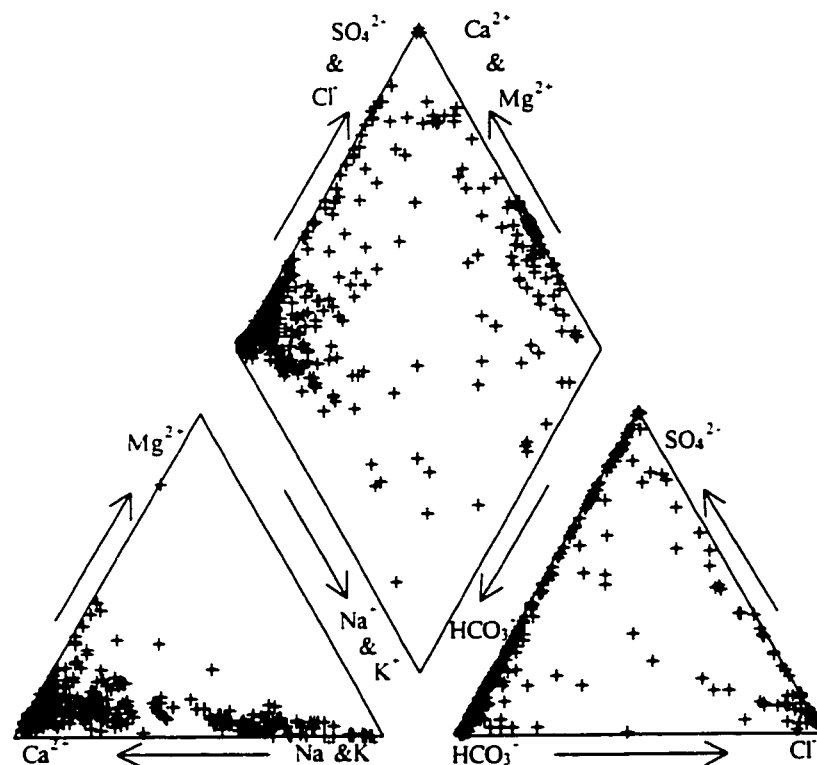


Figure 3-4 Piper diagram of surface and ground waters. There is almost complete coverage of the central diamond by waters from the Myra Falls mining camp.

3.8.2 Major Ion Classification (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , and Cl^-)

Distinct trends in water compositions are evident from piper plots generated for surface and ground waters from various areas of the mining camp.

Surface waters are Ca^{2+} - HCO_3^- dominated, contain minimal Cl^- , and only contain Mg^{2+} and significant proportions of SO_4^{2-} when they have been influenced by mine workings or infrastructure (i.e., Lynx open pit, waste rock dumps, and road building with mined rock). Acidic waters contain high proportions of SO_4^{2-} and Mg^{2+} . Whereas 'pristine' surface waters have low TDS, circum-neutral pH and high DO (Table 3-4 and Appendix A).

Ground waters sampled from upper Price (levels 4, 5, and 9; 626, 580, and 416 m, respectively) plot dominantly in the field covered by 'pristine' surface waters, with few

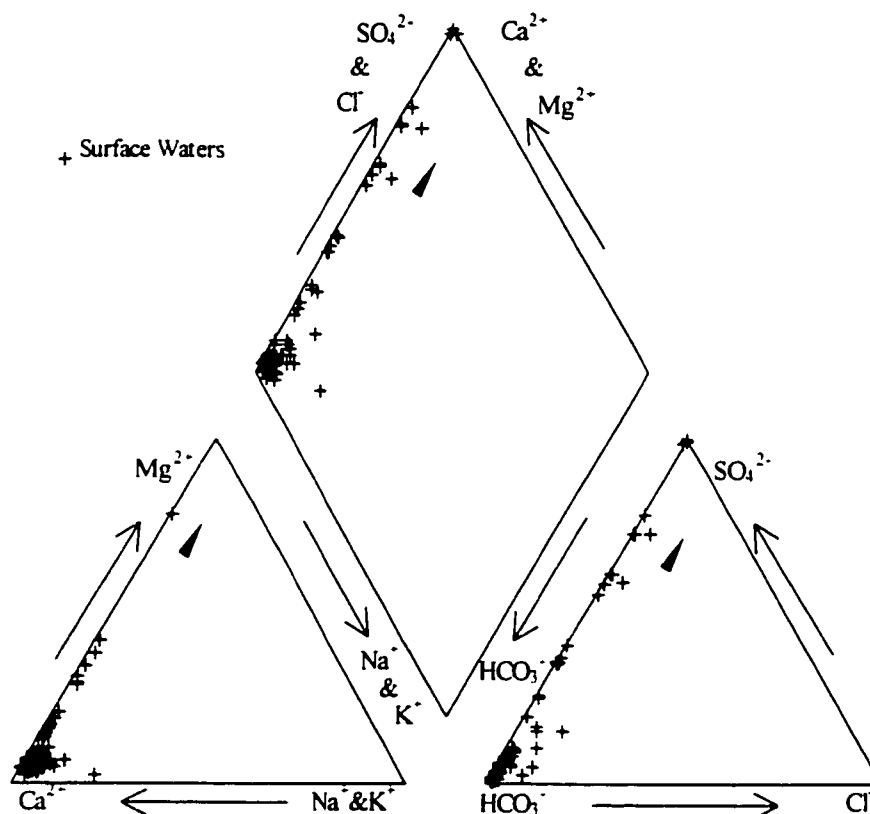


Figure 3-5 Piper plot of surface waters. Arrows inside fields show the effect of mining activity of surface water composition.

waters that diverge away from the Ca^{2+} apex on the cation triangle (Figure 3-6). There is a greater proportion of Na^+ and Mg^{2+} in ground waters from levels 4 and 5 than level 9. Anions from levels 4 and 5 have a greater range with greater proportions of SO_4^{2-} than those from Price 9 level; the result of oxidation of sulphide minerals. Total dissolved solids are low, generally less than 200 ppm in ground water accessed from all three of these drifts. Level 9 ground waters tend to have the lowest TDS. Dissolved solids tend to increase slightly with an increasing proportion of SO_4^{2-} , especially in ground waters from 5 and 9 levels (Figure 3-7).

Level 5 generally underlies the Price deposit to a greater extent than Price 4 level and in most cases ground waters will have traversed slightly greater distances before draining into 5 level. Greater sulphate and slightly higher TDS in a few waters from level 5 as compared to 4 level is evident in Figure 3-7. Weathering mafic rocks which overly Price 4 and 5 levels may be responsible for the greater proportion of Mg^{2+} in these ground waters. Higher proportions of Na^+ occur towards the core of the M-P ridge where ground waters have had to

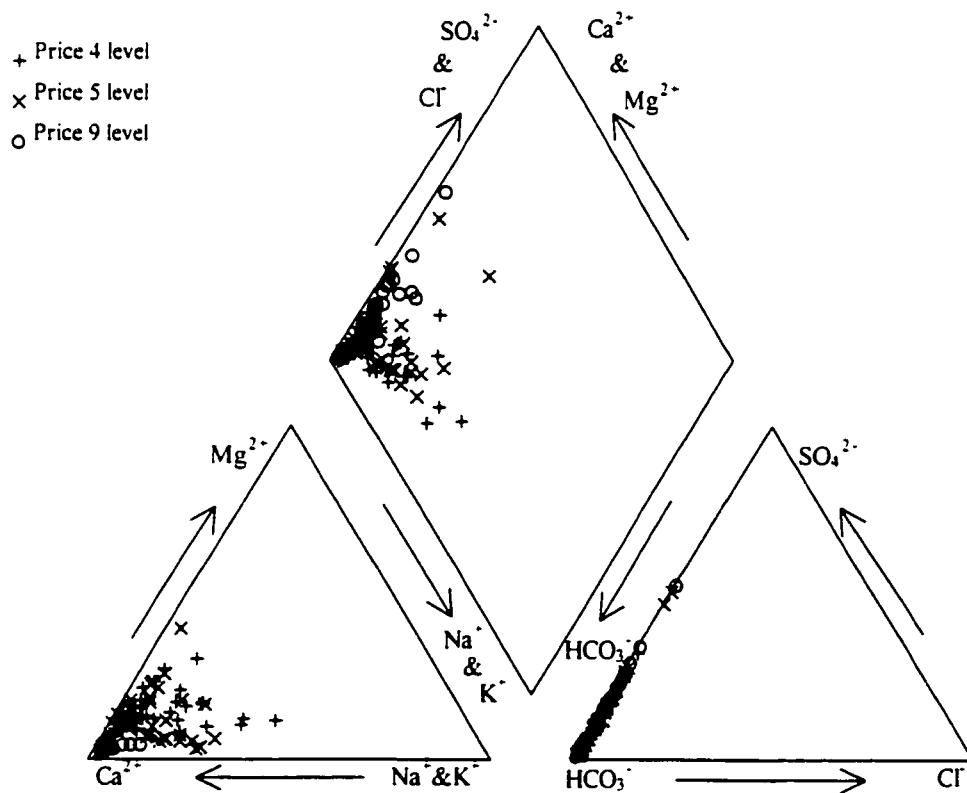


Figure 3-6 Piper diagram of upper Price ground waters.

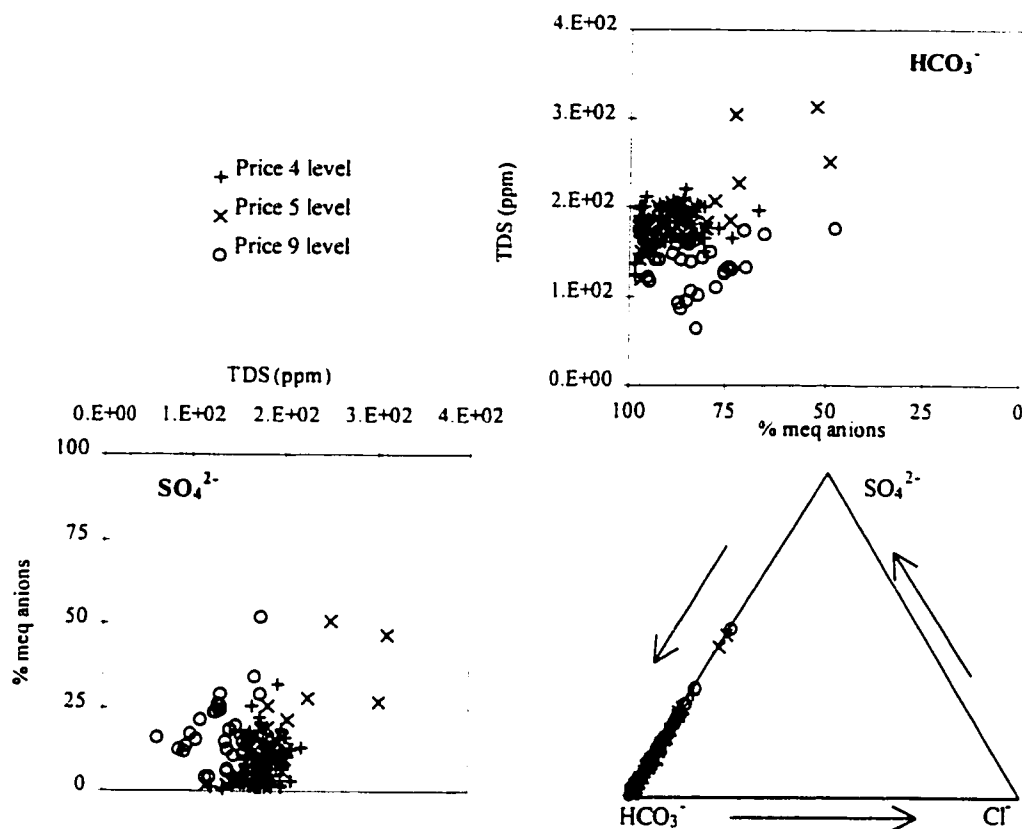


Figure 3-7 Relationships between total dissolved solids and dominant anions (% meq) for ground waters accessed from upper Price levels. For ground waters from levels 5 and 9 increased TDS corresponds to higher proportions of SO_4^{2-} .

traverse greater distances and may have an influence from the damaged rock overlying the end of Price 4 drift believed to be the Myra-Price fault (Hamilton, 1993; and Section 1.7.6). Finely ground rock will be subject to greater weathering than bulk rock and therefore to the development of clays during the weathering process which have the ability to exchange cations (Langmuir, 1997).

Ground waters from upper levels of Myra mine, the Myra decline ramp, and drifts accessed from the ramp tend to have higher proportions of SO_4^{2-} and Na^+ (Figure 3-8) than ground waters from the upper Price area (Figure 3-6).

Low TDS ground waters from the upper Myra drifts are characterized by Ca^{2+} - HCO_3^- chemistry similar to 'pristine' surface waters. Increasing TDS is accompanied by an increasing proportion of SO_4^{2-} (Figure 3-8). Chloride is very low in all of these ground waters and only in waters accessed at the end of Myra 10 level in an area of recent drifting and

exploration drilling is there a noticeable Cl^- component. Ground waters with Cl^- are also Na^+ rich; as is another water from the Myra decline (#2484). The Myra 10 level waters with a noticeable Cl^- component are accessed from the Myra-Price fault or an area underlying the fault in the central region of the Myra-Price ridge.

The $\text{Na}^+ - \text{SO}_4^{2-} - \text{HCO}_3^-$ waters from the end of Myra 10 level drift (near the centre of M-P ridge; see map in back pocket) do not contain measurable tritium (Section. 2.8) and have a longer residence time in the rock than ground waters near the ridge carapace.

The influence of mine workings on major ions in ground water can clearly be seen in waters accessed from 13 level Myra and Price (Figure 3-9). Total dissolved solids (calculated) are low in ground waters accessed from Price 13 level (median TDS = 203 ppm, with a range of 91 to 540 ppm), whereas median TDS from waters accessed from Myra 13 level is twice as high (median TDS = 457 ppm, range of values is from 152 to 4840 ppm).

Sulphate dominated waters from Price 13 have relatively low TDS (<540 ppm) and have high proportions of Na^+ (>75% of cation meq) (Figure 3-17) as compared to SO_4^{2-} dominated waters from Myra 13 which have TDS values that can be greater than 4,000 ppm and low proportions of Na^+ (generally <25% of cation meq). In areas near the centre of the M-P ridge underlying the M-P fault, high proportions of Na^+ are present in waters from Myra and Price 13 drifts similar to what occurs in Myra 10 level waters; although, Cl^- is absent in the waters from 13 level. These same waters tend to have TDS less than ~500 ppm. Since Cl^- is very low in waters with high proportions of Na^+ albite (plagioclase) weathering or cation exchange are the likely sources of Na^+ in these waters (Figure 3-10). Silicate weathering of minerals with low concentrations of Na^+ will result in high $\text{SiO}_2/(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$ molar ratios; whereas, albite weathering will result in lower ratios. Albite is relatively stable in the weathering environment and may only contribute small amounts of Na^+ . Whereas sodium resulting from cation exchange will be readily available and results in very low molar ratios of $\text{SiO}_2/(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$ (Hounslow, 1995).

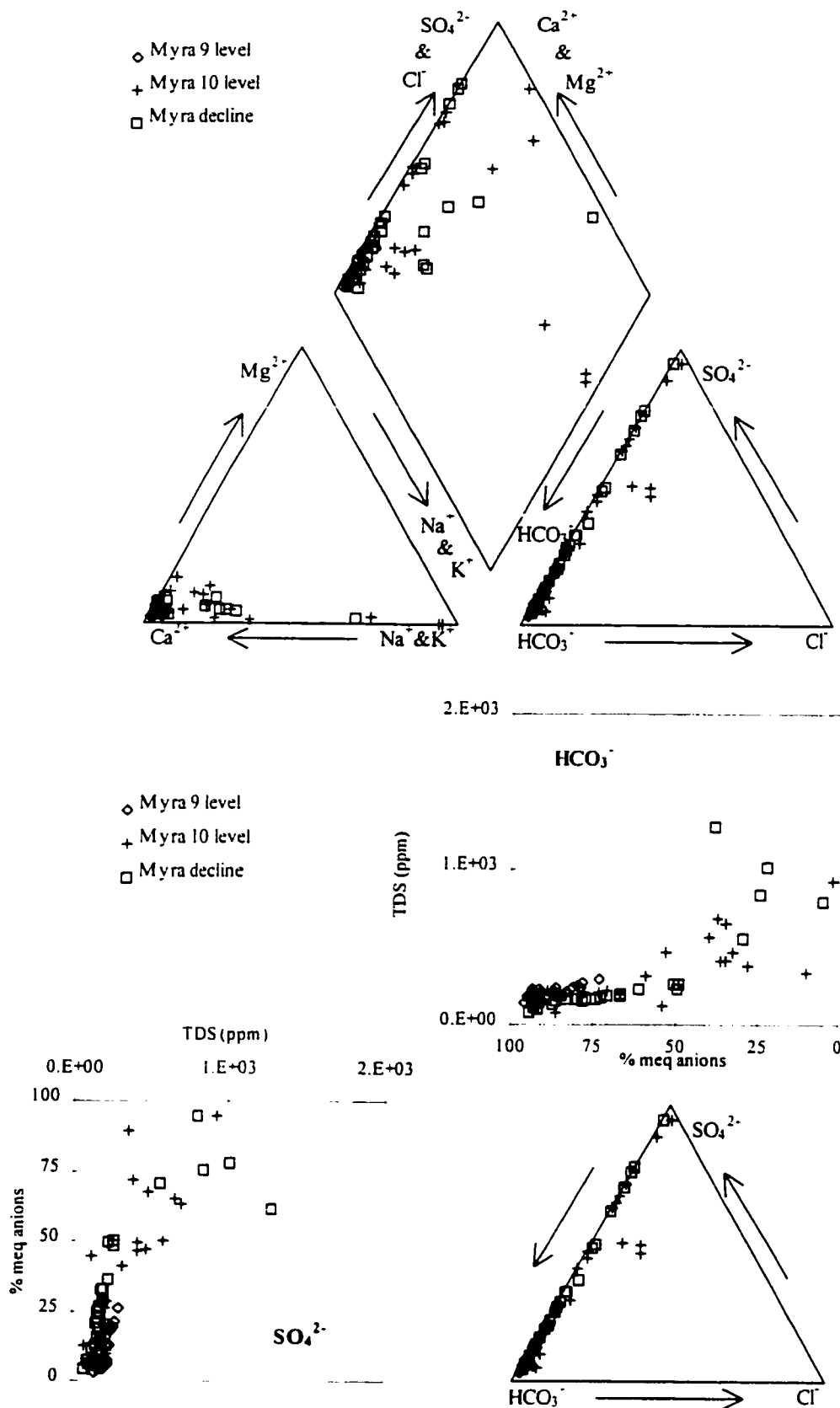


Figure 3-8 Major ion relationships of ground waters from Myra 9 and 10 levels and Myra decline. Top diagram is a piper plot of these ground waters, whereas the bottom diagrams show the relationship of % meq SO_4^{2-} and HCO_3^- with total dissolved solids.

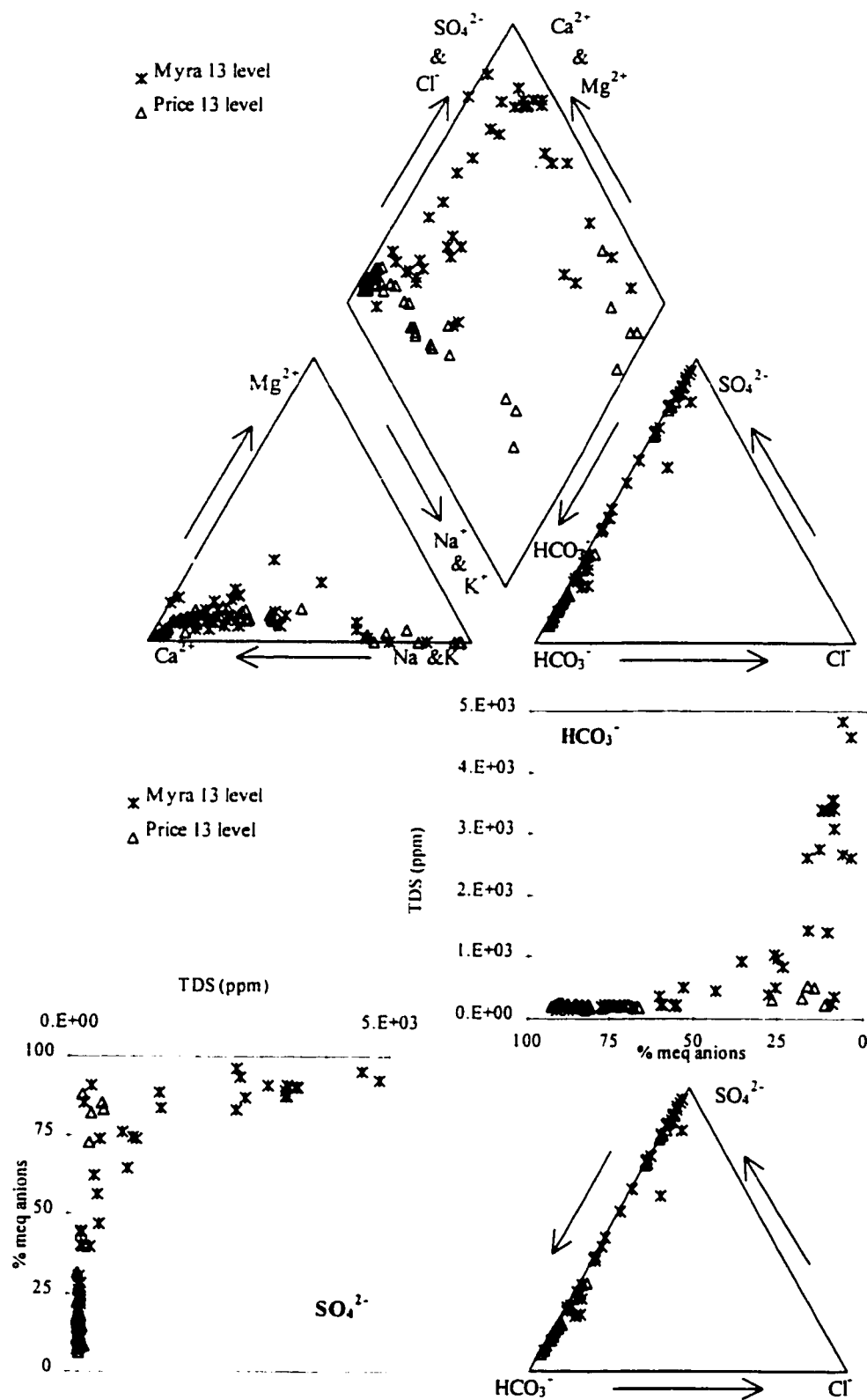


Figure 3-9 Piper plot of ground waters from Myra and Price 13 levels (upper) and relationship of % meq HCO₃⁻ and SO₄²⁻ with TDS (lower). High TDS waters are exclusively SO₄²⁻ composition from regions of Myra 13 underlying old mine workings.

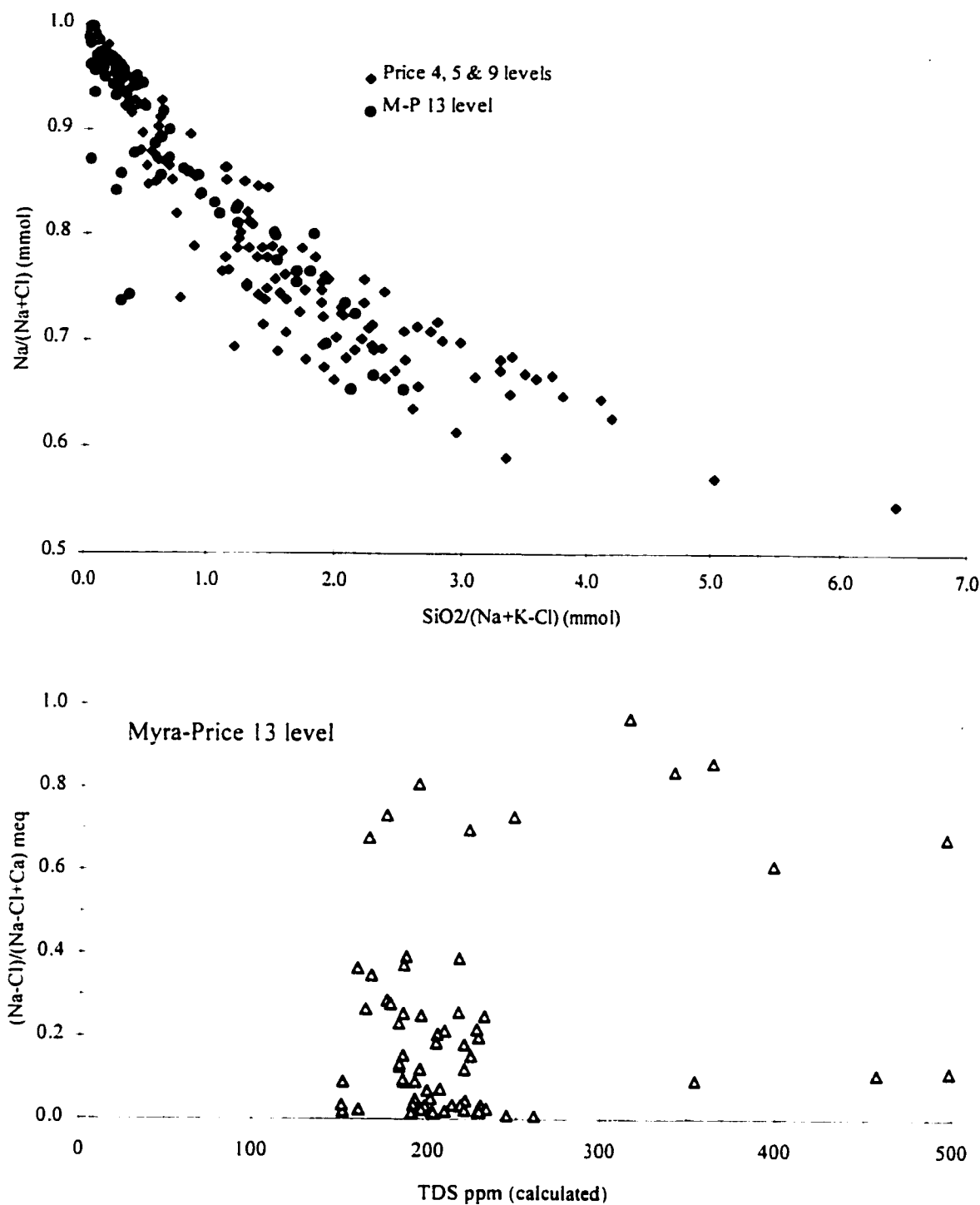


Figure 3-10 Potential sources of Na^+ in waters from M-P ground waters. (Top) High silica to non-halite source of Na^+ is would indicative of rock weathering (Na^+ and Cl^- mmol are both low in these waters), whereas higher ratios of $\text{Na}^+ / (\text{Na}^+ - \text{Cl}^-)$ and lower $\text{SiO}_2 / (\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$ are indicative of albite weathering or more likely, cation exchange. (Bottom) Ground waters (TDS < 500 ppm) from Price 13 level have high proportions of Na^+ (unsupported from halite) with similar TDS as Ca^{2+} dominated waters. This is highly indicative of cation exchange processes adding Na^+ in exchange for Ca^{2+} in waters of equivalent TDS.

Ground waters accessed from deeper workings (HW mine) beneath the M-P ridge show a different anion character (Figure 3-11) than waters from the upper portions of the ridge (Figure 3-6 to Figure 3-9). Waters, with the exception of two which are related to the North fault on HW20 level, are dominated by Na^+ and span the full range of the SO_4^{2-} - Cl^- axis on a Piper diagram (Figure 3-11).

The two Na^+ - HCO_3^- ground waters on Figure 3-11 are draining the North fault (N-fault) and the damaged zone in close proximity to the fault. These waters associated with flow from the N-fault have major chemistry (high proportion of Na^+ , HCO_3^- , and low TDS) similar to waters overlying the central portions of the M-P ridge sampled on 13 level (Figure 3-9). The ground water draining the North fault on 20 level contains tritium (Section. 2.8). The chemical and isotopic characteristics of these two waters are anomalous for waters from the HW mine and likely represent modifications to the natural flow by mining activities.

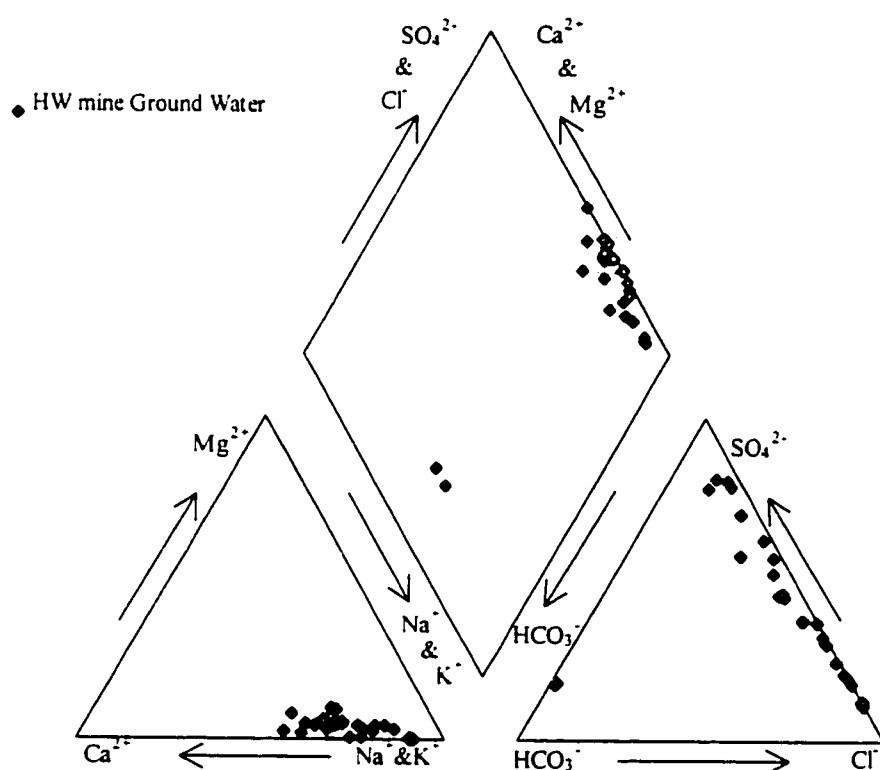


Figure 3-11 Piper plot of ground waters accessed from the HW mine. Circles in triangles and the central diamond mark the chemistry of the most saline water component.

The remainder of the sampled ground waters from the HW mine show mixing between SO_4^{2-} waters with varying proportions of a saline Cl^- water (Figure 3-11, Figure 3-12) which was uncovered at shallow depth beneath the mine and also in Thelwood Valley.

Cations in the HW mine waters are dominantly Na^+ (Figure 3-11) (K^+ contributes only a small proportion of the total Na^+ & K^+). Many of the SO_4^{2-} dominated waters have a higher proportion of Na^+ than the saline Cl^- waters.

Low TDS ground waters from the HW mine may contain up to approximately 50 meq % Cl^- (Figure 3-12). This results from small amounts of the high TDS saline water mixing with a larger proportion of a lower TDS SO_4^{2-} water which will then produce high proportions of Cl^- in the resulting water (Figure 3-15).

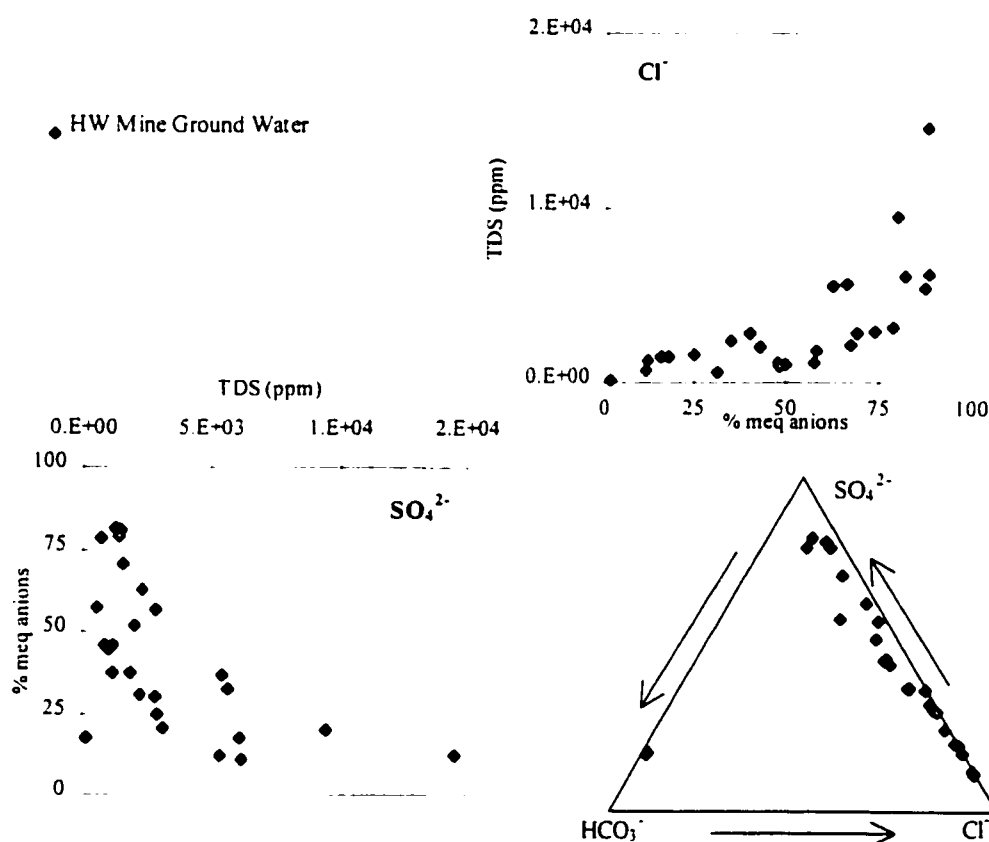


Figure 3-12 Relationship between Cl^- , SO_4^{2-} (% meq anions) and TDS in ground waters from the HW mine.

The ground waters from Thelwood Valley display a somewhat different pattern on a Piper diagram (Figure 3-13) as compared to HW mine ground waters or ground waters from Price and Myra areas (Figure 3-11 and Figure 3-11). Shallow ground waters intercepted by drilling at the base of the Price hillside (PR 97, 100, 101, 102, 111, 112, and 116-119) tend to flow at the ground surface. They also have major element chemistry somewhat similar to shallow recharge in upper levels of Price (Figure 3-6 and Figure 3-9). Ground waters accessed at depth from drill holes situated on the flank of Price hillside (PR 73 and 97) tend to have a higher proportion of Na^+ , while HCO_3^- dominates the anions. This character is similar to ground waters from sluggish flow systems within the central M-P ridge (Figure 3-9). Ground waters from PR92 and PR84 have higher proportions of Na^+ and SO_4^{2-} than other ground waters in Thelwood Valley.

The highest salinity ground waters sampled within this study are from Thelwood Valley. Maximum calculated TDS of the Cl^- waters exceeds 32,000 ppm (Figure 3-14). The field of major chemistry of the most saline waters are outlined by circles in Figure 3-13.

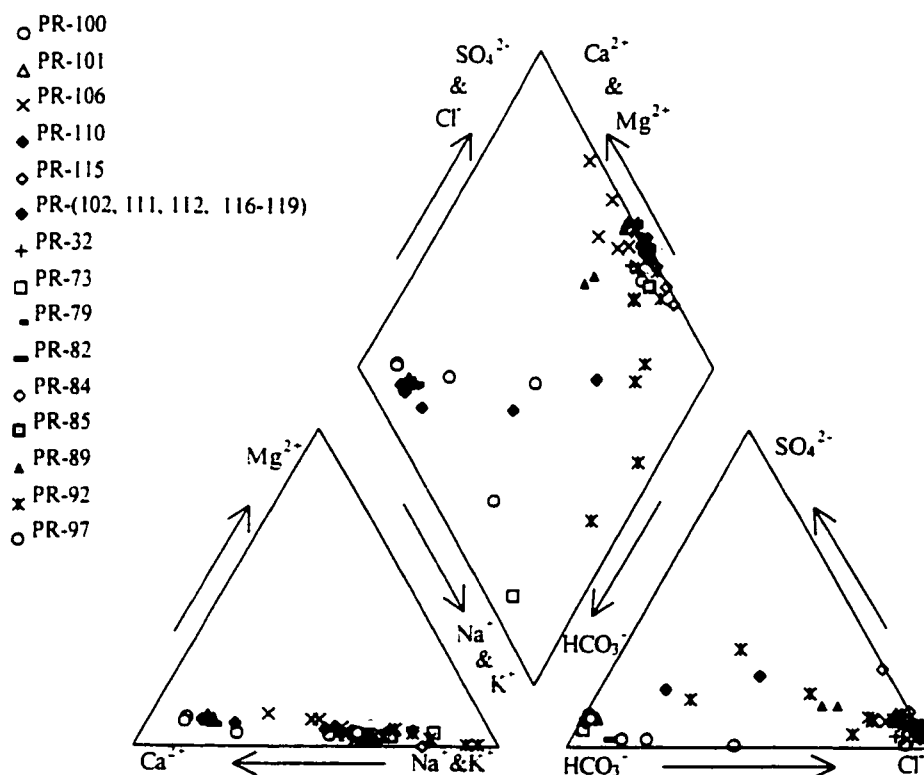


Figure 3-13 Piper plot of major elements in ground waters from Thelwood Valley and lower Price hillside. Drill holes PR-73 and Pr-97 are located on lower Price hillside less than 100 metres above the elevation of Thelwood Valley. The circle designates the major chemistry of the most saline ground water.

The meq proportion of Na^+ in the most saline waters is between 60 and 65% of the total cation meq. Lower salinity waters plot with both lower and also higher proportions of Na^+ than the most saline waters (Figure 3-14). Low salinity waters from shallow ground-water flow paths on the edge of the Price hillside tend to have a low proportion of Na^+ . Ground waters with a higher proportion of Na^+ include non-saline waters accessed at depth from the Price hill fringe (lower Price hillside; PR 73), and ground waters with a measurable SO_4^{2-} component (PR 92, 102, 118, and 119).

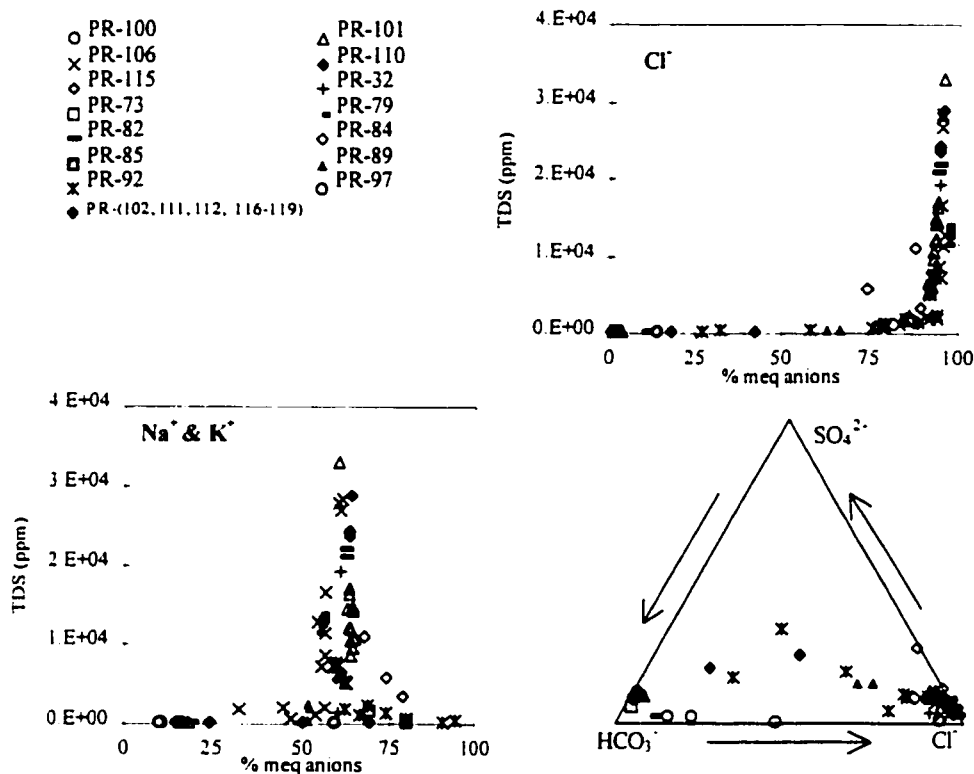


Figure 3-14 Relationship between TDS and %meq Cl^- , also TDS and % meq Na^+ in ground waters from Thelwood Valley and lower Price hillside (PR-73 and PR-97).

Piper (1944) indicated that two component mixing on his diagrams would plot as a straight line with the resulting mixture plotting between the end-members of different water quality (if the major solutes remain in solution). There sometimes appears to be a gap in the central portion of the diamond or in the anion triangle in the Thelwood Valley ground water Piper plot (Figure 3-13) which may result in criticism that mixing with Cl^- waters is not always apparent. Mixing of a dilute water with a water having much higher TDS will result in significant movement across the Piper fields towards the high TDS end-member with only small additions of the saline water to the dilute source. A simulation was carried out using water chemistry encountered in this study for various end-members (end-members were represented by: HCO_3^- , ground water #2022; SO_4^{2-} , ground water #1221; and Cl^- , ground water #2246; analyses in Appendix A). Mixtures of 0.1%, 1.0%, 5.0%, 10% and 50% of the

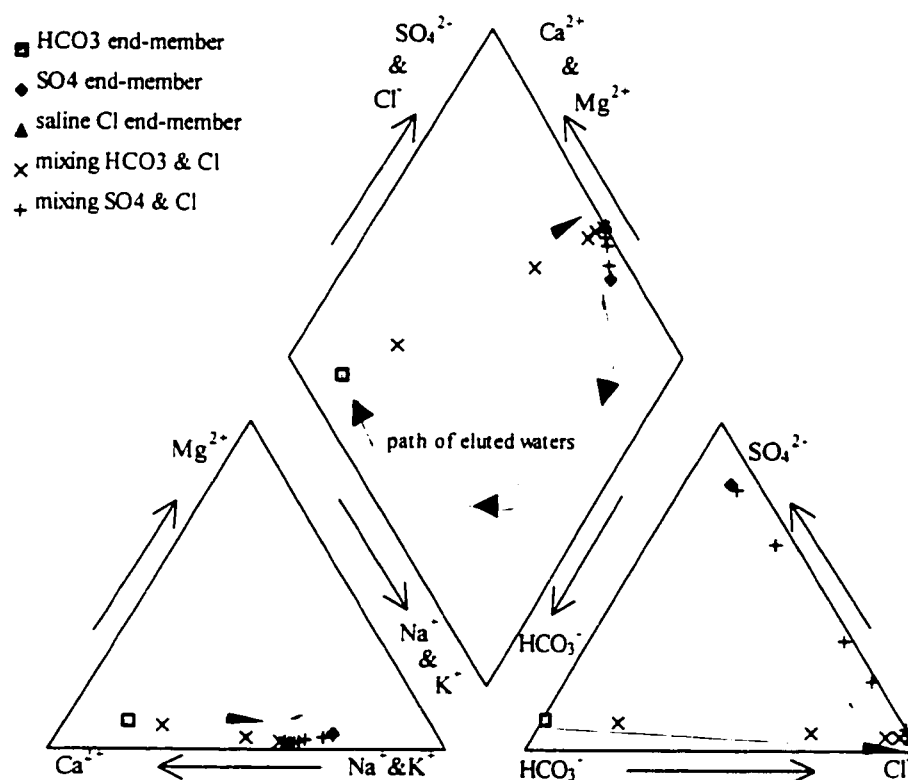


Figure 3-15 Ideal conservative mixing simulation of a dilute HCO_3^- ground water with a Cl^- ground water, and a SO_4^{2-} ground water with the same Cl^- end-member. The amount of saline water added is 0.1, 1.0, 5.0, 10, and 50% as points progress towards the saline Cl^- end-member for both HCO_3^- and SO_4^{2-} waters. Arrows with solid darts and open darts indicate the direction of movement with increased mixing of saline water with the HCO_3^- and SO_4^{2-} ground waters, respectively. In the central diamond the generalized path of eluting waters undergoing cation exchange is also shown.

saline Cl^- end-member were added to both the HCO_3^- and SO_4^{2-} low TDS waters. The resulting mixtures will plot very close to the high TDS (Cl^-) end-member, shown in an ideal mixing simulation of HCO_3^- and SO_4^{2-} dilute waters, and Cl^- water (Figure 3-15).

However, for soils impacted by oil field brines, mixing is not represented by a straight line on a Piper diagram (Cates et al., 1996) as ion exchange processes develop a 'hardness halo' at the leading edge of the brine front. Mixing between the brine and 'fresh' ground water leads to an almost immediate Cl^- signature for the resulting mixture. Cations, however lag behind due to exchange processes and tend to plot above and to the left of a straight line joining the end-members. Likewise, in the central diamond mixing waters plotted well above a straight line meant to describe mixing between the two end-members (Cates et al., 1996). It can therefore be expected that for systems where saline waters have been displaced from the system by meteoric waters (aquifer flushing or freshening) Ca^{2+} (and a minor amount of Mg^{2+}) within the recharging waters is exchanged for residual Na^+ adsorbed to charged

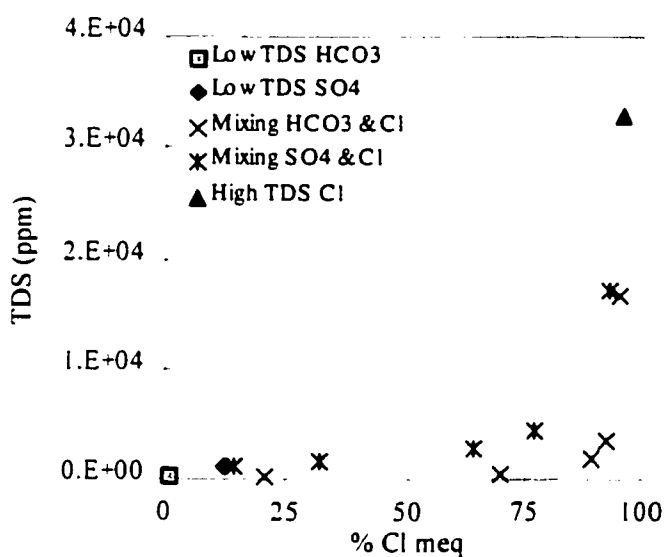


Figure 3-16 Calculated TDS for ideal conservative mixing seen in Figure 3-15 vs. % Cl^- meq. Plotting symbols and mixing ratios are the same as the previous diagram. The SO_4^{2-} water has greater initial TDS than the HCO_3^- water and therefore has a lower % Cl^- with the same proportion of mixing. A small contribution of Cl^- water (<5%) will still result in a 50% of the anions being Cl^- .

mineral surfaces. This process would be expected to occur for some time (several pore volumes of water) after the more mobile elements have been displaced (Valocchi et al., 1981; Appelo et al., 1993; Appelo, 1994); resulting in meteoric waters moving through the mountain containing a greater proportion of Na^+ than expected. As well, zones or flow paths with sluggish displacement would contain mineral surfaces with Na^+ available for exchange that would have been previously removed in more active flow systems. Diffusion from secondary (matrix) porosity

would also add residual Na^+ and possibly other ions to the water.

High meq proportions of Na^+ (greater than that can be supported by NaCl dissolution), which are even greater than the highest salinity ground waters, occur in ground waters from the HW mine (Figure 3-11) and Thelwood Valley (Figure 3-13 and Figure 3-14). A similar finding occurred in ground waters from Myra 10 level near the central part of the M-P ridge (Figure 3-8). Some of the sodium in these ground waters may originate from albite weathering. However, TDS generally does not increase with an increasing proportion of Na^+ in most ground waters, and weathering plagioclase in a low temperature environment is reasonably slow (Langmuir, 1997). Therefore, cation exchange processes are likely the dominant source of Na^+ in ground waters that have high proportions of cations as Na^+ . The generalized chemical evolution of eluting ground waters undergoing cation exchange during 'aquifer freshening' is shown in (Figure 3-15). Many of the ground waters in Thelwood Valley (Figure 3-13) demonstrate this general chemical trend rather than a simple binary mixing of cations.

3.8.3 Major Ion - Myra-Price Ridge Transect

Price and Myra 13 levels pass through the M-P hillside at approximately 240 m elevation. Ground waters entering 13 level have been recharged at varying elevations, which generally increase towards a maximum elevation near the centre of the tunnel (see stable isotopes Section 2.2.5). The ground waters sampled near the centre of the tunnel may have undergone contact with a greater volume of rock and in general have likely had longer residence times as compared to ground waters sampled near the hill fringes.

Major ions show definite spatial patterns moving through the M-P ridge on 13 level (Figure 3-17). Ground waters sampled near the hill fringes have Ca^{2+} and HCO_3^- dominant chemistry similar to surface water (Figure 3-5). Moving towards the centre of the ridge Na^+ dominates the cations while SO_4^{2-} replaces HCO_3^- as the dominant anion on the Myra (West) side of the ridge. The dominance of SO_4^{2-} coincides with elevated total dissolved solids (TDS) as shown in the increase in total dissolved milli-equivalents (meq) (Figure 3-17). The increased dissolved load underlies portions of the now exhausted Myra mine. Total meq concentrations remain relatively low on the Price side of 13 level and is dominated by HCO_3^- .

Towards the centre of the ridge, Na^+ concentrations increase at the expense of Ca^{2+} , in waters where the total TDS remains fairly uniform. This results from $\text{Ca}^{2+} \Rightarrow 2\text{Na}^+$ exchange. Waters within the central core of the rock volume making up the M-P ridge have had longer contact and higher rock to water ratios than waters within the hill fringes. A residual Na^+ and possibly effects of dual porosity have added Na^+ to the water. TDS remains low throughout regions that have higher proportions of Na^+ precluding mixing between low TDS Ca^{2+} waters and waters with concentration of Na^+ high enough to dominate cations.

Higher SO_4^{2-} and TDS in ground waters under previously mined regions may be associated with greater rock exposure (oxidation) as the result of mine openings and back filling of stopes with gangue minerals.

High Ca^{2+} and SO_4^{2-} in ground waters within parts of the Myra decline (~32+46 m E) results in precipitation of gypsum. Gypsum precipitates (i.e., sample S2040 Appendix E) from drips on the drift ceilings which form fragile hollow stalactite 'straws'. High concentrations of Ca^{2+} are likely added to the waters from the use of cement added to back-fill in at least some of the stopes overlying this area.

Both chloride concentrations and Cl^- as % of the total anion meq remain low in the ground waters sampled through 13 level (Figure 3-17). Magnesium concentrations and its contribution to cations (% meq) is also low, with the exception of ground waters heavily influenced by waters from the mined out Myra stopes (Figure 3-17).

The summary of water chemistry for Myra and Price 13 levels, along with other areas, is presented in Table 3-4.

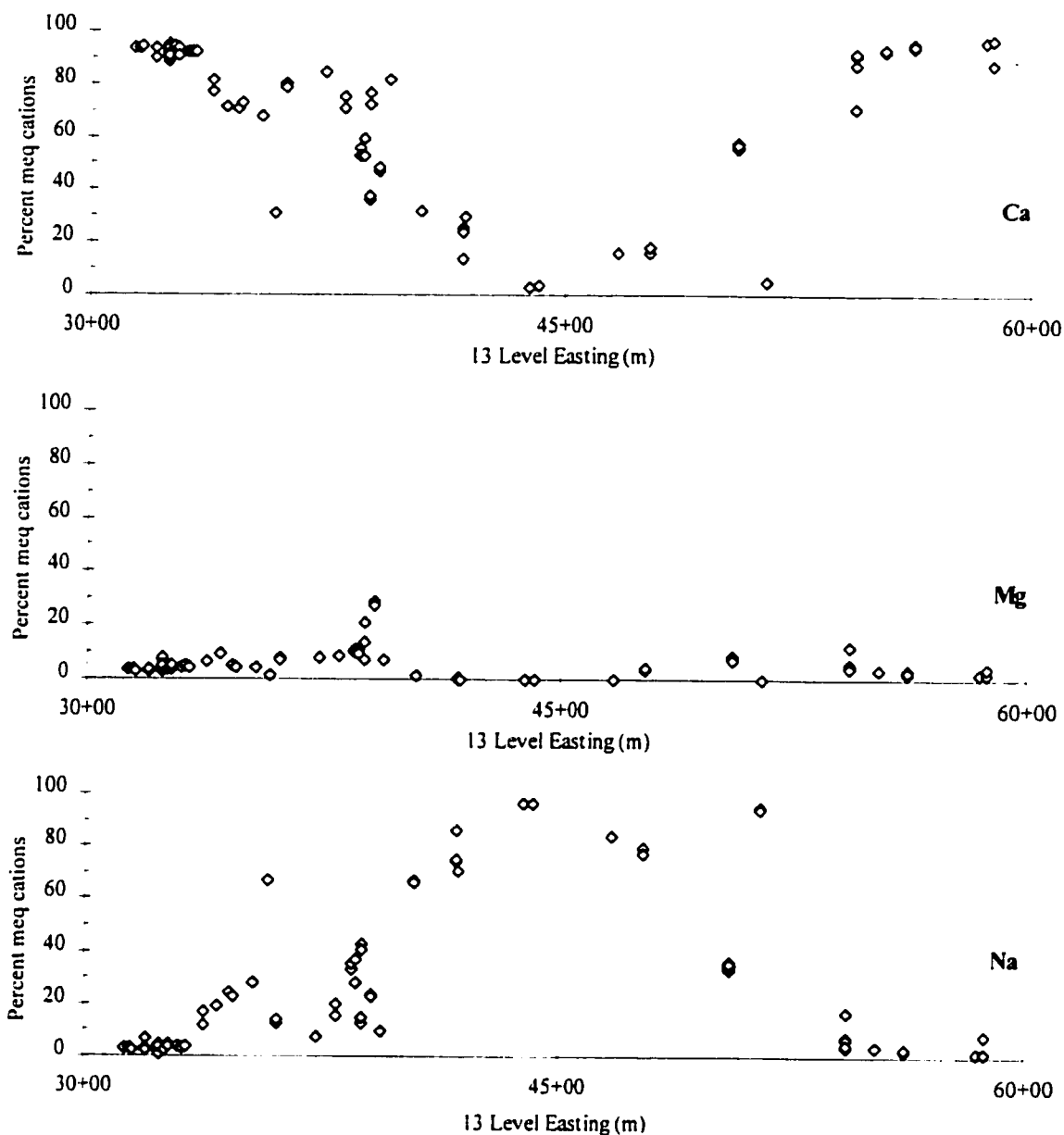


Figure 3-17 Spatial relations of major ions from ground waters sampled from Myra (left) and Price (right) 13 level. Continued on next page. Cations shown on this page; anions and total meq are shown on the next page. See text for discussion.

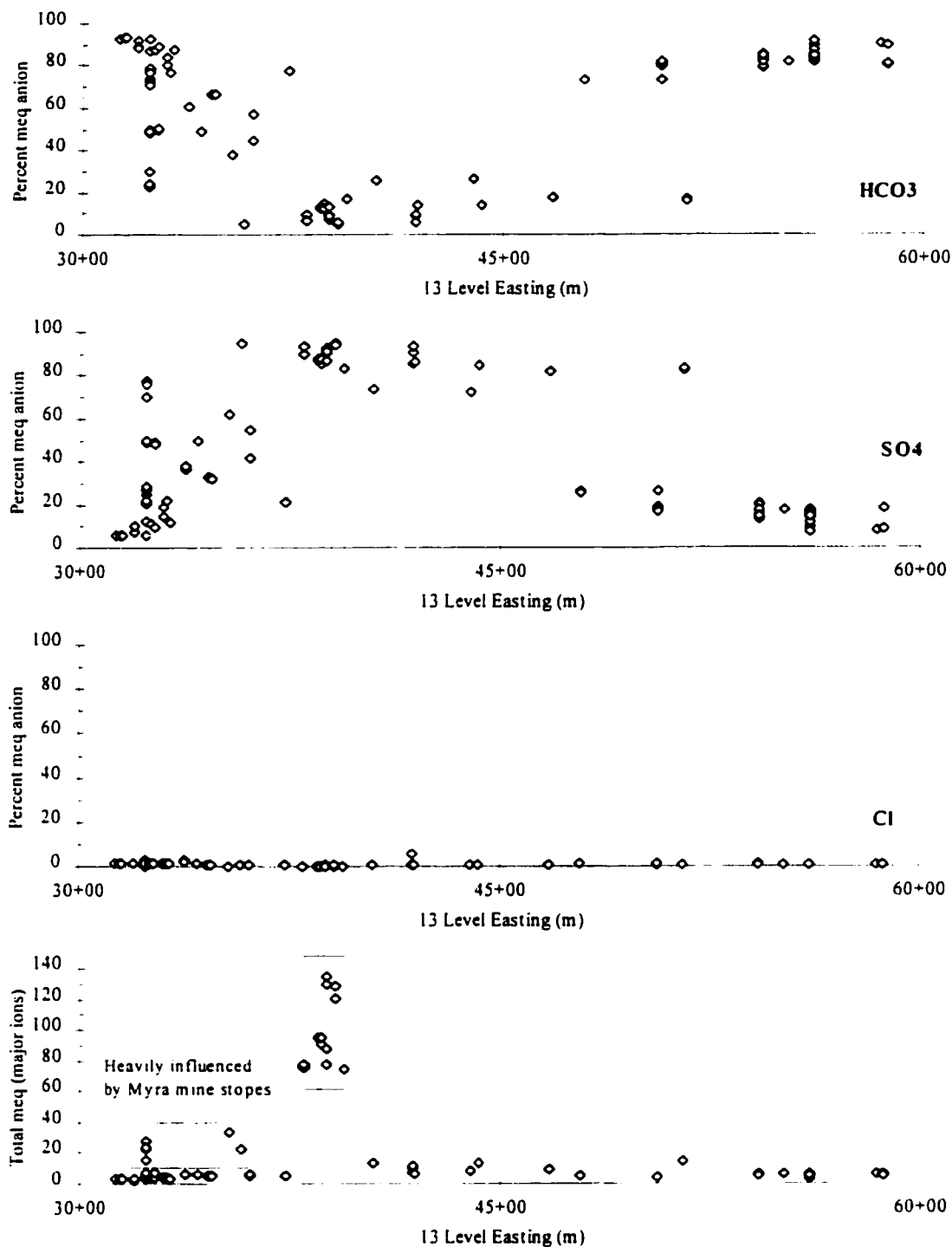


Figure 3-17 continued. Spatial relationship of major anions (% meq) and total meq for ground waters sampled along 13 level (Myra on left; Price to the right). Refer to text for discussion.

3.9 Element Trends and Saline Ground Water Chemistry

There is a general increase in Cl^- and TDS with increasing depth within waters from Thelwood Valley and the HW mine (Figure 2-9b). It is not known if the most saline ground waters sampled in this study represent the maximum salinity of ground waters in this setting, or if higher salinity water exist at greater depth. However, the use of composition diagrams and element ratios can be useful in discerning the end-member composition of saline ground waters (Stoessell, 1997).

3.9.1 Discussion

The behavior of ions that are hydrochemically conservative (have little tendency to react once in solution), are helpful in determining the provenance of the saline water, as well as the mixing characteristics of these waters. Through the use of composition diagrams, conservative mixing of important element ratios may be illustrated and the composition of the saline end-member may be deduced. Element diagrams were constructed for Myra Falls ground waters using Cl^- as the abscissa co-ordinate representing a conservative tracer.

Chloride, Br^- , and I^- are relatively conservative in the hydrochemical realm. The ratios of Br^-/Cl^- and I^-/Cl^- are fairly uniform in Cl^- dominated ground waters from Myra Falls. The Br^-/Cl^- mass ratio is approximately 0.0018. Sea water Br^-/Cl^- mass ratio is around 0.0034, while the same ratio for evaporitic deposits is less than 0.0003 (Mazor, 1997 [Mazor reports the ratio of Cl^-/Br^- , which is >3000]). The I^-/Cl^- mass ratio in Cl^- dominated ground waters, like Br^-/Cl^- is quite uniform (Figure 3-18d) at $5.7 \cdot 10^{-5}$. The I^-/Cl^- ratio in sea water is $3.2 \cdot 10^{-6}$. In relationship to sea water (SW), chloride ground waters from Myra Falls (MF-Cl) have $(\text{Br}^-/\text{Cl}^-)_{\text{MF-Cl}}/(\text{Br}^-/\text{Cl}^-)_{\text{SW}}$ and $(\text{I}^-/\text{Cl}^-)_{\text{MF-Cl}}/(\text{I}^-/\text{Cl}^-)_{\text{SW}}$ mass ratios of approximately 0.53 and 17, respectively.

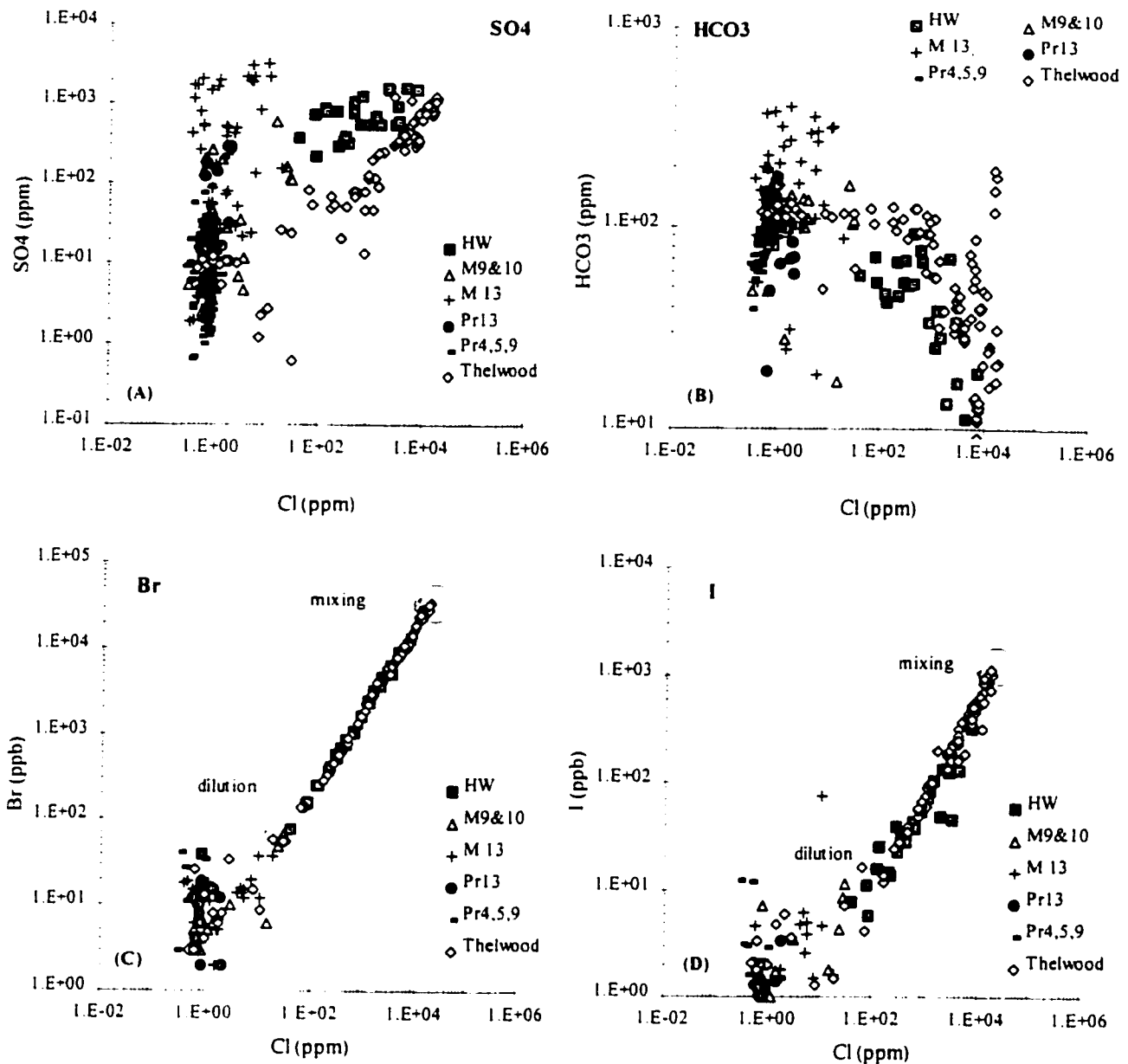


Figure 3-18 Composition diagrams featuring anion vs. Cl⁻ variation. Sulphate is concentrated in some non-saline ground waters greater than saline waters (A). This leads to distinctive mixing between saline and young meteoric waters in Thelwood Valley and a more disperse mixing between the saline and higher SO₄²⁻ HW mine waters. This process is also visible on Figure 3-11 and Figure 3-13. Bicarbonate concentrations decrease with increasing Cl⁻ with the exception of a few waters where HCO₃⁻ has been added from oxidation of organic carbon (B). Bicarbonate in these waters will be controlled by the precipitation of carbonates. Bromide (C) and I⁻ (D) are concentrated in the saline waters as compared to dilute waters and show a much more linear (ideal) mixing between the most saline ground waters (circled) and dilute waters. Many of the Myra mine waters have similar Br⁻/Cl⁻ ratios as the saline waters, indicating a common source of Cl⁻ for these waters.

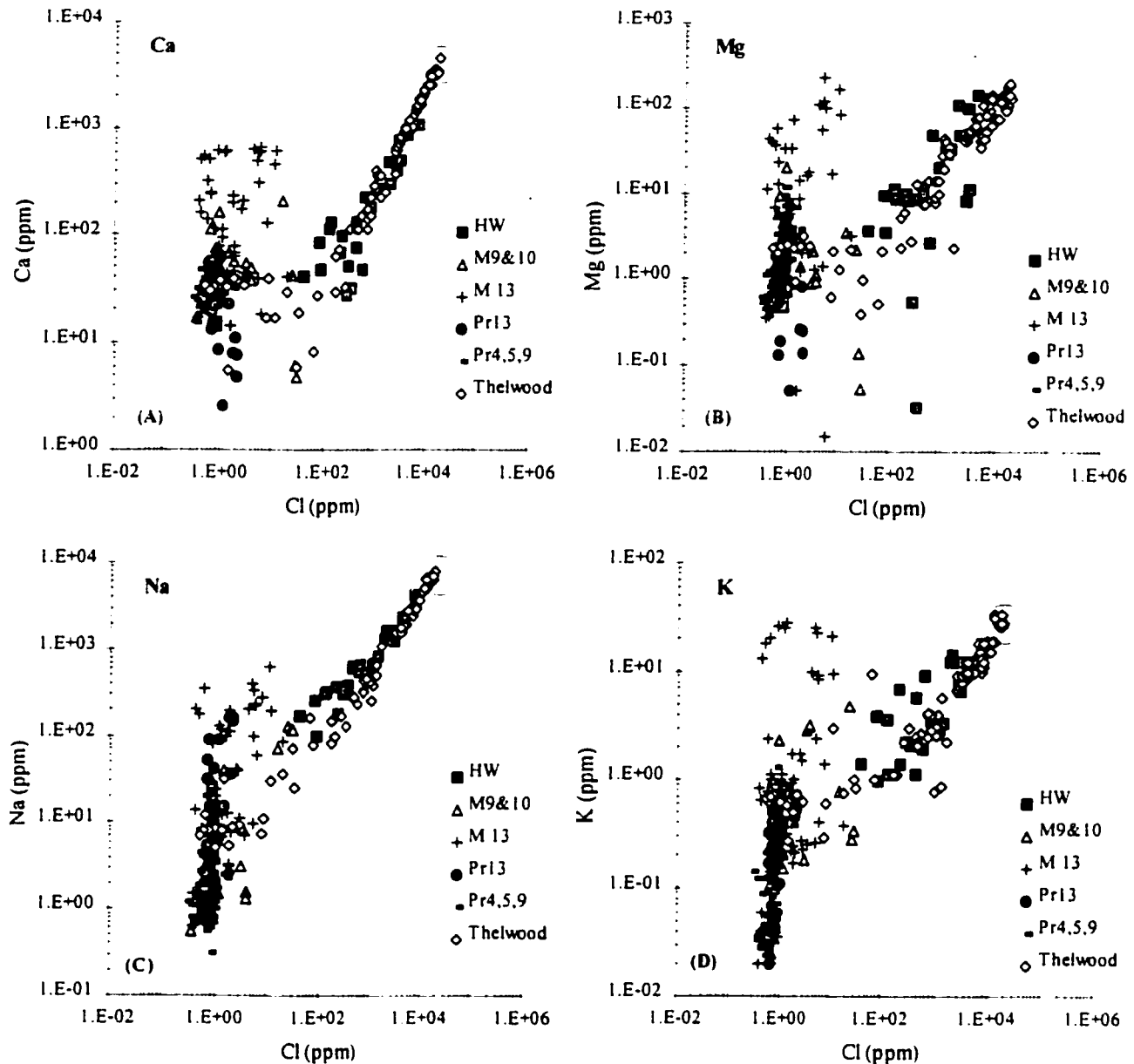


Figure 3-19 Composition diagrams featuring cation vs. Cl^- mass variation. Calcium is concentrated in saline ground waters, and saline mixing with more dilute waters is demonstrated in A. Magnesium concentrations increase with increasing Cl^- in the HW and Thelwood Valley ground waters (B). Myra 13 level waters, including acidic waters, also mobilize relatively high concentrations of Mg^{2+} . There is a wide range of Mg^{2+} concentrations in low Cl^- waters and many waters have lower than expected concentrations for ideal mixing between the most saline waters (circled) and more dilute ground waters. Sodium (C) demonstrates reasonably ideal mixing in ground waters in Thelwood Valley but many ground waters from HW mine and low Cl^- waters from Myra lie above this trend. Potassium is low in most waters but is concentrated in acidic and non-acid waters from Myra 13 level (D). Potassium in ground waters from HW also tend to lie above the mixing trend in Thelwood Valley ground waters. Many of the HW mine waters plot intermediate to the Myra 13 and more saline ground waters with respect to cations.

There is an excellent agreement and binary ideal mixing between ions such as Br^- and I^- concentrations with Cl^- concentrations in high Cl^- ground waters (Figure 3-18 c, d). The dilute modern ground waters from the upper drifts have low concentrations of Br^- and I^- . Low Cl^- ground waters from Myra 10 level sampled near the center of the M-P ridge have Br^-/Cl^- and I^-/Cl^- mass ratios similar to the mixing lines of dilute waters with saline ground waters (triangle plotting symbols at the base of the dilution arrow; Figure 3-18 c and d). As well, ratios of Br^-/Cl^- and I^-/Cl^- indicate that many upper level waters, especially on Myra 9, 10, and 13 levels have similar ratios as the saline waters. These ions are likely derived from the saline ground water.

Linear relations suggest that water-rock interaction and mineral reactions have been insignificant following mixing. Waters that deviate from the linear relationships have likely been altered during or after mixing.

The $\text{SO}_4^{2-}/\text{Cl}^-$ for the most saline ground waters from Thelwood Valley are fairly linear (Figure 3-18). Low TDS ground waters from the upper levels and from the HW mine

often have higher SO_4^{2-} concentrations than Cl^- dominated waters. This was previously shown in Piper diagrams (Figure 3-11 and Figure 3-12). Mixing Cl^- ground waters with these mine waters results in variable SO_4^{2-} concentrations for low and moderate concentrations of Cl^- (Figure 3-18 a).

Bicarbonate concentrations have greater variability with increasing Cl^- in ground waters from the HW mine and Thelwood Valley (Figure 3-18b). There is a general decrease in HCO_3^- concentration with increasing salinity and a

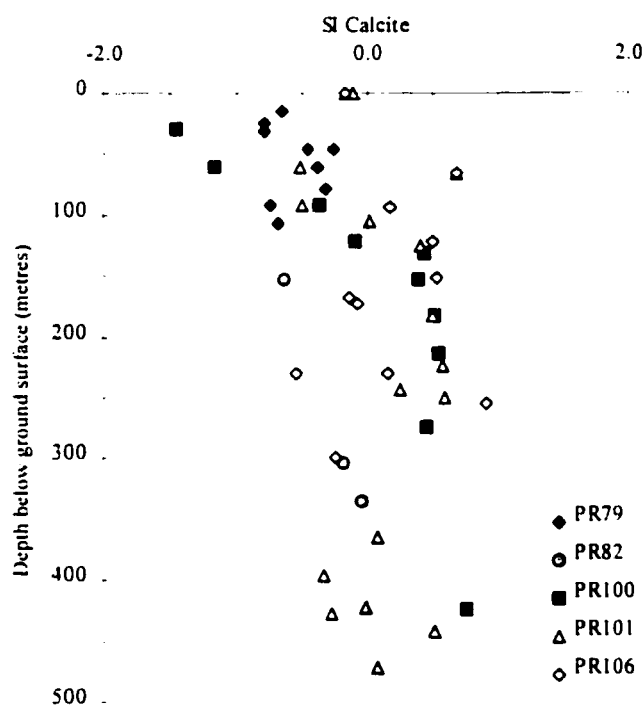


Figure 3-20 Calcite saturation indices (SI) tend to increase with depth below ground surface in ground waters from exploration drill holes located in Thelwood Valley.

corresponding increase in Ca^{2+} concentration. The precipitation of carbonates would be expected to be a major factor in decreasing HCO_3^- concentrations in the saline ground water. Shallow, low TDS waters from Thelwood Valley are generally undersaturated with respect to calcite (Figure 3-20). Visual observation of drill core from Thelwood Valley [pointed out by J.V. Hamilton while logging PR-106] confirms that calcite lined fractures are being (or have been) dissolved in the shallow bedrock. A few saline waters with higher HCO_3^- concentrations have been impacted by SO_4^{2-} reduction (due to the use of organic vegetable oil during drilling) and the subsequent increase in DIC.

Major cation concentrations of Na^+ and Ca^{2+} and to a lesser extent K^+ , and Mg^{2+} are elevated in saline ground waters. The divalent cations, Ca^{2+} and Mg^{2+} , show a reasonable ideal (straight line) mixing in ground waters with the highest Cl^- concentrations (Figure 3-19 a and b). The linear relationship indicates that relatively conservative mixing processes are occurring in the most saline ground waters. However, there tends to be some divergence from the straight line mixing relationship in ground waters with Cl^- concentrations ranging from approximately 10 ppm to 800 ppm. Sodium and K^+ concentrations likewise show reasonable linear relationships in the most saline ground waters (Figure 3-19 c and d), except within the above noted Cl^- range where Na^+ and K^+ concentrations tend to lie above the linear mixing line. Sodium adheres to this observation more so than K^+ , which has slightly greater scatter. Within the range of approximately 20 ppm to 1,000 ppm Cl^- , Na^+ and K^+ diverge from the ideal mixing generally seen in Thelwood Valley ground waters. This relationship can be seen more clearly on Figure 3-21 where cations are converted to milli-equivalents (meq) and are shown in relationship to an ideal mixing line between typical recharge waters and saline ground water.

Elution or aquifer freshening is the likely cause of the divergence seen in mixing behavior of cations and the ideal Br^- and I^- behavior in ground waters with very low Cl^- concentrations. Modeling aquifer freshening, Appelo (1994) found that nearly all Cl^- should be removed with one pore-volume of recharge water containing no Cl^- (neglecting dispersion and matrix porosity). However, cations do not follow the same process as anions and cation elution is retarded as compared to conservative elements due to exchange processes. Several pore water volumes are required to pass through an aquifer material before the cation chemistry of the effluent water reflects that of the influent water. This will be dependent upon

the cation exchange capacity of the aquifer material and does not take into consideration diffusion of solutes from water trapped in immobile zones such as dead-end pores and matrix porosity.

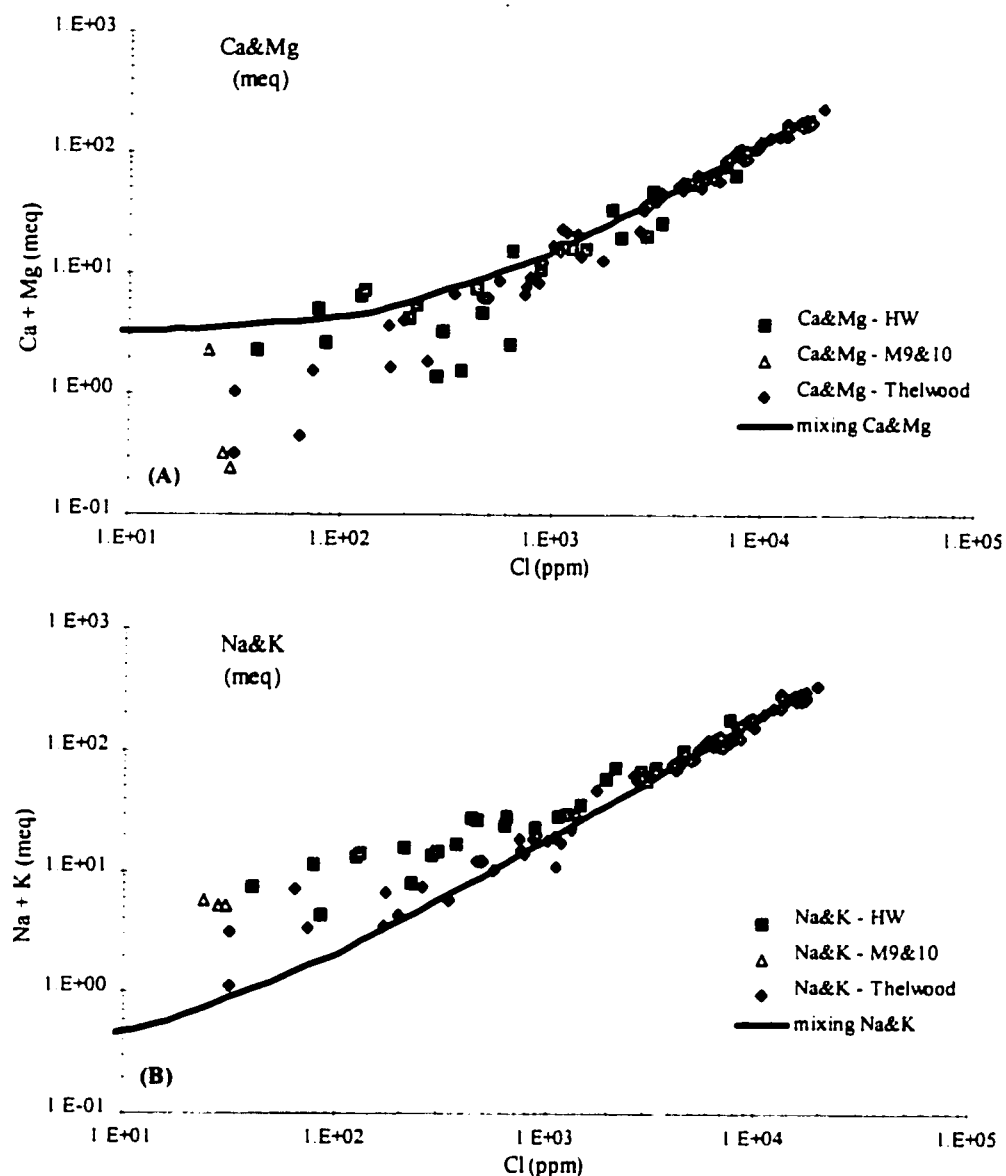


Figure 3-21 Major cation meq vs. Cl^- concentration ($\text{Cl}^- > 20$ ppm). Calcium and Mg^{2+} plot below an ideal mixing line (A), while Na^+ and K^+ lie above an ideal mixing line (B) between typical recharge concentrations and saline water. Ideal mixing lines are between saline water and typical recharge water with the following cation concentrations: Ca, 55; Mg, 5; Na, 7; and K, 0.4; all in ppm.

The saline end-member of ground waters from Myra Falls has the following mass ratios: $\text{Ca}^{2+}/\text{Cl}^-$, 0.22; $\text{Mg}^{2+}/\text{Cl}^-$, 0.01; Na^+/Cl^- , 0.42; K^+/Cl^- , 0.0019; $\text{SO}_4^{2-}/\text{Cl}^-$, 0.070. Bicarbonate to Cl^- mass ratios are variable in the saline waters but many waters have very low HCO_3^- concentrations.

The molar ratio of Na^+/Cl^- is 0.65 in the saline ground waters. This ratio along with the mass ratios of Br^-/Cl^- and I^-/Cl^- largely rule out halite or a modern (post-glacial) sea water as the singular source of Cl^- in the saline end-member ground water.

Chloride concentrations are linearly correlated with most of the major ions for the majority of the Cl^- -rich ground waters in Thelwood Valley. In ground waters from the HW mine the correlations are less linear depending on the concentration of the ions in the lower salinity water which can be highly variable for ions such as: SO_4^{2-} , HCO_3^- , Mg^{2+} , Na^+ , and K^+ . The elution of cations (Na^+ , and K^+) during the flushing of low TDS ground waters is contributing to the non-linear behavior of the concentrations of these cations and Ca^{2+} and Mg^{2+} . Perturbations to the natural hydrology from mining activities in the HW mine has brought a recent elution of previously adsorbed cations. The effects of the process of elution are seen in ground waters from the central portion of the M-P ridge on Myra 10 level where waters have low, but measurable Cl^- , Br^-/Cl^- and I^-/Cl^- mass ratios similar to saline waters, but have a high proportion of Na^+ (Figure 3-8). This suggests that only a limited number of pore volumes of meteoric water have traversed this portion of the mountain.

There have been no recent major perturbations to ground water hydrology in Thelwood Valley from mining activity with the exception of the drill holes themselves, and ground waters from this area display more of an ideal mixing behavior between shallow non-saline and deeper saline waters. As well ground waters from Thelwood Valley exhibit a much sharper mixing interface than ground waters from the HW mine. A condensed mixing zone allows less contact with minerals capable of exchanging cations.

Table 3-4 Summary statistics for major ions, dissolved silica, physical parameters and TDS (calculated) in surface and ground waters from various locations within the Myra Falls study area. Continued on next page (Price and Thelwood Valley). Complete analyses for individual waters are found in Appendix A.

	Temp	E C	pH	Eh	DO	SiO2	Ca	Mg	Na	K	HCO3	SO4	Cl	TDS
	(°C)	uS/cm		(V)	(ppm)			(ppm)				(ppm)		(ppm)
Surface ("Pristine?")														
Min	6.9	11.0	6.0	0.2	4.2	1.05	1.30	0.10	<DL	<DL	4.1	0.40	0.19	7.9
Median	11.0	130	7.3	0.4	9.7	3.64	24.0	0.84	0.74	0.03	73.9	0.98	0.60	104
Mean	11.6	131	7.3	0.4	9.3	3.47	22.9	0.82	0.73	0.17	68.4	1.43	0.69	98.8
Stdev	3.4	47.1	0.6	0.0	1.8	1.09	10.0	0.44	0.43	0.70	30.4	1.23	0.64	42.3
Max	21.4	307	9.0	0.5	12.2	5.56	40.0	2.70	2.90	5.00	119	6.36	5.29	167
n =	91													
Surface (Anthropogenic Influence)														
Min	7.0	111	2.3	0.3	3.7	1.78	11.0	0.43	0.32	0.02	0	1.63	<DL	44.5
Median	11.1	325	7.4	0.4	9.5	5.13	43.0	6.50	1.10	0.13	58.0	60.7	0.69	232
Mean	11.9	773	7.0	0.4	9.1	11.9	68.2	55.4	1.60	0.17	71.3	607	0.75	937
Stdev	3.0	2092	1.4	0.1	1.9	32.4	94.9	224	2.15	0.14	49.0	2486	0.50	3381
Max	19.0	10340	8.4	0.7	11.8	160	490	1080	11.0	0.48	150.3	12000	2.17	16435
n =	23													
Myra 9 level														
Min	7.0	153	6.2	0.2	2.9	2.78	32.0	0.73	0.66	0.03	97.0	2.49	0.66	138
Median	10.6	265	8.1	0.4	9.0	3.74	50.5	0.94	0.94	0.17	141	9.86	0.87	210
Mean	10.3	268	7.9	0.4	8.7	3.88	51.5	1.19	1.17	0.19	139	14.7	1.02	213
Stdev	1.7	63.5	0.5	0.1	1.5	0.87	8.68	0.59	0.67	0.15	16.6	11.8	0.57	35.4
Max	12.8	471	8.8	0.4	10.0	5.56	72.0	3.00	3.20	0.56	167	46.7	3.31	295
n =	22													
Myra 10 level														
Min	7.0	147	5.4	-0.2	0.4	2.78	4.8	0.05	0.57	<DL	17.2	3.5	<DL	74.9
Median	8.5	259	7.6	0.3	7.4	5.88	43.5	2.05	2.90	0.43	112	34.7	0.90	213
Mean	8.5	414	7.8	0.3	6.7	7.11	64.8	3.23	23.8	1.00	114	106	5.0	330
Stdev	0.9	253	0.9	0.2	3.1	5.10	53.7	4.18	41.8	1.27	47.3	135	9.2	211
Max	11.5	1045	10.1	0.4	11.0	25.7	210	20.0	130	4.80	206	595	30.2	927
n =	24													
Myra decline														
Min	6.7	91.5	2.3	0.3	2.5	2.35	17.0	0.36	0.65	<DL	0.0	1.89	0.38	75.6
Median	8.0	218	7.3	0.4	9.6	4.71	39.0	1.15	1.50	0.13	94.0	19.7	0.71	161
Mean	8.0	483	7.1	0.4	8.6	5	69	7	15	0.3	99.3	169	1	273
Stdev	0.7	638	1.2	0.1	2.1	3	74	21	40	0	64.3	377	1	291
Max	10.1	3040	8.0	0.8	10.8	19	310	120	190	2	396	1822	5	1277
n =	34													
Myra 13 level														
Min	7.4	185	6.8	0.1	1.8	4.06	14.0	0.02	0.82	0.04	18.3	6.37	0.42	15

Table 3-4 continued. Summary statistics for major ions, dissolved silica, physical parameters and TDS in Price and Thelwood Valley ground waters. Statistics for Myra and surface waters are on previous page. Complete analyses for individual waters are found in Appendix A.

Temp	E.C	pH	Eh	DO	SiO2	Ca	Mg	Na	K	HCO3	SO4	Cl	TDS	
(°C)	uS/cm		(V)	(ppm)			(ppm)				(ppm)		(ppm)	
Price 13 level														
Min	7.5	182	6.8	0.1	0.8	4.28	2.60	0.05	1.30	0.02	19.3	7.15	0.61	151
Median	8.6	238	7.5	0.4	8.4	6.63	41.0	1.05	4.60	0.35	124	15.9	0.82	202
Mean	8.7	279	7.6	0.4	7.6	6.78	36.1	1.38	23.6	0.33	115	44.5	0.94	230
Stdev	0.8	141	0.6	0.1	3.0	1.78	17.3	0.94	42.8	0.18	32.5	75.1	0.40	91.1
Max	11.9	782	9.3	0.4	13.1	11.3	63.0	3.80	160	0.73	177	286	2.17	540
n =	42													
Price 4&5 levels														
Min	5.8	125	6.4	0.2	2.1	3.00	21.0	0.45	0.31	<DL	82.7	0.66	0.40	118
Median	6.4	197	7.4	0.4	9.8	5.35	38.0	2.45	2.00	0.26	119	8.23	0.85	180
Mean	6.5	201	7.4	0.4	9.0	5.54	37.5	3.00	3.94	0.32	119	10.7	0.85	182
Stdev	0.5	32.4	0.4	0.0	2.4	1.70	6.93	2.15	4.28	0.25	14.2	12.7	0.17	25.9
Max	8.9	372	8.8	0.5	11.4	9.84	72.0	12.0	21.0	1.30	170	90.4	1.81	312
n =	116													
Price 9 levels														
Min	6.0	76.3	6.7	0.4	3.8	2.10	15.0	0.44	0.60	<DL	38.8	2.7	0.29	63.4
Median	7.0	166.8	7.9	0.4	10.4	3.21	32.5	0.81	1.20	0.05	82.1	12.9	0.48	136
Mean	7.1	164.6	7.8	0.4	9.6	3.56	31.7	0.81	1.59	0.07	79.1	14.7	0.48	132
Stdev	0.5	38.5	0.3	0.0	3.3	1.13	6.59	0.24	1.11	0.06	15.9	10.9	0.10	27.3
Max	8.6	253.0	8.2	0.4	18.3	6.20	46.0	1.20	4.70	0.31	101	57.2	0.68	176
n =	30													
HW mine														
Min	13.0	175	6.3	0.0	0.0	5.13	14.0	0.03	22.0	0.37	11.3	13.6	0.87	143
Median	13.0	2870	7.1	0.3	4.4	7.49	130	10.0	540	3.30	51.1	576	458	2002
Mean	13.2	4466	7.3	0.2	4.2	7.46	241	29.7	805	5.15	49.0	699	1276	3127
Stdev	0.4	4895	0.8	0.2	2.7	1.11	275	41.1	886	4.79	22.6	437	1762	3231
Max	14.6	23180	8.9	0.4	9.3	10.1	1070	140	4180	18.0	92.8	1562	7653	14574
n =	27													
Thelwood Valley <5,000 TDS														
Min	7.9	181	7.0	-0.1	0.4	1.84	5.40	0.39	2.30	0.21	31.5	0.62	0.53	85.7
Median	12.9	642	7.9	0.1	1.6	7.70	38.5	2.45	79.5	1.00	114	27.8	69.1	406
Mean	13.3	1337	8.0	0.1	2.2	7.73	99.6	8.24	182	1.82	102	51.5	371	828
Stdev	4.2	1382	0.5	0.2	1.6	1.90	106	10.8	226	1.77	26.4	59.9	487	846
Max	24.0	5450	9.1	0.4	8.5	12.8	390	43.0	1070	9.40	131	250	1782	3418
n =	44													
Thelwood Valley >5,000 TDS														
Min	8.5	8120	6.6	-0.2	0.0	3.42	370	35.0	1270	6.60	0	258	2635	5071
Median	13.0	18445	7.3	0.0	0.0	7.70	1710	78.5	2890	12.0	30.4	457	7549	12770
Mean	13.3	21670	7.3	0.0	0.2	8.07	1834	90.1	3514	16.2	44.0	596	8411	14591
Stdev	2.4	11408	0.4	0.1	0.5	2.44	993	40.8	1944	8.35	44.6	287	4623	7824
Max	21.9	47000	8.7	0.2	2.2	15.8	4430	200	8000	34.0	194	1209	19000	32912
n =	60													

3.10 Price Deposit Ground Water Baseline Metal Concentrations: Comparisons To Myra Mine Ground Waters

3.10.1 Introduction

Trace metals entering the environment are a concern for base-metal and other mining camps and strict guidelines are enforced for waters leaving metal extraction areas. Yet, in areas with naturally high concentrations of metals, background levels may naturally exist at levels greater than legislated concentrations.

Assessing the natural background chemistry of ground waters associated with the Price deposit is important for remediation activities after mining the Price deposit (if this were to occur). Stratigraphically and mineralogically, the Price deposit is similar to the Myra deposit and the chemical baselines determined in the Price ground waters may also be of importance in assessing possible background concentrations of ground waters related to the Myra deposit. Where pre-mining water chemistry is not available this method of comparing mined to similar non-mined areas is a useful approach in determining background chemical levels (Runnels et al., 1992).

3.10.2 Trace Metal Concentrations (Price and Myra)

Diagrams summarizing the trace metal chemistry of both Myra mine (9, 10, decline, and 13 levels) and the Price deposit (4, 5, and 13 levels) are presented in Figure 3-22 and Figure 3-23, respectively. The maximum concentration, minimum concentration, range of concentration for the majority of waters ($\text{mean} \pm \sigma_{n-1}$), and median concentrations are outlined in a box and whisker diagram format.

If pre-mining baseline concentrations of metals within the Myra mine ground water can be extrapolated from Price ground water compositions, then the result of mining is not always an increased element (median) concentration in ground water within this stratigraphy. Median concentrations are higher in Price ground waters as compared to Myra mine ground waters for: Sr, Ba, Cr, Mo, As, Sb, and U. Likewise, elements whose maximum

concentrations are greatest in the Price ground waters are: Ba, V, Mo, and Sb. Understandably Ba concentrations are higher in Price ground waters due to the lower SO_4^{2-} concentrations in these waters as compared to Myra (i.e., 16 and 167 ppm for Price 13 level and Myra 13 level, respectively; Table 3-4). Higher concentrations of V, Cr, As, and Mo in the Price waters (either maximum or median concentrations) may be related to the slightly higher oxidizing conditions in the Price waters (Table 3-5). Vanadium, Cr, As, and Mo tend to be transported as oxy-anions or have higher solubilities in their higher oxidation states; although, Mo solubility may be limited by the presence of Ca^{2+} (Hem, 1989). The chemistry of Sb is similar to As (Hem, 1989) and therefore higher concentrations of Sb would be expected with elevated As. The remainder of the minor and trace elements have been mobilized to a greater extent in the ground waters related to the Myra mine as compared to the Price ground waters as a consequence of mining this deposit.

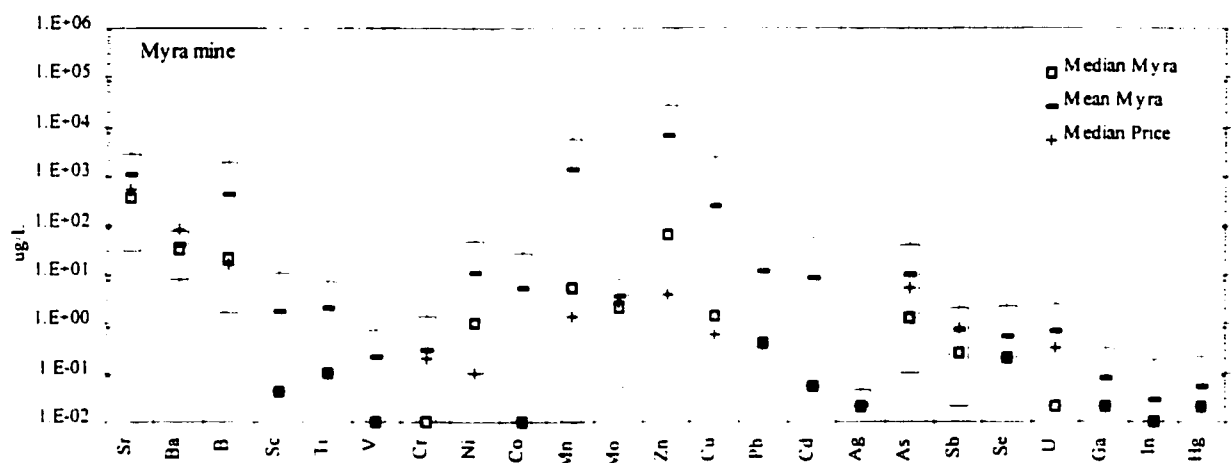


Figure 3-22 Box and whisker plot of minor and trace elements in ground waters associated with the Myra mine. Boxes cover the range of mean concentration $\pm 1\sigma$, and often extend to the less than the detection limit. Whiskers extend from minimum to maximum concentrations where applicable. Mean and median concentrations indicate that the distributions are highly positively skewed. Median values for Price ground waters are plotted for reference as a possible pre-mining value.

Silver, Ga, and In concentrations do not exceed the detection limit in any of the ground waters from the Price levels. Whereas, Ag and In are only mobilized in the acidic waters from Myra 12 and 12+50 levels. Gallium is also mobilized in these acidic waters and it also has measurable concentrations in a limited number of ground waters from Myra mine.

Median, mean, and maximum concentrations of Zn and Cu are considerably greater in the Myra mine waters as compared to the Price ground waters. This may be the result of mining techniques or back-filling operations. High metal loading of ground waters, especially in regards to Zn, occur in water accessed from Myra 13 level underlying exhausted mine workings.

Exposure of sulphides to increased oxidizing conditions or the improper installation of back-fill may be the greatest risks in increasing metal loading of the associated waters. Based on the metal load of the Myra mine ground waters, the metals that potentially have the greatest risks of increase in mine drainage due to developing the Price deposit are Zn and Cu.

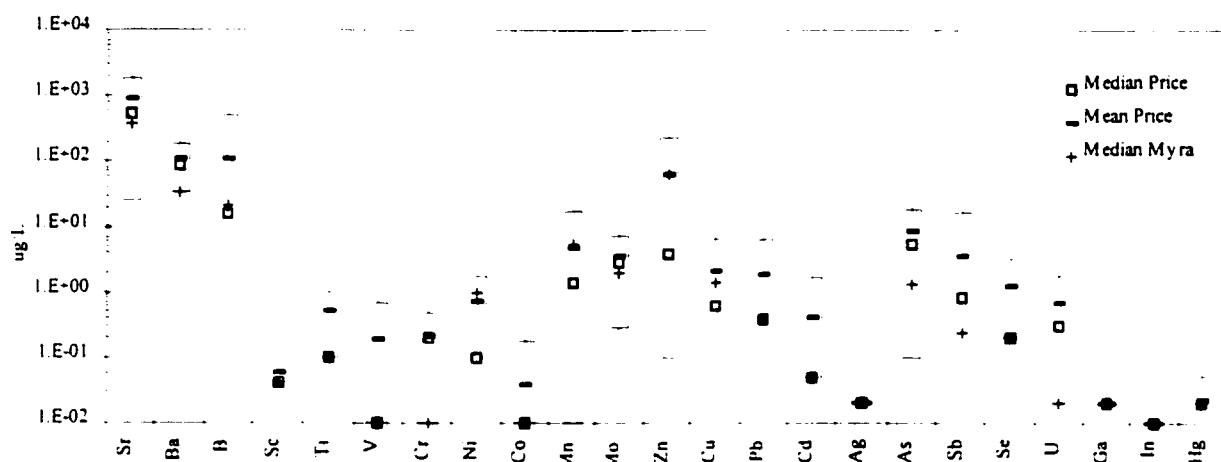


Figure 3-23 Box and whisker plot of minor and trace elements in ground waters from Price 4, 5, and 13 levels. Boxes cover the range of mean concentration $\pm 1\sigma$, and often extend to the less than the detection limit. Whiskers extend from minimum to maximum concentrations where applicable. Mean and median concentrations indicate the element distributions are highly skewed. Median values from Myra mine are plotted for reference.

Table 3-5 Summary statistics of selected minor and trace metals from ground waters sampled from Price area and Myra mine.

Temp	E.C	pH	Th	DO	Al	Fe	Sr	Ba	B	Sc	Ti	V	Cr	Ni	Co	Mn	Mo	Zn	Cu	Pb	Cd	Ag	As	Sb	Se	U	Ga	In
(°C)	uS/cm		(V)	(mg/L)																								
ppb																												
Myra Mine (9, 10, decline, and 13 levels, n = 125)																												
Min	6.7	92	2.3	-0.22	0.4	0.05	<DL	30	3.7	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Median	8.3	278	7.7	0.38	9.1	4.1	10	370	33	21	<DL	<DL	<DL	1.00	<DL	5.5	2.0	65	1.4	0.39	<DL	<DL	1.3	0.24	<DL	<DL	<DL	<DL
Mean	8.7	723	7.6	0.35	8.2	79	1012	1072	42	431	1.7	0.2	0.3	10.38	5.45	1346	3.6	6465	249	11	8.7	<DL	9.9	0.73	0.55	0.70	0.07	0.03
Stdev	1.3	948	0.9	0.13	2.4	706	4633	1773	34	1388	8.7	5.1	0.6	1.1	35.52	21.47	4267	4.0	21520	2164	90	47	30	1.4	1.67	1.7	0.25	0.15
Max	12.8	4350	10.1	0.77	11.0	7800	33000	9500	170	9900	71	4	11	300	140	29000	19	150000	23000	900	370	0.3	260	8.3	16	11	2	2
Price (4, 5, and 13 levels, n = 157)																												
Min	5.8	125	6.4	0.23	0.8	1.1	<DL	25	8.8	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Median	6.6	199	7.5	0.41	9.5	3.8	10	520	84	16	<DL	<DL	<DL	<DL	<DL	1.4	2.9	3.9	0.61	0.38	<DL	<DL	5.3	0.83	<DL	0.31	<DL	<DL
Mean	7.1	221	7.4	0.40	8.4	4.9	19	878	110	106	0.1	0.5	0.2	0.2	0.73	0.04	4.7	3.7	62	2.1	1.88	0.41	<DL	8.5	3.61	1.26	0.67	<DL
Stdev	1.1	84	0.5	0.04	2.7	4.0	44	911	76	395	0.1	0.5	0.3	1.0	0.14	1.3	3.4	175	4.32	4.53	1.3	30	1.4	1.3	1.98	1.1	0	0
Max	11.9	782	9.3	0.47	13.1	12	510	6800	380	2900	1.2	1.4	1.6	7.6	1.4	110	20	1100	28	28	12	<DL	67	130	12	6.7	<DL	<DL
Water Quality Guidelines, Freshwater Aquatic Life*																												
6 5-9.0 5.0-9.5 5-100 300																												
25-150																												
2.4 1-7 0.2-1.8 0.1 50** 1																												

* Water Quality Branch, Environment Canada;

Maximum concentrations vary depending on other parameters when a range is given

** Subject to change to 5 ppb in 1998

3.11 Rare Earth Elements

3.11.1 Introduction

Rare earth elements (REE) consist of a group of trace elements (La to Lu) which behave rather coherently and that substitute predominantly for Ca in the structure of Ca bearing minerals. They are strongly concentrated in apatite, garnet, and titanite, and to a lesser extent in feldspars, pyroxenes, and amphiboles. There is a progressive decrease in ionic radii with increasing molecular weight, with the result being different patterns of element partitioning into different minerals. Garnets and pyroxenes incorporate more heavy rare earth elements (HREE: Tb-Lu), while feldspars and apatite take in more light rare earth elements (LREE: La-Gd) (Henderson, 1984).

Concentrations of REE are generally displayed after normalizing the concentrations. This is accomplished by dividing measured concentrations by abundances in a reference material to eliminate the abundance variation between elements of odd and even atomic number. The reference material used for normalizing is chondrite meteorites or more commonly in waters abundances of REE in shales is used (de Baar et al., 1988, Fee et al., 1992).

Europium unlike other REE which are trivalent in igneous rocks, can be di- or trivalent. Divalent Eu is preferentially incorporated into feldspars, a progressive amount is partitioned into lower anorthite member plagioclases and alkali feldspars (Zielinski, 1975). Significant fractionation of Eu can occur during hydrothermal alteration due to the stability of Eu^{2+} at elevated temperatures (Sverjensky, 1984). During sericite alteration of feldspars divalent Eu is not incorporated into sericite which leads to high Eu in the hydrothermal fluids or minerals that can incorporate Eu^{2+} . At near neutral pH in the aqueous environment Eu^{3+} , and related complexes should dominate except under extremely reducing conditions where SO_4^{2-} is absent (Sverjensky, 1984).

The only other multivalent REE is Ce. Cerium generally exists as Ce^{3+} , but under oxidizing conditions such as in surface oceanic environments it is oxidized to Ce^{4+} and is then removed from solution as highly insoluble CeO_2 or as oxy-hydroxide coatings on

precipitating minerals (Fee et al., 1992). Iron-Mn hydroxides can readily concentrate REE (Fleet, 1984; Fee et al., 1992) especially LREE, leading to HREE-enriched patterns in waters relative to shales.

Rare earth elements in this program were pre-concentrated by a chelation procedure (Hall et al., 1995) that removes alkali and alkaline earth elements before analyses using ICP emission spectrometry, graphite furnace atomic absorption spectrometry and/or ICP mass spectrometry at the GSC labs.

3.11.2 Results and Discussion

Concentrations of REE are low in all 27 waters analysed and the result of replicate analyses show that there is poor reproducibility for these elements. Concentrations of REE in the Myra Falls waters show no relationships with increasing Cl^- concentrations. The rare earth abundance patterns normalized to shale (Haskin and Haskin, 1966; Haskin et al., 1968; de Baar et al., 1988) display saw tooth shapes, have a greater variation in the light REE, and are slightly enriched with increasing atomic weight (Figure 3-24). There are many below detection values in the data especially with respect to the HREE (Table 3-6). Some zigzag REE abundance patterning is still apparent but in the opposite pattern of cosmic abundances (in this case the odd atomic number elements are high) which suggests over compensation when dividing measured REE concentrations by average shale concentrations. The enrichment of HREE suggests that adsorption to hydroxides may be a factor.

No Ce anomaly (depletion) is present in any waters sampled including the oxidizing waters. This is not wholly surprising as Ce^{3+} , as well as all REE, hydrolyze and strongly complex with carbonate and bicarbonate ions (de Baar et al., 1988; and references therein).

Europium is slightly enriched as compared to the LREE, but is fairly flat with the remaining heavier elements. All three waters with above detection Eu are reducing and only one water #4001 (Table 3-6) shows any enrichment over the HREE. Water #4001 is also the most enriched for Ho and has one of the most extreme REE saw-tooth patterns of any of the waters. Europium anomalies may be associated with hydrothermal minerals such as: barite, siderite, and galena (Morgan and Wandless, 1980; in Sverjensky, 1984), which may be the source of Eu in water 4001.

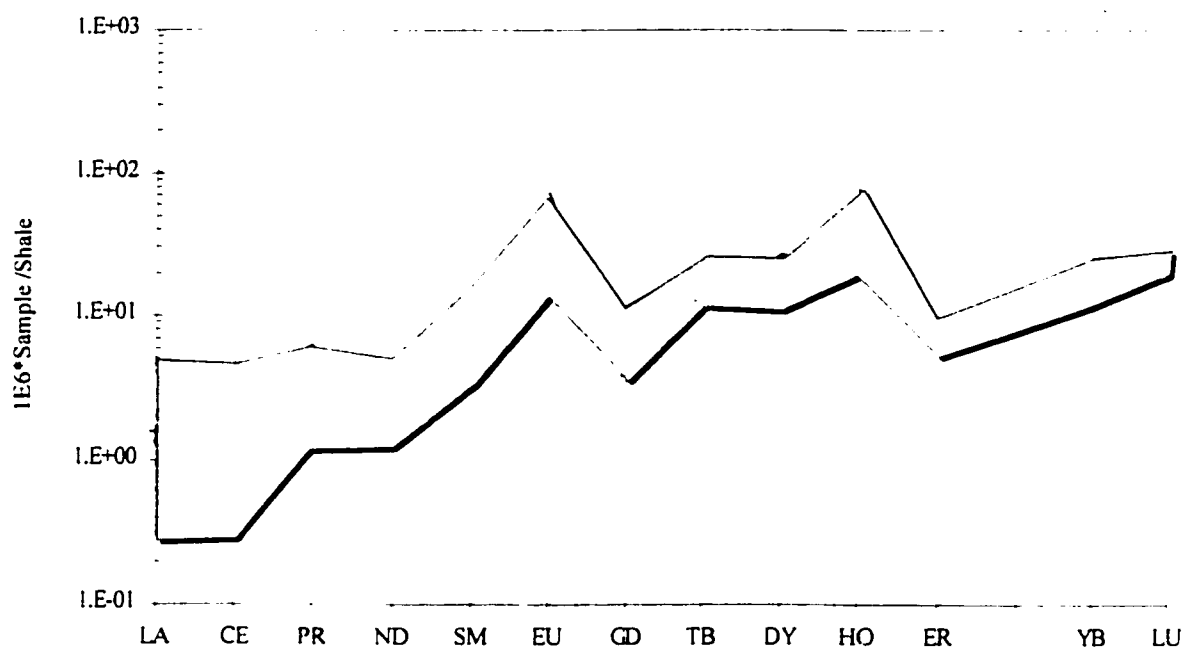


Figure 3-24 Range of rare earth elements all samples normalized to North American shale (Haskin and Haskin, 1966; composition outlined in Table 3-6)

Geochemical processes affecting the REE are difficult to determine and therefore implications towards evaluating the source of cations in the saline waters are difficult to assess from the REE patterns. Adsorption of REE, likely to oxyhydroxides, especially HREE seems to be a likely mechanism for the enriched HREE.

Table 3-6 Rare-earth element data for select ground waters. Many elements are below detection and the results of duplicate analyses are poor

Sample	Site	DDH	Depth (bgs) (m)	pH	DO mg/L	Eh (V)	Cl ppm	LA	CE	PR	ND	SM	EU	Gd	Tb	DY	HO	ER
3544	W20-415de	HW20-832		7.13	5.52	0.391	7133	0.02	0.05	0.01	0.07	<0.02	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3552	W20-415de	HW20-832		7.13	5.52	0.391	7157	<0.01	0.03	<0.01	<0.04	<0.02	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
		mean						Mean	0.04									
		sd						σ	0.01									
		sd/mean						C V	0.35									
3349	surf dddh	Th-101	423	7.77	0	-0.089	7985	0.03	0.08	<0.01	<0.04	<0.02	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3354	surf dddh	Th-101	423	7.91	0	-0.118	8142	<0.01	<0.02	0.01	<0.04	0.03	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
		mean						Mean										
		sd						σ										
		sd/mean						C V										
3183	surf/ddh	Th-106	300	7.27	0	0.088	16896	0.08	0.13	0.02	0.10	<0.02	<0.02	0.12	0.03	0.12	0.03	0.05
3189	surf/ddh	Th-106	300	7.27	0	0.088	16988	0.05	0.10	0.01	0.12	0.03	<0.02	0.04	0.01	0.16	0.02	0.02
		mean						Mean	0.07	0.12	0.02	0.11		0.08	0.02	0.14	0.03	0.04
		sd						σ	0.02	0.02	0.01	0.01		0.06	0.01	0.03	0.01	0.02
		sd/mean						C V	0.33	0.18	0.47	0.13		0.71	0.71	0.20	0.28	0.61
3346	surf/ddh	Th-73	299	7.09	2.08	0.152	1	0.01	0.02	0.03	0.04	0.09	<0.02	<0.02	0.02	<0.03	<0.02	<0.02
3316	r13-930dw	Pr13-36		8.08	10.16	0.426	2	0.01	<0.02	<0.01	<0.04	0.02	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3385	surf/ddh	Th-101	105	7.86	0.42	0.184	2	0.02	0.04	<0.01	<0.04	<0.02	<0.02	0.03	<0.01	<0.03	<0.02	<0.02
3343	surf/ddh	Th-92	123	8.55	3.32	-0.002	31	0.04	0.04	<0.01	0.06	<0.02	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3345	surf/ddh	Th-92	170	7.8	4.77	-0.026	64	<0.01	<0.02	<0.01	0.05	<0.02	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3274	surf/ddh	Th-92	276	8.82	0.94	0.206	172	0.13	0.21	0.05	0.04	0.02	<0.02	<0.02	<0.01	0.05	<0.02	<0.02
3318	surf/ddh	Th-92	149	9.1	1.64	-0.104	257	0.05	0.10	0.01	0.05	0.03	<0.02	0.02	<0.01	<0.03	<0.02	<0.02
3258	surf/ddh	Th-106	122	8.09	0.98	0.056	341	<0.01	<0.02	<0.01	<0.04	<0.02	<0.02	<0.02	<0.01	0.03	<0.02	<0.02
3257	surf/ddh	Th-106	152	8.02	1.33	0.139	553	0.01	<0.02	<0.01	<0.04	<0.02	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3273	surf/ddh	Th-106	66	8.04	3.56	0.333	1101	0.02	0.03	<0.01	<0.04	0.03	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3271	surf/ddh	Th-106	93	7.52	1.65	0.225	1109	<0.01	<0.02	0.01	<0.04	<0.02	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3216	surf/ddh	Th-106	172	7.39	1.01	0.021	1194	0.01	<0.02	0.02	<0.04	<0.02	<0.02	<0.02	0.01	<0.03	<0.02	<0.02
3277	surf/ddh	Th-92	250	8.58	1.4	0.084	1381	0.01	0.02	<0.01	<0.04	<0.02	<0.02	0.02	<0.01	<0.03	<0.02	<0.02
3356	surf/ddh	Th-115	292	8.45	0.83	-0.099	1782	0.01	0.03	0.01	0.05	0.04	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3366	surf dddh	Th-84	266	7.91	0.27	0.036	2635	<0.01	<0.02	<0.01	<0.04	0.03	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
4001	surf/ddh	Th-106	167	7.3	0	0.06	4970	0.16	0.05	0.01	<0.04	<0.02	0.09	0.02	0.01	<0.03	0.08	0.02
3363	surf dddh	Th-101	250	8.22	0	-0.128	6318	0.15	0.31	0.03	0.14	0.04	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3181	surf/ddh	Th-106	230	7.28	0.02	0.077	6748	0.01	<0.02	<0.01	<0.04	0.02	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
4002	surf/ddh	Th-106	230	8.02	0	0.225	7526	0.02	<0.02	<0.01	<0.04	0.04	0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3321	surf/ddh	Th-101	442	8.1	0	-0.083	8490	0.05	0.08	0.01	<0.04	<0.02	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3083	surf/ddh	Th-106	255	8.72	0	0.128	9803	0.03	0.06	0.01	0.05	<0.02	0.02	<0.02	<0.01	<0.03	<0.02	<0.02
3429	surf/ddh	Th-100	425	7.36	0	-0.174	15462	0.05	0.09	<0.01	<0.04	0.02	0.02	0.03	<0.01	<0.03	<0.02	<0.02
3184	surf/ddh	Th-106	275	7.12	0	0.005	16345	0.02	0.06	0.01	<0.04	0.04	<0.02	0.06	0.02	0.07	<0.02	<0.02
3365	surf/ddh	Th-106	353	6.61	0	-0.05	17070	0.03	0.08	0.01	0.05	<0.02	<0.02	<0.02	<0.01	<0.03	<0.02	<0.02
Method Level of Detection																		
REE: shales (ppm) Haskins and Haskins (1966) de Baar et al (1988)																		
								0.01	0.02	0.01	0.04	0.02	0.02	0.02	0.01	0.03	0.02	0.02
								32	70	79	31.0	57	12	52	0.85	6.0	1.0	34

3.12 Conclusions

The major anion facies in the Myra Falls ground waters in many ways correspond to the three hydrologic zones outlined by Domenico (1972; as reported in Freeze and Cherry, 1979). This observation is rather amazing considering the limited areal extent of the study area as compared to studies of large regional ground water systems.

The ground waters of Myra Falls consist of an upper HCO_3^- zone (Zone 1) dominated by flushing of meteoric water. This zone may also include SO_4^{2-} waters due oxidation of sulphide minerals in this setting and dissolution of anhydrite. Cations in this zone are typically dominated by Ca^{2+} . Magnesium concentrations are generally very low due to the slower dissolution of Mg-bearing minerals except in areas of anthropogenic influence. Near the centre of the Myra - Price ridge there is a more sluggish zone (Zone 2) of flushing which allows for greater oxidation of sulphide minerals. Ground waters in this zone are typically characterized by higher Na^+ concentrations resulting from cation exchange processes. The elution of saline ground water from the central core of the M-P ridge is likely a fairly recent phenomena or at least the result of only a low number of pore-water volumes of meteoric water. This is observed since Cl^- has been flushed but Ca^{2+} and Mg^{2+} cations have been retarded. Low but measurable Cl^- (>10 ppm) may result from diffusion of Cl^- from dead-end pore spaces and possibly matrix porosity in zones where ground-water flow is slow. The deeper zone of saline ground water (Zone 3) which may have low circulation is characterized by old Cl^- dominated waters.

Zone one (of Domenico classification) has typically developed on the Myra Price hill fringes, and in areas of relatively high permeability. Zone two is largely centered in the core of the Myra-Price Ridge and below that, in the HW mine. High salinity Cl^- ground waters (Zone 3) exist below zone two in the HW mine and beneath a narrow interface of HCO_3^- ground water in Thelwood Valley. Mixing between the saline Cl^- waters and the other two water types has resulted in waters exhibiting a full spectrum of major anions intermediate between the three (anion) water types. Only a slight proportion of high salinity Cl^- water is required to mix with HCO_3^- or SO_4^{2-} water to shift the water to chemistry dominated by Cl^- .

The Cl^- saline ground water is characterized by element mass ratios of: $\text{Ca}^{2+}/\text{Cl}^-$, 0.22; $\text{Mg}^{2+}/\text{Cl}^-$, 0.01; Na^+/Cl^- , 0.41; K^+/Cl^- , 0.0017; $\text{SO}_4^{2-}/\text{Cl}^-$, 0.059. Bicarbonate to Cl^- mass ratios are variable in the saline waters but many waters have very low HCO_3^- concentrations (~20 ppm). The molar ratio of Na^+/Cl^- is 0.64 in the saline ground waters. This ratio along with the mass ratios of Br^-/Cl^- and I^-/Cl^- largely rule out evaporites or a modern (post-glacial) sea water as the source of Cl^- in the saline end-member ground water.

Trace element chemistry of Myra and Price mine ground waters indicates a wide overlap of individual element concentrations. Ground waters associated with the unmined Price deposit have higher median concentrations of elements mobile as oxy-anions such as: V, Cr, As, and Mo. Mining activity has the greatest effect on the concentrations of Zn and Cu in Myra ground waters as compared to baseline levels determined from the Price ground waters.

4. Physical Speciation (Filtration Studies)

4.1 Introduction

The weathering of Fe, Al, and Mn containing minerals can produce oxide or hydroxide precipitate phases capable of removing metals from solution. The study of the loss of metals by adsorption on these phases crosses several scientific disciplines reflected in past research carried out by chemists, soil scientists, geologists, hydrologists, and engineers. The attenuation and transport of metals is of interest in ground and surface water studies, soil research, and water treatment.

Metals within natural and artificial waters may exist as: dissolved inorganic ions; inorganic or metal-organic complexes; bound to suspended or colloidal clays, oxides, hydroxides or oxy-hydroxides (e.g. Fe, Mn, Al) or humic acids (Kedziorek and Bourg, 1996; Stumm and Morgan, 1996). The objective set forth in this chapter is to investigate the presence of suspended/colloidal material within the Myra Falls ground water domain, the degree of association of metals to these non-aqueous phases and how that association affects the mobility of the main metals of interest; that is Fe, Mn, Zn, Cu Pb, and Cd.

Bound metals may be adsorbed to the surface of a solid, or co-precipitated with the solid. The formation of (hydr)oxides (oxides, hydroxides, oxy-hydroxides) in the presence of metals may result in co-precipitation, in addition to adsorption on the forming (hydr)oxide this may result in an even greater sink for metals than adsorption on pre-existing (hydr)oxides. The processes of co-precipitation and adsorption will be collectively referred to as sorption since these processes are difficult to assess separately.

Adsorption results from attraction of ions to a pH-dependent charge on a surface. In general, adsorption of metals on (hydr)oxides is limited at low pH, as metals are in competition with H^+ ions for adsorption sites. With increasing pH the degree of adsorption for metals will increase. Adsorption will start, and over a narrow pH range, the adsorption edge which will vary for each metal and for each substrate, there is a progression from little to full adsorption (e.g. Hayes and Leckie, 1986; Evans, 1989; Stumm and Morgan, 1996).

The amount of adsorption may also be dependent upon the age of the (hydr)oxide; as a freshly precipitated phase may have a greater charge imbalance. Aging of the precipitate may lower its' adsorption capacity due to increased crystallinity and the loss of surface area by organic coatings (Lee, 1975). Also, the presence of the metal in the solution at the time of (hydr)oxide precipitation may increase the uptake through co-precipitated (Gadde and Laitinen, 1973; Lee, 1975). Iron and Mn (hydr)oxides tend to be fine grained with surface areas in the order of 200 to $>300 \text{ m}^2\text{g}^{-1}$ (Jenne, 1968; Drever, 1988), and can exert a chemical activity far in excess of their concentration, making them capable of removing large concentrations of metals from solution (Jenne, 1968). The greatest reservoirs and control of metals in the weathering environment is due to adsorption reactions with Fe and Mn (hydr)oxides or organic matter (Lee 1975; Jenne, 1977), and any discussion of metal cycling or transport within natural systems should include the role of these hydr(oxides).

The degree, and processes that will affect adsorptive losses may include: the concentration of metal in solution; pH; presence of and competition by soluble organic chelates and inorganic complexes (e.g. $\text{Me}^y(\text{OH})_x^{y-x}$, $\text{Me}^y(\text{Cl})_x^{y-x}$) (Jenne, 1968); competition for sites among competing metals (Gadde and Laitinen, 1974; Lee, 1975); Eh, particle parameters such as surface area, exchange capacity, adsorption site density per unit area of the adsorbent, chemical composition of the surface (McKinley and Jenne, 1991; Stumm and Morgan, 1996); colloid surface area per unit volume (McKinley and Jenne, 1991; Kooner, 1993); adsorption kinetics (Santschi, 1984; Honeyman and Santschi, 1988); temperature, age of the adsorbent, presence of metals at the time of adsorbent formation (Lee, 1975); catalysis reactions on the formation of the sorbate and on its' surface (Jenne, 1968; Lee, 1975); and the presence and amount of organic matter in solution (Jenne, 1968; Kedziorek and Bourg, 1996).

Iron (hydr)oxides, besides having a great affinity to sorb metals may also be a major sink for Mn and Al. Up to 30 mole % Al or Mn can isomorphically substitute for Fe in the goethite structure (Ebinger and Schulze, 1989; Schwertmann and Taylor, 1989); amorphous phases would likely equal or exceed this amount. Diffusion into a porous or a micro-porous solid may also be important during metal retention and may have implications on diffusional transport of metals. Papelis (1995) has shown this to be the case for Cd and Se with porous

Al oxides. Most experimental studies of metal adsorption attempt to understand these processes in simpler, often binary trials (e.g. Swallow et al., 1980; McKinley and Jenne, 1991). There have been few trials using actual aquifer material (i.e., Coston et al.; 1995; Zachara et al., 1989); or investigating competition amongst adsorbates (Gadde and Laitinen, 1974); or the presence of organic acids (Kedziorek and Bourg, 1996); but generally the phases and processes in natural systems are too complicated to duplicate in laboratory studies. Weber et al. (1991) in their review of sorption theory warn against extrapolating experimental data to conditions not so easily quantified; thereby suggesting that site specific studies should be carried out where adsorption processes are of interest.

The mobility of suspended solids and associated trace metals are of interest in examining the total metal load being transported within the surface and ground water regimes. The total metal load of a water may be considerably greater than that measured in the dissolved form. Total recoverable or non-filtered metals may represent a threat to the biosphere, especially by filter feeding organisms or by direct ingestion (Lee, 1975) and metals that are unaccounted for in dissolved analyses may become available after redox changes in natural waters (Lee, 1975; Speliethoff et al., 1995). Determining the modes of transport and sinks for trace metals in the natural environment is important in understanding metal cycling. The understanding of the degree of association of metals with (hydr)oxides in the natural environment is also important in the retardation and transport on colloids of some daughter products of nuclear reactions (Buddemeier and Hunt, 1988).

A site specific study is necessary to understand the hydrogeological fate and sinks of metals (mobility) in waters at the Myra Falls location. A study of this nature has implications towards environmental mitigation and applications towards hydrogeochemical prospecting.

4.2 Method

Any study of metal adsorption must include the differentiation between particulates and dissolved phases. Filtration is the most widely accepted method of separating a particulate phase from the dissolved phase. The overwhelming choice of filter pore size as the cut-off to describe dissolved species in recent literature and in regulated industries (i.e., copper in water, ASTM D1688-95, 1996) is $0.45\mu\text{m}$ which is clearly an operational choice rather than a scientific one, as suspended particles may have diameters $<10^{-6}$ m and colloidal material may have diameters $<10^{-8}$ m (Stumm and Morgan, 1996). No distinction between suspended particles and colloids is made within this study and for ease of reporting, all concentrations retained during filtration will be lumped together, and the terms particulate, colloid or suspended will be used interchangeably.

Filtration of samples through porous membranes of various pore size diameters is a rapid and simple method for separation of particles within natural waters which can be carried out under field conditions. This technique enables the processing of samples to occur on site with as little delay as possible after sample collection and consequently should represent as near as possible the in-situ chemical make-up of the water.

Aliquots of a single water sample were filtered at 0.45, 0.22, 0.10, and $0.05\mu\text{m}$ pore spacing and one aliquot remained non-filtered (total recoverable = TR). Filters were pre-loaded with sample, which was then used to rinse the sample bottle. The initial filtrate was then discarded. Where sample volumes were not sufficient, a lesser number of aliquots were processed, and in some cases, especially during the initial stages of the sampling program, prior to being supplied with filtration equipment, sites were subjected to non-filtered and $0.45\mu\text{m}$ filtration only. The sites with a lesser number of filtered aliquots were included since they broaden the areas sampled and variety of water quality within this study.

Membrane filters used were of the 'tortuous path' (TP) variety. The TP filter will tend to trap particles on its' surface and within the membrane. The filter pore-size tends to be more variable in TP variety than a 'sieve' (S) style that traps the sediment only on its' surface. The advantage of TP membranes over the S type lies in their ability to process greater volumes of sample before plugging and are therefore a favorable choice in studies of

waters related to mining. The overwhelming majority of samples processed by the United States Geological Survey are with the TP style of membrane (Horowitz et al., 1992).

Two different filter materials were used for filtering. Gelman 47 mm Supor membrane filters composed of polysulfone were used for the 0.45 μm pore-size filtering and Millipore 47 mm diameter mixed cellulose esters of acetate and nitrate were used for the 0.22, 0.10, and 0.05 μm pore-size filtering. Lately, there has been discussion in the literature of the effects on metal concentrations using different processing procedures especially the use of membranes of different composition (Taguchi et al. 1989; Horowitz et al., 1992; Hall et al., 1996; Horowitz et al., 1996). Hall et al. (1996) compared the effects of using various 0.45 μm filter membranes (TP and S type) which included filter membranes composed of polysulfone (Gelman) and cellulose acetate/nitrate (Millipore). They found that variations in element concentrations from different sample processing (filtration artifacts) were matrix dependent and in 'acid mine drainage' waters, pH 7.39 and suspended load of 11.9 mgL^{-1} (composition not given), there was low variability in metal concentrations between the different filters, and there were no distinctive trends with regards to membrane composition on trace metal concentrations. The relative standard deviation of element concentrations between the filters for the mine drainage was lowest of any of the five water types tested and was within the range of analytical error. The difference in composition of the filter paper would therefore not be expected to affect the analysed concentrations in this present study. As well the presence of alkali and alkaline earth cations, which are readily abundant in the Myra Falls waters, should reduce or limit the losses of trace metals by preferential adsorption to the filter membrane during filtration (Buffle, et al., 1992).

4.3 Results and Discussion

Waters of diverse (major-element) chemistry, representing the dominant water types in the Myra Falls mining complex, were sampled for physical speciation of various metals; namely Fe, Al, Mn, Zn, Cu, Pb, and Cd (Figure 4-1).

Ratios of filtered concentrations divided by total recoverable (TR) non-filtered concentrations were calculated to develop a better understanding of the partitioning of metals between various fractions of suspended solids (e.g. $C_{F(0.45)}/C_{TR}$, is the ratio of the concentration of an element in the filtrate processed through a 0.45 μ m pore-size membrane to the non-filtered concentration). One-tenth of the detection limit concentration was substituted where concentrations were below the method of detection in the filtered aliquot. This would result in a minimum of 0.1 for C_F/C_{TR} fraction where the TR concentration is at the detection limit. Where the TR concentration was below the detection limit all aliquots were removed from further calculations for that particular analyte at the given site.

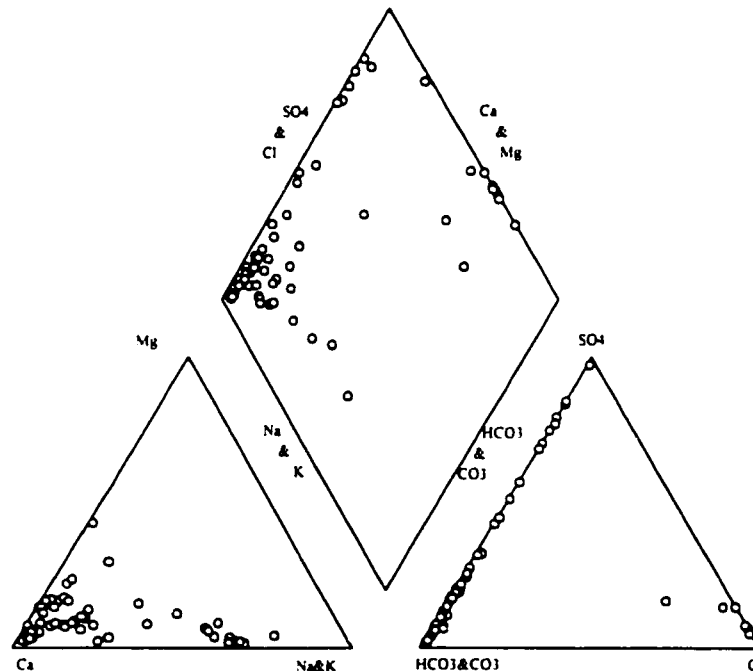


Figure 4-1 Piper diagram of major ions for ground waters used in filtration study.

4.3.1 Partitioning of Metals in Acid Mine Drainage

Only two highly acidic waters were sampled, and their results will be discussed separately from the non-acidic waters, since they are atypical of waters encountered in this study. The two sites, 2579 and 2676, have pH values of 2.3 and 3.0, respectively. Each of these sites had associated precipitate samples taken and analysed for crystal structure (XRD) and trace elements. Site 2676 drains a portion of Myra 12 level, which is an access drift to a portion of the now-exhausted Myra mine. The precipitate sample (S3003) that was taken at the 2676 site has an XRD pattern identifying it as Goethite (α -FeO(OH)). This is the only iron precipitate sampled within the mining complex that was not amorphous (Appendix E). Selected trace element concentrations of the precipitate S3003 (Table 4-1) shows that trace element accumulation, co-precipitation and adsorption, are still relatively high considering the pH of the water passing over the precipitate surface. The more acidic water, site 2579, is located at the base of the mine's main waste rock pile and contained an Fe stained microbial(?) gel-sludge precipitate (S2006) that also has relatively high metal concentrations in relationship to the total concentration of metals in solution. Several metals, i.e., Ag, In, and Ga, were rarely above detection in this study but are mobilized in these acidic waters. The precipitate to aqueous concentration ratios are less at the lower pH site 2579 than at site 2676, except for Pb which is higher in 2579 and, Zn and Cd which are about the same at both sites. Co, Zn, Cu, and Cd are less strongly partitioned into the solid phase than the other metals at both sites. The element order of precipitate/dissolved ratios are similar between the two sites with the exception of Pb. The association of dissolved metals with the Fe-precipitates is $\text{Ag} \gg \text{Mo} > \text{Pb}_{(2579)} > \text{Ga} > \text{Cr} > \text{In} > \text{Pb}_{(2676)} > \text{Ni}_{(2579)} > \text{Cu} > \text{Zn} > \text{Cd} \approx \text{Co}_{(2579)}$.

Under these highly acidic conditions in similar studies the amount of metals adsorbed should be quite low. Less than approximately 5% of the Pb and Zn were adsorbed in a laboratory batch experiments with synthesized goethite at pH 4 (Kooner, 1993). While adsorption of Cd, Pb, Cu, and Zn was less than 10% of the dissolved concentration under acidic conditions (metal concentration was $5 \times 10^{-5} \text{M}$) (Benjamin and Leckie, 1981); while laboratory experiments of natural sediments by Coston et al. (1995) had 20+ % of the Pb and Zn sorbed at pH 4. Under acidic ground water conditions associated with a waste-rock dump, Herbert (1996) found Al, Cu, and Ni were preferentially associated with poorly crystalline

solids; while, Zn was more preferentially associated with more crystalline precipitates. These two sites (2676 and 2579) would receive a continuous supply of water from which to scavenge metals rather than a set initial concentration as in a batch experiment. At low pH values metals such as: Ag, Mo, Cr, In, Ga, and Pb have high precipitate to water ratios. Molybdenum, soluble as a oxyanion, is readily sorbed to amorphous Fe hydroxides at low pH (Reyes and Jurinak, 1967). Elements with greater solubility, such as Zn, are have lower precipitate to water ratios. At these low pH values it is also quite possible that anions may be adsorbed, although this has not been determined in these samples.

Table 4-1 Metal concentrations for waters from acidic sites and corresponding precipitates. All concentrations are in ppm.

	----- Site 2676 -----			----- Site 2579 -----		
	H2O	Precipitate (S3003)	Precipitate/ Water	H2O	Precipitate (S2006)	Precipitate/ Water
pH	3.0	--	--	2.3	--	--
T (°C)	8.1	--	--	19	--	--
EC (mS/cm)	2.92	--	--	10.34	--	--
Fe	35	$6.2 \cdot 10^5$	18000	1490	$1.1 \cdot 10^5$	74
Al	14	$0.4 \cdot 10^4$	300	520	$6.2 \cdot 10^5$	119
Mn	19	100	5	280	$1.7 \cdot 10^3$	6
V	<0.0005	5.0	--	<0.0005	75.0	--
Cr	0.013	81	6200	0.14	32	230
Ni	0.31	<10	--	0.95	15	16
Co	0.16	<5	--	3.2	18	6
Mo	0.00081	46	57000	0.0013	6.8	5200
Zn	140	760	5	300	2200	7
Cu	7.5	290	39	81	650	8
Pb	0.36	200	560	0.18	370	2000
Cd	1.3	3.7	3	1.5	9.6	6
Ag	0.00042	51	120000	0.00057	16	28000
In	0.00061	1.4	2300	0.0082	0.23	28
Ga	0.00079	6	8000	0.01	8.4	800

4.3.2 Iron

Iron can exist in two oxidation states, Fe^{2+} and Fe^{3+} . In the aquatic environment Fe^{2+} is soluble, while Fe^{3+} is sparingly soluble, except at low pH, and will form relatively insoluble oxides, hydroxides, and oxy-hydroxides ((hydr)oxides). The kinetics of the oxidation of Fe^{2+} is quite rapid at pH values >3.5 and the half life of Fe^{2+} at 25 °C and pH 7.5 in the presence of O_2 would be in the minutes range (Eary and Schramke, 1990). Oxidation insitu of Fe within the majority of sampled waters which contain dissolved oxygen (DO) would be expected to be fairly rapid.

The source of Fe in waters of the Myra Falls mining complex is from sulphide minerals, dominantly: pyrite, chalcopyrite, and sphalerite; the same sources as many of the other metals in solution. The fresh precipitation of amorphous Fe-(hydr)oxides would be expected to be a major sink for trace metals by co-precipitating in isomorphic substitution, or adsorption to charged surface sites on the freshly precipitated Fe-(hydr)oxides. These processes may remove more metals with the freshly formed (hydr)oxides than would be removed on aged or crystalline (hydr)oxides (Gadde and Laitinen; 1973, Lee, 1975).

As would be expected, SO_4^{2-} waters have the greatest concentrations of Fe (primarily from the oxidation of pyrite); while, HCO_3^- waters have the lowest. In non-acidic SO_4^{2-} waters $\text{Fe}_{(\text{TR})}$ ranges from 7 to 140000 ppb; and has a median value of 1530 ppb (Table 4-2). Chloride dominated waters have minimum, maximum and median $\text{Fe}_{(\text{TR})}$ concentrations of 130, 39000, and 410 ppb, respectively. Summary statistics for $\text{Fe}_{(\text{TR})}$ in HCO_3^- waters are the lowest and range from below detection to 4300 ppb, with a median value of 45 ppb.

Where all filter sizes are available for comparison, the 0.45 μm filter appears to adequately remove particulate Fe from the water. There is little additional removal of Fe particulates using a pore spacing less than 0.45 μm . This is apparent for sites from all water types. This observation is quantified by running a one-way analyses of variance on the Fe ratios for various filter sizes which indicates there is no difference in filtered aliquots between the C_F/C_{TR} ratios for 0.45, 0.22, 0.10, and 0.05 μm filter pore sizes for all three anion dominated water types (Appendix C). Therefore, the 0.45 μm filter membrane is as effective as smaller pore sizes (down to 0.05 μm) at removing particulate Fe. The ratio and

amount of Fe removed is not consistent across the major water types. Estimated median concentrations of suspended Fe are 1.0, 0.13 and 0.072 ppm for SO_4^{2-} , Cl^- , and HCO_3^- waters, respectively.

Dissolved $\text{Fe}_{\text{F}(0.45)}$, with the exception of acidic waters, tends to have an upper Eh barrier that decreases with increasing dissolved Fe (Fig. 5.2b). This is also true for DO; although, it is less pronounced. There are no clear relationships between DO, EC, or pH with the concentration of particulate Fe ($C_{\text{TR}} - C_{\text{F(avg.)}}$). The pH values for these waters are near neutral and within each water type redox conditions (Eh) exert the strongest control on Fe

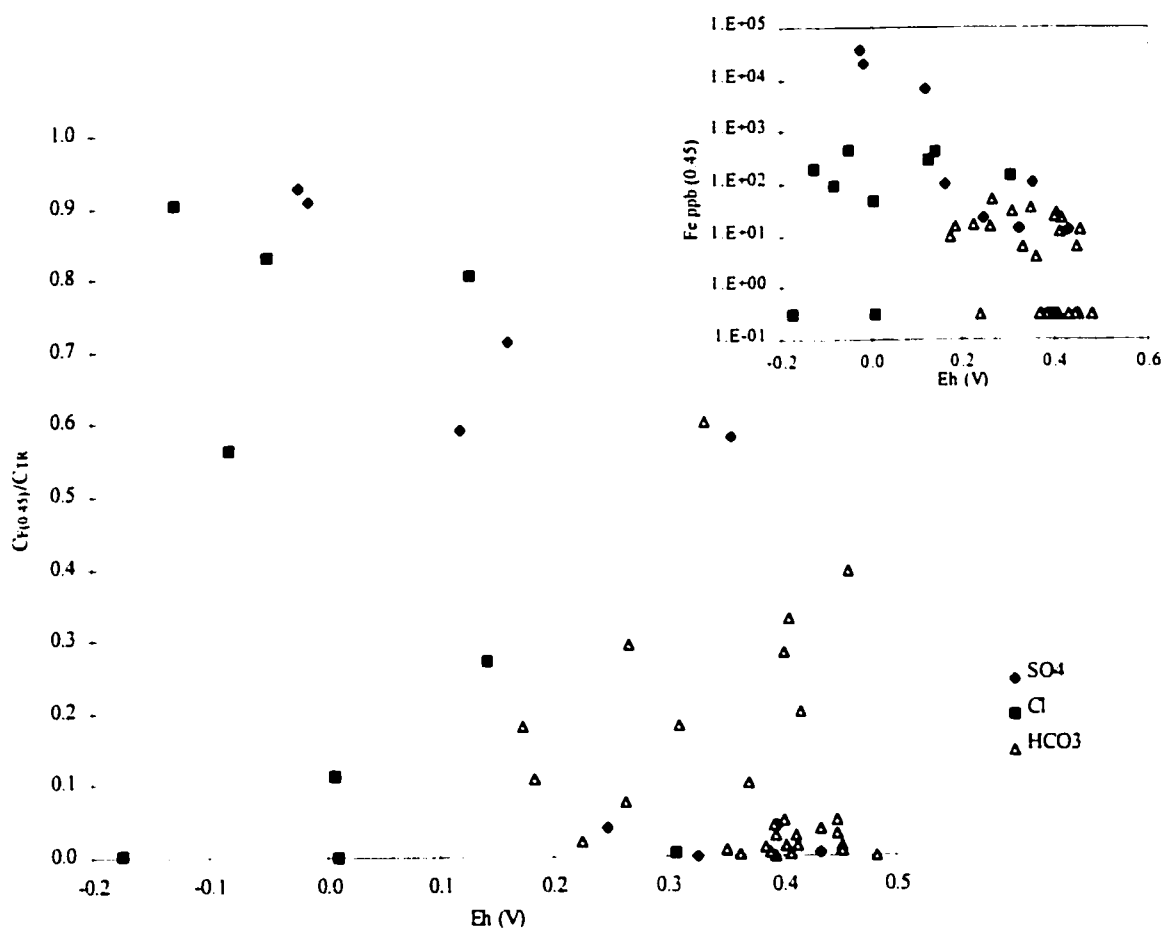


Figure 4-2 Eh vs. $C_{\text{F}(0.45)}/C_{\text{TR}}$ (ratio of dissolved Fe (0.45 μm filtrate) showing Eh control on suspended Fe. High Eh corresponds to greater suspended Fe. Insert: Dissolved Fe concentration in 0.45 μm filtrate vs. Eh. Below detection concentrations plot along the bottom of graph.

species and therefore influence the fraction of Fe that is suspended ($C_{F(0.45)}/C_{TR}$); or conversely, the measured redox potential is influenced by the Fe^{2+}/Fe^{3+} ratio. The ratio C_F/C_{TR} increases with decreasing Eh for SO_4^{2-} and HCO_3^- dominated waters (Figure 4-2). Formation of Fe particles is influenced in the SO_4^{2-} waters by the lower redox values that would favour Fe^{2+} in solution over Fe^{3+} . While there is not as clear a relationship between redox and Fe particulates in Cl^- dominated waters, since the three samples that have low Eh also have high Fe losses in the filtered aliquots. Two of the three waters with low C_F/C_{TR} ratios, (low Eh waters #2622 and #2627) are bailed samples from Thelwood Valley drill hole PR-89, and represent mixed saline/non-saline waters. Iron (hydr)oxides may have been entrained by the bailer or advected by non-saline water during the natural mixing process. The third sample (#3429) is a highly reducing water from a straddle packed zone in drill hole PR-100. Iron (hydr)oxides should not be stable in a reducing environment and may possibly represent particles advected to areas where they would not normally precipitate. At these locations dissolution of (hydr)oxide particles may be slow as conditions are non-acidic. Only in SO_4^{2-} waters is there a slight trend in decreasing C_F/C_{TR} with increasing DO. The presence of any DO should readily oxidize ferrous Fe. It is evident that the relationship between Fe (hydr)oxides, DO, Eh and pH are not straight forward. The C_F/C_{TR} ratios of Fe indicate that Fe particulates removed are HCO_3^- waters $> Cl^- \cong SO_4^{2-}$.

Saturation indices (SI) were calculated for Fe species in all waters using the ion-association speciation code PHREEQC (Parkhurst, 1995; using the WATEQ4F data base (Ball and Nordstrom, 1991)) with the intent of finding the possible forms in which Fe is precipitating. Saturation indices calculated for goethite ($\alpha\text{-FeOOH}$, $\log K_{sp} = -1.0$) are greater than 1 for all except samples from a single site. Saturation indices are calculated by $\log_{10} SI = \log_{10} IAP - \log_{10} K$; where SI is saturation indices, IAP is the ion activity product and K_{sp} is the equilibrium constant for goethite at the sample temperature. Maximum logSI values were greater than 10 and in most cases were around 5 to 7. Equilibrium modeling programs do not account for the kinetics of nucleation and precipitation; however, the extreme values of over-saturation for goethite indicate that the precipitation of goethite is likely not controlling Fe concentrations. Crystalline Fe-(hydr)oxides generally require elevated temperature or pressure, or a period of aging to form (Swallow et al., 1980). Goethite, being more structured

than amorphous Fe-hydroxide ($\text{Fe}(\text{OH})_{3(a)}$) would not be expected to be the first Fe phase to precipitate. The log SI values for $\text{Fe}(\text{OH})_{3(a)}$ are < 3 , and more within a range including zero (saturation). Goethite, as previously mentioned was only identified as the Fe precipitate at one site (site 2646), whereas at other locations where precipitates were formed, the Fe precipitates were amorphous in XRD analyses. The $C_{F(0.45)}/C_{\text{TR}}$ ratios decreases with increasing Fe_{TR} SI($\text{Fe}(\text{OH})_{3(a)}$) in SO_4^{2-} waters showing an increased $\text{Fe}(\text{OH})_{3(a)}$ precipitation with increasing SI_{TR} (Figure 4-3). The pattern, for reasons mentioned earlier, is not as uniform in Cl^- waters. In the HCO_3^- waters virtually all sites are over-saturated with respect to $\text{Fe}(\text{OH})_{3(a)}$ in the TR and $0.45\mu\text{m}$ aliquots, and have low C_F/C_{TR} values. Where log $\text{SI}_{0.45}$ approaches SI_{TR} associated with correspondingly higher C_F/C_{TR} , there tends to be less loss of Fe which may indicate a kinetic hindrance to precipitation or be the result of analytical variation.

Shapiro (1964) found that the presence of organic acids in water tended to limit the growth of Fe hydroxides. Where natural dissolved organic matter was absent, the bulk of Fe hydroxides could be removed by $0.45\mu\text{m}$ pore size; but in the presence of organic matter, 0.1 to $0.45\mu\text{m}$ was the dominant particle size. This was also demonstrated by Liang and Morgan (1990) where coagulation of colloidal hematite particles was reduced by the presence of humic, fulvic, and polyaspartic acids. Humic acid was also found to stabilize smaller Fe hydroxide particles, that is to reduce coagulation, in a sandy coastal aquifer (Ryan and Gschwend, 1990). The amount of dissolved organic carbon (DOC) was not measured in the Myra Falls ground waters. However, the bulk of Fe(hydr)oxides can be removed with a $0.45\mu\text{m}$ pore size which may indicate that hydroxide surfaces were not coated by organic matter. In addition to the steric hindrance, the presence of humic acid has the ability to lower total recoverable metals as humic acid would retain sorbed metals after acidification (Kedziorek and Bourg, 1996).

The presence of Cu in solution may also play a role in promoting oxidation of Fe. Copper may act as a catalyst in the oxidation of ferrous sulphate by DO. The Cu is then available to be sorbed by the newly formed Fe hydroxide (Stumm and Lee, 1961).

Co-precipitation is likely occurring as well as adsorption since the metals are present in solution at the time of the solid phase formation. Co-precipitation, as compared to pure

adsorption, will be largely a non-reversible process (Gadde and Laitinen, 1973), as trace metals are not readily desorbed. In this case Fe (hydr)oxides would act as a semi-permanent sink for co-precipitated metals until dissolution in an anoxic environment. However, metals would continue to be removed in an anaerobic environment since the formation of H_2S under low redox conditions would precipitate metals as insoluble or very low solubility metal-sulphides.

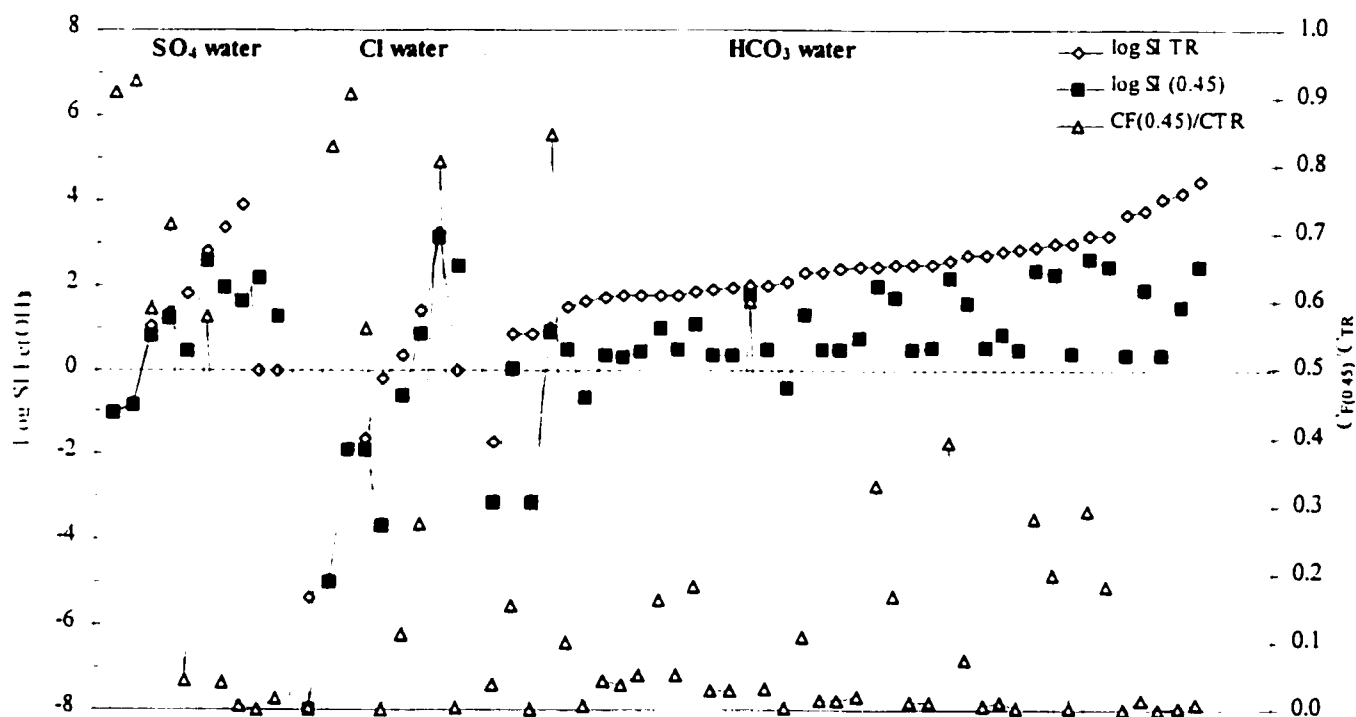


Figure 4-3 Comparison of saturation indices for amorphous Fe-hydroxide and the filtration ratio $CF(0.45)/CTR$. Sites ordered by increasing saturation indices of non-filtered aliquot for each major water type.

4.3.3 Manganese

Manganese (hydr)oxides make up the second group of inorganic particles that are capable of scavenging metals from solution. Manganese can exist as Mn^{2+} , Mn^{3+} , Mn^{4+} , Mn^{6+} , and Mn^{7+} ; however, the highly oxidized ions Mn^{6+} and Mn^{7+} are generally unimportant in natural waters. The Mn^{2+} ion is soluble while the solubilities of the Mn^{3+} and Mn^{4+} ions are highly limited. Manganese oxides act as significant scavengers in concentrating metals, especially Cu, Ni, and Co, as in deep sea Mn-nodules (Jenne, 1968; Drever, 1988; Hem, 1989). The kinetics of Mn oxidation are slower than that of Fe and require a higher pH for similar oxidation rates (Stumm and Morgan, 1996) without the intervention of surface reactions or microorganisms (Lee, 1975).

Total recoverable Mn concentrations range from 0.7 to 5100 ppb, 65 to 2800 ppb, and from below detection to 150 ppb for SO_4^{2-} , Cl^- , and HCO_3^- waters, respectively (Table 4-2). Median values, in the same order, are 1700, 1100, and 4.2 ppb.

For the SO_4^{2-} dominated waters only two of ten waters decrease in Mn concentration with increasing filtration pore size. Median values of aqueous Mn concentrations for SO_4^{2-} waters are 1.0, 1.1, 1.0, and 1.0 ppm for 0.45, 0.22, 0.10, and 0.05 μm pore sizes, respectively. Median values of C_F/C_{TR} in SO_4^{2-} waters are 0.98, 0.97, 0.99, and 0.99 for 0.45, 0.22, 0.10, and 0.05 μm pore sizes, respectively. Ratios of filtrate to total recoverable concentrations (C_F/C_{TR}) indicate that in the majority of SO_4^{2-} waters Mn is transported as a dissolved species (Table 5-2).

Only one of the nine Cl^- waters has a significantly lower Mn concentration after filtering (2606); median C_F/C_{TR} ratios are 0.99, 1.00, 1.00, and 1.00 for filter pore-sizes in decreasing order. Manganese is dominantly exists as dissolved ions in Cl^- waters, whereas for HCO_3^- waters, 29 of the 46 waters with concentrations above the detection limit have $C_F/C_{TR} < 0.75$. The median C_F/C_{TR} values are 0.39, 0.57, 0.45, and 0.40 in HCO_3^- waters. A one-way analyses of variance indicates there is no difference between the C_F/C_{TR} ratios for Mn between the different filter pore sizes (Appendix C). The 0.45 μm is as effective as smaller filter sizes at removing approximately 50% of the Mn in HCO_3^- water. The median concentration of suspended Mn in HCO_3^- waters is 0.0025 ppm.

The kinetics of the oxidation of Mn is considerably slower than the oxidation of Fe, and Mn^{2+} can coexist with O_2 in water for some time (Lee, 1975). There is no relationship between DO content and the amount of Mn removed by filtering in HCO_3^- waters. There is a very slight trend of lower C_F/C_{TR} values with decreasing DO in SO_4^{2-} waters. In other words the precipitation of Mn from the direct oxidation by O_2 may not be the controlling influence on the form of Mn particles in suspension. Laboratory experiments (Davies, 1986) show that Fe oxy-hydroxides (lepidocrocite) kinetically may be more important in removing Mn from solution by complexing the Mn on the lepidocrocite surface. The effects of surface reactions on oxidation of Mn in natural waters is not known.

The initial solid state Mn species expected to form from the oxidation of Mn^{2+} is hausmannite (Mn_3O_4) (Hem and Lind, 1983; Murray et al., 1987). Equilibrium saturation calculations using PHREEQC (Parkhurst, 1995; with the WATEQ4F database (Ball and Nordstrom, (1991))) indicate that none of the waters have any of the following Mn minerals above saturation: birnessite ($\text{Na}_4\text{Mn}_{14}\text{O}_{27} \cdot 9\text{H}_2\text{O}$), bixbyite ($(\text{Mn,Fe})_2\text{O}_3$), hausmannite, $\text{Mn}_2(\text{SO}_4)_3$, $\text{Mn}_3(\text{AsO}_4) \cdot 8\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, MnSO_4 , nsutite ($\gamma\text{-MnO}_2$) and pyrolusite (MnO_2). A single water (#3470) was saturated with respect to rhodochrosite (MnCO_3), pyrochroite ($\text{Mn}(\text{OH})_2$), and manganite ($\text{MnO}(\text{OH})$); and one other water (#3250) was slightly saturated with respect to manganite ($\text{MnO}(\text{OH})$). The $C_{F(0.45)}/C_{TR}$ for Mn in water at site 3470 is the lowest of any SO_4^{2-} waters; while $C_{F(0.45)}/C_{TR}$ at site 3250 is in good agreement with other HCO_3^- waters. The only identified Mn mineral precipitate (XRD) sampled at Myra Falls; although, not associated with any of the filtration sites, was todorokite, $((\text{Mn}^{2+}, \text{Ca, Mg})\text{Mn}_3^{+4}\text{O}_7 \cdot \text{H}_2\text{O})$ (Appendix E) precipitated on a wet wall on Myra level 13 (34+27.5 m E). None of the above listed mineral phases appear to be controlling particulate Mn at the majority of sites.

A plot of concentration of suspended Mn particulates vs. suspended Fe particulates (Figure 4-4) shows the relationship of increasing particulate Mn with increasing particulate Fe concentrations. Although Mn in the SO_4^{2-} and Cl^- waters is largely dissolved, for individual waters the filter-retained Mn is still associated with the suspended Fe. Ebinger and Schulze (1989) have shown that Mn can substitute up to 30% for Fe in synthesized goethite. Possibly, the greatest loss of Mn from solution is through association, bound to or co-

precipitated with, Fe-(hydr)oxide particles rather than as Mn minerals. Individual molar ratios of Mn/Fe range up to 5.7, though the median molar ratio value of 0.045 could quite likely be easily accommodated in amorphous Fe- (hydr)oxide. The oxidation state of suspended Mn being removed from the solution is not known.

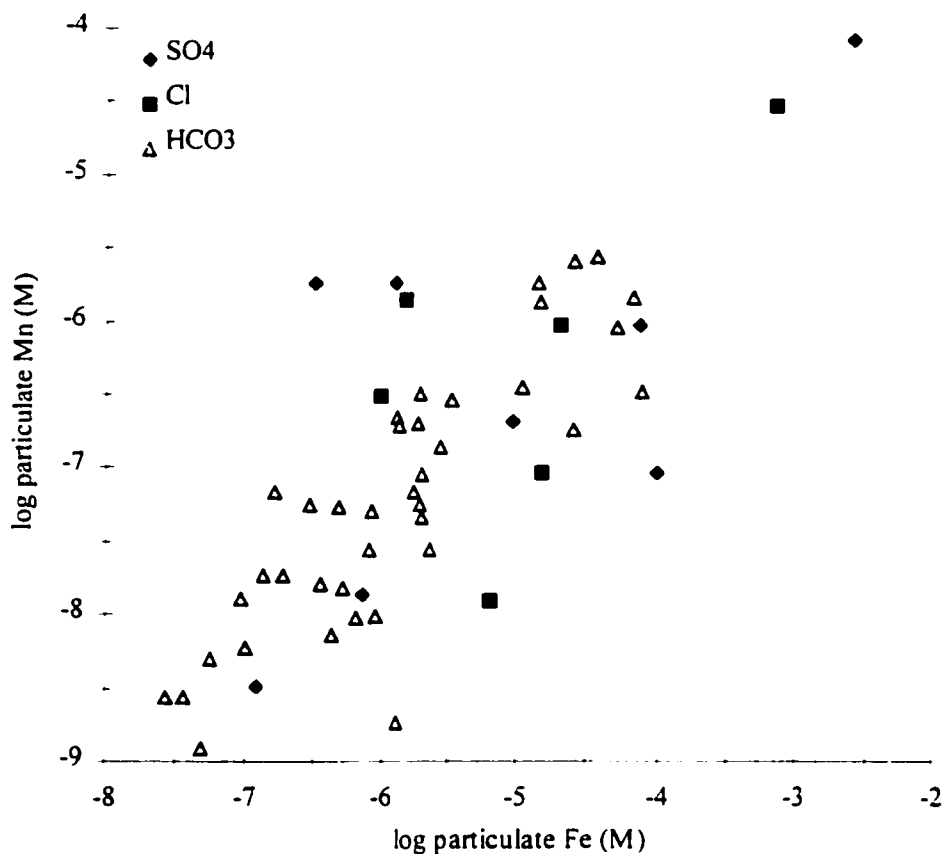


Figure 4-4 Particulate (suspended) Mn (moles) vs. particulate Fe (moles) for water types. Particulate concentration calculated as non-filtered less mean filtrate.

4.3.4 Aluminum

The aqueous hydrogeochemistry of Al is somewhat simpler than for Fe and Mn since Al exists in only one oxidation state (Al^{3+}). Aluminum has low solubility at intermediate pH, and tends to remain behind during chemical weathering (e.g. development of laterites and bauxites).

Total recoverable Al concentrations range from 5.0 to 2300 ppb, 13 to 5900 ppb, and from 1.2 to 1600 ppb for SO_4^{2-} , Cl^- , and HCO_3^- waters, respectively (Table 4-2). Median values for TR, listed in the same order, are 16, 60, and 15 ppb. Aqueous Al concentrations are low. Median values are 6.8, 12 and 4.8 ppb in the 0.45 μm aliquot for SO_4^{2-} , Cl^- , and HCO_3^- waters, respectively. Moderate to high filter retention of Al occurs in all water types. Median C_F/C_{TR} ratios within the SO_4^{2-} waters are 0.41, 0.43, 0.45, and 0.50 for the 0.45, 0.22, 0.10, and 0.05 μm pore-sizes, respectively. Ratios of filtrate to total recoverable concentrations (C_F/C_{TR}) indicate a slightly greater percent of suspended Al in Cl^- waters. Median values of C_F/C_{TR} in Cl^- waters are 0.16, 0.24, 0.22, and 0.73 for 0.45, 0.22, 0.10, and 0.05 μm pore sizes, respectively. There tends to be greater variability in the Al analyses resulting in greater variability of C_F/C_{TR} in some sites and several C_F/C_{TR} values are greater or much greater than unity. The higher $C_{F(0.05)}/C_{\text{TR}}$ value (0.73) as compared to larger filter sizes in Cl^- waters is the result of two of the five waters filtered at this pore-size have a $C_{F(0.05)}/C_{\text{TR}}$ value of >1 . Suspended Al ratios in HCO_3^- waters is similar to SO_4^{2-} waters. Median C_F/C_{TR} ratios are 0.34, 0.43, 0.36, and 0.48 for filter pore-sizes in decreasing order. A one-way analysis of variance indicates there is no difference between the C_F/C_{TR} ratios between the different filter pore sizes for all three water types (Appendix C). The 0.45 μm filter is as effective as smaller filter pore-space in removing approximately 50 or more percent of the Al. The median concentration of suspended Al in SO_4^{2-} , Cl^- , and HCO_3^- waters is 0.0066, 0.040, and 0.0092 ppm.

The phases of particulate Al could be Al-(hydr)oxides, entrained alumino-silicates, and/or Al sorbed to other solid phases. If clay minerals (e.g. illite) were present in suspension then metals would have to compete with alkali and alkaline earth elements for exchange sites on the clays (Jenne, 1968; O'Conner and Kester, 1975). Higher Na concentrations in solution

would be reflected by a greater amount of Na associated with exchange sites on the clays since metal and major cation selectivity coefficients are similar for exchange reactions, but concentrations of major cations are much greater than metal concentrations; whereas, metal distribution coefficients (K_d s) are much greater than major cations K_d values for adsorption reactions due to their ability to hydrolyze in water. Kharkar et al. (1967) found that adsorbed trace elements were always released from suspended solids in low ionic strength water upon contact with sea water due to displacement of ions by Na and Mg. There is no indication of a shift in $C_{F(0.45)}/C_{TR}$ values for metals, lower sorption in the presence of higher mole % Na in the Myra Falls waters. Lower sorption would be expected with increasing Na concentration if clays were present and Na was competing for exchange sites. Indirect evidence suggests that suspended clays likely do not contribute to measured Al retained during filtering.

Within the pH range of the waters sampled the most likely Al phase to first precipitate

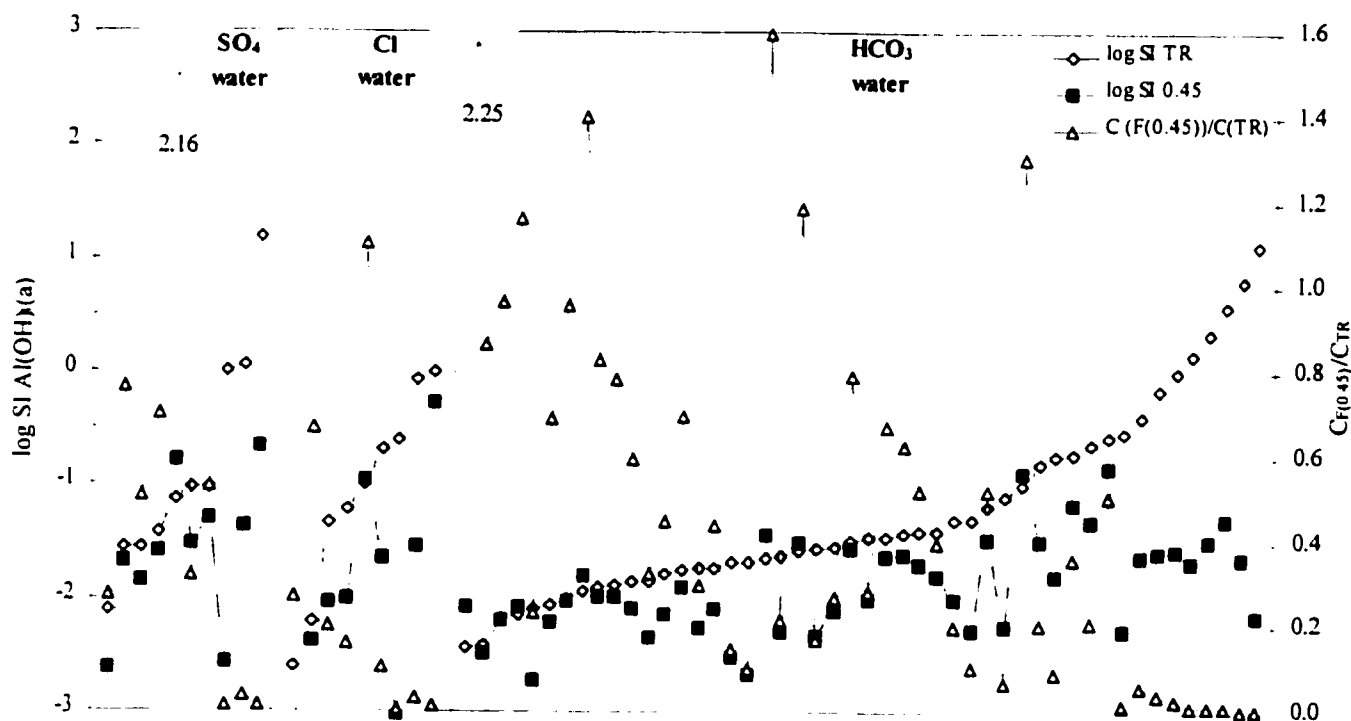


Figure 4-5 Comparison of saturation indices for amorphous Al-hydroxide and the filtration ratio $C_{F(0.45)}/C_{TR}$. Sites ordered by increasing saturation indices of non-filtered aliquot for each major water type. Above approximately $SI_{TR} -0.5$ all Al is removed by filtering

would be an amorphous Al-hydroxide. Sites that are near- or over-saturated with respect to

$\text{Al}(\text{OH})_3$ have $C_{F(0.45)}/C_{\text{TR}}$ values approaching zero indicating that $\text{Al}(\text{OH})_3$ may be a plausible phase in Al removal (Figure 4-5). In all three water types, $C_{F(0.45)}/C_{\text{TR}}$ approaches zero (removal of all Al during filtering) when $\log \text{SI}_{\text{Al}(\text{OH})_3}$ approaches -0.5. However, C_F/C_{TR} ratios are also low at many other sites where amorphous Al hydroxide is not near or over saturated suggesting that this may not be the only mode of Al removal. Where, $\text{Al}(\text{OH})_3$ is vastly under-saturated, even in the TR fraction, Al may be lost due to co-precipitation with, or adsorption to Fe (hydr)oxides.

Schulze and Schwertman (1987) demonstrated that Al has the ability to substitute for Fe up to 30 mole % in the goethite structure: and synthetic Al-goethite formed at lower temperatures (25 vs. 70 °C) was able to incorporate more Al and also had greater crystal defects. Herbert (1996) estimated that 5.5 mole % of Al was incorporated into the goethite structure in ground water polluted from a waste-rock dump in Sweden. Goethite is isostructural with diaspore ($\alpha\text{-AlO}(\text{OH})$), which may account for the high substitution. Al adsorption on goethite has been shown to occur with an adsorption edge between pH 3.5 and 4.5, (Lövgren et al., 1990) and it is suspected that the Al is adsorbing as $\text{Al}(\text{OH})_2^{+}$ onto the FeO surface. The form of particulate Al removed by filtering in the Myra Falls study has not been determined. Figure 4-6 illustrates the close relationship between the increase of Al particles to Fe particles retained in the 0.45 μm filter pore-size aliquot. There are likely a combination of sinks to account for the Al losses during filtering.

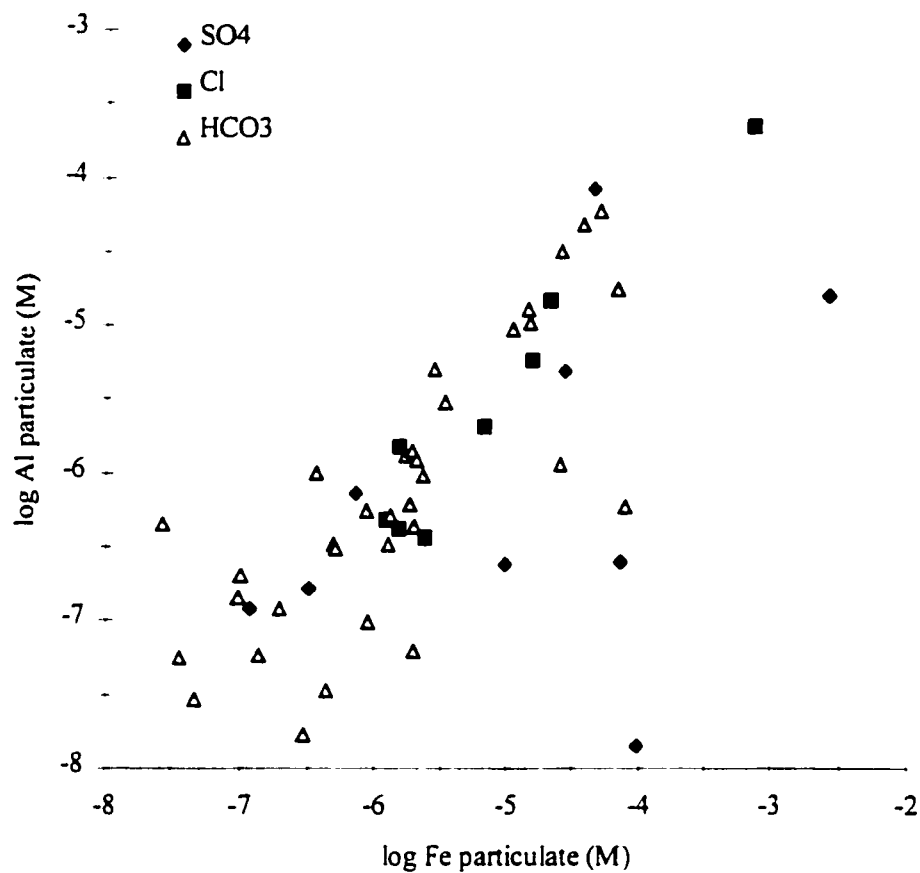


Figure 4-6 Particulate (suspended) Al (moles) vs. Fe (moles) for major water types. Particulate concentration calculated as non-filtered less mean filtrate.

4.3.5 Zinc

Zinc is one of the primary metals of interest in this study since sphalerite is the most common ore mineral in the Myra Falls deposits. The concentration of Zn in waters ranges from less than detection to 28 ppm in the 0.45 μ m filtrate (Table 4-3). Median total recoverable concentrations of Zn are 5950, 45, and 24 ppb, and 3650, 24, and 13 ppb, in the 0.45 μ m filtrate for the SO_4^{2-} , Cl^- , and HCO_3^- waters, respectively.

Precipitating phases would limit the concentration of dissolved Zn, and thereby limit the degree of sorption, since adsorption is dependent upon the dissolved concentration. The solubility of Zn in carbonate, sulphate, and chloride waters was investigated by Mann and Deutschler (1980), who suggested that zincite (ZnO), Zn(OH)_2 , smithsonite (ZnCO_3), hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$), $\text{Zn}_4(\text{SO}_4)(\text{OH})_6$, and $\text{Zn}_2\text{Cl(OH)}_3$ are possible phases that might be expected to first precipitate as secondary minerals associated with Cu-Zn-Pb ore deposits. No waters at Myra Falls were saturated with respect to these phases as calculated with the PHREEQC speciation program (Parkhurst, 1995), with the exception of hydrozincite, which is not included in the mineral database; although, PHREEQC does include $\text{Zn(CO}_3\text{)H}_2\text{O}$, which is also under-saturated for all waters. Removal of Zn from solution should be attributable to sorption on solid (Fe, Mn, Al) phases with no loss from the precipitation of secondary Zn phases.

Zinc is very-slight to moderately associated with the solids retained in the TR fraction; although, there is a great degree of variability between water types. In SO_4^{2-} dominated waters Zn is largely dissolved (Table 4-3) and although the concentrations associated with solids retained on the filter can be high, as compared to other waters, the proportion of loss is negligible to slight (Appendix C). The median C_F/C_{TR} Zn values for various filter sizes in SO_4^{2-} waters ranges from 0.94 to 0.98.

Ratios of Zn removed during filtering as compared to TR in Cl^- waters is moderate to high. The C_F/C_{TR} ranges from 0.03 to >1 (the $C_{\text{F}(0.45)}/C_{\text{TR}} = 2$ at site 3365 is likely due to contamination or analytical problems; removing this point results in a highly significant ANOVA for Cl^- waters including the non-filtered aliquot (Appendix C). The median C_F/C_{TR} Zn values for Cl^- waters are 0.54, 0.54, 0.47, and 0.49 for the 0.45, 0.22, 0.10, and 0.05 μ m

pore-size filtrates, respectively (Table 4-3). Where all pore-sizes are available for comparison, the Zn concentrations and C_F/C_{TR} are very consistent at each site.

Around 10% or less of Zn is associated with the filtered particles in HCO_3^- waters. The median C_F/C_{TR} Zn values are 0.87, 0.95, 0.95, and 0.95 for the 0.45, 0.22, 0.10, and 0.05 μm pore-size filtrates, respectively. Once again, as was seen with the Cl^- waters, there is no difference in C_F/C_{TR} ratios between filter sizes.

Where the concentration of Zn in waters is above the detection limit, the amount of Zn sorbed increases with increasing dissolved Zn (Figure 4-7). The sorption of Zn in Cl^- waters appears to have a steeper slope vs. aqueous Zn as compared with Zn sorption in SO_4^{2-} waters. The sorbed amount also increases, though with more scatter, with increasing molar $\text{Fe}_{(s)}$ (Fe-(hydr)oxide) (Figure 4-8). These controls on the sorption of Zn are greater than the relationship of sorbed Zn (C_F/C_{TR}) to pH. Waters range from pH 6 to almost 9 and the lack of sorbed relationship to pH is puzzling. Many other factors will influence the adsorption of metals including ionic strength, concentration and form of adsorbent, and water temperature (variable between sites); each of which would play a role in the lack of apparent relationship with pH. These waters would also have a much greater H^+ buffering capacity than de-ionized waters used in laboratory experiments of metal adsorption. In this study the degree of sorption of Zn, is much more dependent upon the sample matrix, the concentration of aqueous Zn, and the concentration of Fe-(hydr)oxide and shows no relationship to pH within the pH range of 6 to 9.

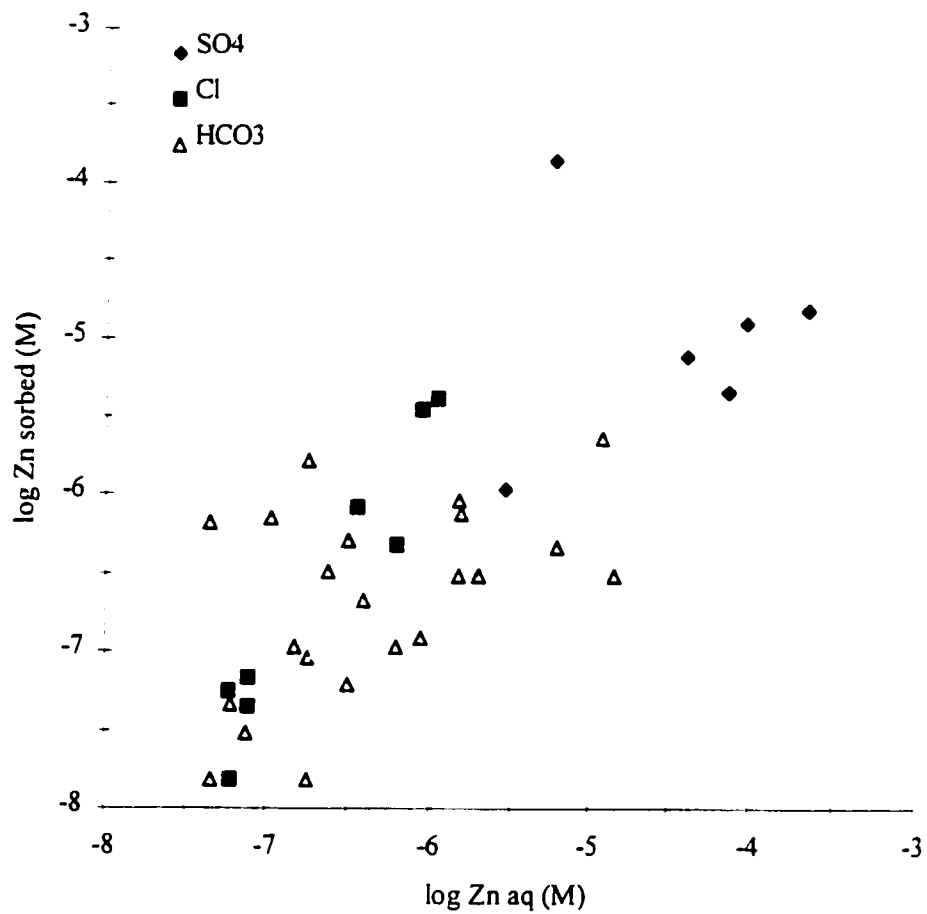


Figure 4-7 Sorbed Zn (moles; non-filtered (TR) - 0.45 μ m filtrate) vs. dissolved Zn (moles; 0.45 μ m filtrate) in major water types.

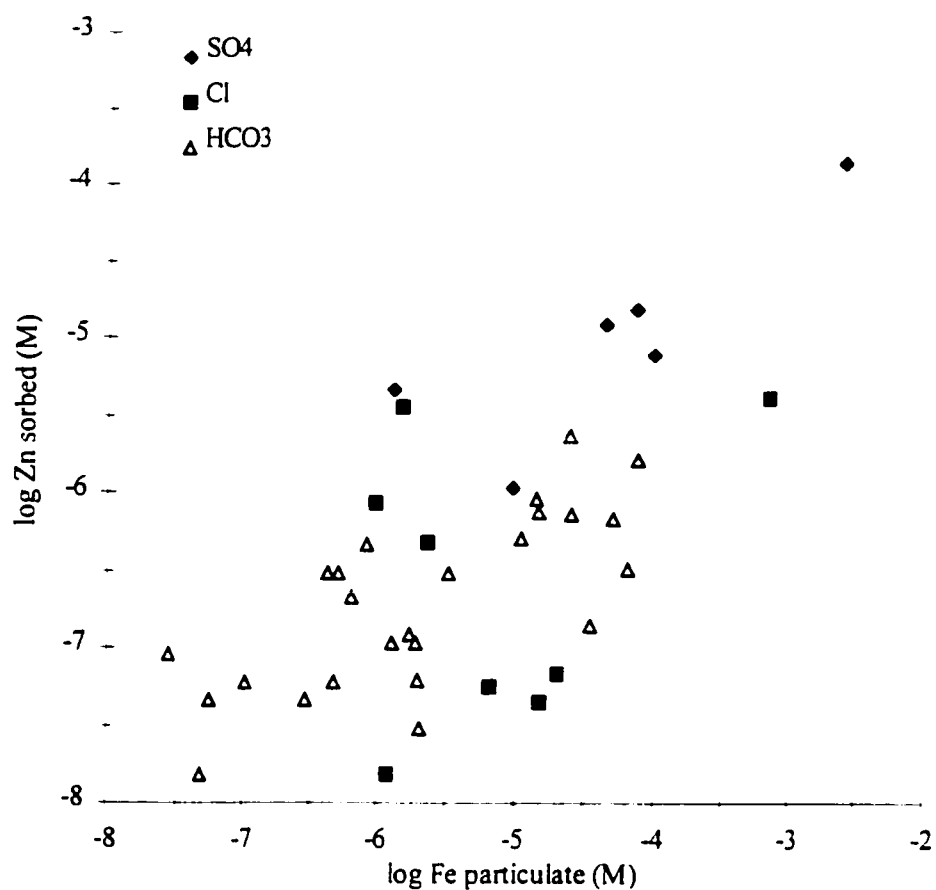


Figure 4-8 Sorbed Zn (moles; non-filtered (TR) - 0.45 μ m filtrate) vs. particulate Fe (moles; non-filtered (TR) - mean filtrate) in major water types.

4.3.6 Copper

Aqueous Cu concentrations are considerably lower than Zn in most waters. Copper concentrations in the 0.45 μm filtrate range from less than the detection limit to 82 ppb in SO_4^{2-} waters, less than detection limit to 98 ppb in Cl^- waters, and less than detection limit to 30 ppb in HCO_3^- waters. Median concentrations are: 4.2, 22, and 3.4 ppb for the TR fraction; and for the 0.45 μm filtrate are 2.9, 22, and 1.5 ppb, for the SO_4^{2-} , Cl^- , and HCO_3^- waters, respectively.

The first Cu phase to precipitate from solution would be expected to be $\text{Cu}(\text{OH})_2$ (Swallow et al., 1980); while, other secondary Cu phases that may precipitate might include antlerite ($\text{Cu}_3(\text{SO}_4)(\text{OH})_4$), brochantite ($\text{Cu}_4(\text{SO}_4)(\text{OH})_6$), atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), and malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) depending on the anion matrix (Mann and Deutschler, 1977). PHREEQC (Parkhurst, 1995) saturation indices indicate that none of these phases are over-saturated in any water. There should be no confusion about loss of Cu due to precipitation of secondary Cu minerals with losses due to sorption onto solids retained by filtration.

Copper is slightly to moderately associated with the solids in the TR fraction retained during filtration. In SO_4^{2-} dominated waters Cu is moderately associated with filtered solids. The median Cu C_F/C_{TR} values for SO_4^{2-} waters are 0.64, 0.49, 0.55, and 0.60 for the 0.45, 0.22, 0.10, and 0.05 μm pore-size filtrates, respectively (Table 4-3).

There is little sorption of Cu onto filter-retained solids in Cl^- waters. The median C_F/C_{TR} values for Cu in Cl^- water are 0.83, 0.94, 1.00, and 1.08 for the 0.45, 0.22, 0.10, and 0.05 μm pore-size filtrates, respectively. Only two Cl^- dominated waters show appreciable losses of Cu. Site 2606 has only TR and 0.45 fractions, while 2622 has a TR concentration of 1.3 ppb and filtered aliquots are quite variable with no trend. These two sites alone would lower the $C_{F(0.45)}/C_{\text{TR}}$ value to account for the higher median C_F/C_{TR} values with the larger filter size. There is little loss of Cu by sorption for most Cl^- dominated sites. Waters from 2606 and 2622 sites contain more DO than the remaining waters. Speciation calculations indicate that for the remainder of the sites the prevalent form of Cu is Cu^+ as compared to Cu^{2+} in the oxidizing sites. The lower charge on the Cu^+ ion would greatly reduce adsorption

verses divalent metals. The lower proportion of Cu sorbed in Cl^- waters is likely attributable to Cu valence.

In HCO_3^- waters Cu is moderately associated with filtered solids. The median C_F/C_{TR} values are 0.58, 0.73, 0.76, and 0.66 for the 0.45, 0.22, 0.10, and 0.05 μm filtrates, respectively. There tends to be more analytical variability in some waters with Cu concentrations nearing the detection limit. Within each of the three dominant water types there is no significant difference between the C_F/C_{TR} among the different filter pore-sizes (Appendix C). The C_F/C_{TR} ratios of removal of Cu in Cl^- waters is considerably less than for other water types which is the opposite of Zn behavior.

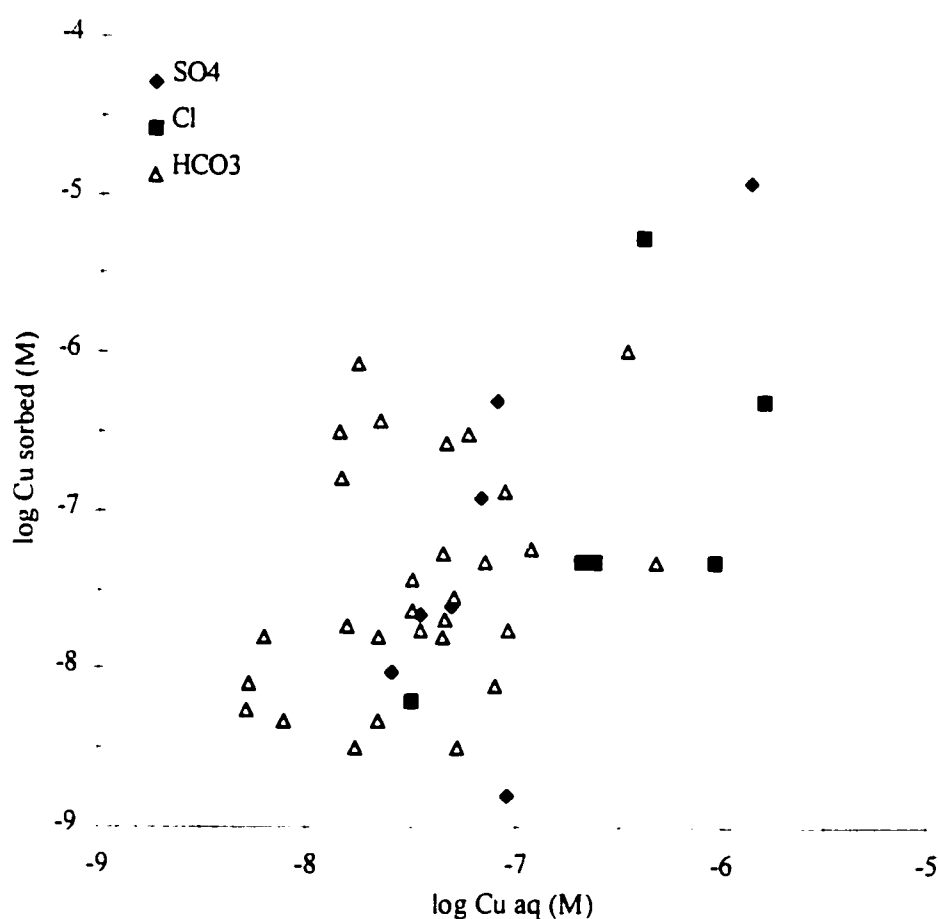


Figure 4-9 Sorbed Cu (moles; non-filtered (TR) - 0.45 μm filtrate) vs. dissolved Cu (moles; 0.45 μm filtrate) in major water types.

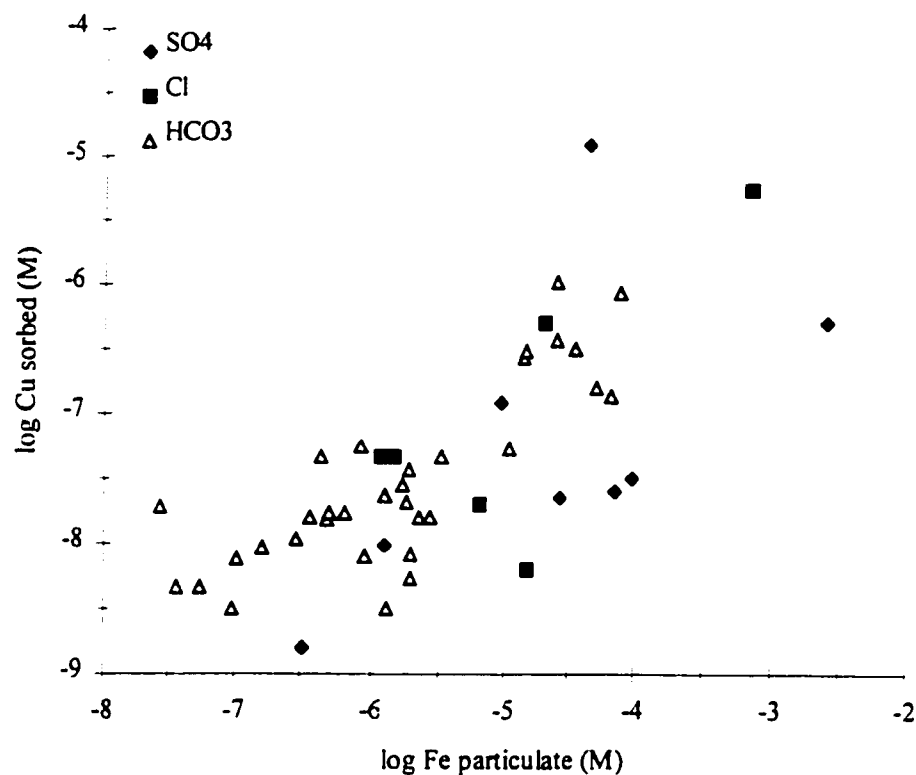


Figure 4-10 Sorbed Cu (moles; non-filtered (TR) - 0.45 μ m filtrate) vs. particulate Fe (moles; non-filtered (TR) - 0.45 μ m filtrate) in major water types.

There is less of a relationship between adsorbed and dissolved Cu as compared to Zn, especially with respect to HCO₃⁻ waters; although, SO₄²⁻ and Cl⁻ waters generally have an increased amount of sorbed Cu with increasing aqueous Cu (Figure 4-9). Bicarbonate waters show a much stronger relationship between sorbed Cu and the molar concentration of suspended Fe (Figure 4-10). In this study the degree of sorption of Cu is much more dependent upon the sample matrix, the concentration of aqueous Cu (especially for SO₄²⁻, and Cl⁻ waters), the concentration of Fe-(hydr)oxide (especially for HCO₃⁻ waters), and especially the valence of Cu. The pH of waters (6 to 9) has little control over the amount of Cu sorbed.

4.3.7 Lead

Lead concentrations are considerably lower than Zn or Cu concentrations in the 0.45 μm pore-size filtrate. Aqueous Pb concentrations range from less than the detection limit to 3.1 ppb in SO_4^{2-} waters, less than the detection limit to 1.4 ppb in Cl^- waters, and less than the detection limit to 36 ppb in HCO_3^- waters. Median concentrations are 3.9, 1.3, and 1.2 ppb for the TR fraction, and in the 0.45 μm pore-size aliquot they are 0.64, 0.41, and 0.40 ppb for the SO_4^{2-} , Cl^- , and HCO_3^- waters, respectively.

If Pb compounds were precipitating, the amount of secondary mineral caught on the filter might be considered as Pb lost to adsorption. Secondary Pb phases expected to precipitate would include $\text{Pb}(\text{OH})_2$ (Swallow et al., 1980) or, cerussite (PbCO_3), anglesite (PbSO_4), cotunnite (PbCl_2), and phosgenite ($\text{Pb}_2(\text{CO}_3)\text{Cl}_2$) depending on the anion matrix (Mann and Deutschler, 1977). No waters were saturated with respect to any of these phases as calculated with PHREEQC (Parkhurst, 1995). All loss of Pb to the filtered fraction should therefore be the result of sorption processes.

Lead is strongly associated with the filter-retained solids in all waters. The median C_F/C_{TR} Pb values for SO_4^{2-} waters are 0.23, 0.29, 0.13, and 0.32 for the 0.45, 0.22, 0.10, and 0.05 μm pore-size filtrates, respectively (Table 4-3). The median C_F/C_{TR} values for Pb in Cl^- waters are 0.25, 0.22, 0.24, and 0.44 for the 0.45, 0.22, 0.10, and 0.05 μm pore-size filtrates, respectively. The median C_F/C_{TR} values in HCO_3^- waters are 0.30, 0.50, 0.33, and 0.46 for the 0.45, 0.22, 0.10, and 0.05 μm pore-size filtrates, respectively. As with Cu, there tends to be greater analytical variability for Pb in waters with near-detection limit concentrations. This leads to some of the variability seen in the C_F/C_{TR} within each water since Pb concentrations tend to be quite low. Within each of the three dominant water types there is no significant difference between the C_F/C_{TR} for Pb among the different filter pore-sizes (Appendix C).

There appears to be no relationship between adsorbed and dissolved Pb (Figure 4-11), while there is increasing sorption of Pb with increasing Fe-(hydr)oxide concentration in all water types (Figure 4-12). The degree of sorption of Pb is much less dependent upon sample matrix, concentration of aqueous Pb, or the solution pH.

Swallow et al. (1980) have shown that sorption of Pb to $\text{Fe}(\text{OH})_{3(a)}$ decreases in Cl^- waters ($\text{NaCl} = 0.5\text{M}$) as compared to low ionic strength water; whereas, there was no decrease with Cu. It is believed that Cl^- competes successfully with Pb in forming complexes which lessen the Pb adsorption. Sorption losses of Pb in the Myra Falls waters are not markedly different between the major water types suggesting competition by Cl^- complexation in Cl^- dominated water may not be a major factor. Lead has a lower first hydrolyses constant than Zn and Cu, and has a higher percentage adsorption than Zn or Cu at a given pH. Median $C_{F(0.45)}/C_{\text{TR}}$ values for Pb at Myra Falls are in the 0.2 to 0.3 range; which is higher than the up to 100% Pb adsorption at pH 6 in studies by Coston et al. (1995). The Myra Falls results are closer to the ranges of sorbed Pb shown by Swallow et al. (1980) in which 70-90% Pb was sorbed at pH 7. Kooner (1993) showed that the percentage of Pb

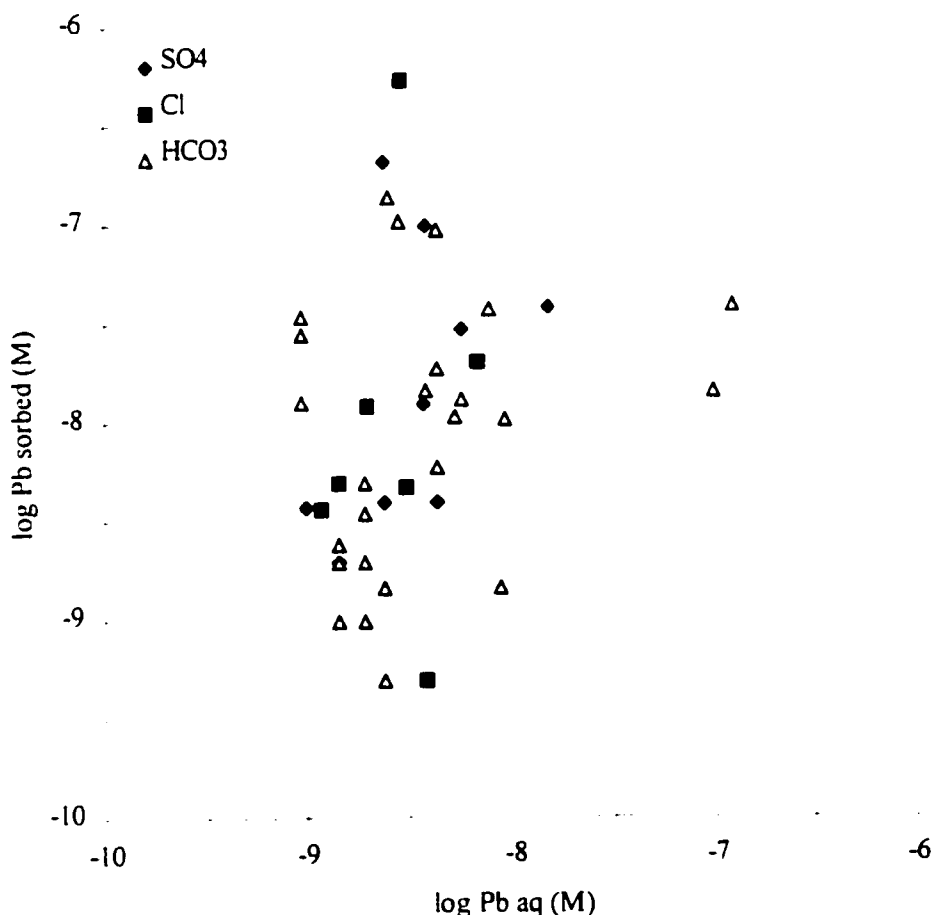


Figure 4-11 Sorbed Pb (moles; non-filtered (TR) - 0.45 μm filtrate) vs. dissolved Pb (moles; 0.45 μm filtrate) in major water types.

sorbed on goethite was dependent upon the surface area of the sorbate per volume of solution. At low $Pb_{(total)}$ concentrations (2 ppm) a lower percentage of Pb was sorbed onto $30\text{ m}^2\text{ L}^{-1}$ surface area of goethite than 60 or $120\text{ m}^2\text{ L}^{-1}$. Gadde and Laitinen (1974) have shown that Pb is very competitive for sorption sites on Mn-hydroxide, and is preferentially sorbed over Zn, Cd, and Tl, even if the other ion was sorbed first. They also showed that Pb was preferentially sorbed to Mn-hydroxide > Fe-hydroxide > Al-hydroxide at similar pH values and that 0.28 moles of Pb could be sorbed per mole of Fe^{3+} in goethite at pH 6. No waters at Myra Falls approach this molar ratio (maximum molar ratio of Pb/Fe is 0.09). Even though Pb is currently highly sorbed it is unlikely that these waters have reached the maximum concentration of Pb that can be sorbed.

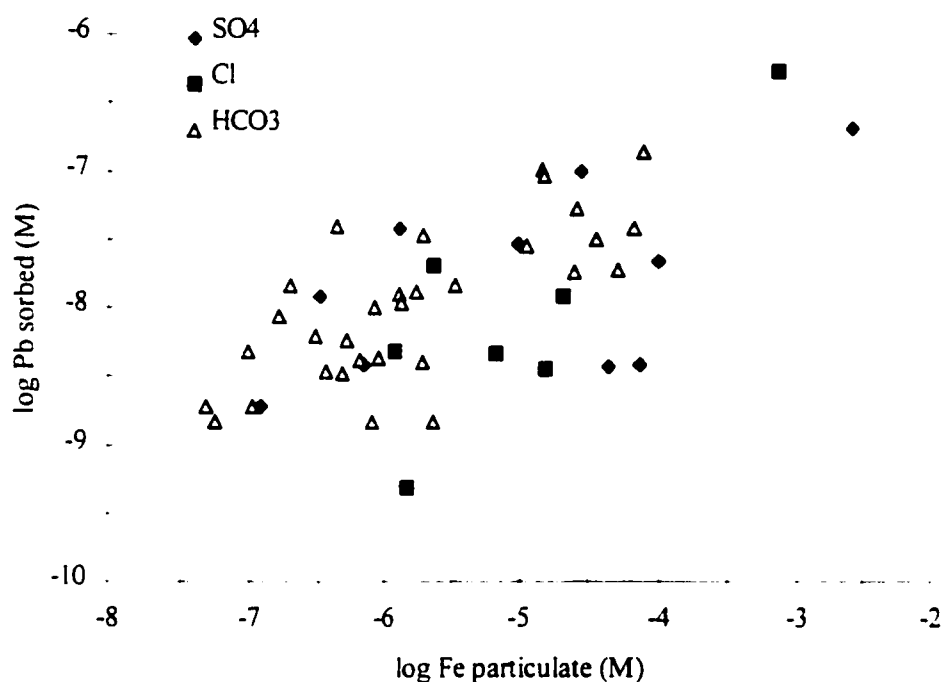


Figure 4-12 Sorbed Pb (moles; non-filtered (TR) - $0.45\mu\text{m}$ filtrate) vs. particulate Pb (moles; non-filtered (TR) - $0.45\mu\text{m}$ filtrate) in major water types.

4.3.8 Cadmium

The vast majority of waters have below detection values for Cd. The remainder generally have concentrations very close to the detection limit with the inherent problem of poorer precision (greater analytical noise) at low concentration. Fifteen waters have dissolved Cd above detection values in HCO_3^- waters. The median TR Cd concentration of these sites is 1.0 ppb, while, median C_F/C_{TR} values are very similar to Zn values in HCO_3^- waters, with median values that range from 0.86 to 0.89. Four SO_4^{2-} waters have Cd above detection, although two sites have low TR concentrations when compared to filtered aliquots. Cadmium concentrations are quite uniform in the filtered aliquots and suggest that Cd in SO_4^{2-} waters remains in solution, similar to Zn. In reducing waters, greenockite (CdS) would readily precipitate in the presence of S^{2-} which would remove Cd from water and would account for the below detection values in Cl^- waters. Otavite (CdCO_3), the only other Cd mineral in PHREEQC-WATEQ4F database (Parkhurst, 1995; Ball and Nordstrom, 1991) is under-saturated for all waters.

Table 4-2 Summary statistics for Fe, Al, and Mn concentrations (ppb) in major water types (upper) and C_F/C_{TR} (filtered / non filtered) ratios (bottom) [TR = total recoverable (non-filtered); F = filtered, 0.45, 0.22, 0.10, and 0.05 μm filtrates].

	Fe					Al					Mn				
	TR	0.45	0.22	0.10	0.05	TR	0.45	0.22	0.10	0.05	TR	0.45	0.22	0.10	0.05
SO₄ waters															
n	10	10	7	6	6	10	10	7	6	6	10	10	7	6	6
n > DL	10	8	6	5	5	10	10	7	6	6	10	10	7	6	6
Minimum	7.0	0.3	0.3	0.3	0.3	5.0	1.7	4.2	4.2	4.5	0.7	0.6	0.5	0.6	0.4
Maximum	140000	38000	36000	21000	21000	2300	32	65	59	87	5100	5000	3700	3400	3400
Median	1525	61	140	103	115	15	7	8	9	8	1700	1025	1100	1030	1040
Mean	21741	6476	8850	4452	4343	296	10	16	17	21	2175	1712	1629	1289	1292
Cl waters															
n	9	9	7	7	5	9	9	7	7	5	9	9	7	7	5
n > DL	9	7	5	6	4	9	8	7	6	5	9	9	7	7	5
Minimum	130	0.3	0.3	0.3	0.3	13	0.1	4.1	0.1	16.0	65	63	66	64	540
Maximum	39000	440	480	420	450	5900	73	32	41	57	2800	1800	1900	1800	1800
Median	410	150	63	120	160	60	12	14	12	39	1100	1100	1100	1000	1000
Mean	4793	180	179	192	198	747	22	18	14	39	1181	985	1039	1055	1166
HCO₃ waters															
n	48	48	30	33	28	48	48	30	33	28	48	48	30	33	28
n > DL	40	22	20	17	14	48	48	30	33	28	46	41	26	29	24
Minimum	0.3	0.3	0.3	0.3	0.3	1.2	1.1	2.5	1.5	1.7	0.01	0.01	0.01	0.01	0.01
Maximum	4300	50	72	64	250	1600	77	25	23	140	150	130	63	63	63
Median	45	0.3	5.0	3.0	1.7	15	4.8	5.9	5.9	6.5	4.2	1.0	1.0	1.2	1.2
Mean	414	8.1	12	8.3	19	126	7.6	7.7	7.5	14	24	8.1	5.2	5.4	5.8
C_F/C_{TR} (concentrations in filtrate/total recoverable) sites with below detection total recoverable have been removed															
	Fe					Al					Mn				
	TR	0.45	0.22	0.10	0.05	TR	0.45	0.22	0.10	0.05	TR	0.45	0.22	0.10	0.05
SO₄ waters															
n	10	10	7	6	6	10	10	7	6	6	10	10	7	6	6
Minimum		0.0001	0.004	0.002	0.01		0.01	0.03	0.03	0.03		0.12	0.71	0.86	0.57
Maximum		0.93	0.91	0.95	0.95		2.2	0.94	0.84	1.3		1.0	1.0	1.0	1.0
Median		0.31	0.71	0.54	0.53		0.41	0.43	0.45	0.50		0.98	0.97	0.99	0.99
Mean		0.38	0.54	0.46	0.48		0.53	0.49	0.44	0.52		0.83	0.94	0.97	0.92
Cl waters															
n	9	9	7	7	5	9	9	7	7	5	9	9	7	7	5
Minimum		0.0004	0.0004	0.002	0.002		0.003	0.03	0.003	0.04		0.43	0.96	0.91	0.91
Maximum		0.90	0.91	0.83	0.85		1.10	0.83	0.84	4.38		1.00	1.02	1.01	1.03
Median		0.27	0.25	0.57	0.37		0.16	0.24	0.22	0.73		0.99	1.00	1.00	1.00
Mean		0.39	0.35	0.45	0.44		0.28	0.33	0.30	1.49		0.92	1.00	0.98	0.98
HCO₃ waters															
n	48	40	25	27	22	48	48	30	33	28	48	46	30	32	27
Minimum		0.0001	0.0002	0.0002	0.003		0.004	0.004	0.01	0.01		0.003	0.003	0.003	0.003
Maximum		0.85	2.8	1.1	1.5		2.3	1.8	3.3	5.1		2.1	1.5	2.3	1.3
Median		0.03	0.16	0.05	0.05		0.34	0.43	0.36	0.48		0.39	0.57	0.45	0.40
Mean		0.11	0.36	0.19	0.18		0.49	0.52	0.57	0.75		0.45	0.51	0.54	0.46

Table 4-3 Summary statistics for Zn, Cu, Pb, and Cd concentrations (ppb) [top] and C_i/C_{TR} ratios (bottom) [TR = total recoverable (non-filtered); F = filtered, 0.45, 0.22, 0.10, and 0.05 μm filtrates].

		Zn					Cu					Pb					Cd				
		TR	0.45	0.22	0.10	0.05	TR	0.45	0.22	0.10	0.05	TR	0.45	0.22	0.10	0.05	TR	0.45	0.22	0.10	0.05
SO4 waters																					
n		10	10	7	6	6	10	10	7	6	6	10	10	7	6	6	10	10	7	6	6
n > DL		10	10	7	6	6	10	9	5	5	5	10	9	6	4	3	5	5	4	3	3
Minimum		4.0	5.0	5.0	5.0	5.0	0.60	0.02	0.02	0.02	0.02	0.70	0.02	0.02	0.02	0.35	0.05	0.05	0.05	0.05	0.05
Maximum		28000	28000	14000	11000	11000	850	82.0	120	110	110	43	3.1	5.3	2.4	3.0	17	140	140	140	150
Median		5950	3650	4700	3700	3700	4.2	2.9	1.5	1.3	1.8	3.9	0.6	0.5	0.6	0.5	0.83	0.73	1.6	14	14
Mean		7878	6700	5461	4088	4038	92	11	18	19	20	9.5	0.8	1.1	0.8	0.9	3.1	21	27	33	35
Cl ⁻ waters																					
n		9	9	7	7	5	9	9	7	7	5	9	9	7	7	5	9	9	7	7	5
n > DL		9	9	7	7	5	9	8	7	6	5	7	7	7	5	2	1	1	0	0	1
Minimum		5.0	3.9	4.2	4.5	9.0	1.30	0.02	1.0	0.02	14.0	0.02	0.02	0.02	0.02	0.02	0.05	0.05	0.05	0.05	0.05
Maximum		340	90	34	34	43	370	98	140	150	140	110	1.4	1.2	1.4	4.0	1.4	0.66	0.05	1.90	1.90
Median		45	24	5.2	14	22	22	22	17	24	54	1.3	0.4	0.3	0.2	0.0	0.05	0.05	0.05	0.05	0.05
Mean		95	34	13	16	21	74	32	41	45	58	14	0.5	0.4	0.4	0.9	0.20	0.12	0.05	0.05	0.42
HCO3 waters																					
n		48	48	30	33	28	48	48	30	33	28	48	48	30	33	28	48	48	30	33	28
n > DL		46	43	28	32	26	45	38	25	30	25	44	33	25	30	24	16	14	8	9	8
Minimum		0.1	0.1	0.1	0.1	0.1	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.05	0.05	0.05	0.05	0.05
Maximum		1200	1200	1200	1300	1300	88	30	29	30	29	36	36	36	34	33	5.2	5.9	3.5	4.1	3.8
Median		23.5	13.0	12.0	12.0	13.0	3.4	1.5	2.1	2.1	1.6	1.2	0.4	0.6	0.6	0.5	0.05	0.05	0.05	0.05	0.05
Mean		168	155	118	113	130	8.8	3.6	3.2	3.4	3.4	5.3	2.2	2.6	2.5	2.8	0.64	0.69	0.48	0.48	0.51
C _i /C _{TR} (concentrations in filtrate/total recoverable) sites with below detection total recoverable have been removed																					
		Zn					Cu					Pb					Cd				
		TR	0.45	0.22	0.10	0.05	TR	0.45	0.22	0.10	0.05	TR	0.45	0.22	0.10	0.05	TR	0.45	0.22	0.10	0.05
SO4 waters																					
n		10	10	7	6	6	10	10	7	6	6	10	10	7	6	6	10	10	7	6	6
Minimum		0.04	0.81	0.84	0.84	0.84	0.01	0.01	0.03	0.03	0.03	0.004	0.02	0.004	0.02	0.02	0.88	1.59	1.59	1.59	1.65
Maximum		1.3	1.3	1.3	1.3	1.3	4.5	0.80	0.87	1.47	1.47	0.53	0.62	0.92	0.57	0.57	70	70	70	70	75
Median		0.94	0.94	0.98	0.98	0.98	0.64	0.49	0.55	0.60	0.60	0.23	0.29	0.13	0.32	0.32	1.2	7.0	8.8	8.8	10
Mean		0.86	0.97	0.99	0.99	0.98	0.94	0.40	0.46	0.62	0.62	0.23	0.25	0.25	0.31	0.31	17	26	27	27	29
Cl ⁻ waters																					
n		9	9	7	7	5	9	9	7	7	5	9	9	7	7	5	9	9	7	7	5
Minimum		0.20	0.03	0.07	0.03	0.03	0.02	0.77	0.02	0.02	0.88	0.01	0.02	0.15	0.02	0.02	0.47	1	0	0	0
Maximum		2.0	1.0	1.2	1.1	1.1	1.0	1.1	1.2	1.1	1.1	0.89	0.41	0.33	0.73	0.73	0.47	0.47	0.47	0.47	0.47
Median		0.54	0.54	0.47	0.49	0.49	0.83	0.94	1.0	1.1	1.1	0.25	0.21	0.22	0.15	0.15	0.47	0.47	0.47	0.47	0.47
Mean		0.64	0.57	0.53	0.51	0.51	0.70	0.93	0.88	1.0	1.0	0.31	0.21	0.23	0.30	0.30	0.47	0.47	0.47	0.47	0.47
HCO3 waters																					
n		48	46	30	32	27	48	45	29	31	26	48	44	29	31	26	15	15	6	6	6
Minimum		0.01	0.01	0.03	0.03	0.01	0.01	0.02	0.02	0.02	0.03	0.002	0.002	0.03	0.03	0.02	0.07	0.08	0.08	0.08	0.08
Maximum		1.8	2.0	1.8	1.5	1.5	1.8	2.2	8.4	8.9	8.9	3.8	1.5	1.4	3.5	2.5	1.1	1.3	1.1	1.0	1.0
Median		0.87	0.95	0.95	0.95	0.95	0.58	0.73	0.76	0.66	0.66	0.30	0.50	0.33	0.46	0.46	0.89	0.87	0.87	0.86	0.89
Mean		0.77	0.90	0.94	0.94	0.87	0.58	0.72	1.4	1.1	1.1	0.47	0.55	0.86	0.86	0.56	0.71	0.82	0.76	0.76	0.76

4.4 Metal Mobility

Elements with superior mobility in the environment surrounding base-metal (Cu - Zn - Pb) deposits will be useful as pathfinder elements in mineral exploration programs. The mobility of Zn, Cu, and Pb have been estimated for different sulphide deposits in a variety of settings (Table 4-4). The applicability of metals as pathfinders will be dependent upon their concentrations and mobility in natural settings. Losses of these metals is generally due to precipitation of saturated secondary phases and/or sorption to (hydr)oxides. Zinc has superior mobility under a wide range of chemical and physical conditions in studies outlined in Table 4-4. A marked increase in Cu mobility in Cl^- waters (due to reducing conditions) is only seen in this study. The presence of Cl^- waters was not noted in any of the other studies. The decreased adsorption in Cl^- waters is in contrast to studies by Swallow et al. (1980) for amorphous Fe-hydroxides with the addition of Cl^- and Balistrieri and Murray (1982) with goethite and a synthetic sea-water, that found no decrease in Cu sorption due to increased Cl^- concentration. Swallow et al. (1980) did measure a decrease in Pb adsorption with the addition of Cl^- (0.5 M NaCl and synthetic ocean water); whereas Balistrieri and Murray (1982) did not see such an effect. Possibly the form of adsorbent, or as Balistrieri and Murray (1982) suggest the concentration of Fe-hydroxide may be the difference between the results of those studies. In the Myra Falls waters redox conditions affects the mobility of Cu in Cl^- waters; Cu^+ being less prone to sorption than Cu^{2+} .

Because the formation of oxy-hydroxides (especially Fe) is relatively quick and sorption to (hydr)oxide surfaces is generally considered to be fairly rapid, elements strongly partitioned in/on precipitating Fe-Mn-Al-(hydr)oxides could be lost from ground waters proximal to the ore and the remaining dissolved ions will quickly lose their effectiveness as pathfinders. The exception to this observation may be in cases where total ore minerals oxidized is reasonably high as compared to pyrite oxidized. This will result in low sorption of metals since the total concentration of Fe (hydr)oxides will be low.

Possibly either the TR fraction, providing there is no entrained rock-flour from drilling or re-suspended solids incorporated into the sample, could be used in hydrogeochemical exploration programs or filter-retained solids could be analysed, if enough water was processed. Higher concentrations of readily sorbed phases may act as a geochemical 'trail', with higher metal concentrations acting as a vector leading to the deposit.

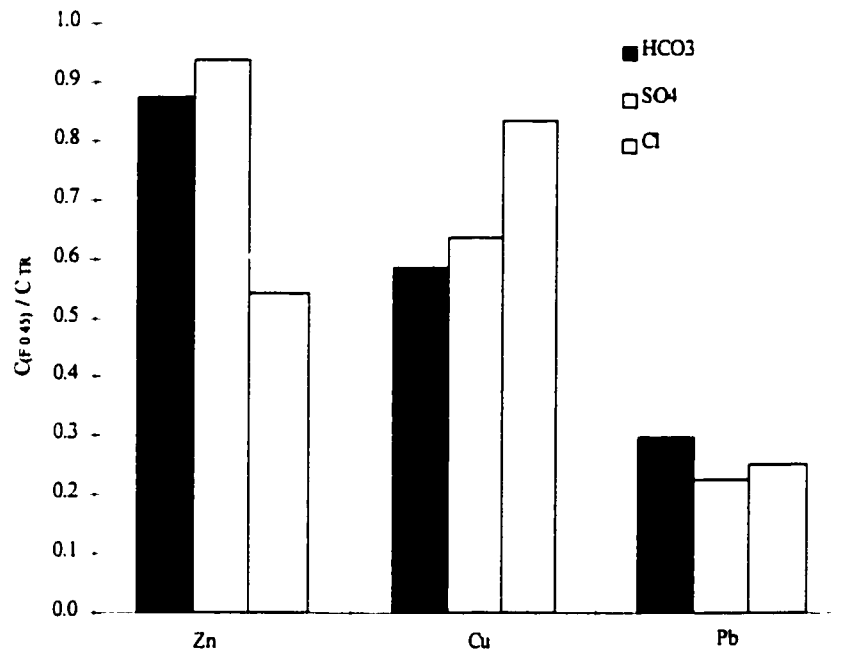


Figure 4-13 Summary median ratio values of 0.45 µm filtrate to total recoverable (TR) Zn, Cu, and Pb by water type.

Table 4-4 Comparison of element mobilities in the vicinity of sulphide minerals/deposits.

Location	Author(s)	Solution Constraints		Relative Mobility	Remarks
		pH	Matrix		
Myra Falls	This Study	6.8-8.4	[SO ₄] 110-2000mg/l [Cl] 0.4-5.1mg/l [HCO ₃] 17-430 mg/l	Zn > Cu > Pb	
Myra Falls	This Study	6.6-8.7	[SO ₄] 55-1400mg/l [Cl] 200-17000mg/l [HCO ₃] 17-150 mg/l	Cu > Zn > Pb	Lower redox conditions- predominantly of Cu ⁺
Myra Falls	This Study	6.1-8.4	[SO ₄] 1.4-92mg/l [Cl] 0.2-3.3mg/l [HCO ₃] 44-150 mg/l	Zn, Cd > Cu > Pb	
Brittany (France)	Laville-Timsit and Wilhelm (1989)	?	?	Zn > Cu, Pb	Poly-metallic deposits at several sites in Brittany. Ground waters correlate with sediment sampling Zn anomalies.
Copper Cliff (Ontario, Canada)	Coggans et al. (In Press)	3.7 to ~7	[SO ₄] <=8470mg/l	Fe, Ni, Co > Zn, Pb > Cu	Ni, Cu tailings containing sphalerite, chalcocopyrite and galena.
Huogeqi (China)	Ren et al. (1989)	6.0-8.5	[SO ₄] 500-2000 mg/l	Zn > Cu	Stratabound Cu-Pb-Zn deposit and new prospects
Glogfawr (Wales)	Andrews et al. (1984)			Zn > Cu, Pb	Indirect evidence from soil-retained metals. Zn too mobile to be used in soil sampling.
Rush-Zinc (Arkansas, U.S.A.)	Dilday (1982)	6.8-8.3	[SO ₄] <5-12mg/l [Cl] 1.1-10.2mg/l [CaCO ₃] 70-300mg/l	Zn > Pb	Mississippi Valley Type of mineralization. Pb more indicative of proximity to mineralization as Zn is more mobile
Woodlawn (N.S.W., Australia)	Giblin (1978)	6.8-8.0	DO free, and 60°C	Zn > Pb ~ Cu	Dependent upon flow rate of experiment. At low flow all metals lost.
Northampton (W.A., Australia)	Nunn and Riches (1978)	6.6 3.3		Zn > Pb > Cu Zn > Cu > Pb	
Shasta County (California, USA)	Potter and Nordstrom (1978)	2.4		Zn, Cu > Pb	
Agnicola Lake (N.W.T., Canada)	Cameron (1978)	med=6.8		Zn > Cu > Pb	Surface waters; acidic to alkaline pH show similar trend.
Captain's Flat (N.S.W., Australia)	Craze (1977)	2.9		Zn > Cu > Pb	
New Brunswick (Canada)	Govett et al. (1976)	7		Zn > Pb > Cu	
Yukon and British Columbia (Canada)	van Everdingen et al. (1985)			Zn > > Pb > Cu	Fe bearing springs from mineralized carbonates and shales, all contain Fe-oxyhydroxides and/or jarosite or gypsum precipitates

4.5 Metal mass-balance

4.5.1 Introduction

High potentiometric gradients (Stapinsky personal communication, 1997) and the associated higher flow velocities within highly permeable zones within the study, area especially in the regions influenced by mine workings may be expected to entrain suspended colloids and precipitating (hydr)oxide particles further than what may normally be expected during ground-water flow. Some of the recently precipitated (hydr)oxide particles entrained in the flow would be expected to settle-out or be naturally filtered during transport. Since suspended particles, as defined by filtration, are so efficient at scavenging metals from solution it would be expected that there would be attenuation of sorbed metals during decrease of the suspended particles load.

In the non-saline, non-reducing ground waters, the SO_4^{2-} ion should behave rather conservatively. If the only source of sulphur is from 1) input from rainfall, and 2) dissolution of minerals, primarily sulphides and barite; then a mass balance approach can be used to determine what proportion of the total metals (minerals) dissolved is represented by metals in the total recoverable (TR) fraction.

4.5.2 Method

A mole-balance approach was used to partition (allocate) S and metals present in the non-filtered (TR) aliquot to potential source mineral phases. The mineral phases and stoichiometry used are shown in Table 4-5. Arsenopyrite was chosen as the As mineral source: although, tennantite is present within the ore (Wilson, 1993; Pearson, 1994). This choice may slightly underestimate the moles S accounted for by measured metals within the sample; however, allocating all the As into tennantite only accounts for an average of 0.04 additional moles of S removed.

The only common SO_4^{2-} mineral that is saturated ($\log \text{SI} > 0$) in the $0.45\mu\text{m}$ aliquot (SI calculated with PHREEQC; Parkhurst, 1995) is barite. The amount of SO_4^{2-} lost from

solution by precipitating barite would be balanced by the SO_4^{2-} gained from the original dissolution of barite less the moles of Ba left in solution. This assumes that barite is the only, or at least the most common source of Ba in solution. The common ion effect of additional SO_4^{2-} entering the solution from sulphide dissolution would lower the amount of Ba in solution through additional precipitation of barite as sulphides are dissolved. It is unlikely that there would be any other sink for SO_4^{2-} under oxidizing conditions.

Moles of S were proportioned into the minerals listed in Table 4-5. All Ba was partitioned into barite. Zn and Cd into sphalerite, Pb into galena, Sb and the corresponding Cu into tetrahedrite, As into arsenopyrite, the remainder of Cu not allocated for tetrahedrite into chalcopyrite, and the remainder of Fe not partitioned into sphalerite, arsenopyrite, and chalcopyrite was partitioned into pyrite. The equation used to determine the moles of S excess not accounted for by metals in the TR fraction is:

$$[\text{S}]_{\text{excess}} = [\text{S}]_{\text{dissolved}} - [\text{Ba}] - ([\text{Zn}] + [\text{Cd}]) - [\text{Pb}] - \frac{13}{4}[\text{Sb}] - [\text{As}] - 2([\text{Cu}] - 3[\text{Sb}]) - 2([\text{Fe}] - ([\text{Zn}] + [\text{Cd}]) - [\text{As}] - ([\text{Cu}] - 3[\text{Sb}]))$$

Where [] designates molar quantities.

Table 4-5 Mineral phases and stoichiometry used for S mass-balance, and comparisons to the composition of HW ore samples from Wilson (1993).

Minerals	Stoichiometry used in calculation	Stoichiometry (Wilson)
Barite	BaSO_4	--
Sphalerite	$(\text{Zn,Cd})\text{S}$	$(\text{Fe}_{0.01}\text{Zn}_{0.98}\text{Cu}_{0.004})\text{S}$
Galena	PbS	
Tennantite	--	$\text{Fe}_{0.81}\text{Cu}_{0.83}\text{Zn}_{1.24}\text{Sb}_{0.24}\text{As}_{3.7}\text{S}_{13}$
Tetrahedrite	$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$	--
Arsenopyrite	FeAsS	--
Chalcopyrite	CuFeS_2	CuFeS_2
Pyrite	FeS_2	$\text{Fe}_{1.02}\text{S}_2$

4.5.3 Results and Discussion

Approximately 6% of the SO_4^{2-} in solution can be assigned to the total metal load of the TR aliquot (Figure 4-14). The mole imbalance between S and metal can be explained by; 1) another SO_4^{2-} source which is not being accounted for and/or 2) the metals accompanying the original dissolution of sulphides have been greatly attenuated along the flow path due natural filtering of particles laden with sorbed metals and/or 3) other sinks exist for the metals in question. Calculated SI indicate there are likely no phases limiting the solubility of As, Pb, Cu, or Zn.

Particle aggregation and/or settling (natural filtering) of suspended (hydr)oxide colloids during transport may influence the concentration of particles transported and hence also any sorbed metals. Colloid removal by capture on fixed surfaces is controlled by Brownian motion of the colloids and the efficiency of attachment after colloid-surface contact (Buddemeier and Hunt, 1988). The transport of latex microspheres was studied by Harvey (1989) who showed that removal of particles during transport in a sandy aquifer with a flow velocity of 0.33 m day^{-1} decreased with increasing particle size ($1.35 \mu\text{m} > 0.91 \mu\text{m} > 0.23 \mu\text{m}$). The fraction of particles removed from a sampling well 6.9 m from an injection well as compared to particle concentrations injected ranged from 0.0001 to 0.031. Attenuation within the aquifer was $\geq 97\%$ for all sizes of spheres under natural gradients. The inverse relationship between the size of the synthetic microspheres and attenuation is believed to be the result of colloid filtration (collector theory, Yao et al., 1971). Smaller microspheres contact and sorb to stationary surfaces with greater frequency than larger sizes due to a greater impact of Brownian motion during transport, especially during gravitational settling. The attenuation of microspheres in the study by Harvey (1989) is in close agreement with the excess S as compared to metals in the Myra Falls waters.

Loss of small colloids during transport may explain why the bulk of suspended (hydr)oxides in the Myra Falls ground waters are retained during processing through the largest filter size ($0.45\mu\text{m}$) and also the mass-balance deficit of metals vs. SO_4^{2-} in solution. Iron (hydr)oxides and/or Al-(hydr)oxides may also coat minerals along the transport route leading to a loss of metals including Fe during transport. Albeit, oxy-hydroxides have a greater surface area than alumino-silicates and quartz per unit mass; alumino-silicates would

likely have a far greater total surface area in contact with water in which to react. Quartz with thin surface coatings of Fe and Al bearing minerals of variable composition were found to be very efficient scavengers of Zn (85%) and Pb (90%) due to their ubiquitous nature in a sandy aquifer (Coston, et al., 1995). The attenuation of metals during transport may be strongly affected by (hydr)oxide coatings on common minerals along the flow-path. The combination of these mechanisms, natural filtration/particle settling coating common minerals, may greatly reduce the total metals being delivered into the drift openings of the mining complex. These processes alone are likely responsible for the attenuation of the majority of metals, assuming that the degree of sorption along the flow path is in the same proportion as that calculated for metals at the sampling sites.

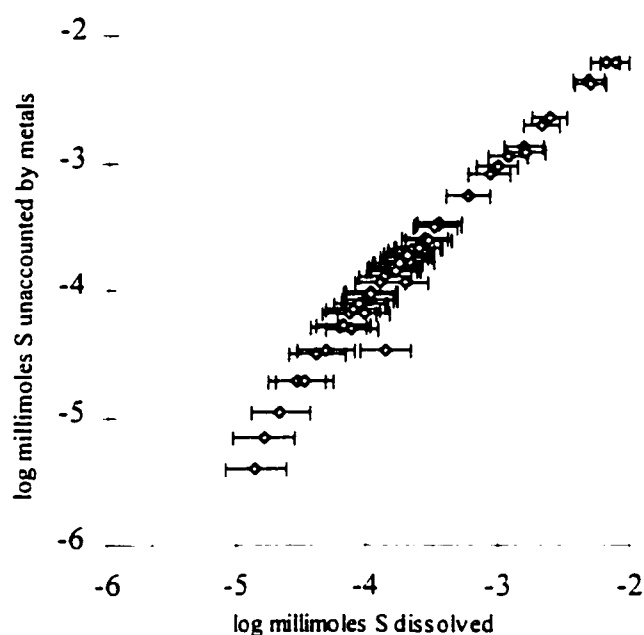


Figure 4-14 Plot of S dissolved not supported by metals vs. total dissolved S. Only about 5% of the dissolved S in solution can be accounted for by the metals in the total recoverable fraction and therefore approximately 94% of the dissolved S (sulphate) is not stoichiometric balanced by metals.

4.6 Conclusion

For ground waters in the Myra Falls mining complex, the 0.45 μ m pore-size filter removes most suspended Fe-Mn-Al (hydr)oxides particles. The presence of mainly the large colloids may be due to: 1) enhanced Fe-(hydr)oxide formation due to the presence and catalytic effect of Cu, 2) the low concentrations of DOC in these waters, 3) colloidal filtration of the smaller fraction of (hydr)oxides along the flow-path, or 4) a combination of some or all of these processes.

The adsorption of a metal is also dependent upon the charge of multivalent metals. In reducing conditions a lower charge to radius ratio will result in lower sorption as seen in Cu in reducing conditions of Cl water.

The formation of Fe-Al-(hydr)oxides likely occurs in the presence of metals in solution which may account for the high degree of metal loss from solution. The fate (retardation) of metals in ground water at normal ground water gradients may be greatly influenced by the formation of Fe-hydroxides. The strong role of Fe-hydroxides in metal transport may in part be due to the enhanced kinetics of Fe oxidation in higher pH waters. The rate of Fe oxidation increases 10^2 times for each rise in pH since the hydrolyzed Fe reacts faster with O_2 than the non-hydrolyzed Fe (Stumm and Morgan 1996).

Goethite and amorphous Fe(hydr)oxides are present in acidic drainage at Myra Falls and high concentrations of metals are sequestered by the Fe-(hydr)oxide structure even at low pH.

In this study of metal transport in natural mine waters, it has been shown that amorphous Fe-(hydr)oxides +/- Al-(hydr)oxides can act as major sinks of Pb and Cu (SO_4^{2-} and HCO_3^- waters), and Zn (Cl^- waters). A small portion of the (hydr)oxides which are formed within the oxidizing waters are then transported to drift openings under the hydraulic conditions present at Myra Falls. Likely a much greater proportion of metals are removed from the water before being delivered into the drifts. Under the natural conditions at Myra Falls sorption of Zn and Cu is highly dependent upon the solution matrix and suspended Fe concentration. The sorption of Pb is greater than Zn and Cu and is affected little by the solution matrix. In HCO_3^- waters the extent of metals sorbed to particles is $Pb > Cu > Cd \sim Zn$; which follows the order of first hydrolyses for these metals. In SO_4^{2-} waters the order is

$Pb > Cu > Zn$; while, in Cl^- waters it is $Pb > Zn > Cu$ (Figure 4-13). The order of element mobility has implications toward understanding of the natural in situ metal attenuation and metal transport of pathfinder metals used in hydrogeochemical prospecting in different ground water facies, as well as in studies of the environmental impact of metals emanating from the sulphide deposits.

The total metal loading of waters is greater than that of the dissolved metal load. Environmental planning and decision making based only on the dissolved metal load may overlook the effects on aquatic life after mine waters have been delivered to water bodies. Mine waters from the upper levels of the Price deposit (4, 5, and 9) are released untreated into the surface environment. The presence of atmospheric oxygen would stabilize (hydr)oxides which would remain in the surface environment on rocks and soil. Price 13 level drains into Thelwood valley into a dry pond with a coarse rock bed. Water quality may be affected downstream of effluent if changes in redox conditions occur. This may result during sedimentation or in anoxic bottom waters of Buttle Lake. As seen in reducing waters Cu will be less strongly partitioned onto Fe hydroxides and will be released into interstitial sedimentary water or lake water.

For non-turbid samples, total recoverable (non-filtered) samples may be an alternative for multi-element hydrogeochemical prospecting as compared to filtered waters. Since non-filtered samples were not collected at all sites the preferred element for hydrogeochemical exploration is Zn due its ability to remain in solution under the conditions (aerated and dominantly bicarbonate-sulphate anion composition) encountered in the Price area mine waters verses other metals associated with the Price ore deposit.

5. Chemical Speciation: As and S

5.1 Introduction

Many elements that occur in waters have more than one oxidation state. The oxidation state of an element in natural systems will be sensitive to the redox conditions of the water and may be modified or controlled by biologic activity, or redox reactions may experience kinetic hindrances. Either of these processes may keep a redox couple in disequilibrium with other species or with the solution as a whole. The redox state of elements is of considerable interest in ground and surface water studies, because it often determines the chemical behavior of an element.

Two redox couples, As(V)/As(III) and S(VI)/S(-II), were investigated in selected waters from the Myra Falls study area to determine predominant oxidation species and the relationship between different couples. Preliminary work on a third redox couple, Fe(III)/Fe(II) (ferrozine spectrophotometric method), was discontinued due to poor analytical results. The main cause of the poor results was likely do to the very limited holding time before analysis (preferably <60 min), and to Cu^+ and Cu^{2+} interference (Ball and Nordstrom, 1982; Stookey, 1970). Sampling logistics were such that the holding time could not be met from the time of sampling to time of analysis. Sulphide-sulphate redox measurements were also unsatisfactory for reasons discussed in a subsequent section (Section 5.3).

Chemical data for individual sites is listed in Appendix F and Appendix A. Refer to page F1, Appendix F, for materials and methods used in this chapter. Computed As molalities using p_e from As(V)/As(III) ratios and saturation indices of various As-bearing phases are given in Table D2, Appendix D.

5.2 Arsenic

5.2.1 Introduction

Arsenic is stable in four oxidation states (+5, +3, 0, and -3) (Ferguson and Gavis, 1972). Metallic arsenic occurs only rarely; and As^{-3} occurs in only very reducing conditions. Arsenic in most aqueous solutions exists in the As^{3+} and As^{5+} oxidation states. Arsenic(V) (arsenate) species are prevalent in oxidizing conditions and cover a large stability field (Figure 5-1). Arsenic(III) (arsenite) is dominant in reducing conditions especially above the sulphate-sulphide redox boundary. In low redox settings and in the presence of sulphide, As will be removed from the system as various As-sulphide minerals (i.e. Realgar, AsS ; Orpiment, As_2S_3 ; Tennantite, $(\text{Cu,Fe})_{12}\text{As}_4\text{S}_{13}$), or as elemental As. The predominant aqueous As species are $\text{As}(\text{OH})_3^0$, $\text{As}(\text{OH})_4^-$, and the arsenates, $\text{H}_n\text{AsO}_4^{n-3}$ ($n = 0$ to 3). With the exception of H_3AsO_3^0 and $\text{As}(\text{OH})_3^0$, all of the dominant As species are anions.

Thermodynamically, Fe and Mn (oxy)hydroxides and molecular oxygen can oxidize As^{3+} (Oscarson et al., 1981; De Vitre et al., 1991). However, the oxidation of As^{3+} by oxygen at neutral pH is kinetically slow (Cherry et al., 1979). Results of studies of the oxidation of As^{3+} by iron (oxy)hydroxides have been inconsistent. Oscarson et al. (1980) found no oxidation of As^{3+} with a prepared Fe(III) oxide at near neutral pH. Whereas Cherry et al. (1979) found oxidation of As^{3+} in highly acidic solutions ($\text{pH} = 2$), but no oxidation at neutral pH. Using natural and prepared Fe (oxy)hydroxides, De Vitre et al. (1991) measured appreciable rates of As^{3+} oxidation (50-75%) invariant of pH. These authors attributed the discrepancy between their findings and those of Oscarson et al. (1980) primarily to the very high Fe:As ratios that they had used (3,400:1). These high ratios were representative of natural conditions found in shallow lake bottom sediments of their study. Arsenic is also oxidized by Mn, and in experiments of Oscarson et al. (1981) up to approximately 20% of the MnO_2 present was reduced during As oxidation. The resulting As^{3+} is more soluble and more mobile than As^{5+} compounds (Thanabalasingam and Pickering, 1986). It is believed that Mn hydroxides are the primary oxidants of As^{3+} in sediments and solution (Oscarson, et al., 1980; Korte and Fernando, 1991) and is more thermodynamically favourable than oxidation by Fe hydroxides.

Arsenic can be removed from the ground water domain by co-precipitation and adsorption to iron, manganese, and aluminum hydroxides, ion exchange with clays, or, by precipitation of As-sulphides (Anderson et al., 1976; Frost and Griffin, 1977; Davis et al., 1989; CEPA, 1993; Cheng et al., 1994; Scott et al., 1995). Results of these studies are contradictory in identifying the preferred As species adsorbed. Arsenic (V) is believed to be more readily adsorbed than As^{3+} species (Ferguson and Gavis, 1972; De Vitre et al., 1991) and therefore As^{3+} is generally felt to be more mobile in the ground water domain. However, Pierce and Moore (1980) indicated that arsenite was adsorbed to Fe-(oxy)hydroxides, using low concentrations of arsenite (10^{-7} to 10^{-5} M) and that maximum adsorption occurred at pH 7. It appears that both arsenite and arsenate can be sorbed to amorphous (oxy)hydroxides, and the differential magnitude of adsorption for these two species may depend on the individual setting.

Conversely, arsenic can be added to the ground water through the dissolution of Fe and Mn (oxy)hydroxides containing sorbed As, following redox decreases. This can result in high concentrations of As released to ground waters (Korte, 1991; Korte and Fernando, 1991; Masscheleyn et al., 1991).

Although arsenic can be cycled by biologic activity (Cullen and Reimer, 1989), in the vicinity of base-metal deposits or mining/processing activities arsenic would be expected to be mostly in the inorganic form (CEPA, 1993). In ground water environments, As is primarily present as inorganic species (Korte, 1991; Masscheleyn et al., 1991); biologic activity in As redox reactions is more important in surface water environments.

The study of arsenic in the natural environment goes beyond the study of redox-couples and equilibrium reactions. Arsenic is a known toxin and a suspected carcinogen (Ferguson and Gavis, 1972; CEPA, 1993). Relatively, high concentrations of arsenate have been consumed without known deleterious effects, whereas low doses of As have proven to be fatal (Ferguson and Gavis, 1972). In humans, aqueous arsenite compounds are reportedly 25 to 60 times more toxic than arsenates (Ferguson and Gavis, 1972; Korte and Fernando, 1991). For this reason developing an understanding of arsenic species in natural settings is important in understanding As cycling, toxicity, and mitigation.

Concerns regarding arsenic in the environment have recently been addressed by the Canadian Environmental Protection Act (Guidelines Division) which is currently in the

process of lowering the maximum total arsenic that can be released to freshwater aquatic life to 5 ppb from the current 50 ppb value (U. Schneider, personal communication). However, the Canadian regulatory process has to this time not addressed the toxicity differences between the various oxidation states, and under the current and pending guidelines no provisions are made for the various As species.

Since the inorganic arsenic species are relatively stable they are very well suited to redox-couple studies in natural ground water systems containing As (Cherry et al., 1979; Mok, et al., 1988).

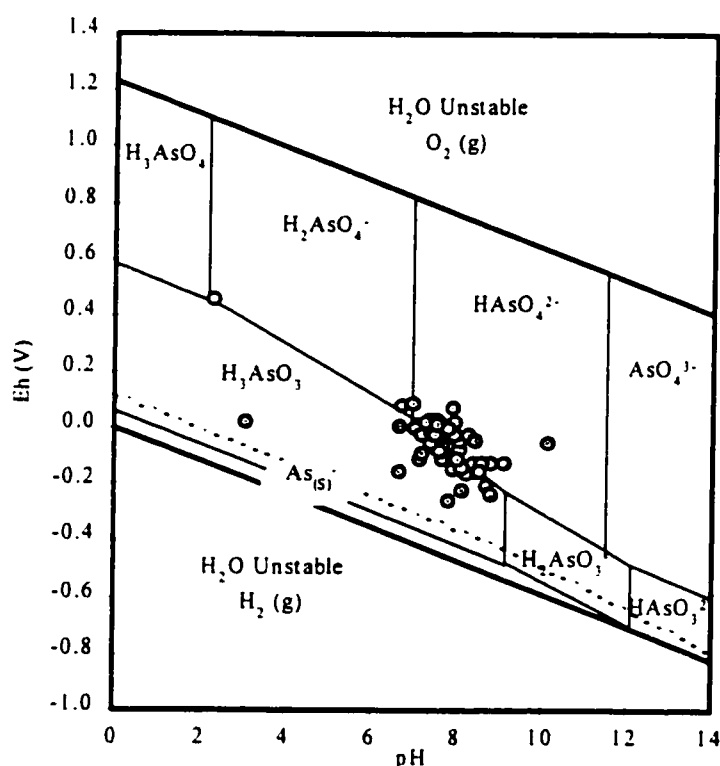


Figure 5-1 Eh-pH diagram for the systems As-O-H using thermodynamic equations from Cherry et al., 1979. Plotted Eh values are calculated from the As(V)/As(III) redox couple. Dashed line at bottom represents aqueous As(III) equal to 10^{-3} m which is within the range of As concentrations of high As(III) waters.

5.2.2 Controls on Arsenic Speciation and Arsenic attenuation (adsorption and precipitation)

The predominant arsenic sources within the study area are massive sulphides and argillaceous sedimentary units within the mine stratigraphy (Table 1.2). These sources have As concentrations between 150 and 350 ppm. Other stratigraphic units within the mine sequence have whole rock As concentrations less than 20 ppm, with typical values around 4 ppm. The predominant arseniferous minerals include arsenopyrite and tennantite.

Arsenic concentrations range up to 377 ppb in waters sampled for As speciation. Chloride dominated waters contain the highest concentrations of As. High arsenic levels tend to be predominantly As(III), although there are waters with high As(V) concentrations as well (Figure 5-2).

The As concentration of ground waters in the Price area is not systematically related to the concentrations of economic minerals as a whole. Nor, do As speciation ratios, for mineral exploration, correlate spatially to mineralization. However, total As concentrations can be used as an anomaly enhancement pathfinder in waters which already have anomalous zinc concentrations (see Chapter 7 Ground Water Hydrogeochemical Exploration Methods). There is no overall relationship between As(V) / As(III) ratio and metal content (Zn, Cu, Pb, and Cd; individually, or combined). The lack of consistent correlation between total As and Zn (mineralization) is due to the fact that As is not only concentrated in massive sulphides but is also elevated in argillaceous sediments.

There is a wide distribution of As(V)/As(III) ratios (range is $\sim 10^4$) in ground waters from Myra Falls. Generally As(V)/As(III) decreases with increasing As concentration in Cl^- waters, many SO_4^{2-} waters, and a few HCO_3^- waters (Figure 5-2). The species distribution in HCO_3^- waters is very censored since many of these waters have As^{3+} below detection.

There is no relationship between As species ratios and pH, or with dissolved oxygen (DO). The lack of relationship between As species and DO is likely due to the very slow kinetics of As oxidation by DO, while DO is consumed during other reactions (i.e. those outlined in Table 3-2).

There is a tendency of increasing As(V)/As(III) ratio with increasing measured Eh (Figure 5-3). This indicates that As(V)/As(III) ratio is sensitive to bulk redox conditions within the water (or that As contributes to the measured redox). However, Eh calculated from As species tends to be lower than measured redox values (Figure 5-7).

Four Cl⁻ and two SO₄²⁻ waters have much greater As(V)/As(III) than the majority of Cl⁻ waters (Figure 5-2 and Figure 5-3). These anomalous As ratios may result from poor

preservation, dissolution of Fe-(oxy)hydroxides releasing As⁵⁺ to the water, or mixing of waters, one containing a high As⁵⁺ end-member.

In an earlier study of mine effluent waters, Mok et al. (1988) found high As(V)/As(III) ratios corresponded to acidic waters with high metal loads. Acidic waters will promote the oxidation of As³⁺ (Cherry et al., 1979). In Myra Falls waters acidic ground waters are dominated by As⁵⁺ but to a lesser extent than many other oxidizing waters.

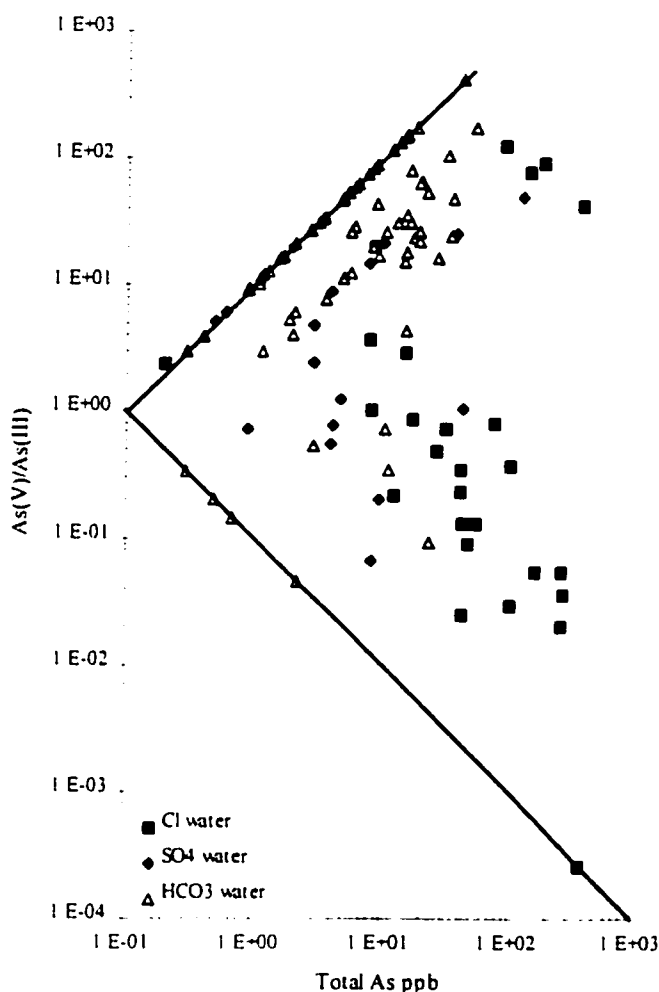


Figure 5-2 As(V)/As(III) vs. total As concentration. A very wide range of species ratios and concentrations are present in the Myra Falls waters. Waters plotting along bold lines are censored due to the choice of 0.1 ppb As for values of either species below the detection limit. The 1 σ error plots within symbols.

5.2.2.1 Controls on Arsenic Concentrations and As(V)/As(III) Ratios

The dominant controls on As concentration once arsenic has entered ground waters are the sorption and co-precipitation of arsenic to Al, Fe, and Mn (oxy)hydroxides (Anderson et al., 1976; Pierce and Moore, 1980), and the precipitation of arsenite sulphides or arsenates such as $\text{Mn}_3(\text{AsO}_4)_2$ (Cullen and Reimer, 1989; Masscheleyn et al., 1991).

All waters are undersaturated with respect to $\text{Mn}_3(\text{AsO}_4)_2$ (calculated with PHREEQC; Parkhurst, 1995). While virtually all waters are saturated with respect to $\text{Ba}_3(\text{AsO}_4)_2$ (maximum SI > 14). Cullen and Reimer (1989; and references therein) dispute the thermodynamic data for this phase and suggest there is no geologic evidence that it exists. For oxidizing waters at Myra Falls there does not appear to be a precipitating arsenate phase controlling the As concentration.

In reducing waters precipitating arsenite species include the As-sulphide minerals Orpiment (As_2S_3) and, at higher pH, Realgar (AsS). There is also the possibility of soluble

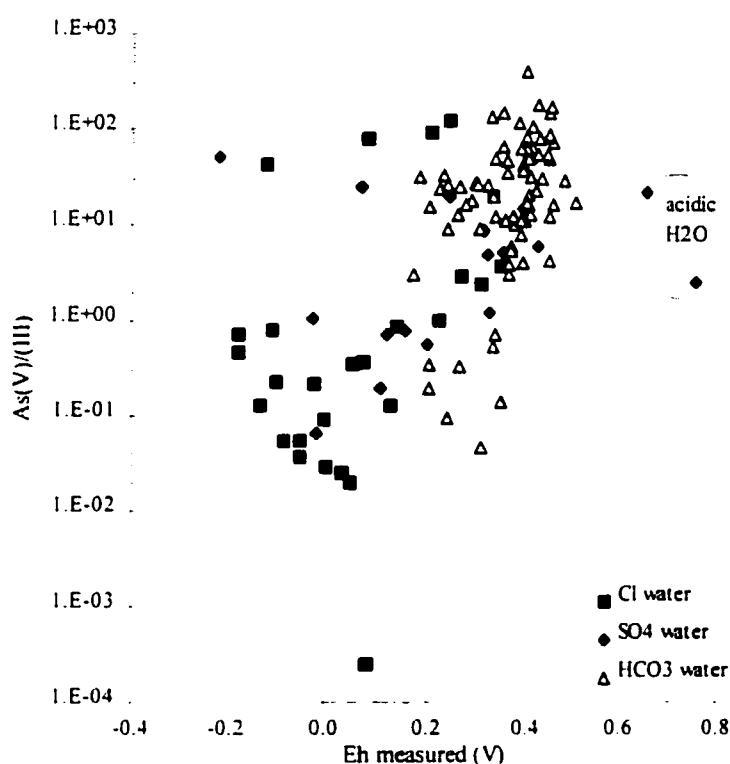


Figure 5-3 As(V)/As(III) vs. measured Eh.

sulphide polymers existing in solutions at low Eh especially in neutral to alkaline solutions (Cullen and Reimer, 1989). Saturation indices of Realgar are all below 0 (calculated with PHREEQC; Parkhurst, 1995). Virtually any sulphide and As^{3+} in the water results in oversaturation values with respect to Orpiment ($\log K = -60.8$). As is noted below (Section 5.3), sulphide determinations suffer from poor reliability. The precipitation of AsS would preferentially remove As^{3+} from water, although competition

from other ions for S^{2-} may limit the extent that this reaction controls the As concentration (Cullen and Reimer, 1989). Some waters have a distinguishable H_2S odour and other ground waters have elevated $\delta^{34}S_{SO_4}$ indicating SO_4^{2-} reduction is occurring (Section 2.4.3). In these waters the precipitation of orpiment is a possible mechanism for removal of As. However, arsenic concentrations tend to be highest in reducing waters and therefore the precipitation of AsS likely has little control on the As concentrations in these waters (Figure 5-4).

Arsenic(III) and As^{5+} species can be sorbed to Fe (oxy)hydroxides. Many factors will affect the degree of sorption (see Section 4.1) including the physical characteristics of the adsorbent, pH of the water, and competition from other ions and complexes. In the previous chapter (Chapter 4) it was shown that the majority of suspended solids in ground waters were Fe (oxy)hydroxides. In waters from Myra Falls the relationship between As species ratios and suspended Fe is not straight forward, but there is a tendency toward decreasing As concentrations with increasing suspended Fe at high Fe concentration. This trend is evident in HCO_3^- waters with suspended Fe concentrations greater than approximately 20 ppb Fe.

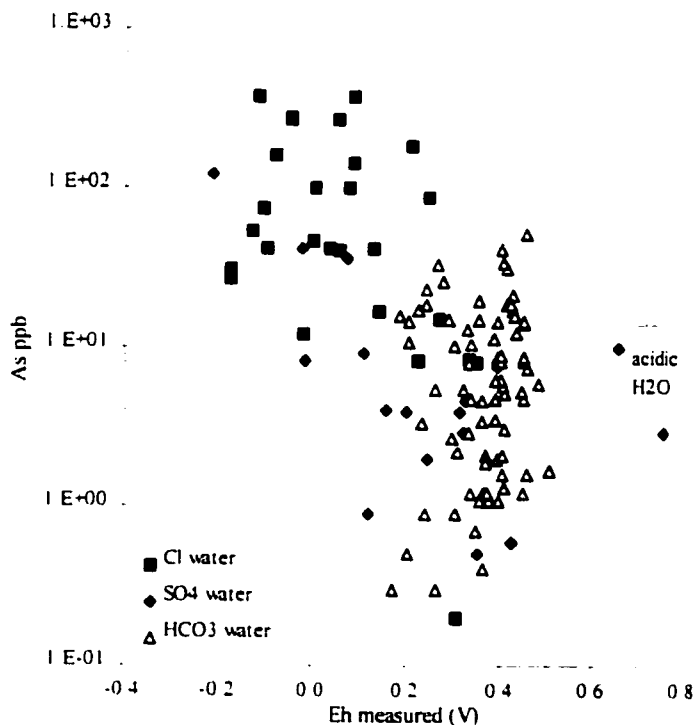


Figure 5-4 Total arsenic concentration vs. platinum electrode Eh.

Suspended Fe concentrations in Cl^- waters (where data is available) is low and As concentrations tend to be the highest in these waters.

Manganese in higher redox states is a strong oxidizer and is capable of oxidizing arsenite (Oscarson et al., 1981). In ground waters from Myra Falls there is a tendency of increasing arsenate/arsenite ratios with increasing suspended Mn (i.e. low dissolved Mn/suspended Mn ratios) (Figure 5-7). In experiments by Oscarson et al. (1981) only a portion of the Mn-oxide reacted during arsenite oxidation. A

maximum of ~19% of the original Mn^{4+} was reduced to Mn^{2+} . Manganese appears to be at least a partial control on the As species in the Myra Falls ground waters.

As was shown in Chapter 4 the majority of suspended particles in solution are greater than $0.45\mu\text{m}$ in size. The absence of Mn (hydr)oxides in solution after filtering has likely aided the preservation of the As^{3+} in solution.

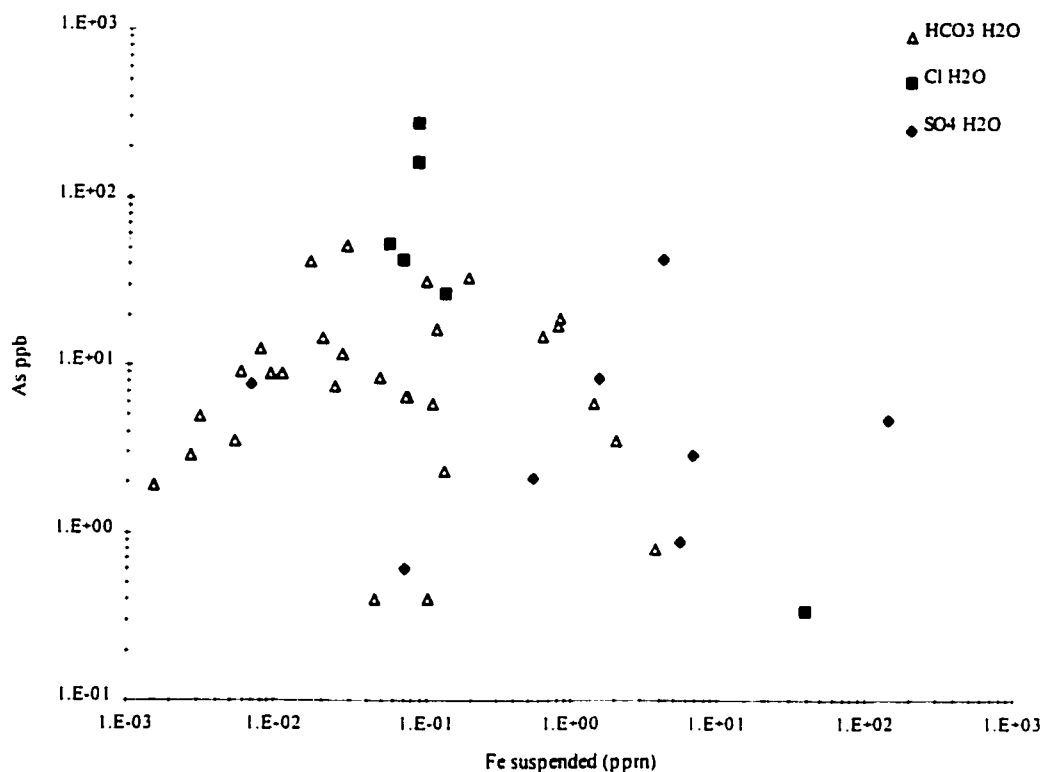


Figure 5-5 Arsenic concentration vs. suspended iron for different water types.

5.3 Sulphide/Sulphate

5.3.1 Introduction

Few of the waters analysed by the difference method (all S oxidized to SO_4^{2-} less SO_4^{2-} aliquot treated with a bactericide) had a variation of SO_4^{2-} between the two aliquots greater than the estimate of analytical precision. Estimated laboratory precision is $\pm 5\%$; total precision from duplicate analyses during this study also gives a precision of $\pm 5\%$. Analytical data and methods and materials are presented in Appendix F. The results for the sulphide/sulphate speciation will only be presented qualitatively in redox comparisons by other methods in Section 5.4.

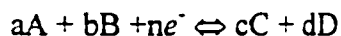
5.3.2 Recommendations

Under rugged field conditions the ability to perform delicate chemical analyses is greatly curtailed and therefore there is a requirement to process waters under controlled laboratory conditions. The sulphide / sulphate redox couple would have been best calculated from the gravimetric analyses of sulphide in solution after precipitation with a sparingly soluble metal (i.e. Cd). The amount of Hg used as a bactericide in this study was not great enough to precipitate more than a minor amount of sulphide from the water. A simple method that can be used under harsh field conditions to determine sulphide would require that Cd-acetate be added to a sample aliquot at sampling. Filtering the aliquot would remove any precipitate for later gravimetric analyses. The remaining filtrate would be analysed for dissolved SO_4^{2-} .

5.4 Comparisons of Measured Eh and DO, and Eh Calculated from Redox Couples

The transfer of electron(s) under equilibrium conditions can be described in terms of half-reactions and the Nernst equation. The half-reaction written in terms of reductions, and the resulting theoretical voltage are described by:

Equation 5-1



$$Eh(V) = E^\circ - \frac{RT}{nF} \ln \frac{(C)^c (D)^d}{(A)^a (B)^b}$$

where A and B are the reactants, C and D are the products, lower case letters denote the stoichiometric coefficients, and n is the number of electrons (e^-) transferred. In the Nernst equation E° is the standard (state) potential of the half-reaction in volts, R is the universal gas constant, T is the absolute temperature, and F is Faraday's constant; other designations are the same as in the reduction reaction. The sign of the second part of the last equation is dependent upon whether products or reactants are in the numerator (this is dependent upon whether the equation is written with products or the oxidized species on the right-side of the upper equation).

Individual redox couples rarely reflect the measured or 'bulk solution' redox values (Lindberg and Runnells, 1984; Holm and Curtiss, 1989; Stumm and Morgan, 1996). There are a multitude of reasons for this apparent discrepancy. Chemical reactions often move to completion (i.e. are irreversible) and therefore equilibrium conditions may not be met under natural conditions; redox reactions may be biologically mediated; or individual redox couples may be able to buffer redox changes to varying degrees and therefore are not in equilibrium with other redox couples.

Researchers have tried to develop relationships between measured redox values (platinum electrode) and speciation of various elements (redox couples) (Holm et al., 1986), but Eh in natural systems rarely reflect calculated 'equilibrium' potential (Barcelona, et al., 1989). Only in single redox-couple solutions in the absence of O_2 (such as Fe^{3+}/Fe^{2+} , pH 3; and $Fe(CN)_6^{3-} / Fe(CN)_6^{4-}$, pH 6; in Kempton et al., 1990) does the Nernst equation describe

the measured response. The redox couple which can best fit calculated Eh from the Nernst equation under natural conditions is $\text{Fe}^{3+}/\text{Fe}^{2+}$ in mine drainage with high Fe content (Back and Barnes, 1965; Holm, et al, 1986, Kempton et al., 1990).

Moreover, platinum electrode redox values are more importantly an indicator of mixed potential or 'bulk solution' redox qualities; and as such, are informative of the redox sequence resulting from the consumption of oxidants in flow systems (Back and Barnes, 1965; Champ et al., 1978; Baedecker and Back, 1979)

In this study comparisons between the fields of redox from platinum electrode measurements and those calculated from redox couples are made for general interest and are similar to the findings of the much more extensive study by Lindberg and Runnels (1984)

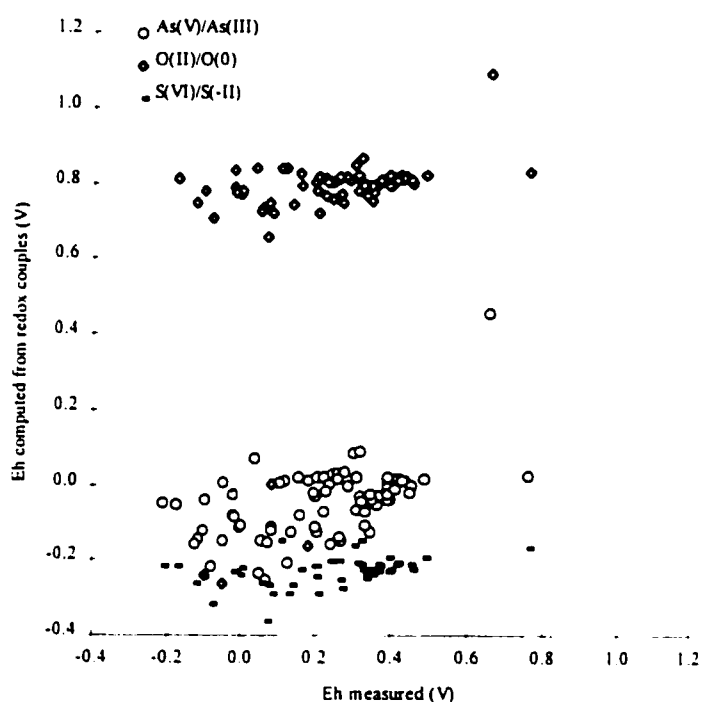


Figure 5-7 Eh computed vs. Eh measured in ground waters from Myra Falls. Calculated redox from a few DO measurements are in the same vicinity as potentials from As (no potentials are calculated for DO = 0 mg/L). Potentials from S(VI)/S(-II) couple tend to be the lowest. No Eh computed from single redox couples agree with the measured redox. The dashed line represents Nernstian behavior of redox couples (i.e. equal potential to the measured electrode Eh).

(although As was not included in their inter-comparison of available data). Quite simply, no single redox couple adequately describes the measured redox potential of the water. The comparison of computed Eh (PHREEQC; Parkhurst, 1995) show that the potential calculated from the measurement of DO ($\text{O}_{2(\text{aq})}/\text{H}_2\text{O}$) tends to be the highest, except with very low DO concentrations (DO = 0 mg/L are not calculated) and are consistently above the measured Eh. Redox potentials calculated by As species tend to be below the measured redox values and only fall in the same region as measured Eh at low potentials. The potentials from the available

sulphate-sulphide data (see above for precautions about the sulphide data) tend to be the lowest and are included for comparison only.

Redox comparisons between measured platinum electrode and those calculated from As (III/V) redox couple rarely show a good correlation (Korte and Fernando, 1991). However, depending on the nature of the study, Eh values calculated from As(V)/As(III) may be beneficial. Studies of arsenic mobility and cycling will likely benefit most from Eh calculated from As redox couple.

As was pointed out by Lindberg and Runnels (1984) there is little reason to expect agreement between redox values measured from concentrations of various redox couples. The simplest reason for this disagreement is the wide variation in reaction E° values. The calculated Eh values are dependent upon the E° value in the Nernst equation and to a much lesser degree upon ratio of activities of the dissolved redox couple. Large differences in redox ratios in the second half of the right hand side of Equation 5-1 will have a minimal effect on the calculated Eh. For example a difference in As redox ratios of 1000 at standard temperature and pressure will only result in a 0.089V difference in computed Eh.

5.5 Conclusions

As(V)/As(III) ratios in ground waters of Myra Falls varied by more than three orders of magnitude. The highest As concentrations are found in waters with the lowest Eh. These waters also tend to have the lowest As(V)/As(III) indicating that As^{3+} is more mobile in this setting. Higher aqueous As concentrations may be related to the instability of (oxy)hydroxides in the lower Eh conditions. Manganese may be influential in establishing the redox state of As in these ground waters.

The platinum electrode potential only crudely estimates the predominant As species present. Solution Eh values should not be estimated from As(V)/As(III) redox values. The values of As(V)/As(III) ratios and computed Eh may be useful in systems where As is of key concern, and by analogy may also prove useful for understanding species mobile as oxyanions and with similar aqueous behavior as arsenic such as Sb, Mo, Se, V and Cr (at high Eh).

6. Ground Water Circulation and Saline Ground Water Source

6.1 Introduction

The effects of underground mine openings on ground-water flow has implications in the mining industry and also for interested groups involved in the safe siting of spent nuclear waste repositories. The resulting changes in ground water chemistry due to perturbations results from changes to natural hydrology through the creation of underground mine openings. These ground water chemical changes are of concern to mine operators, in part due to the entrained oxygen delivered to greater depths than pre-mining conditions. This results in increased oxidation of sulphide minerals and increased metal loading of mine waters.

In a fractured media, ground water circulation to deeper mine workings is difficult to predict. In this environment discrete fractures may carry the majority of ground-water flow into deeper strata. This deeper circulating ground water will be identified by the chemical and isotopic signature of its recharge source.

Isotopic and geochemical processes in ground waters have been discussed in detail in Chapters 2 and 3, respectively. They are used in this section to discuss ground-water flow in a fractured medium, illustrate the affects of mine openings on ground water circulation, and discuss ground water circulation processes in general. The source of the saline ground waters is of interest in this setting since it exists at such shallow depth and have $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic compositions similar to the isotopic trends seen in sedimentary basinal brines.

6.2 Discussion

6.2.1 Areal Extent of Saline Ground Waters

From this current study it has become apparent that the saline Cl^- -dominated ground waters exist throughout the lower Thelwood Valley, external to active mine workings in HW mine (North of HW-21 level, South of HW-20 level, and East of HW-20 level), and below active mine workings in the HW mine. It is not known if saline waters are currently present in Myra Valley. Portions of the HW mine, Myra mine, and Lynx mine underlie areas of Myra Valley. It would be expected that the mining activity in this area has affected the pre-existing hydrology and hydrochemistry of ground waters within Myra valley.

Ground waters sampled by bailer from drill holes within Myra Valley have been non-saline. A ground water sampled from an elevation of approximately -80 metres (relative to sea level) from drill hole W195 on the southern edge of the Lynx workings (along the road to level 8 adit) had a conductivity of $305 \mu\text{S cm}^{-1}$ (sample #3320). A second drill hole in Myra Valley (W129) located above the HW mine had a conductivity of $230 \mu\text{S cm}^{-1}$ (sample #3545). Both of these ground waters have likely been affected by their proximity to mining activity. Underground production commenced in Myra, Lynx, and HW mines, in 1972, 1976, and 1985, respectively.

The existence of saline ground water on the western edge of the mining camp would have to be tested in new exploration drill holes on this frontier of the mining camp. It is not known at this time how regionally extensive the Thelwood Valley saline waters might be.

6.2.2 Saline Ground Water Discharge Into Thelwood Creek and Buttle Lake?

No salt-licks are reported or were found during this study in the valley bottoms. Some drill holes do discharge water to the surface but this water is fresh.

Information garnered from this study indicate the fresh ground water / saline ground water interface in Thelwood Valley is below the elevation of Thelwood creek. A sampling program was initiated on September 4th 1995, during a period of low creek flow to determine if there was any recognizable Cl^- (saline) discharges into Thelwood creek. Sampling included

Jim Mitchell lake (water sample 3526), the water source for generating hydro-electricity, which is the primary source of water in Thelwood creek during the late summer, and within the creek from Thelwood powerhouse to the creeks mouth in Buttle Lake (water samples 3528, 3530, 3532, and 3533). All of these waters had less than 1 ppm Cl^- indicating there is no discernible amount of saline ground water discharging into Thelwood creek. It is possible that small discharges of saline water would soon be diluted by the main creek flow. A surface water collected from a marshy area near the creek and Thelwood Valley drill holes PR-101, on the same day as the Thelwood creek waters, had Cl^- concentration of 6.2 ppm. This marshy area is believed to be hydraulically connected to fracture zone(s) intercepted while drilling exploration holes in the immediate vicinity (see Section 6.2.4).

The extent of saline ground water found underlying Thelwood Valley to the fringes of mining activity in HW mine raises the question whether saline waters are more regionally extensive within the Buttle lake uplift, and if saline waters are discharging into Buttle lake? Copper levels in lake waters have been greater than expected from being solely derived from Myra creek discharges (Rudy van Dyk, personal communication 1994; Aquamin, 1996). This raises the question whether discharging saline waters could be responsible for a portion of the copper. Further work would be needed to evaluate this source. Discharges into lake bottoms could occur along permeable faults and may be difficult to isolate; nevertheless, discharges if found would be easily identifiable since they would correlate to elevated Cl^- levels during sampling of lake bottom waters. Buttle lake averages 45 metres in depth (Deniseger, et al., 1990), with a deeper south basin close to Thelwood and Myra creek discharges. It is quite conceivable that the elevation of the south basin is below the fresh ground water / saline ground water interface.

6.2.3 Ground Water Gradients in Thelwood Valley

Several fracture zones from various drill holes located in Thelwood Valley were sampled by means of dedicated and portable packer systems. The portable packer system was equipped with a pressure transducer to measure the hydrostatic pressure isolated between the two packers in the system, [Note: The packer system equipped with the pressure transducer was 'lost' down PR-115 (ground water #3356) and subsequent sampling system using a back-up set of packers was not equipped with a pressure transducer]. Dedicated packer systems isolating either the bottom of drillholes or assembled in pairs to isolate specific zones within drill holes were not equipped with pressure transducers. Although not equipped with a pressure transducer, qualitative determinations can be made when isolated zones flowed at the surface. [For information regarding temporal water static levels in Thelwood Valley the reader should consult a more thorough coverage of this subject by M. Stapinsky (Ph.D. in progress, U. of Ottawa).]

Many drill holes located in Thelwood Valley are flowing at the surface (i.e. PR-32, 92, 100, 101, 109, 111, 112, 115, 116, 117, 118, 119; see map in back pocket for locations). Water flowing at the surface had chemical composition resembling recently recharged meteoric water (low TDS, measurable DO, and measurable ^3H).

Ground waters sampled from drill hole PR-92 (see site map in back pocket for location) located near the edge of the Price hillside in Thelwood Valley have low to moderate TDS and contain only a small proportion of the saline Cl^- dominated water. PR-92 is artesian, and has low flow rates from the open drill hole at the ground surface. Unlike other drill holes sampled in Thelwood Valley, fresh to brackish water exist to greater depths within PR-92. PR-92 also has a TDS inversion, as the deepest water sampled has lower TDS than ground waters from overlying zones (Figure 6-1). There is generally a downward gradient within PR-92 that allows mixing of meteoric waters with saline waters and the subsequent flushing of saline ground waters from the rocks. Packed zones encountering low TDS ground waters have the highest piezometric heads. Higher piezometric hydraulic heads were measured from sampling points located at 101, 52, and -52 metres elevation. The two zones located at -8 and -25.5 metres elevation have hydraulic heads below the constant head boundary of the flowing

open hole suggesting these two zones are actually zones of net loss from the drill hole. PR-92 appears to have very heterogeneous flow since several zones are delivering meteoric water to the drill hole and there is not a progressive increase in salinity with depth.

Often, the hydrostatic pressure within isolated zones is greater than the pressure measured in the open drill hole indicating fracture zones are capable of delivering ground waters to the drill holes. Other drill holes do not have enough piezometric measurements to define gradients within them. However, ground waters sampled from packed zones (dedicated packers without pressure transducer) located at 423 and 445 metres below ground surface in PR-101 were artesian during early development. The pressure from the main flow zone (-105 metres below ground surface; Section 2.8) was not measured since the transducer had been previously lost down a drill hole.

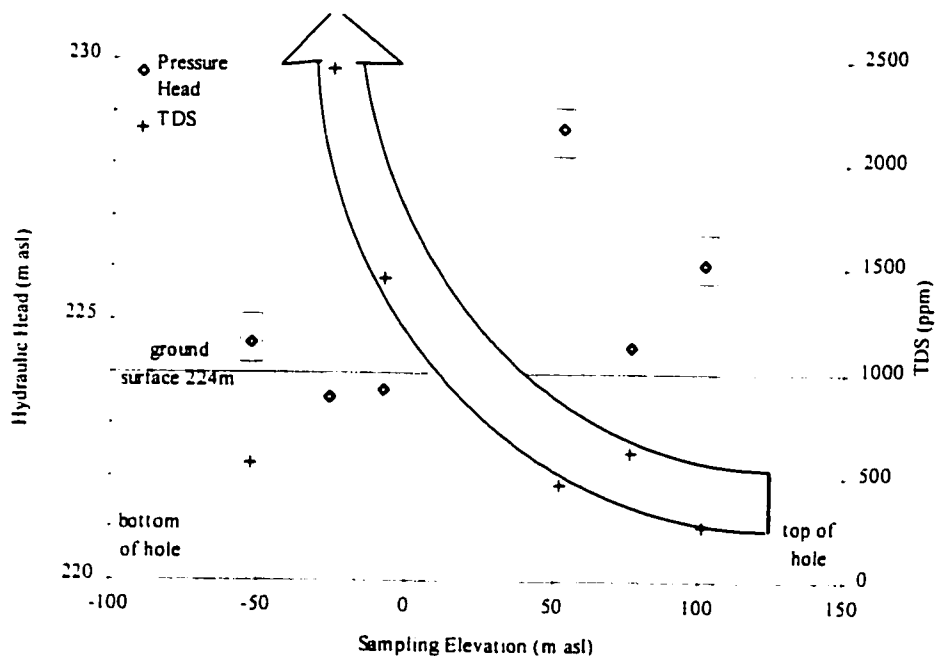


Figure 6-1 Piezometric heads and corresponding sample TDS vs. sampling elevations for drill hole PR-92. This drill hole is flowing at the ground surface (224 m). Arrow shows general trend of expected TDS increase. Zones with low TDS (rectangles around points) correspond to higher heads. Ground waters from Pr-92 have lower salinity than corresponding depths in other Thelwood Valley drill holes due to the influx of low TDS waters at depth.

6.2.4 Fresh/Saline Water Interface and Fracture flow in PR-101, Thelwood Valley

A single fracture at 105 metres depth delivers modern meteoric water (4.1 ± 0.5 TU; Section 2.8) to the drill hole PR-101. Based on Cl^- concentrations, the flow from this fracture constitutes the majority of the discharge at the surface from this artesian drill hole. The interface is very sharply defined at or just below the depth of this fracture and has fresh water in the drill hole immediately overlying saline water (delineated by open hole profile discrete interval ground water sampling (Figure 6-3) and by geophysical logging (Figure 6-2)). The Cl^- concentration in ground water at the inflow is approximately 2 ppm while immediately below the freshwater saline water interface the saline water has concentrations >5000 ppm Cl^- . Unlike PR-92, the salinity within the ground water below the freshwater interface in PR-101 increases progressively with depth as found in most of the drill holes which were sampled at various depths.

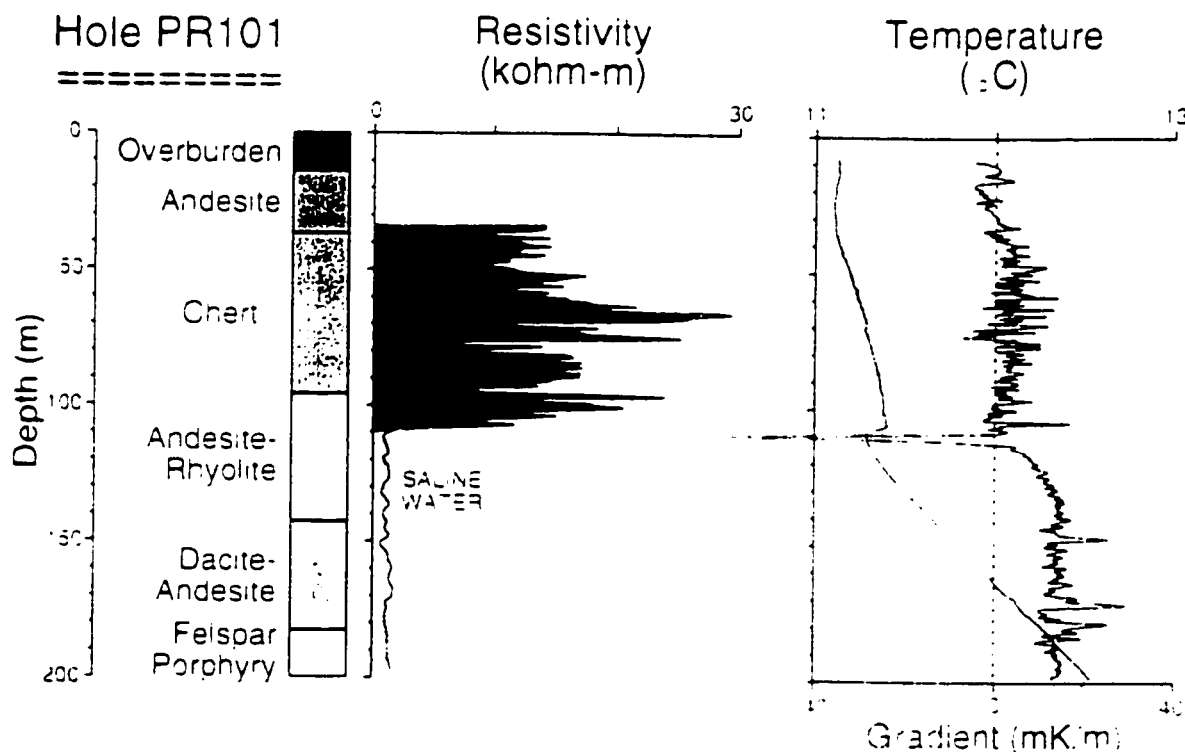


Figure 6-2 Geophysical resistivity and temperature logs from the top 200m of PR-101 showing the fresh/saline water interface. A single fracture delivers meteoric water to the drill hole. (from Mwenifumbo, 1995).

The majority of the flow at the surface from PR-101 is from this fracture (Cl^- concentrations from the flowing hole are 0.7 to 1.5 ppm; sampled in 1993 and 1994; sample #'s 1040, 2022, and 2434).

The flow at 105 metres depth within drill hole PR-101 may 'short-circuit' the discharge of non-saline water from the Price hillside into Thelwood Valley. Recent drilling of new exploration holes in this area resulted in disturbances in surface waters on the Thelwood creek side of the road (opposite side of the road to the drilling). Surface waters in a marshy area near Thelwood creek became impacted by drilling fluid. The marsh must be

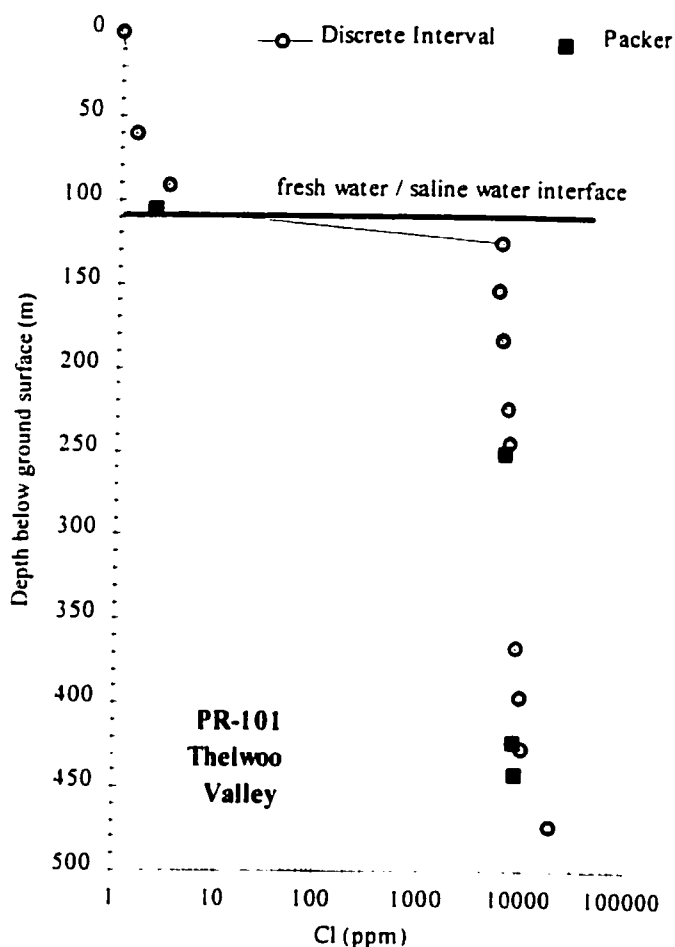


Figure 6-3 Variation of Cl^- with sampling depth in PR-101. The fresh/saline water interface is very sharp in this drill hole. Below the interface there is a gradual increase in Cl^- . There is a very good agreement between the Cl^- profile from open hole discrete interval sampling and sampling by packers.

hydraulically connected to the drill holes as rock flour and drilling fluid from drilling were being discharged from springs underlying the marsh (G. Dirom personal communication, 1995).

From the comparison of the $\delta^{18}\text{O}$ (-12.9‰) of this ground water (PR-101, 105 m bgs) with ground waters accessed within Myra-Price 13 level, it has likely been recharge on the middle to upper Price hillside. The $\delta^{13}\text{C}$ value (-11‰ VPDB) and HCO_3^- concentration (123 ppm), indicate it was likely recharged through a soil zone. It is saturated with respect to calcite which indicates that it has time to have equilibrated with calcite, but still retains measurable tritium.

Below the fresh water - saline water interface the saline waters gradually become increasingly saline with depth (Figure 6-3). Piezometric head measurements are not available from the packed zones in PR-101, but the two lower packed zones were artesian during early development (Figure 6-3). The fresh water heads are likely greater than the more saline water (as seen in PR-92; Figure 6-1) and are enough to keep the saline water largely constrained below the fresh/saline ground water boundary.

6.2.5 Influence of Mine Workings on Water Circulation (mixing of meteoric and saline ground waters)

The result of mixing modern (tritium bearing) and saline (high chloride, tritium-free, and ^{14}C -free; Chapter 2) ground waters was investigated for ground water from drill holes located in HW mine level 20-371 cross cut south (HW20-653; 245 m, +45°). This heading is an area of recent drifting and drilling (1990), and is in a region underlain by brackish water (HW20-650; 262 m, -90°; sample #3267; Figure 6-4). Whereas, drill holes oriented above the drift have between 130 and ~600 ppm Cl^- (Figure 6-4).

Results from binary ideal mixing, using Cl^- as a conservative tracer, indicate that ground water HW20-653 may result from approximately 5% brackish water from HW20-650 (similar chemistry to water underlying the area) mixing with low chloride meteoric water (1 ppm Cl^-). The ground waters discharging from HW20-653 contain 1.2 ± 0.4 TU. Using the same percentage (5%) to resolve the tritium content of the brackish waters results in negative tritium values for brackish water component. Therefore, either the modern water is originally low in tritium (~1.2 TU), and the chloride component is the result of piston flow along fractures incorporating a salt residue (grain boundary salts) or diffusion from bimodal and/or matrix porosity. This would result in incorporation of a Cl^- source with no dilution of the tritium. Or more likely, a modern water (with >1.2 TU) is mixing with a less saline partially eluted water. Other drill holes with less horizontal extent in the vicinity of HW20-653 have undergone less dilution than water from HW20-653, and contain a greater saline water component (~400 ppm Cl^-). Resolving binary mixing results in a contribution of 30% of the water in HW20-653 possibly originated from ground water with similar Cl^- (436 ppm) as HW20-654. Using this proportion to solve for the original tritium in the modern water mixing

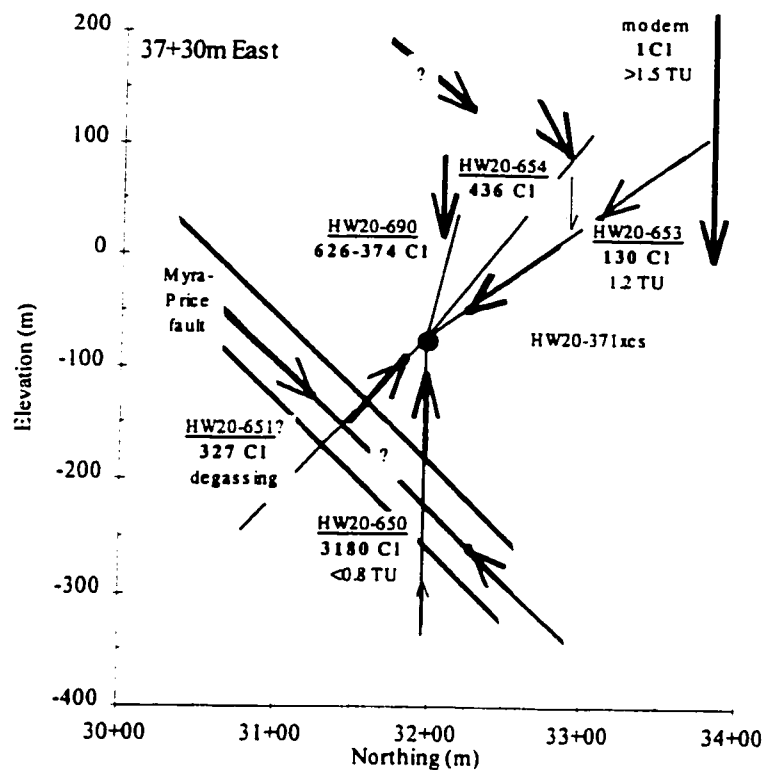


Figure 6-4 Mixing flow paths of ground waters from HW20-371xcs (37+30E). Arrows represent ground-water flow. Chloride concentrations are in ppm. Water entering the drift from drill hole 653 may result from mixing 30% water similar to 20-654 water with modern meteoric water. See text for description.

with HW20-654, results in the meteoric water containing no more than 1.7 TU (mixing water = 0 TU). Note, this is not a unique solution as the low CI water will contain less than this amount if the second water containing ~400 ppm Cl^- has a tritium component (i.e., 1.5 TU in meteoric water if mixed with brackish water having 0.5 TU). The ^3H concentration and likely the Cl^- content in HW20-653 ground water is clearly the result of mixing modern waters with older, Cl^- bearing waters either in fractures or within the drill hole itself. The heterogeneous and complex nature of the ground-water flow paths becomes apparent in Figure 6-4.

The above example of the downward migration of modern meteoric water and mixing between non-saline tritium containing, and saline ground waters which is occurring on the meso-scale, can also be seen on a larger mine-wide scale. Ground waters from beneath the M-P ridge were all sampled from within mine workings. The areas of the HW mine in which sampling occurred show the influence of mine drifting and drilling on the natural(?) hydrology of the area, as compared to the hydrology of the ground waters underlying

Thelwood Valley. In Thelwood Valley the local hydrology has been unaffected by underground drifting but may be slightly modified due to exploration drilling.

The modifications to hydrology due to perturbations from mine workings are investigated in the two longitudinal diagrams (Figure 6-6 and Figure 6-7), approximately mine west - east from Myra Valley to Thelwood Valley (across the M-P ridge). The result of mine workings on the hydrology can be seen on the tritium concentrations and chloride isopleths through the two diagrams.

Chloride gradients in areas of Thelwood Valley with unaltered hydrology may be slightly steeper in the more northerly section (Figure 6-6; there is also tighter control on drill hole sampling chemistry in this section). In both sections Cl^- concentrations greater than 10^4 ppm are encountered around 200 to 250 metres below ground surface in Thelwood Valley. There is a paucity of information under the M-P ridge in the northern section (Figure 6-6). Nevertheless, the three drifts that intercept this section all show that meteoric waters have migrated to these levels displacing saline ground waters. The displacement of saline water is more pronounced in the western portion (west of the M-P ridge crest). HW mine workings at equivalent elevation to these levels and at greater depths are located south of this section in the western half of the diagram. The mine workings may influence the ground water hydrology on HW 20 and 21 levels. The North fault intersection with HW 20 level drift is a permeable damaged rock zone 10 or more metres wide which has circulated modern meteoric waters down to depths of around -50 m. There is no mine development above this location, and nearby exploration holes drilled into the floor contain brackish to saline water. Oxygen-18 from the North fault waters suggests the ground water is recharged at an elevation of approximately 900 metres. The drift that intersects the North fault was driven during the fall of 1989; modern waters were first sampled from this location during August 1993. The presence of tritium and HCO_3^- water at this location implies high ground water velocities have delivered modern meteoric water to this location. Some monthly (seasonal) variability is apparent in the $\delta^{18}\text{O}$ in Figure 2-2, suggesting piston like flow with moderate seasonal attenuation of the isotope signal.

Within Thelwood Valley a sharp interface exists between fresh water above and saline water below. A single fracture in PR-101 at 105 metres depth delivers modern meteoric water

(4.1 ± 0.5 TU) to this drill hole in Thelwood Valley (Figure 6-6). The fresh water in the drill hole immediately overlies saline water (Section 6.2.4). Chloride containing waters are closest to the surface in the vicinity of PR-106 (~1000 ppm at 66 metres below ground surface; #3273) and the 'freshest' ground waters may be confined to high flow rates within coarse valley fill. Geophysical logging by J. Mwenifumbo (GSC) of temperature and temperature gradient in the cased portion of PR-106 and the adjacent PR-107 drill holes, indicate high flows between 30 and 60 metres depth through the overburden material.

A chloride profile south of, but similar to, the more northerly longitudinal section (Figure 6-6) is shown in Figure 6-7. In this profile the effect on local hydrology of level 13, which dissects the M-P ridge at 240 m elevation, can be seen. Modern meteoric waters have been drawn down into this access drift. Tritium containing ground waters were sampled within all but the central portion of the M-P ridge (Price levels 5, 9, and 13). In the central core of the M-P ridge on Myra 10 level there is tritium-free and slightly higher Cl^- (up to ~30 ppm Cl^- ; #3444) ground water from recently developed bedrock. Recent drilling on Myra 10 level is in an area not directly underlain or overlain by mining activity.

Ground water from areas within the M-P ridge with a more prolonged mining history typically have very low Cl^- concentrations (<10 ppm). Within the margins of the M-P ridge Cl^- concentrations are typically similar to rainfall recharge (~1 ppm).

Ground waters at lower elevation within the HW mine (20 level; Figure 6-6) show the influence of the lower mine workings on chloride profiles and tritium concentrations under the M-P ridge. Meteoric waters have been drawn down to working depths within the HW mine. These waters are mixing with and eluting residual water contain moderate Cl^- concentrations (Figure 6-4 and Figure 6-6). Ground waters above 20 level overlie tritium free brackish waters (<0.8 TU and 2860 ppm Cl^-) located below 20 level.

Tritium was not analysed in ground waters sampled from drill holes located in Thelwood Valley on this profile (Figure 6-6), but Cl^- concentrations have a similar pattern as the profile down valley (Figure 6-7), and the 10^3 ppm contours are at approximately similar elevations in both Figure 6-6 and Figure 6-7.

The sampling locations in the HW mine, at the extreme northern edges of drifting on HW-20 and HW-21 levels (Figure 6-6) and on the extreme southern edge of exploration activity on HW-20 level (Figure 6-7), are located at the lowest elevation of mining activity in these areas. The downward migrating meteoric water would be expected to be at even lower elevations in the area between these sections (west-central area of the sections Figure 6-6 and Figure 6-7; HW main zone, map in back pocket), in the midst of the main mining activity in HW mine. Deepest drifts in the HW mine are located at -328 metres elevation (relative to sea level).

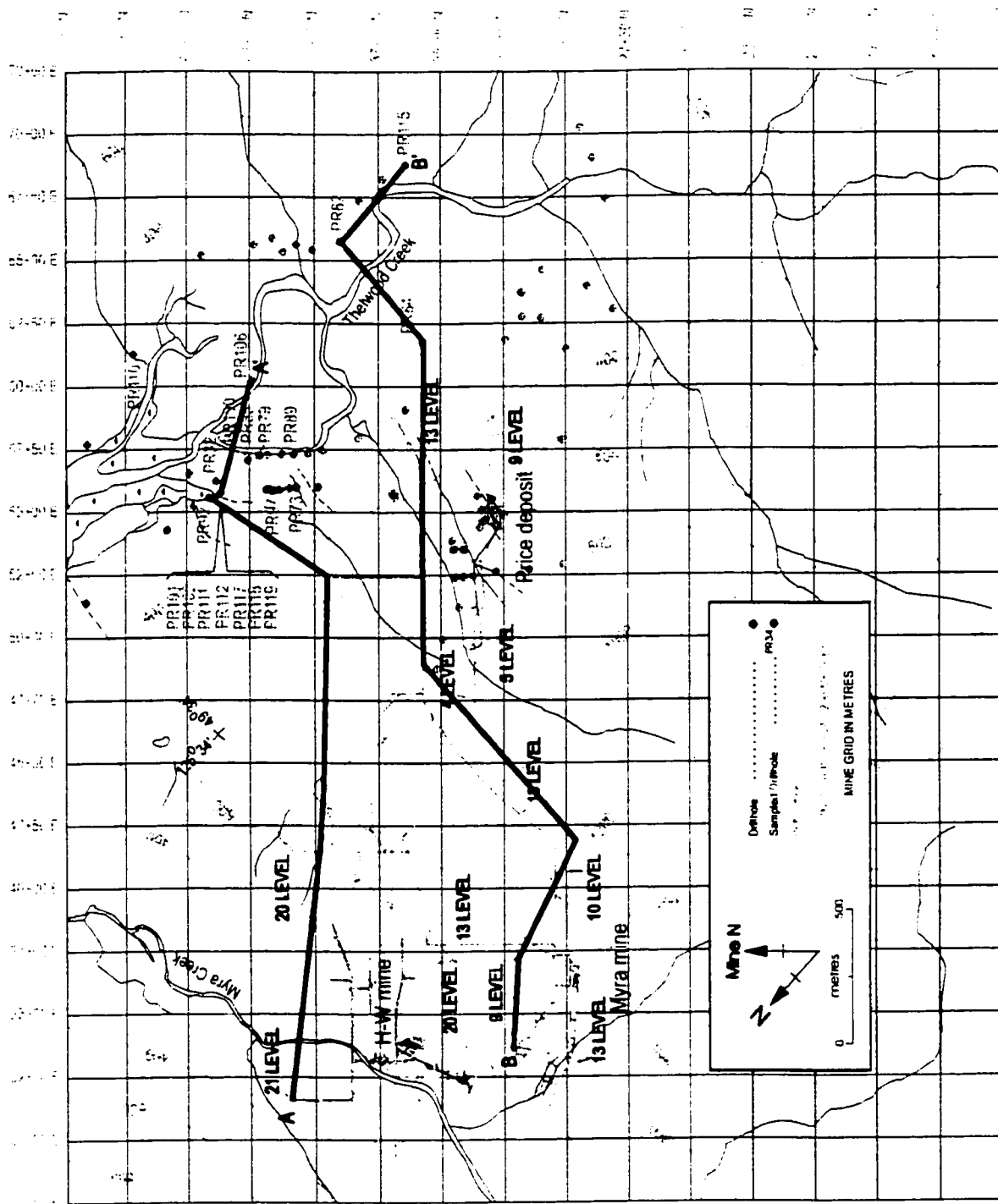


Figure 6-5 Plan map of Myra Falls study area showing the location of chloride and tritium profile.

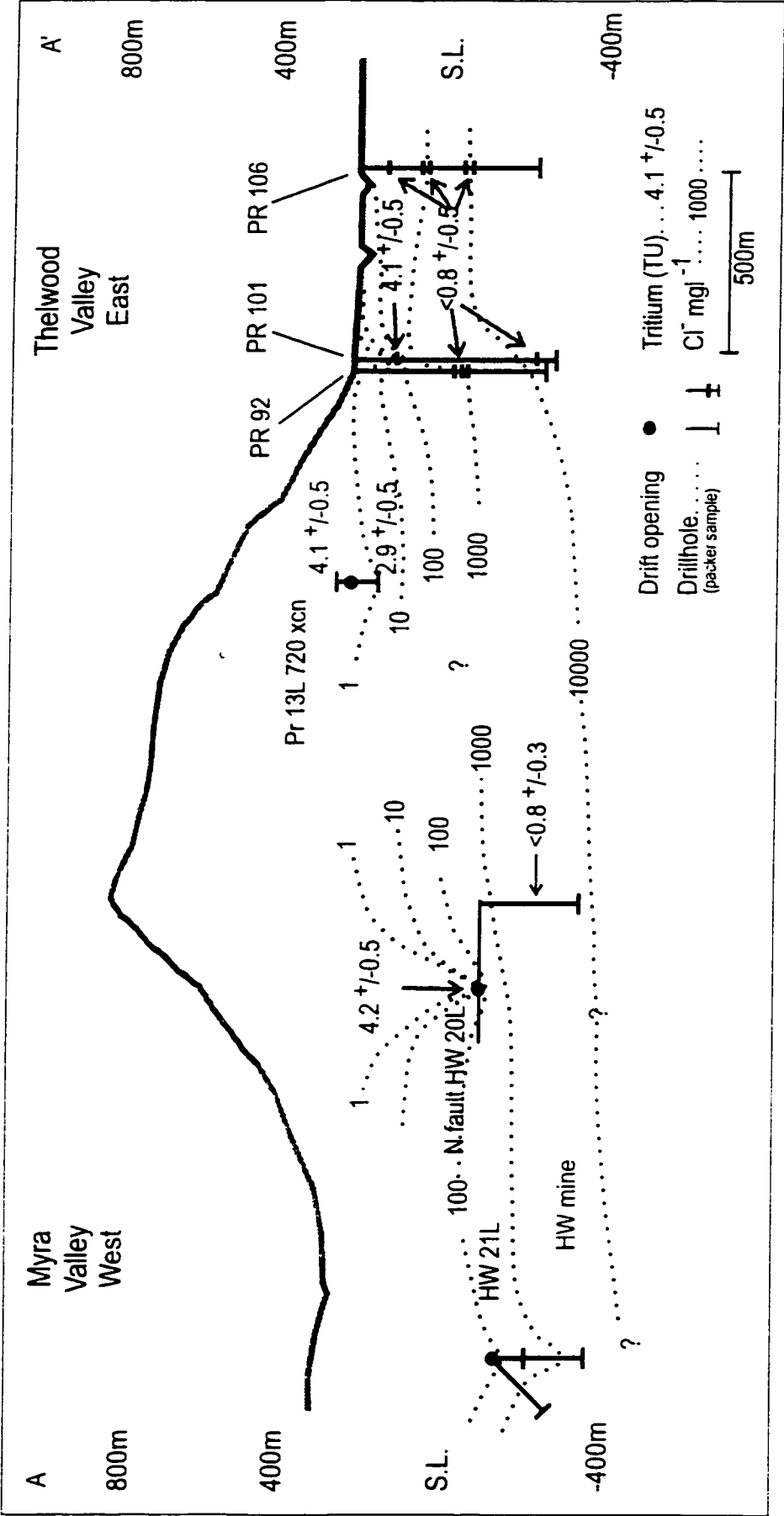


Figure 6-6 Tritium and chloride profile under northern Myra-Price ridge, from Myra valley (west) to Thelwood Valley (east). See text for description and Figure 6-5 for location.

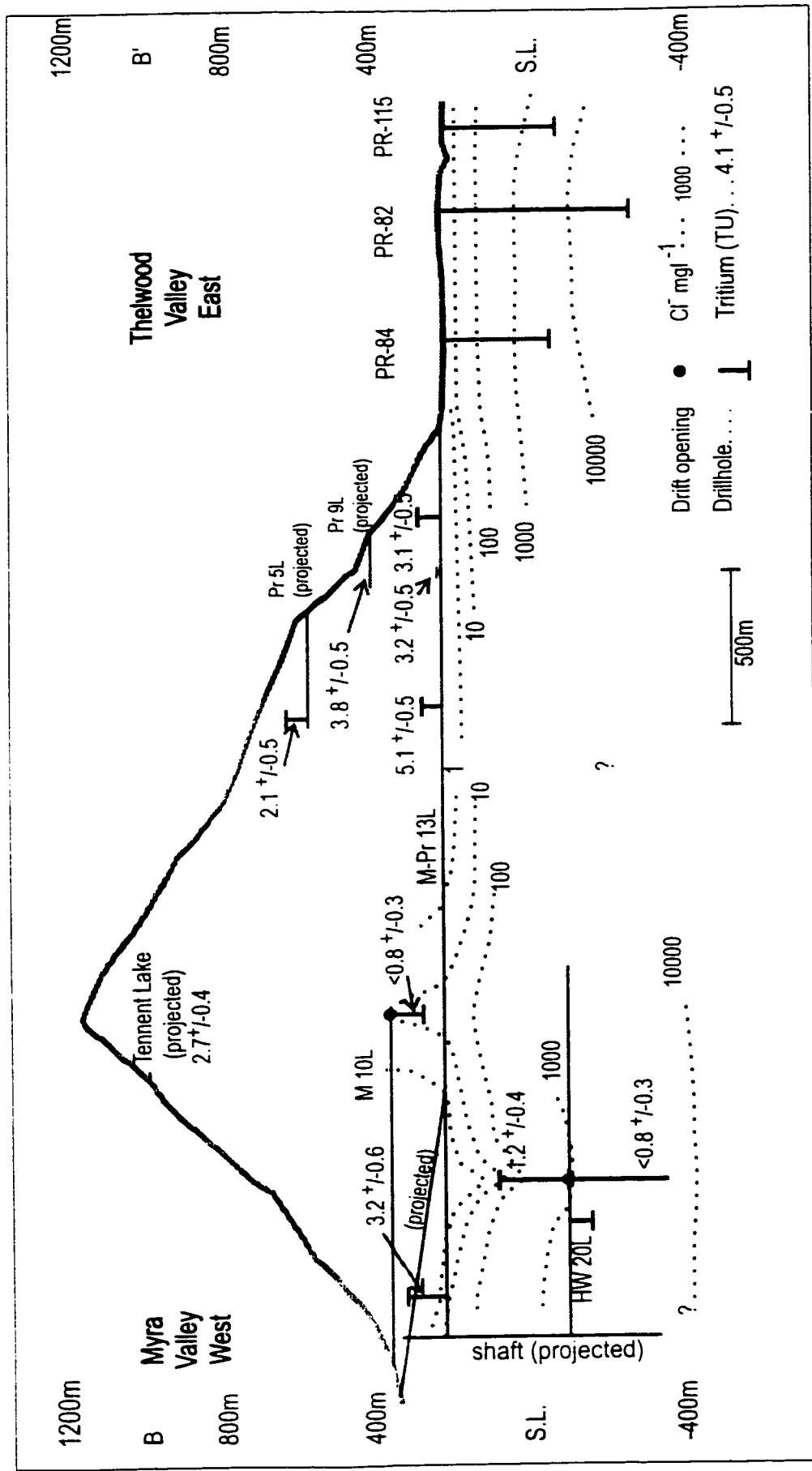


Figure 6-7 Tritium and chloride profile under northern Myra-Price ridge, from Myra valley (west) to Thelwood Valley (east). See text for description and Figure 6-5 for location.

6.2.6 Possible Origin of Saline Ground Water

The characteristics and possible origin of saline waters in crystalline rocks have been the focus of several studies (including: Frape et al., 1984; Fritz and Frape, 1987; Nordstrom et al., 1989; and Bottomley et al., 1994). Stable isotopes, $\delta^{18}\text{O}$ and $\delta^2\text{H}$, in the Thelwood Valley saline ground waters do not share the stable isotope signature of saline waters from crystalline rocks (i.e. shield brines), which typically plot above the meteoric water line.

Oddly enough, the stable isotopes ^{18}O and ^2H in the Thelwood Valley saline ground waters have a trend typical of sedimentary basinal brines (Clayton et al., 1966), and plot below the meteoric water line with a slope less than 8. The $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ line describing these recently discovered saline waters has a slope of 5.6. The Thelwood Valley saline waters are clearly the result of mixing modern meteoric waters with a saline water occurring at depth (Chapters 2 and 3). The slope of the stable isotope chloride trend line is defined by mixing modern meteoric waters with the end-member isotopic ratios rather than an increasing water-rock exchange processes that would lead to enrichment of $\delta^{18}\text{O}$ greater than $\delta^2\text{H}$.

The saline water that is encountered at increasing depth in the Myra Falls area contains components removed from the local rock as well as extrinsic components. The minerals in the local rock itself, including grain boundary salts and fluid inclusions, likely contain too little chloride to have been the source of Cl^- in the ground water, even if very long time periods were invoked for the process of leaching Cl^- from the rocks. The first logical choice for the saline water source, mainly based on Cl^- concentration, is a sea water source. Stable isotopes, and conservative element ratios quickly rule out an unmodified sea water as the source of the saline water (Chapters 2 and 3).

Several possibilities exist for the origin of the Thelwood Valley saline waters and may include: a residual connate or hydrothermal (metamorphic?) fluid, or a sedimentary brine.

The presence of a Devonian age connate fluid would be impossible in these rocks. Original fluids in Myra Falls rocks would have been displaced by post-depositional fluid events. These would include events related to greenschist metamorphism, and fluid events related to the later intrusion of the granitic Bedwell batholith on the edge of the mining camp.

Jurassic aged intrusions on Vancouver were emplaced at depth of 3-6 km, at a depth where large convective hydrothermal systems can readily develop (Magaritz and Taylor, 1986). Fluid related to a convective hydrothermal cell would replace pre-existing fluid in the vicinity.

Some evidence of the salinities of formational and later fluids have been preserved in the fluid inclusions in quartz crystals within the mine rocks of Myra Falls. Fluid inclusions in primary quartz, some of which are within the massive sulphide mineralization, have salinities ranging from 3.2 to 8.1 equivalent weight %, or, on average are about twice as saline as sea water (Barrett and Sherlock, 1996). Fluid inclusions from late quartz-calcite-chlorite veins that cross-cut the stratigraphy have lower salinities, from 0.2 to 5.6 equivalent weight % NaCl, and average 2.1 wt. % (Barrett and Sherlock, 1996). The hydrothermal event responsible for the late veining has too little Cl to represent the end-member saline ground water now seen in rocks of the Buttle lake uplift. The late stage veining is likely pre-Jurassic age and formed during peak metamorphism (Berry, 1995; see Section 1.7.6).

Fluids involved in the hydrothermal alteration of the granitic Jurassic intrusions on Vancouver Island are believed to have been of marine pore fluid origin (Magaritz and Taylor, 1986). These same fluids are also believed to have been involved in the low-grade (prehnite-pumpellyite facies) metamorphism of the mainly basaltic Karmutson formation (which is stratigraphically younger than the mine sequence). These waters had a $\delta^{18}\text{O}$ and $\delta^2\text{H}$ enriched composition. The ^{18}O of the fluids involved in these events was likely slightly positive, possibly an isotopically shifted marine water ($\delta^{18}\text{O}_{\text{H}_2\text{O}} \geq 0$; Magaritz and Taylor, 1986).

The Thelwood Valley saline waters are not the only Cl^- -rich ground waters on Vancouver Island. Saline waters have been encountered from other regions of Vancouver Island. Notably in sediments, volcanics, and granodiorites in the North Saanich peninsula (Al-Mooji, 1982; Fritz, et al., 1983), Mayne Island (Dakin et al., 1983), in thermal waters from Hot-Spring Cove from the west coast (Phillips, 1994), and within sediments of the Naniamo group (Souther and Halstead, 1973). The possibility that the saline waters at Myra Falls may be related to some of these other saline waters on Vancouver Island is explored further.

The similarities in the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of the water between the Thelwood Valley saline ground waters and basinal brines, suggests the possibility that the Thelwood Valley saline waters have a sedimentary origin. Sediments with saline water are present in the vicinity of Vancouver Island. These are hosted in the Cretaceous age Naniamo group.

The sediments of the Naniamo Group (Cretaceous) -Chukanut Formation (Tertiary) are currently found on many of the Gulf Islands and Naniamo lowlands, and may have originally covered much of Vancouver Island (Monger and Journeay, 1992). Sediments of the Naniamo group are currently found within 25 km of the Myra Falls mining camp, and host actively mined coal deposits within ~40 km of Myra Falls.

Fernwood spring on Salt Spring island is fed from Cretaceous age sediments and is almost 100% dominated by Na-Cl ground waters (Al-Mooji, 1982; Souther and Halstead, 1973). It has a TDS of greater than 70,000 ppm (Dakin et al., 1983). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of the

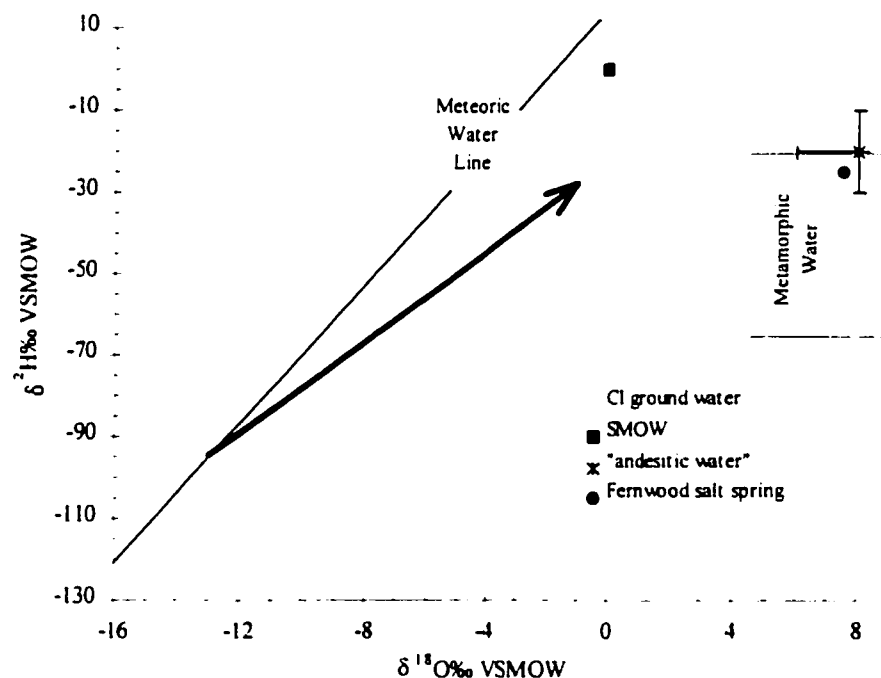


Figure 6-8 Deuterium vs. ^{18}O of Thelwood Valley saline water trend (grey arrow, arrowhead points in the direction of increasing Cl^-) and potential saline water sources. Only a portion of “metamorphic water” field is shown. Metamorphic water from Taylor (1974), “andesitic water” from Giggenbach (1992), and Fernwood salt spring from Dakin et al. (1983).

Fernwood salt springs waters are $\delta^{18}\text{O} \sim 6.5$ to 7.5‰ and $\delta^2\text{H} \sim -20$ to -28‰ SMOW (Dakin et al., 1983). The average values are plotted for reference in Figure 6-8. Major element chemistry for Fernwood salt spring was also reported by Souther and Halstead, (1973) as 27,440 ppm Cl^- , 25,240 ppm Na^+ , and 17,520 ppm SO_4^{2-} with a total of 71,926 ppm TDS. In comparison to Fernwood salt springs the salt springs from Naniamo have greater concentrations of Cl^- and Ca^{2+} , and lower concentrations of Na^+ , Mg^{2+} , and SO_4^{2-} (Dakin et al., 1983).

Ground waters from Saanich Peninsula on southern Vancouver Island with >1000 ppm Cl^- were sampled from shallow wells (30-50 m) in Jurassic aged granodiorites (Al-Mooji, 1982). The salts in these waters were attributed to mixing meteoric waters with pore-waters and water-rock interaction. The general field of major ions are plotted for comparison on a piper plot in Figure 6-9.

Comparisons of the Thelwood Valley saline waters with other saline waters from Vancouver Island show that Cl^- dominates all waters except the Fernwood salt spring which

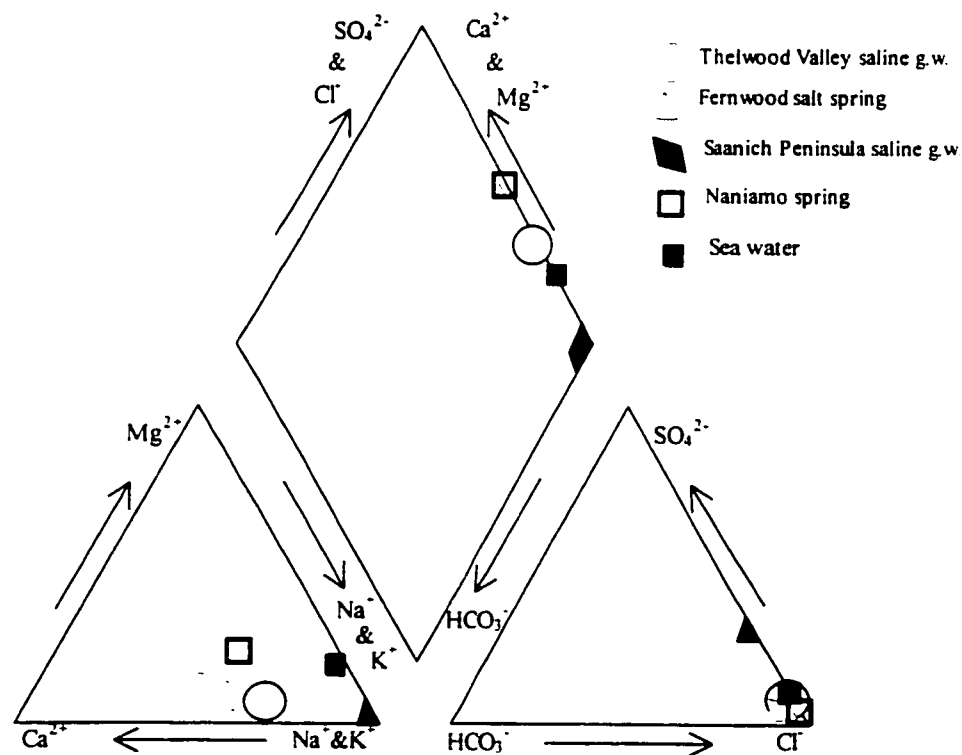


Figure 6-9 Piper plot of various saline waters from Vancouver Island and sea water. Fields of saline water are from Dakin et al., (1983) - Naniamo spring; Al-Mooji (1982) - Saanich peninsula Cl^- ground water; and Souther and Halstead (1973) - Fernwood salt spring.

has a significant SO_4^{2-} component (Figure 6-9). Cations in all of these saline waters are variably Na^+ to $\text{Na}^+ - \text{Ca}^{2+}$ rich. Cations in saline ground waters from Thelwood Valley, Naniamo, and Saanich peninsula Cl^- waters are $\text{Na}^+ - \text{Ca}^{2+}$ dominated.

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water clearly show that the saline ground water from Thelwood Valley is not the result of mixing locally derived meteoric water with a residual saline water of similar character to the Fernwood spring saline water (sedimentary basinal brine)(Figure 6-8).

Major elements from the N. Saanich peninsula ground waters plot very close to the field of the most saline waters from Thelwood Valley, Myra Falls (Figure 6-9). The Br/Cl mass ratio decreases in the N. Saanich ground waters and in the most saline waters ($\text{Cl}^- > 1000$ ppm) are slightly less than the ratio in Thelwood Valley saline ground waters (Figure 6-10). The Br/Cl ratios in the Thelwood Valley saline ground waters are very constant with increasing Cl^- . These Cl^- waters from two different areas of Vancouver Island share some common chemical characteristics.

However, even if these waters have some similar chemical characteristics it is highly unlikely that the Thelwood Valley saline waters acquired their Cl^- from local rock interaction.

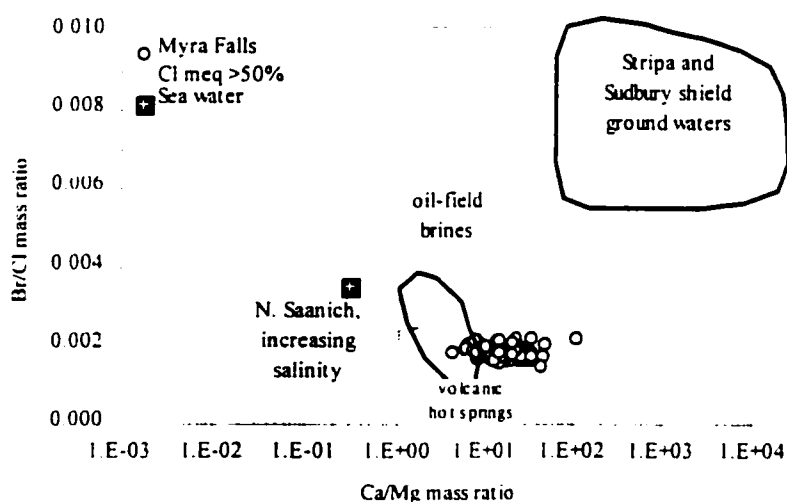


Figure 6-10 Br/Cl vs. Ca/Mg mass ratios of Thelwood Valley Cl^- waters (anion meq $\geq 50\%$ Cl^-). The fields of Stripa and Sudbury brines, and N. Saanich ground waters (Fritz et al., 1983), and oil-field brines and volcanic hot-springs (White, 1957) are plotted for comparison.

Bromide, Cl^- , and Na^+ ratios remain fairly conservative in evaporating sea water until halite saturation is reached (Carpenter, 1978). The Cl^- vs. Br^- trend lies parallel and above the sea water dilution line and therefore does not intersect an evaporative sea water curve (the relationship of Cl^- - Br^- of residual sea water during evaporation). The Br^- vs. Na^+ trend (Figure 6-11) lies sub-parallel to the sea water dilution line and would intersect the concentrated sea water curve above the sea water concentration of Br^- - Na^+ . Bromide and Cl^- are more conservative than Na^+ and would indicate that a residual brine source of salinity does not seem favourable in these waters. However, the Br^- - Cl^- ratio could be produced from a mixture where the total Cl^- results from <10% halite mixed with sea water. A combination of sea water and halite dissolution would also lie above the sea water mixing line for Na^+ , but to a greater degree than the Br^- - Cl^- relationship.

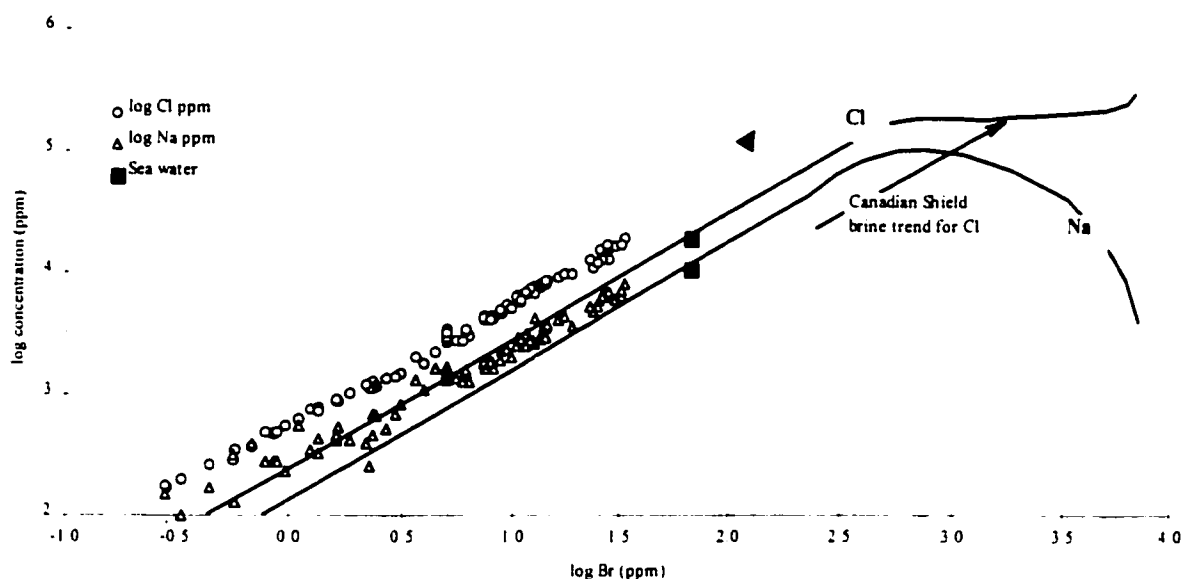


Figure 6-11 Chloride and sodium vs. bromide in ground waters that Cl^- is $\geq 50\%$ meq anions. The Br^- - Cl^- and Br^- - Na^+ trends for evaporating sea water are from Carpenter (1978). Chloride vs. Br^- in Myra Falls water is parallel to a sea water dilution line. The Na^+ vs. Br^- runs sub-parallel to the sea water dilution line and would intersect at a concentrated sea water prior to halite precipitation (inflection point). The large headed arrow indicates the direction of movement when halite ($10^{2.3}$ ppm Br^- and $10^{5.8}$ ppm Cl^-) is added to sea water. The Br^- vs. Cl^- trend of Canadian shield brines (small arrow; Fritz et al., 1983) are plotted for reference.

Up to this point, the possibility of saline water originating as a residual (connate?) fluid or one that has moved into the region from overlying rocks (i.e. sedimentary brines from Cretaceous sediments) has been investigated. There is also the possibility that the saline waters have originated from below the strata in which it is found.

The Myra Falls mining camp is situated on the inboard side of the Juan de Fuca and Explorer plates subduction zones. The modern configuration of convergence beneath Vancouver Island has been continuous under Vancouver Island for ~40 Ma (Clowes et al., 1987). During convergence, underplating beneath Vancouver Island has resulted (Figure 6-12) (Sutherland Brown and Yorath, 1985; Clowes et al., 1987). Much of this underplating was likely pre-Eocene (Lewis et al., 1988) and may consist of marine sediments with pieces of oceanic lithosphere sandwiched in-between or imbricated slices from the top of the subducting oceanic crust (Sutherland Brown and Yorath, 1985; Clowes, et al. 1987). A seaward movement of subduction prior to the late Miocene has been postulated as having left the underplated slab beneath Vancouver Island (Keen and Hyndman, 1979), but this may have been earlier, possibly post Eocene (Sutherland Brown and Yorath, 1985).

Dewatering of subducted sediments through the loss of pore space initially occurs in the deformational front and is often seen in the form of mud-volcanoes (Carson et al., 1991; Moore and Vrolijk, 1992). Further reactions would occur with increasing pressure and temperature as subduction depth increases. Dehydration of sediments and oceanic crust is expected to occur at temperatures above 450 °C (Lewis et al., 1988). The expelled water would move largely up the subducting slab but flow will be controlled by permeable faults and likely occurs sporadically (Moore and Vrolijk, 1992).

Seismic reflector bands located beneath Vancouver Island may represent water driven off the downgoing plate trapped at metamorphic fronts (Lewis et al., 1988) (E1 and E2 on Figure 6-12). These highly conductive zones are presumed to contain saline fluids within interbedded sediments and basalts (Clowes, et al., 1987). As well, these zones tend to occur as isothermal bands in the underplated regions under Vancouver Island which may result from water flow in these regions or temperature buffering due to metamorphic reactions (Hyndman, 1988; Lewis et al., 1988). These zones likely represent permeable layers allowing water movement. Pore water and metamorphic water from the oceanic crust are possible

sources (Lewis et al., 1988). Water is probably being driven from the subducting plate and overlying sediments and moving upwards to lower temperature zones where mineral hydration may be occurring (Lewis et al., 1988). Mineral hydration is one process that will lead to enhanced Cl^- concentrations in water.

Numerous, mainly eastward dipping faults have developed during accretionary tectonic processes under Vancouver Island (Figure 6-12). Many of these faults are believed to carry fluids from greater depth (Lewis et al., 1988). Fluids can travel great distances in convergent zones and may be expelled along lateral distances of 10's of kilometers in accretionary prisms (Moore and Vrolijk, 1992). Extensional veins, common in subduction accretionary prisms illustrate that fluid pressures have exceeded the minimum principal stress. These veins persist as mineral filled fractures to great depths (up to 45 km) (Moore and Vrolijk, 1992). Many of the faults which dislocate the lowest seismic reflector zone extend upwards into the under plated zone beneath Vancouver Island (Sutherland Brown and Yorath, 1985). Other faults extend from the underplated zone into the overlying intrusive rocks and older Triassic and Paleozoic rocks. It is not known whether fluids would travel from the high conductivity zones near the lower sections of the subduction complex upwards into the overlying Wrangellia rocks. It would be presumed that much of this water, if expelled from the subduction zone, would move up-dip along the down-going sediments. Major faulting in the upper portions of the subduction complex (Figure 6-12) may be a more readily accessible pathway for waters moving from the underplated sediments into the overlying crystalline rocks.

There is less knowledge of regarding the composition of water in convergent margins as compared to waters in many other geologic settings (with perhaps the exception of metamorphic water which this setting also includes). Original rock composition is likely important in determining the water composition although, diagenetic and metamorphic reactions and original solute composition may govern the final water composition. Early waters expelled are generally low in Cl^- , as compared to sea water from which they are originally derived. The reasons for this is not completely understood (Kastner et al., 1991), although saline waters may be produced at convergent margins (Martin et al., 1995). If these low Cl^- waters are produced by gas hydrate formation (and degradation) or clay membrane

filtration, then the resulting residual fluid would be a brine (Kastner et al., 1991). Martin et al. (1995) believe that volumetrically little saline Cl^- water would be produced through gas hydration and that clay membranes would be circumvented through permeable faults in convergent tectonics and chemical and isotopic changes in water within convergent margins will be the result of diagenesis and hydration reactions. As well, brines such as CaCl_2 may form from hydration reactions of volcanic ash (Egeberg et al., 1990), or upper oceanic crust (Kastner et al., 1991). Chloride dominated waters can be produced in convergent margins and tracers (isotopic and chemical) may show decoupling of systems at even shallow depths (Kastner et al., 1991).

The relationship between halides in Thelwood Valley saline waters is unusual; $\text{Br}^- / \text{Cl}^-$ is depleted and, I^- / Cl^- is enriched in saline waters from Thelwood Valley relative to sea water (Table 6-1). The relationships between these ions in natural waters are not always fixed, and a wide variety of Br/Cl can result. For example Br/Cl relationships in oil-field brines can be highly variable (Figure 6-10) and high I/Cl ratios have been noted from waters related to west-coast subduction zones (Barnes, 1970). High I^- in these latter waters is believed to result from the decomposition of marine biological remains. In spring waters with similar composition to oil-field brines, but from many different rock types, White et al. (1963) noted that I/Cl ratios may often be elevated with respect to sea water while Br/Cl may be lower (Table 6-1).

Giggenbach (1992) described waters produced from a subduction complex on the North Island, New Zealand. These waters, including saline springs, are expelled during the early stages of the subduction process and have variable ^{18}O and salinities but resemble the trends seen in sedimentary basins. Deuterium was depleted with respect to sea water and ranged from -30 to -20‰. The interaction of sea water with sediments during burial and diagenesis, primarily the role of dehydration of hydrous minerals (clays) was attributed for the changes in the expelled pore water chemistry.

The smectite to illite transition is a kinetic reaction dependent upon temperature and time and requires K in the pore fluids (Moore and Vrolijk, 1992). Complete smectite dehydration produces 35% of the clay's original volume in water (assuming Ca-montmorillonite as the predominant clay in subducting sediments). It can be seen that large

volumes of water may be produced from this reaction. Over-pressuring in petroleum wells often coincides with the intervals of smectite-illite conversion (Moore and Vrolijk, 1992).

Oxygen-18 and deuterium in hydrous minerals such as smectite, illite, and chlorite will be enriched in $\delta^{18}\text{O}$ and slightly depleted $\delta^2\text{H}$ with respect to the water from which these minerals originate. Dehydration of these hydrous minerals will result in an isotopically shifted water. Kyser and Kerrich (1990; Fig. 5.10) illustrate that dewatering pore waters from accreting sediments and water expelled from dehydration of subducting and underplating oceanic crust would plot below the meteoric water line, the result of mixing of meteoric water with an evolved end-member whose ^{18}O and ^2H lies between sea water and metamorphic water. This is the same trend as seen in the saline ground waters from Myra Falls.

Other waters with unique chemistry have been ascribed to the metamorphism of sediments underplating older rock units on west coast convergent margins (Barnes, 1970). Barnes (1970) reported waters of unique character emanating from a variety of rocks along the Pacific coastline, from California to Alaska. In comparison to sea water these waters had high I^- / Cl^- and low $\text{Br}^- / \text{Cl}^-$. These waters also generally have a hydrocarbon association. Some of these waters (i.e. Wilbur Springs, California; Barnes, 1970; pg. 974) have low concentrations of Ca^{2+} and SO_4^{2-} and high H_2S . The reduction of SO_4^{2-} during the oxidation of reduced carbon with the subsequent precipitation of calcite may also account for some the chemical traits.

Although the exact mechanism responsible for the composition of the saline waters found in the area of Myra Falls are not known, it is proposed here that these waters represent a variable mixture of meteoric waters and waters derived from subduction/underplated zones. Underplated sediments lie within approximately 12 km beneath central Vancouver Island. The role of dehydration of hydrous minerals at depth in the subduction complex and possibly the subsequent hydration of minerals at metamorphic fronts higher in the complex may largely control the ^{18}O and ^2H , as well as the Cl^- content of the saline waters. Subducted/underplated waters would have originated as sea water, either in pore water or as water on hydrous minerals in equilibrium with sea water. Pore water would largely be expelled in the initial sediment compaction leaving dehydration reactions to dominate the ^{18}O

and ^2H at greater depths during subduction. The isotopic composition of residual water involved in hydration reactions of minerals at overlying metamorphic fronts would rely upon the temperature dependent fractionation. There may also be effects of membrane filtration occurring in the underplated sediments beneath Wrangellia

Characteristics of major elements and isotopes for the Thelwood Valley saline ground waters are given in Table 6-1. along with general characteristics for some other saline ground waters.

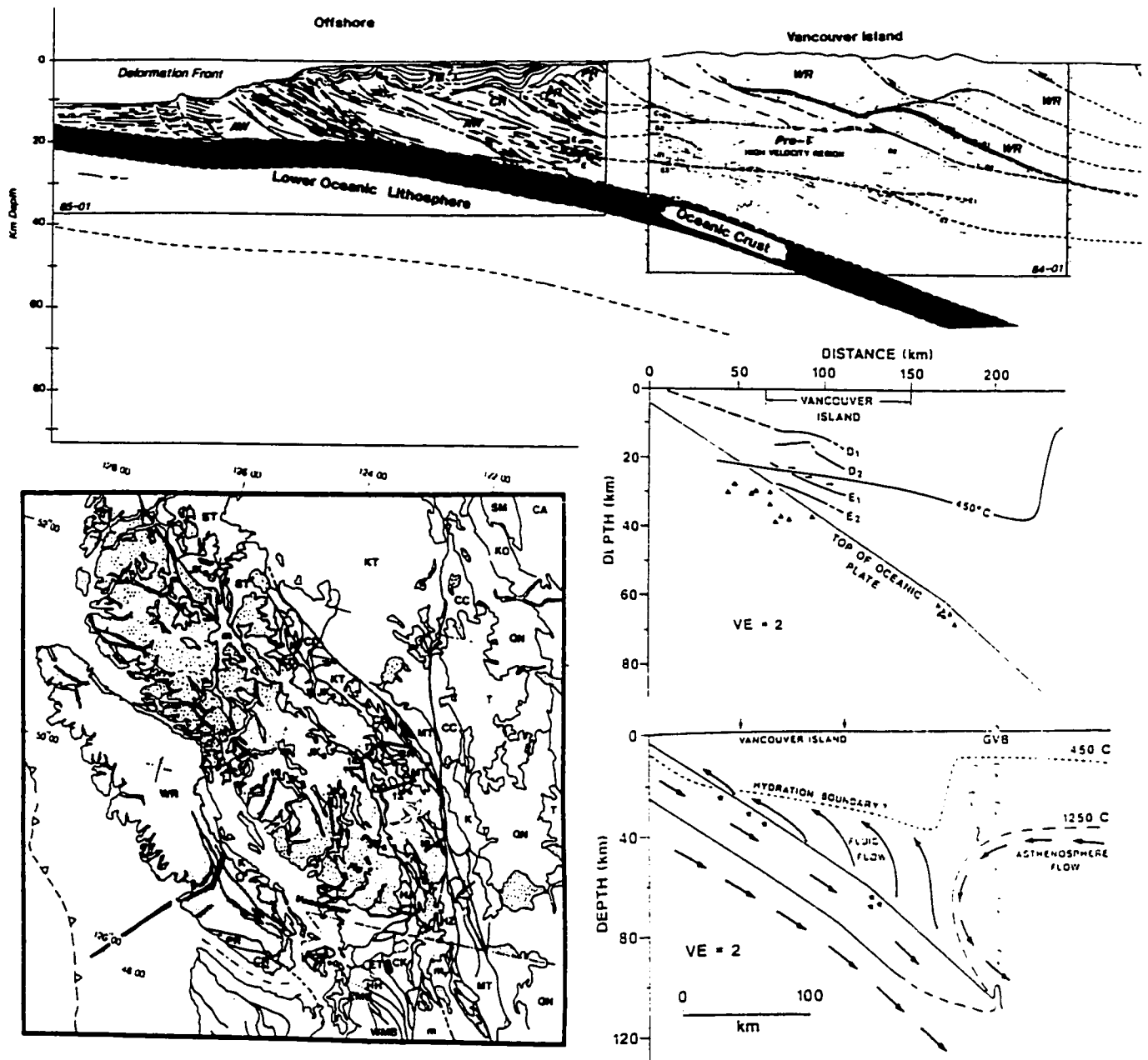


Figure 6-12 Crustal transects through southern Vancouver Island. Top diagram is a seismic interpretation of subduction in the accretionary front and under southern Vancouver Island (from Monger and Journeay, 1992). [WR = Wrangellia; C and D1 = the top of the sediments in the subduction/underplating complex; the HIGH VELOCITY REGION in the central portion of underplated region may be a Cenozoic subduction complex that is bounded top and bottom by sediments; Clowes et al., (1987)] Location of transect is shown on the diagram on the bottom left. Right-centre diagram indicates seismic reflectors and the 450° C isotherm through the same section and diagram (bottom right) indicates that fluid from dehydration flows generally up-dip along the decollement (from Lewis et al., 1988). The 450° C isotherm is progressively shallower towards northern Vancouver Island where the 650° C isotherm may lie at less than 20 km depth (Lewis et al., 1988). The reflectors designated E are near isothermal and likely have high fluid flow.

Table 6.1 Chemical and isotopic summary of the Thelwood Valley saline ground water. Sea water and other chloride waters with unusual chemistry (chloride dominated with high I/Cl) and low Br/Cl relative to sea water) are presented for comparison.

Thelwood Valley Saline Ground Water		Sea Water (Hem, 1985)	Volcanic hot springs (White, 1957b)	Spring water similar to Na-Ca-Cl Oil-field brines (White et al., 1963)	Metamorphic(?) Waters from Undepleted Sediments (Ahoit Hig mine; White et al., 1963)
Water type		Na-Ca-HCO ₃			Na-Cl (high I) (analyses 2, Table 23)
$\delta^{18}\text{O}$ ‰ VSMOW		- Cl(ppm)*0.0007-13.5‰			
$\delta^2\text{H}$ ‰ VSMOW		= 5.6* $\delta^{18}\text{O}$ - 21.8‰			
$\delta^{13}\text{C}$ ‰ VPDB		-9.5 ± -0.5			
$\delta^{34}\text{S}_{(\text{SO}_4)}$ ‰ CDT		-17.5 ± -1.5			
$\delta^{18}\text{O}_{(\text{SO}_4)}$ ‰ SMOW		-11 ± -1			
$^{87}\text{Sr} / ^{86}\text{Sr}$		-0.705 (or lower)			
$\delta^{37}\text{Cl}$ ‰ SMOC		-0.1 to 0.3			
		mass / kg H ₂ O	molar / kg H ₂ O	ppm	mass / kg H ₂ O
Ca		0.22*Cl	0.19*Cl	787	64
Mg		0.010*Cl	0.015*Cl	111	443
Na		0.42*Cl	0.65*Cl	4660	1500
K		0.0019*Cl	0.0017*Cl	60	39
HCO ₃		low ~ <20 ppm		143	2700
SO ₄		0.070*Cl	0.026*Cl	0	467
Cl		variable >17,000 ppm		8870	1900
Br		1.80E-03	8.1E-4*Cl	17	3.8
I		5.7E-5*Cl	1.6E-5*Cl	3.7	6.3
Sr		4.2E-4*Cl	1.7E-3*Cl	51	1.5
B		6.7E-4*Cl	2.2E-3*Cl	35	56
Li		2.4E-4*Cl	1.2E-3*Cl	0.5	2.9E-02*Cl
Other Mass Ratios					
Cu/Na		0.52		0.17	0.043
Li/Na		5.1E-04		1.0E-04	1.2E-03
Mg/Ca		0.045		0.14	6.9
K/Na		0.0045		0.013	0.026

6.2.7 Long term hydrologic stability of the Saline water

No matter what the original source of the saline ground water in Thelwood Valley, the fact that this water currently exists at shallow depth in its present location is of great interest. The mountainous setting in which the saline ground water is situated has high rainfall (Section 1.6), and high piezometric gradients (Stapinsky, 1997) and the saline water encountered at shallow depth was unexpected. Saline waters in crystalline rocks, even in areas of low topographic relief are usually only encountered at considerable depths (i.e. >800 m for Sudbury saline waters, Frape and Fritz, 1982).

Ground waters from rocks within the M-P ridge that have been uplifted and are currently well above the valley floor indicate that saline water flushing is fairly recent. Chemistry of ground water in the upper Myra-Price ridge (Myra 10 level) indicates that elution of components of the saline water is ongoing. Chloride has been flushed from the rocks of the upper M-P ridge but higher than expected Na^+ concentrations in the central core of the ridge suggest that only a small number of pore-volumes of meteoric water have moved through the rock (Section 3.9.1).

Uplift in central Vancouver Island region has been rapid during the Neogene (Parrish, 1983). The Buttle lake uplift has been progressively exhumed over the last 10^7 years and the total uplift in this area over this time period is estimated to be at least $2 \cdot 10^3$ metres. Although Parrish (1983) did not estimate the amount of uplift on central Vancouver Island for periods greater than 10^7 years; regions of the Coastal mountains on mainland British Columbia directly adjacent to central-northern Vancouver Island have undergone uplift estimated in excess of 6 and 8 km over a period of $40 \cdot 10^6$ years. These areas of the Coastal mountains with high uplift over the past $40 \cdot 10^6$ years have estimated uplifts of greater than 4 km in the past 10^7 years (Parrish, 1983) (illustrated in Figure 6-13). Yorath and Nasmith (1995) estimate that as much as 10 km of erosion may have been shed from central and southern Vancouver Island during and after uplift in the Tertiary period. The magnitude of uplift may be responsible for elevating the saline waters into their current location; as the rate of uplift in the Buttle Lake region has outstripped the elution of saline ground waters by meteoric waters (including glacial melt waters).

Contemporary uplift continues throughout the central Vancouver Island region despite subsidence of up to 8 cm in the Campbell River area of Vancouver Island after a 1946 earthquake (Dragert, 1987). Uplift has recently accelerated in this area ($\sim 5 \text{ mm yr}^{-1}$) making it difficult to assign a vertical velocity to this region (Dragert, 1987; Holdahl, et al., 1989); but in the Buttle Lake area, contemporary vertical uplift is in the range of approximately 2 cm per year.

The hydrology within this system has largely remained very stable until perturbed by mine openings. However, once underground caverns have been opened and steep hydraulic gradients are developed, modern meteoric water rapidly moves along permeable pathways to working depths within the mine (i.e. Section 6.2.5).

The saline ground water at shallow depth illustrates that the rate of uplift in the Buttle Lake region has been greater than the degree of flushing of residual saline water by water of meteoric origin. The presence of the saline ground water at shallow depth attests to the long term stability of the hydrologic regime present in this setting.

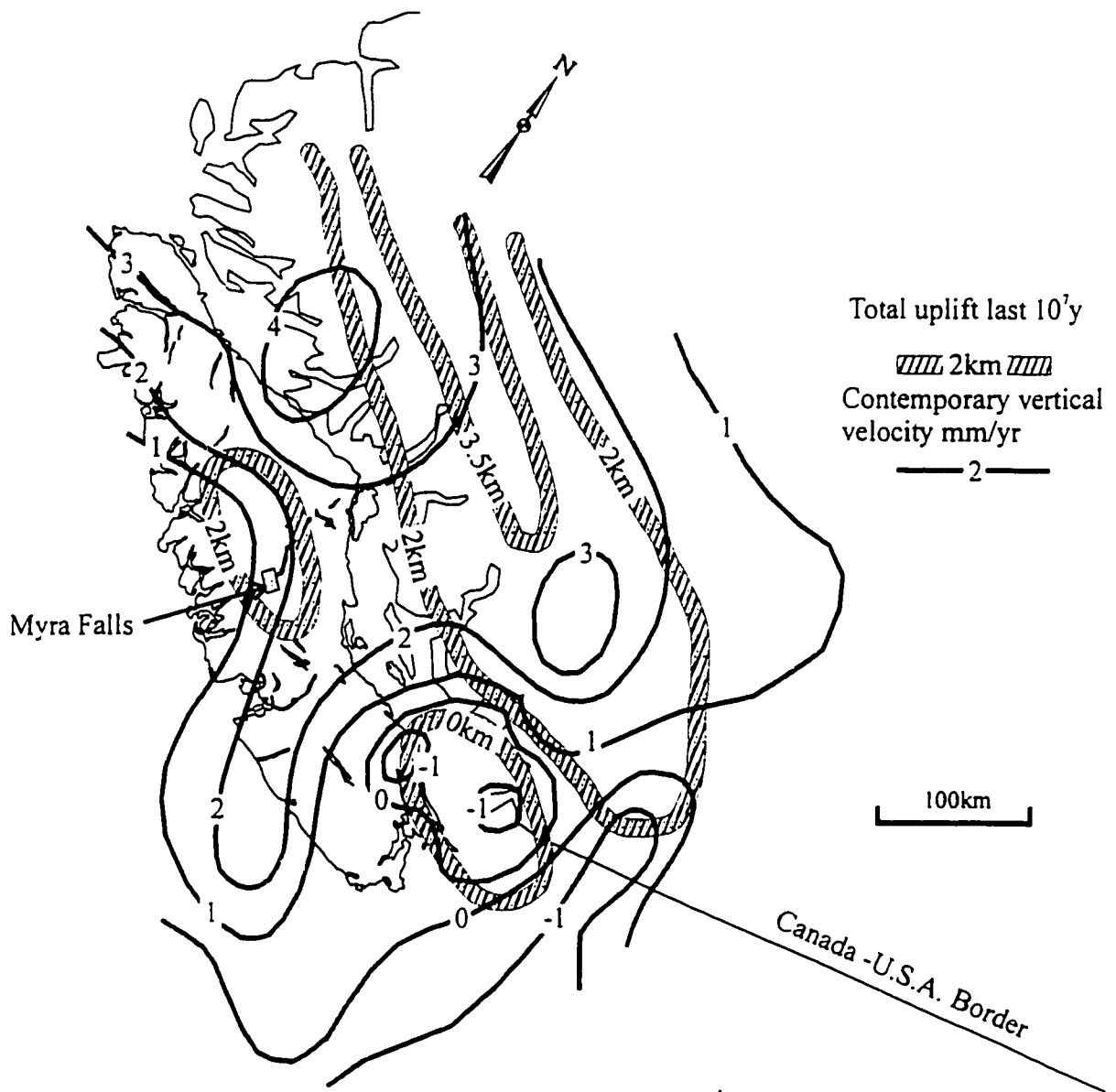


Figure 6-13 Rate of contemporary uplift and magnitude of uplift for Vancouver Island and adjacent mainland British Columbia. The Butte lake region has undergone an estimated >2 kilometers uplift in the past 10^7 years (Parrish, 1983; Monger and Journey, 1992) and continues to be uplifted at an average contemporary velocity of around 2 mm per year (Holdahl, et al., 1989). Areas of the coastal mountain range on mainland British Columbia which have had greater than 3.5 kilometers uplift over this time period have had greater than 5 km (and up to 9 km) uplift over the last $4 \cdot 10^7$ years.

7. Ground Water Hydrogeochemical Exploration Methods

7.1 Introduction

Hydrogeochemistry in mineral exploration offers a third dimensional and deeper penetrating technique presently not available with other geochemical applications. When used together, detailed lithogeochemical surveys, comprehensive structural analyses emphasizing ore and ground water controls, and ground water geochemical programs can be an effective exploration protocol for discovering blind ore deposits. Unfortunately research in ground water geochemical techniques is greatly lacking compared to the other two mentioned methods, despite the fact that analytical methods for waters have been refined to be more reliable, utilize smaller volumes for complete analyses of multi-elements by only a few methods (ICP-MS and ICP-ES for cations and Ion Chromatography and Alkalinity titration for anions), and is capable of detecting cations into the parts per billion and parts per trillion ranges.

Indicator elements are generally major economic components of the ore-body and their presence may indicate proximity to mineralization whereas pathfinder elements are generally non-economic trace elements that occur in association with mineralization and alteration and may often be more readily transported in water than ore-forming elements. Hydrogeochemical elemental dispersion in the vicinity of ore deposits should offer a larger exploration target than lithogeochemical halos.

One of the greatest advantages of using ground waters in exploration programs is the fact that, once waters have traversed an ore zone and/or its alteration halo, they are capable of maintaining a chemical signature of that zone for some distance from mineralization. The chemical signature will be characterized by anomalous concentrations of indicator and pathfinder elements and their differential mobilities will determine both the strength and persistence of the ground water anomalies. Sampling waters flowing from drill holes effectively increases the volume of rock being sampled.

Marchant (1978) conducted a comprehensive historical review of the use of ground waters in geochemical exploration. Much of the work on this subject, especially in regards to base-metal exploration, was conducted in the former Soviet Union where it was found effective in the discovery of a number of ore deposits (e.g. Udodov et al., 1973; Goleva, 1979). In North America, ground water hydrogeochemical exploration methods have not been extensively employed, with the exception of uranium exploration. Recently, ground water hydrochemical exploration methods have been combined with stream sediments (Laville-Timsit and Wilhelm, 1989), surface water geochemical techniques (Cidu et al, 1995), and used independently in regional surveys in arid regions of China (Ren et al., 1989) and Australia (Morris, 1982; Giblin, 1990), and also have been utilized in gold prospecting programs (Grimes, 1992; Grimes et al., 1995).

In a review of hydrogeochemical exploration methods for poly-metallic mineral deposits Miller (1979) suggested that Pb, Zn, Cu, As, Mo, Ni, Ag, Cd, Sb, Se, and Be may act as indicator/pathfinder elements in strongly oxidizing environments. He also indicated that in mountainous terrains with high precipitation and steep hydraulic gradients, the limited contact time between ground water and mineralization may lower element contrasts and thereby restrict the application of hydrogeochemical prospecting methods.

A detailed hydrogeochemical sampling program within the Myra Falls polymetallic volcanogenic massive sulphide mining camp of the Buttle Lake Paleozoic Inlier, Vancouver Island, British Columbia (Figure 1-5) was undertaken to develop methods in hydrogeochemical exploration in mountainous high rainfall terrains. Waters were sampled from 226 sites, including surface waters (n=37) and ground waters accessed from underground workings (n=189) within the Myra-Price ridge. Underground sites included flowing fractures and drill holes, some of which intersect the volcanic hosted poly-metallic massive sulphide Price deposit.

7.2 Field Methods, Sample Collection, and Analytical Techniques

Surface waters were collected from permanent and temporal streams. Ground waters were sampled from flowing drill holes and wet fractures and faults accessed from the Thelwood valley mountain side by four exploration and access tunnels originating at 238 m, 416 m, 580 m, and 626 m elevations; Price 13, 9, 5, and 4 levels, respectively. Most drill holes were arranged in a fan-style vertical orientation that radiated out from drilling stations located at approximately 15.2 m spacing. Drill holes intersecting the Price ore-body were accessed from the 4 and 5 levels. Drill holes intersecting the OCB unit were accessed from 9 level.

Onsite measurements consisted of water temperature, pH, platinum electrode oxidation-reduction potential (Eh), dissolved oxygen (DO), and electrical conductance (EC). Waters were pressure filtered at 0.45 μm . A sample for major cation and trace element analyses was preserved with ultra-pure nitric acid (2% by volume). Samples were refrigerated until analysed at the Geological Survey of Canada Laboratory. Total alkalinity was measured by titration; anions were determined by ion chromatography. Major cations and trace elements were determined using ICP-MS, ICP-ES, and AAS. The concentration of many elements: NO_2 , NO_3 , F, Br, Cs, Be, Sc, Ti, Ag, Ga, In, Hg, Tl and Bi, were below the limit of detection for most waters and their application in exploration have not been pursued further.

7.3 Preliminary Statistical Analyses

Histograms and probability plots were prepared for each variable showing that all variables had some degree of skewness. Multi-modal populations were very evident in Na^+ , SO_4^{2-} , and Ba^{2+} . Variables were transformed into gaussian distributions using the generalized power transform methods of Box and Cox (1964) in the form:

$$y = \frac{(x^\lambda - 1)}{\lambda} \quad (\lambda \neq 0)$$

and

$$y = \ln(x) \quad (\lambda = 0)$$

where x is the original concentration, y is the transformed value and λ is a chosen value to minimize skewness and kurtosis.

Minimizing asymmetry within each variable may introduce a highly peaked distribution; therefore, λ was incrementally adjusted using the weighting scheme that included kurtosis (K) and skewness (S) of the data as suggested by Howarth and Earle (1979) to achieve a minimum value of F in the function:

$$F = 2|S| + |3 - K|.$$

Below detection values and extreme outliers were removed prior to determining λ . To minimize the effect on further statistical procedures below detection values were recoded to values based on fitting the median cumulative probability of below detection values to a normal population. Detection limits, recode values, λ , and median values for select elements and variables of interest are shown in Table 7-1.

Median values are robust estimators of central tendency of distributions and are least affected by outlier and censored data points as compared to other measurements of central tendency such as means; and as such, median concentration values for surface and ground waters are presented in Table 7-1.

7.4 Hydrochemistry

Oxidizing conditions in ground waters circulating through mineral deposits will mobilize elements related to the deposit. Increased fracturing, shearing, and foliation in zones affected by hydrothermal alteration will act as conduits for ground-water flow and increase the contact surfaces for water to react in these zones. The resulting water-rock interaction may impart a specific chemistry to the waters. Complexation of trace metals with HCO_3^- and SO_4^{2-} may enhance the solubility of trace metals; whereas adsorption to hydroxides and clays in the fracture and fault systems, and precipitation due to over-saturation of secondary minerals will remove metals from the water.

Electrical conductivity (EC), an indicator of the total dissolved solids (TDS) in waters, is quite low for both surface and ground waters. Median values of EC are 140 and 198 μScm^{-1} for surface and ground waters, respectively. The pH values are slightly acidic to moderately basic and range from 6.1 to 9.6 with near-neutral median values of 7.3 and 7.5 for surface and ground waters, respectively. Redox (Eh) values range from -0.04 to 0.52 V. Median Eh values are similar for both surface and ground waters at 0.41 V. Dissolved oxygen (DO) is present in all waters; surface waters have a median value of 10.1 mgL^{-1} , which is approximately at saturation with respect to atmospheric oxygen for field conditions. Ground waters have greater variability ranging from 0.8 to 18 mgL^{-1} , with a median value of 9.6 mgL^{-1} .

7.4.1 Surface Water Chemistry

Surface waters are dominated by Ca^{2+} and HCO_3^- (Figure 7-1), and have low dissolved solids as indicated by EC. Median values for all major elements are lower in surface waters than in ground waters; this is especially true for SO_4 , where the maximum surface concentration of 15 ppm is only slightly greater than the median ground water concentration of 12 ppm. The median SO_4^{2-} concentration of surface waters (0.94 ppm) closely reflects rainfall concentration (0.91 ppm). Median Cu and Pb in surface waters are below detection and maximum values of these elements are very low. Median concentrations for the remainder of the trace metals in the surface aqueous environment are below detection, with the exception of Zn and Mn. Zinc concentrations are somewhat higher than Cu or Pb.

and median Zn concentration in surface waters (3.8 ppb) is only slightly less than in ground waters (5.0 ppb). Two surface waters sampled on the upper Price hillside in close proximity to the Lynx-Myra-Price horizon have Zn concentrations of 13 and 17 ppb and may be influenced by oxidation of primary mineralization. In general the surface water environment experiences a high degree of dilution of base flow from the high runoff in this mountainous setting.

7.4.2 Ground Water Chemistry

Ground water major cation compositions are dominated by Ca^{2+} and Na^+ with only a minor contribution from Mg^{2+} ; anion compositions trend from HCO_3^- dominant to SO_4^{2-} dominant waters. Calcium and HCO_3^- concentrations are slightly higher than surface waters reflecting dissolution of fracture calcite (Figure 7-1). The chemistry of many ground waters reflects little interaction with rocks other than contact with quartz-chlorite-calcite lined

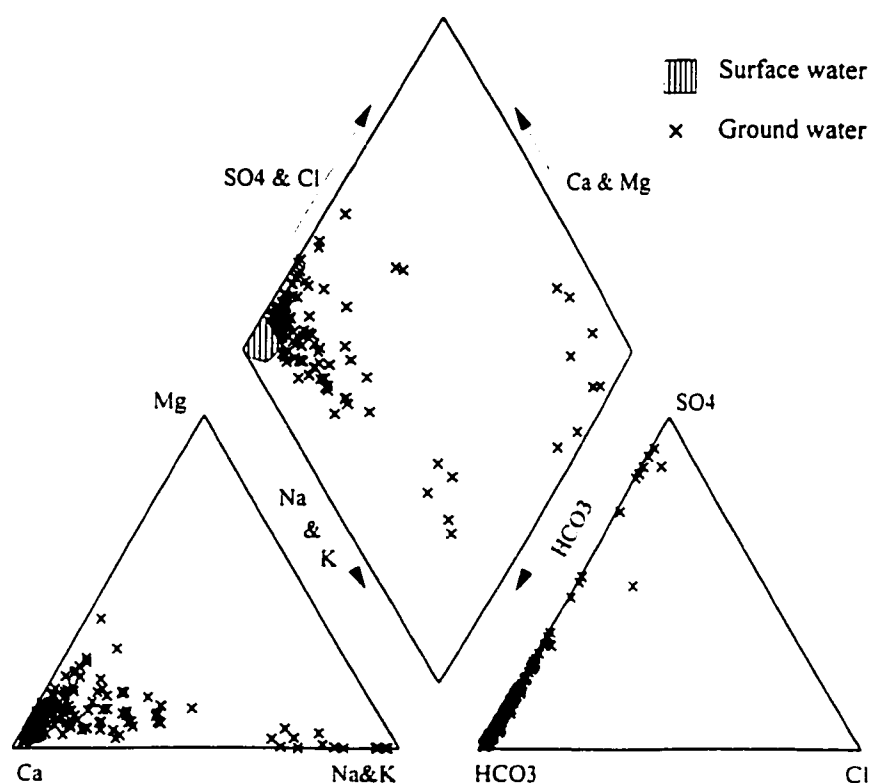


Figure 7-1 Piper plot displaying ground waters and the field of surface waters used for hydrogeochemical prospecting.

fractures. These waters are dominated by Ca^{2+} - HCO_3^- chemistry (Figure 7-1) and have very similar chemistry to surface (recharge) waters. Sources of sulphate include: SO_4^{2-} in recharge waters, dissolution of barite, and oxidation of disseminated and massive sulphides. The proportion of Na^+ tends to increase in ground waters towards the central core of the mountain where ground waters have greater residence time and Ca^{2+} - Na^+ exchange is thought to be occurring. A higher proportion of SO_4^{2-} in some of the Na-dominated ground waters indicates that a greater degree of sulphide oxidation is occurring in some of these waters.

The ore-forming elements (Zn, Cu, and Pb) show large contrasts with Zn concentrations spanning over 3 orders of magnitude (Table 7-1). Minor elements associated with ore forming minerals such as Cd, Sb, and Se, are present but are moderately to heavily censored by values below the detection limit. Cadmium levels tend to be above detection level only when Zn concentrations are high ($\text{Zn} > 50$ ppb), although not all waters with high Zn rigidly conform to this observation. Antimony and U, and to a lesser extent Se, tend to increase with increasing Zn.

Table 7-2 shows correlation coefficients between selected transformed element concentrations in ground waters. The ore-forming elements, Zn, Cu, and Pb, have high correlation coefficients with each other. Zinc is also highly correlated to Mn, Cd, Sb, and U. All but Mn are concentrated in Price massive sulphides. Copper and Pb tend to have lower correlations with ore-accessory elements. Correlations between SO_4^{2-} and ore-forming and ore-accessory elements are low. The strong negative correlation between SO_4^{2-} and Ba results from the increased precipitation of barite during the addition of SO_4^{2-} to water through sulphide oxidation. The low correlation coefficients between SO_4^{2-} and Zn, Cu, Pb, and Cd is probably due to the fact that pyrite is a major source of SO_4^{2-} in solution, however Fe is not correlated to SO_4^{2-} due to the precipitation of Fe-hydroxides in the oxygenated waters and the presence of anhydrite in this setting.

Table 7-1 Detection limits, recode and λ values, and summary statistics for surface and ground water chemical parameters. All concentrations are ppb except where noted.

Element	Detection Limit	Recode Value ^a	Power Transformation λ value ^b	Surface waters			Ground waters		
				Min.	Median	Max.	Min.	Median	Max.
Temp (°C)	-	-	-0.75	7.6	11.5	19.0	5.8	6.7	11.9
EC (μ S/cm)	-	-	0.05	50	140	307	76	198	782
pH	-	-	-0.90	6.1	7.3	7.9	6.4	7.5	9.6
Eh (V)	-	-	3.15	0.36	0.41	0.52	-0.04	0.41	0.48
DO (mg/L)	-	-	1.35	5.7	10.1	12.2	0.8	9.6	18.3
SiO ₂ (ppm)	0.01 as Si	-	0.25	1.1	3.4	4.9	0.9	5.3	19
Ca (ppm)	0.005	-	1.30	2.4	25.0	38.0	2.4	37.0	72
Mg (ppm)	0.002	-	0.20	0.14	0.71	2.7	0.02	1.7	12
Na (ppm)	0.02	-	-0.10	0.052	0.77	2.0	0.31	2.0	160
K (ppm)	0.02	0.01	0.35	0.01	0.029	0.17	0.01	0.26	1.7
HCO ₃ (ppm)	-	-	2.00	6.9	73.9	115	18.3	115	177
SO ₄ (ppm)	50	-	0.00	0.46	0.94	15	0.66	12	286
Cl (ppm)	50	-	-0.45	0.25	0.44	0.75	0.21	0.82	28
Al	0.5	0.48	-0.40	4.6	8.4	56	0.48	4.2	40
Fe	3	1.65	-0.05	1.65	4.0	22	1.65	9.0	160
Li	1	0.13	-0.85	0.13	1.0	2.0	0.13	1.0	79
Rb	0.2	0.003	0.60	0.003	0.003	0.1	0.003	0.003	0.8
Sr	0.03	-	0.15	4.9	20	180	25	410	6550
Ba	0.5	-	0.30	1.0	5.4	63	8.4	77	380
B	16	2.8	0.00	2.8	2.8	49	2.8	2.8	2900
V	0.5	0.07	-0.30	0.07	0.07	0.89	0.07	0.07	4.7
Cr	0.2	0.06	0.30	0.06	0.06	0.7	0.06	0.06	3.0
Ni	1	0.3	0.10	0.3	0.3	0.69	0.3	0.3	7.6
Co	0.2	0.01	-0.05	0.01	0.01	0.05	0.01	0.01	1.4
Mn	0.2	0.18	-0.20	0.18	0.36	2.9	0.18	1.3	110
Mo	0.5	0.01	0.60	0.01	0.01	0.69	0.01	3.1	20
Zn	2	0.44	0.00	0.44	3.8	17	0.44	5.0	1400
Cu	0.5	0.23	-0.15	0.23	0.23	1.8	0.23	0.96	40
Pb	0.2	0.15	-0.80	0.15	0.15	1.3	0.15	0.34	34
Cd	0.5	0.24	-1.45	0.24	0.24	0.24	0.24	0.24	12
As	1	0.58	0.10	0.58	0.58	0.58	0.58	5.1	81
Sb	0.2	0.15	-0.30	0.15	0.15	0.85	0.15	0.87	130
Se	2	1.25	-0.60	1.25	1.25	3.0	1.25	1.25	12
U	0.2	0.07	0.10	0.07	0.07	0.07	0.07	0.3	6.7

^a For samples below detection.^b Box and Cox (1964) power transformation (Ln transformation for $\lambda = 0$)
surface waters n=37, ground waters n=189

Table 7.2 Pearson product moment correlation coefficients for transformed concentrations of selected elements in groundwaters (n=189) from Price hillside. Zinc is highlighted since it is the predominant element in the ore and is the most mobile of the ore forming elements. See text for description of transformations.

	Ca	Ma	Na	K	Fe	SO ₄	Rb	Sr	Ba	B	Mn	Mo	Zn	Cu	Pb	Cd	As	Sb	Se	U
Ca	1.00																			
Ma	0.31	1.00																		
Na	-0.55	-0.07	1.00																	
K	-0.14	0.53	0.63	1.00																
Fe	0.14	0.05	-0.01	0.08	1.00															
SO ₄	-0.27	-0.06	0.75	0.50	0.05	1.00														
Rb	-0.29	0.38	0.60	0.78	0.03	0.47	1.00													
Sr	0.00	0.73	0.49	0.83	0.05	0.39	0.66	1.00												
Ba	0.39	0.42	-0.43	-0.04	0.07	-0.60	-0.20	0.05	1.00											
B	-0.55	-0.02	0.92	0.63	0.02	0.71	0.65	0.52	-0.46	1.00										
Mn	-0.09	0.25	0.18	0.33	0.28	0.25	0.29	0.30	0.09	0.20	1.00									
Mo	-0.24	0.13	0.71	0.59	0.00	0.75	0.50	0.58	-0.36	0.64	0.26	1.00								
Zn	0.33	0.21	-0.18	0.12	0.10	0.14	0.04	0.08	0.18	-0.18	0.41	0.13	1.00							
Cu	0.24	0.14	-0.20	0.08	0.11	0.04	-0.04	0.03	0.20	-0.23	0.30	0.10	0.65	1.00						
Pb	0.20	0.18	0.02	0.22	0.35	0.13	0.07	0.16	0.24	-0.01	0.37	0.17	0.61	0.43	1.00					
Cd	0.22	0.16	-0.19	0.02	0.18	0.03	-0.13	-0.01	0.22	-0.22	0.36	0.03	0.61	0.49	0.43	1.00				
As	-0.09	0.29	0.50	0.61	0.13	0.46	0.53	0.59	-0.06	0.46	0.34	0.68	0.19	0.11	0.25	0.05	1.00			
Sb	0.21	0.42	-0.04	0.27	0.01	0.15	0.11	0.42	0.17	-0.08	0.26	0.43	0.41	0.42	0.28	0.35	0.49	1.00		
Se	0.12	0.14	-0.14	-0.06	-0.22	0.03	-0.15	-0.01	0.10	-0.22	-0.05	0.11	0.28	0.21	0.11	0.25	0.02	0.40	1.00	
U	0.22	0.60	-0.06	0.38	0.08	0.07	0.23	0.48	0.28	-0.08	0.27	0.31	0.38	0.34	0.35	0.33	0.42	0.70	0.40	1.00
CA		MG	Na	K	Fe	SO ₄	Rb	Sr	Ba	B	Mn	Mo	Zn	Cu	Pb	Cd	As	Sb	Se	U

7.5 Zinc Threshold Estimation and Anomaly Detection

Filtration studies of selected ground waters associated with the Price deposit carried out concurrent to this study (Chapter 4; Phipps et al., 1997) show that, of the ore indicator elements only Zn is predominantly transported as dissolved species. Adsorption to suspended particulates, which are dominantly amorphous Fe-hydroxides $>0.45\mu\text{m}$ in size, is quite high for Cu (median loss of 40 to 50% of total Cu in HCO_3^- and SO_4^{2-} dominated waters), and Pb (70 to 80% loss of total Pb); whereas median sorption losses of Zn to suspended solids was around 10% and 5% of the total Zn concentration in HCO_3^- and SO_4^{2-} waters, respectively. Within the bicarbonate and sulphate ground waters associated with the Price deposit and surrounding area, Zn has similar mobility and behavior and therefore these waters can be treated comparably with respect to Zn. The superior mobility of Zn in waters oxidizing sulphide mineralization has been shown by many authors (e.g. Cameron, 1978; Giblin, 1978; Laville-Timsit and Wilhelm, 1989).

Precipitation of secondary minerals will limit the concentration of Zn in solution. Mann and Deutschler (1980) investigated the most probable Zn phases to precipitate in various solution matrices. The first phase to precipitate in bicarbonate and sulphate waters with pH values between 6 and 8 is smithsonite (ZnCO_3). No ground waters in this study were saturated with respect to smithsonite or any other common Zn mineral as calculated using the speciation program PHREEQC (Parkhurst, 1995) and the geochemical data base of WATEQ4F (Ball and Nordstrom, 1991). Other than slight losses by sorption to Fe-hydroxides, Zn would be expected to remain in solution.

Since Zn is a major constituent of the ore deposits and it has the lowest losses due to sorption, it lends itself as an excellent indicator element.

In geochemical surveys it is assumed that both background and anomalous populations are adequately represented in the data set. Estimating the threshold, which is the maximum background or non-mineralized concentration, is the greatest problem encountered in exploration data analyses. While there is no single widely accepted method of threshold estimation; subjective cut-off values such as mean plus 2 or 3 standard deviations would be completely unsatisfactory, especially in an area of known mineralization where anomalous

waters would be expected to account for more than a small proportion of the population. Garrett (1991) states there are no compelling reasons to keep a data-set whole when disaggregating the data set into separate dominant populations will aid in the interpretation. Disaggregating or partitioning data sets into constituent populations for grouping of data sets and for estimating threshold values has been successively demonstrated by Sinclair (1974, 1976, 1991) as an aid in geochemical data analyses.

A gaussian distribution will plot as a straight line on a chart of standardized normal distribution function ($\bar{x} = 0, s = 1$), where $\bar{x}$ is the mean and s is the standard deviation of the element of interest. Deviation from a straight line may indicate the presence of outliers (real or the result of induced errors) a truncated population, or more than one population. The probability plot (Figure 7-2) of natural log (ln) transformed ground water Zn values reveals that a mixture of two populations is present. An inflection point divides the data-set into 82% and 18% proportions. The median and median $\pm 1s$ of each idealized population from transformed values are presented in Table 7-3. The two populations were then recombined at their respective proportions. Selected points are re-plotted and show a good fit to the original data (Figure 7-2).

While there is good separation between the median $\pm 1s$ concentrations within transformed values, there is considerable overlap between the two populations. This can be expected from ground waters in close proximity to massive sulphide mineralization, where some ore-minerals are disseminated outside of the massive mineralization (see Zn concentrations for various rock units in Table 1-3). The result is an overlap of the two Zn populations and therefore a degree of uncertainty must be expected in assigning a threshold value. The degree of uncertainty will decrease as the threshold value is raised. Based on the two constituent populations of Zn there would be approximately 10% of the cumulative population A above a threshold of 20 ppb Zn (Figure 7-2). This value drops to 5% and 1% as the threshold value is raised to 25 and 38 ppb, respectively. By raising the threshold there is less chance of assigning a background Zn concentration as anomalous, analogous to a Type I error, with the consequence of not recognizing anomalous sites (Type II error). The threshold value chosen would have to be based on the acceptable risk of uncertainty (or confidence).

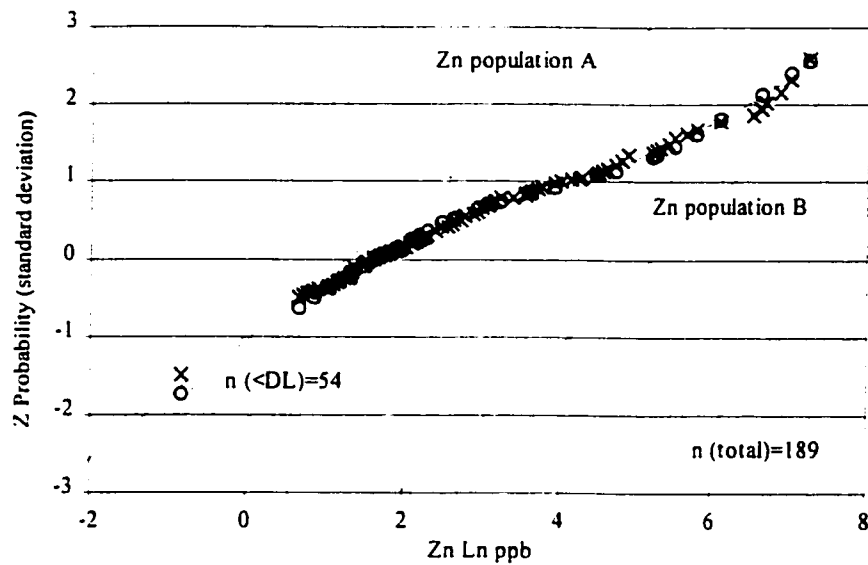


Figure 7-2 Probability plot of ground water Zn partitioned into 2 constituent populations. Original data (x) and recombined ideal mixture of partitioned populations (o) plot in very good agreement. Below detection values are not used in calculation of Zn population A.

Table 7-3 Ground water Zn sub-population parameters. Populations correspond to A and B in Figure 7-2. Sd is standard deviation.

Population	Proportion %	Median transform $\ln(\mu\text{gL}^{-1})$	Median (μgL^{-1})	Transform Sd	Transform -1Sd $\ln(\mu\text{gL}^{-1})$	Median -1Sd (μgL^{-1})	Transform +1Sd $\ln(\mu\text{gL}^{-1})$	Median +1Sd (μgL^{-1})
A	82	1.28	3.6	1.28	0.00	1.0	2.6	13
B	18	5.18	178	1.08	4.11	61	6.3	520

7.6 Applications to Exploration (Price Deposit)

In the Price area the high DO ground waters will oxidize dissolved Fe (predominantly from pyrite) producing Fe^{3+} which is rapidly removed from solution as oxy-hydroxides. The high surface charge of Fe-hydroxides will preferentially remove metals from water by adsorption and co-precipitation ($\text{Pb} > \text{Cu} > \text{Zn}$). Oxidation of economic mineralization (with a low ratio of pyrite to ore minerals) will result in a greater proportion of pathfinder elements entering the water as compared to the iron released from pyrite oxidation. This will result in a lower removal of indicator and pathfinder elements from the water through losses to sorption as Fe-hydroxides precipitate. This is evident by higher Cu and Pb concentrations in ground waters with lower Fe concentrations (Table 7-4). This may allow additional indicator/pathfinder elements to be used in assessing and enhancing the strengths of the Zn anomalies. At greater distances along ground-water flow paths with continued oxidation of ubiquitous pyrite greater losses of metals by adsorption to Fe-hydroxides would be expected.

Ground water chemical data (Table 7-4) for two sections intersecting the Price ore-body, 150 m apart illustrate element contrasts between background and anomalous ground waters draining this ore-body and its surrounding rock units (Figure 7-3). Water emanating from drill holes located above mineralization (drill holes Pr4-54, Pr4-36 and Pr4-35 on section 51+50 m E, and Pr4-103 and Pr5-74 on section 50+00 m E) and water from drill holes Pr5-75 and Pr5-76 on section 51+50 m E display background chemistries. These ground waters (e.g. Pr4-35 and Pr4-36) have concentrations of major ions (i.e., SO_4 , SiO_2 , Na, Sr) similar to surface waters (Table 7-1), and have therefore undergone little rock interaction following recharge.

Zinc concentrations reach maximum values of 1100 and 1400 ppb at anomalous sites on these sections, illustrating that large ground water Zn contrasts can be generated in areas with high relief and high rainfall. Ground waters containing above threshold values of Zn can therefore be designated as anomalous and concentrations of associated pathfinders (Cu and Pb) and indicators (e.g. Cd, Sb, Mn, As, and U) in some cases can be examined to determine the strength of the ground water anomaly and the degree of proximity to ore.

Lithium, Rb, B, and Mo concentrations, although variable, tend to be higher in ground waters at 50+00 m East as compared to those at 51+50 m East and ground waters at section 51+50 m E tend to have higher Ba concentrations than those at 50+00. This illustrates that not all ground waters interacting with ore and alteration minerals will have the same suite of enhanced elements. Strontium tends to be elevated in most ground waters reflecting its elevated concentrations in hangingwall rocks (Table 1-3). Copper, Pb, Cd, and Sb show enrichments in ground waters with anomalous Zn concentrations in both sections, although, this is not always the case in other anomalous waters. Manganese, although not greatly abundant in the ore (Table 1-3) tends to be elevated in most of the anomalous waters. The reason for this is unclear; the origin of Mn may be from overlying mafic rocks (G-flow unit).

Elements with a mafic rock affinity (V, Cr, Ni, and Co) are often elevated in ground waters draining areas underlying the mafic G-flow unit in the Price area.

Uranium, As, and Sb, which are enriched in the ore, tend to be slightly elevated in anomalous waters. These elements in conjunction with other pathfinders are useful in anomaly enhancement.

In summary Zn is a definitive indicator element due to its superior mobility in the ground water environment. Other indicator and pathfinder elements (Cu, Pb, Cd, Mn, As, Sb, and U) may enhance the Zn anomalies and give some indication of proximity to ore.

7.7 Discrimination Between Massive Sulphide Mineralization and Ore Clast Breccia (OCB)

Summary statistics for ground waters with $\text{Zn} \geq 20$ ppb in the vicinity of the Price ore-body (levels 4 and 5) ($n=32$) and from drill holes intersecting the OCB unit ($n=7$), are outlined in Table 7-5. Ore forming elements (Zn, Cu, and Pb) are not definitive as discriminators between the two types of mineralization since both types of mineralization contain similar sulphide minerals. Mean values of K, Rb, B, Sr, and Mg (sericite/muscovite, plagioclase, and chlorite origin), are significantly greater in waters associated with the Price ore-body as compared to the OCB. Barium, Cd, and Sb are the only ore related pathfinder elements that have a much greater mean and maximum concentration in ground waters

related to the Price deposit as compared to ground waters associated with the OCB. The elevated Ba concentrations in the Price waters is related to the higher barite concentration within the Price ore and host rocks. Cadmium is usually only detected when Zn concentrations are high and the higher mean Cd concentration in ground waters related to the Price ore-body is likely due to the higher maximum Zn concentrations in ground waters associated with Price ore. Chromium, although in very low concentrations, is found in ground waters associated with the Price deposit. Chromite is present above the hanging wall of the Price ore-body (Juras, 1987) but this mineral should be resistant to chemical attack. Boyle (1974) reports that Cr is sometimes present as chrome-mica in alteration zones associated with polymetallic sulphide deposits. Weathering of micas would release Cr which would be transported mainly in the form of the anion complex, chromate (CrO_4^{2-}).

Mean U concentrations are also significantly different for these two environments. Uranium is slightly elevated in the massive sulphides (Table 1-3), and is present in specific fault zones as determined by geophysical logging on the property (J. Mwenifumbo, personal communication, 1997). Average U concentration in ground waters related to Price ore is greater than the maximum value from the OCB ground waters.

The use of the elements K, Rb, Ba, Cd, Sb, and U, related to primary depositional processes and host rock alteration, provides an effective tool in discriminating between the Price ore-body and the ore-clast breccia unit after initial delineation of anomalous ground waters using Zn as an indicator element. Elements elevated in overlying stratigraphic units of the Price deposit (i.e., Cr, Sr, Mn, and Mg) may also be helpful in discrimination processes.

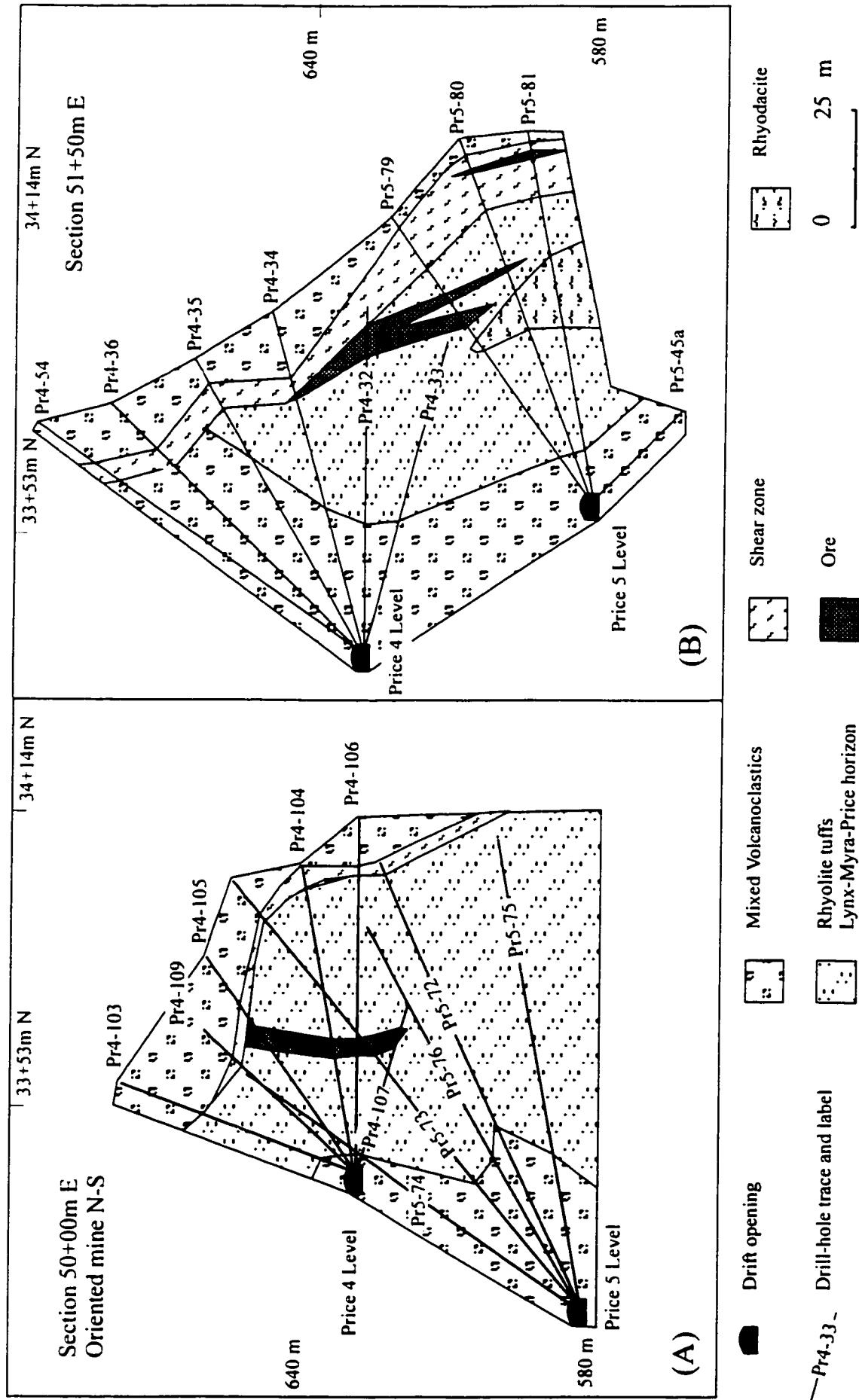


Figure 7-3 Geological section through Price ore-body at 50+00m East (mine co-ordinates) (A), and 51+50m East (B). Hhydrochemistry in ground water flowing from drill holes is outlined in Table 7-4.

Table 7-4 Hydrogeochemistry of groundwaters associated with the Price ore body environment (sections 50+00m E and 51+50m E, mine coordinates). Drill holes correspond to drill holes on Figure 7-3. Concentrations in ppb except where noted (<DL = less than detection).

Element	Section 50+00m E						Section 51+50m E								
	Background			Intermediate			Anomalous			Background			Anomalous		
	Pr4-103	Pr5-74	Pr5-76	Pr5-75	Pr4-105	Pr4-104	Pr4-106	Pr5-73	Pr4-54	Pr4-35	Pr4-36	Pr4-34	Pr4-32	Pr5-80	Pr5-81
Temp (°C)	7.5	6.9	6.5	6.3	7.5	7.2	6.5	6.7	5.9	6.1	6.0	6.1	7.0	6.3	6.3
EC (µS/cm)	186	181	189	192	217	235	198	181	197	196	180	184	199	163	196
pH	7.7	7.6	7.2	8.4	7.6	6.7	7.7	7.0	7.6	7.1	7.0	7.3	7.5	7.6	7.4
Eh (V)	0.39	0.41	0.39	0.38	0.39	0.43	-	0.40	0.42	0.43	0.43	0.42	0.39	0.41	0.40
DO (mg/L)	10.1	-	-	9.8	9.2	-	3.9	-	-	-	-	-	10.4	-	-
SiO2 (ppm)	8.1	7.1	6.0	8.8	9.6	5.8	6.6	5.3	3.9	3.0	0.9	4.3	5.3	6.2	4.5
Ca (ppm)	23.0	30.0	34.0	33.5	33.0	42.0	31.0	34.0	45.0	46.0	41.3	41.0	41.0	33.0	41.0
Mg (ppm)	7.3	1.0	4.7	2.1	4.4	4.2	3.8	3.1	2.6	2.3	1.6	2.6	2.4	3.0	3.7
Na (ppm)	5.7	13.0	3.7	9.8	2.5	3.0	2.6	2.3	1.5	0.8	0.3	1.9	2.0	1.5	1.4
K (ppm)	0.4	0.4	0.5	0.6	0.3	0.4	0.4	0.7	0.2	0.2	0.2	0.3	0.3	0.3	0.4
HCO3 (ppm)	106	109	113	106	110	108	104	108	141	144	130	127	122	109	127
SO4 (ppm)	7.1	14.4	15.3	19.5	5.5	28.8	10.1	11.8	3.2	1.5	1.5	7.0	7.5	5.8	10.8
Cl (ppm)	1.1	1.0	0.9	0.9	1.3	0.9	1.8	1.6	0.8	0.9	0.8	0.9	0.8	0.9	1.0
Al	2.6	4.5	5.4	4.6	2.7	6.1	11	3.1	6.2	9.2	6.4	6.1	5.4	1.3	1.6
Fe	1.7	12	23	2.8	<DL	12	23	14	11	51	41	7.0	<DL	32	41
Li	3.0	3.0	1.0	4.0	3.0	1.0	<DL	1.0	1.0	1.0	1.6	1.0	2.0	<DL	1.0
Rb	0.20	0.23	0.25	0.35	0.20	0.21	0.18	0.35	<DL	<DL	<DL	<DL	<DL	<DL	0.27
Sr	920	1200	1100	1400	340	1150	450	520	1000	130	269	980	950	950	1100
Ba	87	61	64	63	220	80	150	110	130	300	160	210	230	150	130
B	74.0	140	33	105	<DL	29	<DL	<DL	17	<DL	<DL	<DL	<DL	<DL	<DL
V	0.30	<DL	<DL	0.10	0.30	0.25	0.40	<DL	<DL	<DL	<DL	0.90	1.00	<DL	<DL
Cr	<DL	0.35	0.23	0.45	0.40	0.20	0.21	1.20	<DL	0.33	0.27	0.21	0.40	0.30	0.30
Ni	<DL	2.1	1.1	5.0	<DL	2.2	1.1	7.6	1.7	1.6	1.4	1.3	1.0	<DL	1.5
Cu	<DL	<DL	<DL	0.30	<DL	0.41	0.07	<DL	<DL	<DL	<DL	<DL	0.30	<DL	<DL
Mn	0.4	2.4	1.6	0.6	2.3	66	22	16	2.6	4.4	2.7	11	11	1.2	2.5
Mo	6.4	5.7	6.7	4.0	1.0	10	2.7	4.7	1.1	<DL	<DL	1.6	1.4	2.0	5.1
Zn	5.0	6.1	3.5	3.5	22	1400	240	680	<DL	12	14	970	1100	240	810
Cu	0.5	2.0	<DL	0.7	1.1	7.6	3.2	18	1.1	1.6	2.2	19	20	6.5	28
Pb	0.4	0.6	0.5	0.4	0.4	34	6.5	12	0.3	1.5	0.8	19	20	1.6	24
Cd	<DL	4.1	<DL	<DL	<DL	3.2	0.97	12	<DL	0.55	<DL	4.5	5.0	1.4	3.2
As	4.0	9.0	51	12	3.0	17	15	15	2.1	<DL	1.5	8.6	8.0	7.1	8.1
Sb	1.3	1.0	1.5	0.5	1.0	25	3.3	11	0.7	0.2	0.2	6.1	5.8	4.0	18
Se	5.0	<DL	<DL	<DL	5.0	2.0	2.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	5.9
U	0.70	0.27	6.7	<DL	1.0	3.8	2.1	5.8	0.59	<DL	<DL	0.49	0.50	1.6	3.1

Table 7-5 Summary statistics for Zn $\geq$ 20 ppb in groundwaters from the vicinity of the Price ore-body (Price 4 and 5 levels) and ore clast breccia unit (OCB). Recode values from Table 7-1 are used for concentrations less than detection. Concentrations are in ppb except where noted.

Element	Price Ore body (n = 32)			Ore Clast Breccia (n = 7)		
	Min.	Mean	Max.	Min.	Mean	Max.
Temp (°C)	6.0	6.6	9.3	6.7	7.0	7.2
EC (mS/cm)	163	234	458	76	178	277
pH	6.4	7.3	8.1	7.2	7.7	8.1
Eh (V)	0.37	0.41	0.44	0.35	0.40	0.45
DO (mg/L)	3.9	9.3	11.2	5.3	10.0	18.3
SiO ₂ (ppm)	3.2	5.5	9.6	2.1	3.6	4.9
Ca (ppm)	31	41	72	15	35	53
Mg (ppm)	2.4	4.7	12	0.45	0.90	1.3
Na (ppm)	0.56	3.5	29	0.60	1.5	1.9
K (ppm)	0.11	0.45	1.7	0.032	0.045	0.067
HCO ₃ (ppm)	98	124	170	39	86	109
SO ₄ (ppm)	4.3	21	107	5.9	19	47
Cl (ppm)	0.59	0.93	1.8	0.38	0.52	0.61
Al	1.3	4.6	16	4.6	7.1	11
Fe	1.7	16	41	3.0	15	38
Li	0.1	1.2	6.0	0.1	1.0	2.0
Rb	0.003	0.20	0.80	0.003	0.017	0.10
Sr	160	1476	6550	63	150	320
Ba	16	130	330	25	61	90
B	2.8	29	180	2.8	2.8	2.8
V	0.07	0.17	1.0	0.07	0.10	0.25
Cr	0.06	0.23	1.2	0.06	0.08	0.22
Ni	0.30	1.0	7.6	0.30	0.53	1.9
Co	0.01	0.04	0.41	0.01	0.18	0.60
Mn	0.60	14	110	1.1	4.4	11
Mo	0.01	4.3	20	0.01	3.4	6.9
Zn	20	299	1400	22	60	130
Cu	0.23	5.2	28	1.1	9.0	40
Pb	0.15	7.0	34	0.15	0.9	3.0
Cd	0.24	1.7	12	0.24	0.28	0.6
As	0.58	11	43	0.58	5.5	19
Sb	0.15	15	130	0.34	1.8	5
Se	1.3	2.8	12	1.3	2.4	4.2
U	0.07	1.6	5.8	0.07	0.30	0.5

7.8 Conclusions

Zinc concentrations ranged from below detection, to 1400 ppb in ground waters related to the Price ore deposit, illustrate that even in mountainous regions with high rainfall that contact between ore minerals and ground water is sufficient to impart high element contrasts.

Anomalies are first identified using Zn as the preferred indicator element due to its superior mobility in the oxygenated ground waters typical in this setting. Threshold levels were determined by partitioning of the distributions of transformed Zn concentrations into two constituent sub-populations. The background Zn population is represented by 82% of the ground waters and has a median concentration of 3.6 ppb; the second population represents the remainder of the ground waters with a median concentration of 178 ppb. The threshold concentration is dependent upon the willingness to assume uncertainty of designating background ground waters as anomalous and is 20 ppb, 25 ppb, and 38 ppb Zn, for uncertainties of 10%, 5%, and 1%, respectively. Exploration programs in new regions may find cut-off values to differ depending on the distribution of background and anomalous populations.

The strength of the anomaly, after initially being defined on the basis of Zn, can then be further enhanced based on a combination of indicator and pathfinder elements. The list of elements useful in anomaly enhancement include: Cu, Pb, Cd, Mn, B, Sb, and U.

The presence of the ore-clast breccia (OCB) unit presents a problem in developing hydrogeochemical exploration methods in this mining camp. Using Zn as definitive indicator element does not differentiate between anomalous ground waters related to massive sulphide mineralization and the OCB unit. Effective discrimination of ground water anomalies is possible between these two types of mineralization through the use of elements associated with hydrothermal alteration, primary mineralization, and in this setting, elements in the stratigraphy overlying the Price deposit. Elements associated with the hydrothermal alteration such as K, Rb, and B are elevated in ground waters associated with the Price ore deposit as compared to the OCB. Elements concentrated in the massive sulphide mineralization, such as Ba, Cd, Sb, and U, are also important in differentiating between these two types of

mineralization. Elements related to weathering the mafic volcanics overlying the Price ore-body (Sr, Cr, Mg, and Mn) prove advantageous in this setting through additional elements used in discrimination of waters that have been in contact with the mafic units overlying the Price ore.

Hydrogeochemical exploration for volcanogenic massive sulphides in mountainous terrain of Canadian Cordillera can be easily and economically applied since a full suite of elements need not be determined. Anions such as: F, Cl, Br, NO₂, NO₃, HCO₃, are of little efficacy in a hydrogeochemical exploration program for this type of mineralization. Likewise SO₄, which has several sources not exclusively related to massive sulphide mineralization need not be analysed. Major cations are also not essential in determining anomalous waters thus limiting the number of metals analysed allowing for rapid and cost effective analyses of waters using ICP-ES/MS techniques.

8. Conclusions

The primary objectives of this research were of a divergent nature, namely an environmental isotope and hydrochemical assessment, and develop an improved hydrogeochemical method of mineral exploration in the Myra Falls location. The importance of understanding flow systems in a mountainous setting and the mobility of metals in ground waters related to poly-metallic massive sulphide mineralization in this environment is highly relevant in assessing elements to be used in hydrochemical exploration programs, and also in mitigating the environmental consequence of mining these deposits. The following is a reiteration of the primary objectives of this study which are:

- 1.Characterize ground water geochemical facies and determine the geochemical and isotopic evolution of waters, the spatial variations of ground waters, and mean residence times of ground waters within a fractured flow system located in mountainous terrain with high precipitation.
2. Obtain an understanding of the hydrochemical processes that control concentrations and mobility of metals in this setting.
- 3.Develop ground water hydrogeochemical exploration methods that can be used for discovering new mineralization, and/or extensions to existing ore-bodies within the Myra Falls mining camp.
4. Create a quality controlled database of ground and surface water chemistry that can be used in future environmental investigations in this area.

The fourth objective has largely been met in the internal report entitled "GSC-Westmin Resources Industrial Partners Project, Myra Falls Hydrogeochemistry: Sample Quality Control and Hydrochemical Database" by G.C. Phipps, D.R. Boyle and I.D. Clark. Additional information contained within this thesis will also be beneficial for future investigations within this area and will hopefully be of use in areas with similar physiographic settings.

The hydrochemical regimes operating within the mining complex and processes such as recharge, circulation, and mixing can be differentiated on the basis of chemical and isotopic characteristics of the water.

8.1 Water Facies

8.1.1 Precipitation and Surface Waters

Precipitation in the Myra Falls region is high ($>2500 \text{ mm yr}^{-1}$) and predominantly occurs during the fall and winter months. Tritium in precipitation is quite low ($2.7 \pm 0.8 \text{ TU}$), which is typical in a near-coastal setting.

The mean isotopic value of the amount-weighted rainfall is $\delta^{18}\text{O} = -12.0\text{‰}$, and $\delta^2\text{H} = -87.2\text{‰}$ VSMOW, which lies on the global meteoric water line (GMWL) as defined by Rozanski et al. (1993). The winter LMWL, which corresponds to the high precipitation period [Oct. - March, inclusive], is $\delta^2\text{H} = 8.49 \pm 1.47\text{‰} \cdot \delta^{18}\text{O} + 15.1\text{‰}$; with a deuterium excess = 9.1‰ . The winter LMWL lies above the summer LMWL which is $\delta^2\text{H} = 8.39 \pm 0.97\text{‰} \cdot \delta^{18}\text{O} + 3.9\text{‰}$. The local meteoric water lines for Myra Falls rainfall follow the deuterium excess trend of precipitation in Victoria B.C. which is winter deuterium excess being greater than the summer precipitation. The winter LMWL for Myra Falls lies above the LMWL for Victoria B.C. for the same period.

Precipitation at higher elevations, dominantly from snowfall in the winter months, is isotopically depleted from the monitoring station rainfall values. The effect on ^{18}O in precipitation recorded in surface waters due to elevation is $-0.15\text{‰} \delta^{18}\text{O}$ per 100 m rise in elevation in the Myra Falls area.

Surface streams, besides showing the effect of elevation on $\delta^{18}\text{O}$ and $\delta^2\text{H}$, have $\delta^{13}\text{C}_{\text{DIC}}$ averaging -5.1‰ VPDB (mean $P_{\text{CO}_2} = -2.8$; $n=3$) resulting from atmospheric CO_2 equilibration and some contribution from interflow waters previously contacting organically derived CO_2 from soil zones.

The chemistry of local precipitation and surface waters is dominated by Ca^{2+} - HCO_3^- ions. The SO_4^{2-} and Mg^{2+} components increase in surface waters that have had anthropogenic influence and coincides with decreasing pH. This includes waters associated with the Lynx open pit, waste rock dumps and infrastructure (roads etc.) built with waste rock. Chloride, Na^+ , and K^+ have low concentrations in all surface waters.

8.1.2 Shallow Ground Water

Shallow ground waters are of recent meteoric origin, contain tritium, have low (<200 ppm) total dissolved solids (TDS), $\text{Ca}^{2+}\text{-HCO}_3^-$ chemistry, and are nearly saturated with respect to dissolved oxygen (DO). These ground waters are mainly limited to the fractured rock carapace of the Myra-Price ridge, and shallow zones within Thelwood Valley.

Carbon-13 in dissolved inorganic carbon (DIC) is variable ($\sim -8\text{‰}$ to -14‰ VPDB). Shallow ground waters from Price 4 and 5 levels (626 and 580 m elevation, respectively) have an average $\delta^{13}\text{C}$ of -13.0‰ VPDB ($\pm 0.8\text{‰}$ 1σ ; $n=6$). These ground waters are generally close to calcite saturation. The average $\delta^{13}\text{C}$ decreases only slightly from this value in the Price 13 level waters ($-12.6\text{‰} \pm 0.5\text{‰}$ VPDB; $n=4$). In shallow ground waters ^{13}C correlates somewhat to sample location within the Myra-Price ridge. Ground waters with higher bicarbonate (~ 80 to 160 ppm) and lower $\delta^{13}\text{C}$ ($\sim <-10\text{‰}$ VPDB) correlate with ground waters recharged at higher elevations through soil cover. Lower P_{CO_2} and lower $\delta^{13}\text{C}$ ground waters correlate to lower elevations of recharge where there is scant vegetation (i.e. poor soil development due to high topographic gradient and loss of vegetative cover due to a forest fire). Carbon-13, at least in the central portions of the M-P ridge, indicates recharge is occurring in equilibrium with soil CO_2 with a $\delta^{13}\text{C}$ of approximately -27‰ VPDB. The equilibrium with soil CO_2 is highly dependent upon location and topography of the area.

Many of these waters contact sulphide mineralization but have near neutral pH, and SO_4^{2-} remains subordinate to HCO_3^- . In dilute shallow ground waters $\delta^{34}\text{S}$ in SO_4^{2-} ranges from about -8‰ to $+6\text{‰}$ CDT (mean value of 1.2‰), which is within the same range as $\delta^{34}\text{S}$ in local sulphide minerals ($\sim -8\text{‰}$ to $+4\text{‰}$ CDT; mean of 0.9‰) indicating negligible fractionation during oxidation of sulphide minerals. These waters generally have low SO_4^{2-} concentrations, ordinarily less than about 50 ppm. The $\delta^{18}\text{O}$ ($n=2$) in dissolved sulphate in these waters suggest the SO_4^{2-} is largely derived from sulphide mineral oxidation via the Fe^{3+} oxidation mechanism rather than oxidation directly from O_2 .

A progressive shift in dominant cation occurs in shallow to intermediate depth waters which have $\text{Ca}^{2+}\text{-Na}^+\text{-HCO}_3^-$ and $\text{Na}^+\text{-Ca}^{2+}\text{-HCO}_3^-$ chemistry. These ground waters are meteoric and occur within the central core of the Myra-Price ridge. They have gained Na by

cation exchange in rocks previously saturated with $\text{Na}^+\text{-Ca}^{2+}\text{-Cl}^-$ water. Total dissolved solids in these ground waters are similar to $\text{Ca}^{2+}\text{-HCO}_3^-$ ground waters.

8.1.3 Ground Waters of Intermediate Depth

Ground waters of meteoric origin with $\text{Na}^+\text{-Ca}^{2+}\text{-SO}_4^{2-}$ and $\text{Ca}^{2+}\text{-SO}_4^{2-}$ chemistry occur at intermediate depth in areas underlying previously mined areas and in areas where dissolution of sulphates (anhydrite?) has dominated the anion chemistry. Sodium is acquired through exchange processes.

In deeper workings of the HW mine, $\text{Na}^+\text{-Ca}^{2+}\text{-SO}_4^{2-}$ and $\text{Na}^+\text{-SO}_4^{2-}$ ground waters (with variable Cl^-) occur. These waters have TDS, DO and redox intermediate between HCO_3^- and Cl^- dominated ground waters. They also invariably contain some mixture of either $\text{Ca}^{2+}\text{-HCO}_3^-$ meteoric water, or $\text{Na}^+\text{-Ca}^{2+}\text{-Cl}^-$ saline water. The sulphate has $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ similar to the saline water indicating a common source in these waters, which is not the result of sulphide mineral oxidation. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of these water is highly influenced by the amount of Cl^- water component.

8.1.4 Saline Ground Waters

The discovery of saline waters in the Myra Falls mining camp was unexpected. This water exists within a few hundred meters below ground surface in Thelwood Valley and is also present proximal to and underlying developed areas within the HW mine.

Saline, $\text{Na}^+\text{-Ca}^{2+}\text{-Cl}^-$, ground waters (TDS >30,000 ppm) were discovered in areas undisturbed by mining operations. These waters are reducing, have alkaline pH, contain very low HCO_3^- , are most likely ^{14}C -free, and contain a high volume of helium. Similar I^-/Cl^- and Br^-/Cl^- ratios infer a common source of Cl^- in all ground waters (including non-saline). The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are progressively enriched with increasing Cl^- concentration forming a trend similar to sedimentary basinal brines.

Alkalinity for the saline waters is quite variable but tends to be low. The highest salinity waters have alkalinity measurements of less than 20 ppm as HCO_3^- . In saline ground waters an increasing proportion of waters have reached saturation with respect to calcite (mean $\text{Si}_{\text{calcite}} = 0.3 \pm 0.7$) as compared to shallower waters. There are two trends in the

$\delta^{13}\text{C}_{\text{DIC}}$ in saline waters accessed from deeper sampling. The first is a constant $\delta^{13}\text{C}_{\text{DIC}}$ value of $-9.21 \pm 0.9\text{‰}$ VPDB (1σ) in waters unaffected by sulphate reduction. A second separate trend of depleted ^{13}C is apparent in highly reducing waters. The use of canola oil as a drilling additive in new Thelwood Valley drill holes has lead to a depleted carbon source ($\sim 30\text{‰}$ VPDB) as an electron donor for sulphate reduction. The $\delta^{13}\text{C}_{\text{DIC}}$ decreases with an increasing component of oxidized modern organic carbon.

It is apparent that the SO_4^{2-} related to the saline water has a SO_4^{2-} isotopic signature different than the sulphide minerals. Saline waters have SO_4^{2-} concentrations approaching 1500 ppm. These waters are close to saturation with respect to gypsum. The Cl^- concentrations are high and the SO_4/Cl mass ratio is around 0.06. The $\delta^{18}\text{O}_{\text{SO}_4}$ in the saline waters is approximately 10.5 ± 0.5 VSMOW. While the $\delta^{34}\text{S}$ is around $17.5 \pm 2.5\text{‰}$ CDT. Uncertainty in these values exists due to mixing processes, and also because of sulphate reduction in the saline waters. Active sulphate-reducing ground waters have $\delta^{34}\text{S}_{\text{SO}_4}$ values greater than 20‰ CDT. The mean isotopic enrichment ($\epsilon_{\text{SO}_4-\text{H}_2\text{S}}$) is 34.5‰ CDT ($n=3$).

The unique chemical and isotope character of the Cl^- waters imply they are exotic to this setting and are believed to originate from subduction processes, namely dewatering of underplated sediments (and oceanic crust?) beneath Vancouver Island.

8.2 Ground-water flow, Mixing, and Circulation

Ground waters of meteoric origin preserve the $\delta^{18}\text{O}$ elevation variation recorded in precipitation (-0.15‰ per 100 m rise). A transect through the Myra-Price ridge (via 13 level) shows a depletion in the ground waters sampled from the centre of the ridge which corresponds to higher recharge elevations for these waters. The $\delta^{18}\text{O}$ values for ground waters accessed from Myra 10 level (367 m) are quite similar to those from the underlying 13 level (241 m) on the west side of the Myra-Price ridge. This implies a strong vertical or subvertical flow through fractures in the crystalline rock between these two levels. Large continuous structural features, such as the Myra-Price fault, may be the exception to this statement. Waters collected from this same fault system on Myra 10 and 13 levels have quite different $\delta^{18}\text{O}$ values. Ground water from the Myra Price fault on Myra 10 level follow the trend of

other waters with decreasing $\delta^{18}\text{O}$ towards the centre of the M-P ridge; whereas, the ground water sampled from the same fault system from Myra 13 level have higher $\delta^{18}\text{O}$ and appear to be recharged at a lower elevation. Ground waters within this fault system may be subjected to channeled flow.

Flushing of saline water from upper elevations of the Myra-Price ridge and lower HW ground waters has resulted in removal of all or most of the Cl^- and in elution of cations ($\text{Ca}^{2+} \Rightarrow 2\text{Na}^+$ exchange). The $\delta^{18}\text{O}$ - $\delta^2\text{H}$ of low chloride ground waters from the Myra-Price ridge is similar to recent meteoric waters. The low, but detectable Cl^- (~10 to 30 ppm) probably results from diffusion of a residual saline water from bi- or multi-modal porosity of the rock (various scales of fractures, and matrix porosity). The low Cl^- and higher Na^+ concentrations of the eluting waters indicates that only a few pore water volumes have passed through the rock and the flushing process is a recent hydrologic phenomenon. Cations in exchange sites have not yet achieved equilibrium with the water since saline water was displaced from these rocks.

The depth of circulation of meteoric water within the HW mine setting is strongly controlled by the depth of mine workings and subsequent dewatering. Even though the HW mine is very dry, mine openings will act as low pressure zones for water flow. Within the HW mine, waters are drained from the developed areas allowing flushing of Na^+ - Cl^- waters by recent meteoric water. The extent of the flushing is controlled by the rock permeability. High permeability structures, like the North fault, allow rapid flushing of recent meteoric waters down to working depths of the HW mine in short periods of time after mine development. Water emanating from the North fault on HW 20 level contains 4.2 ± 0.5 TU, low TDS (~150 ppm) and low Cl^- (~1 ppm), and is characterized by Na^+ - Ca^{2+} - HCO_3^- chemistry. The $\delta^{18}\text{O}$ of this water suggests recharge around 900 metres elevation, and since the drift was not developed until 1989, high flow rates followed development. This would represent a maximum apparent flow velocity of around $8 \cdot 10^{-6} \text{ m s}^{-1}$. This value is within the same range estimated using tritium for another ground water from the same level flowing from HW-20 653 drill hole. The estimated vertical velocity from this latter water was approximately $6 \cdot 10^{-6} \text{ m s}^{-1}$.

Thelwood Valley is unaffected by mine development. Ground waters in this area exhibit a narrow mixing interface between modern $\text{Ca}^{2+}\text{-HCO}_3^-$ and increasingly saline water from depth. However, the effects of heterogeneous flow in the fractured rock is evident in ground waters sampled from drill holes. In drill hole PR-92, located in Thelwood Valley, a fresh water inversion occurs at depth. Low TDS ground water inflows coincide with higher hydraulic heads.

Mixing of meteoric waters and saline waters in Thelwood Valley appear to be more ideal with less cation exchange as compared to the ground waters from the Myra-Price ridge and HW mine (especially at Cl^- concentrations > 200 ppm) . This may be the result of a more stable zone of mixing in this region. Exchange sites on minerals may have equilibrated with the water composition that is present. No disturbance to the natural hydrology due to mining has occurred in the Thelwood Valley, with the possible exception of the drill hole openings themselves. This information suggests a greater stability of hydrologic and ground water regimes in this area as compared to areas affected by mine development.

Saline water has been displaced from rocks within the Myra-Price ridge and is currently being displaced in areas of new mine development. The elution of Na^+ lags behind Cl^- flushing and is expected to continue as the first few pore volumes of meteoric water move through the rock. The presence of saline water at shallow depth in Thelwood Valley and the current Na^+ elution process in and below the Myra-Price ridge attest to the stability of the local hydrology until it is perturbed by mining development. However, once mine development commences, highly permeable fault and fracture systems can rapidly circulate meteoric waters into working depths within the mine.

The saline ground water at shallow depth illustrates that the rate of uplift in the Buttle Lake region has been greater than the degree of flushing of residual saline water by meteoric water. The presence of the saline ground water at shallow depth attests to the long term stability of the hydrologic regime present in this setting.

8.3 Controls on Metal Transport, Mobility, and Speciation

The pH of ground waters related to the Myra Falls mineral deposits is generally near neutral, and acidic ground waters with high metal loads are extremely rare. Amorphous oxy-hydroxides are common and comparisons from filtrate concentrations (non-filtered, 0.45, 0.22, 0.10, and 0.05 μm) indicate that the majority of suspended particles are greater than 0.45 μm . These particles are composed of Fe oxy-hydroxides but also include Mn and Al. The presence of these particles greatly affects the mobility of Zn, Cu, Pb, and Cd in ground waters. The sorption of Pb is greater than Zn and Cu and is affected little by the solution matrix. In HCO_3^- waters, the order of sorbed metals to suspended particles is $\text{Pb} > \text{Cu} > \text{Cd} \sim \text{Zn}$; which follows the order of first hydrolyses for these metals. In SO_4^{2-} waters the order is $\text{Pb} > \text{Cu} > \text{Zn}$; while, in Cl^- waters the extent to which metals are sorbed decreases in the order of $\text{Pb} > \text{Zn} > \text{Cu}$. The order of element mobility has implications toward understanding of the natural in situ metal attenuation and metal transport of pathfinder metals used in hydrogeochemical prospecting.

The formation of Fe-Al-(hydr)oxides occurs in the presence of metals in solution which may account for the high degree of metal sequestration from solution. The fate (retardation) of metals in ground water at normal ground water gradients may be greatly influenced by the formation of Fe-hydroxides.

A vast range of As(V)/As(III) ratios were found in ground waters of Myra Falls. The highest As concentrations are found in waters with the lowest Eh. These waters also tend to have the lowest As(V)/As(III) ratios indicating that As(III) is more mobile in this setting. Higher aqueous As concentrations may be related to the instability of (oxy)hydroxides in the lower Eh conditions. The presence of oxidized Mn particulates may be influential in establishing the redox state of As in these ground waters.

If the Price deposit is stratigraphically and mineralogically similar to the mined out Myra ore-body, then the consequence of mining the Price deposit may not be an increased mobilization of all trace metals. Comparisons of trace element chemistries of Myra and Price mine ground waters indicates a wide overlap of individual element concentrations. Ground

waters associated with the unmined Price deposit have higher median concentrations of elements mobile as oxy-anions such as: V, Cr, As, and Mo. Mining activity has the greatest effect on the concentrations of Zn and Cu in Myra ground waters compared to baseline levels determined from the Price ground waters.

8.4 Geochemical exploration

Since Zn is the most mobile of ore-related elements in the non-saline, bicarbonate and sulphate dominated ground waters, it is the preferential definitive pathfinder in hydrogeochemical exploration. Hydrochemical anomalies related to the Price Zn-Cu-Pb ore deposit are first identified using Zn as the preferred indicator element. Threshold levels were determined by partitioning of the distributions of transformed Zn concentrations into two constituent sub-populations. The background Zn population is represented by 82% of the ground waters and has a median concentration of 3.6 ppb; the second population represents the remainder of the ground waters with a median concentration of 173 ppb. The threshold concentration is dependent upon the willingness to assume uncertainty of designating background ground waters as anomalous and is 20 ppb, 25 ppb, and 38 ppb Zn, for uncertainties of 10%, 5%, and 1%, respectively. Exploration programs in new regions may find cut-off values to differ depending on the distribution of background and anomalous populations.

The strength of the anomaly, after initially being defined on the basis of Zn, can then be further enhanced based on a combination of indicator and pathfinder elements. The list of elements useful in anomaly enhancement include: Cu, Pb, Cd, Mn, B, Sb, and U.

The presence of the ore-clast breccia (OCB) unit presents a problem in developing hydrogeochemical exploration methods in this mining camp. Using Zn as a definitive indicator element does not differentiate between anomalous ground waters related to massive sulphide mineralization and the OCB unit. Effective discrimination of ground water anomalies is possible between these two types of mineralization through the use of elements associated with hydrothermal alteration, primary mineralization, and in this setting, elements in the stratigraphy overlying the Price deposit. Elements associated with the hydrothermal

alteration such as K, Rb, and B are elevated in ground waters associated with the Price ore deposit as compared to the OCB. Elements concentrated in the massive sulphide mineralization, such as Ba, Cd, Sb, and U, are also important in differentiating between these two types of mineralization. Elements related to weathering the mafic volcanics overlying the Price ore-body (Sr, Cr, Mg, and Mn) prove advantageous in this setting through additional elements used in discrimination of waters that have been in contact with the mafic units overlying the Price ore.

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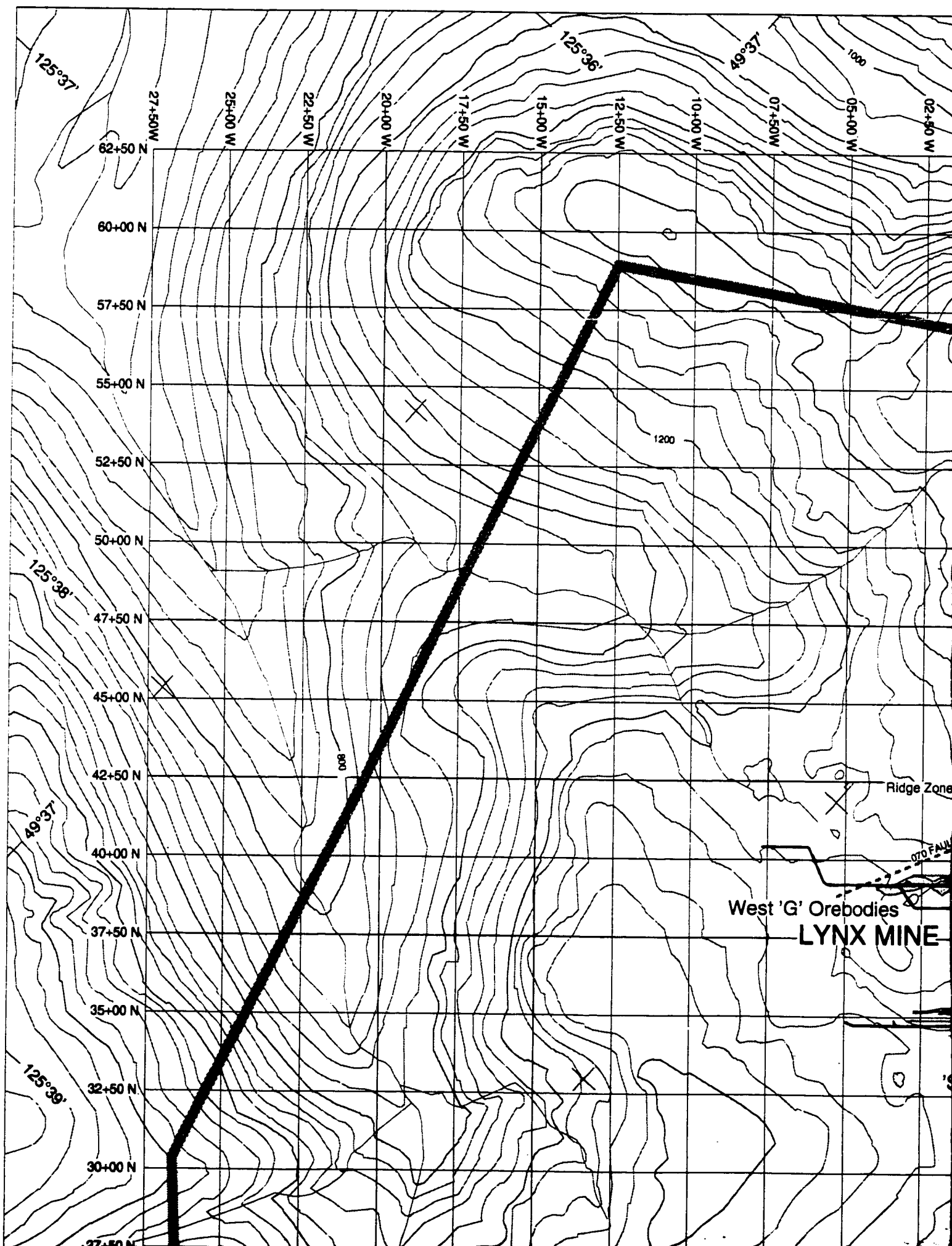
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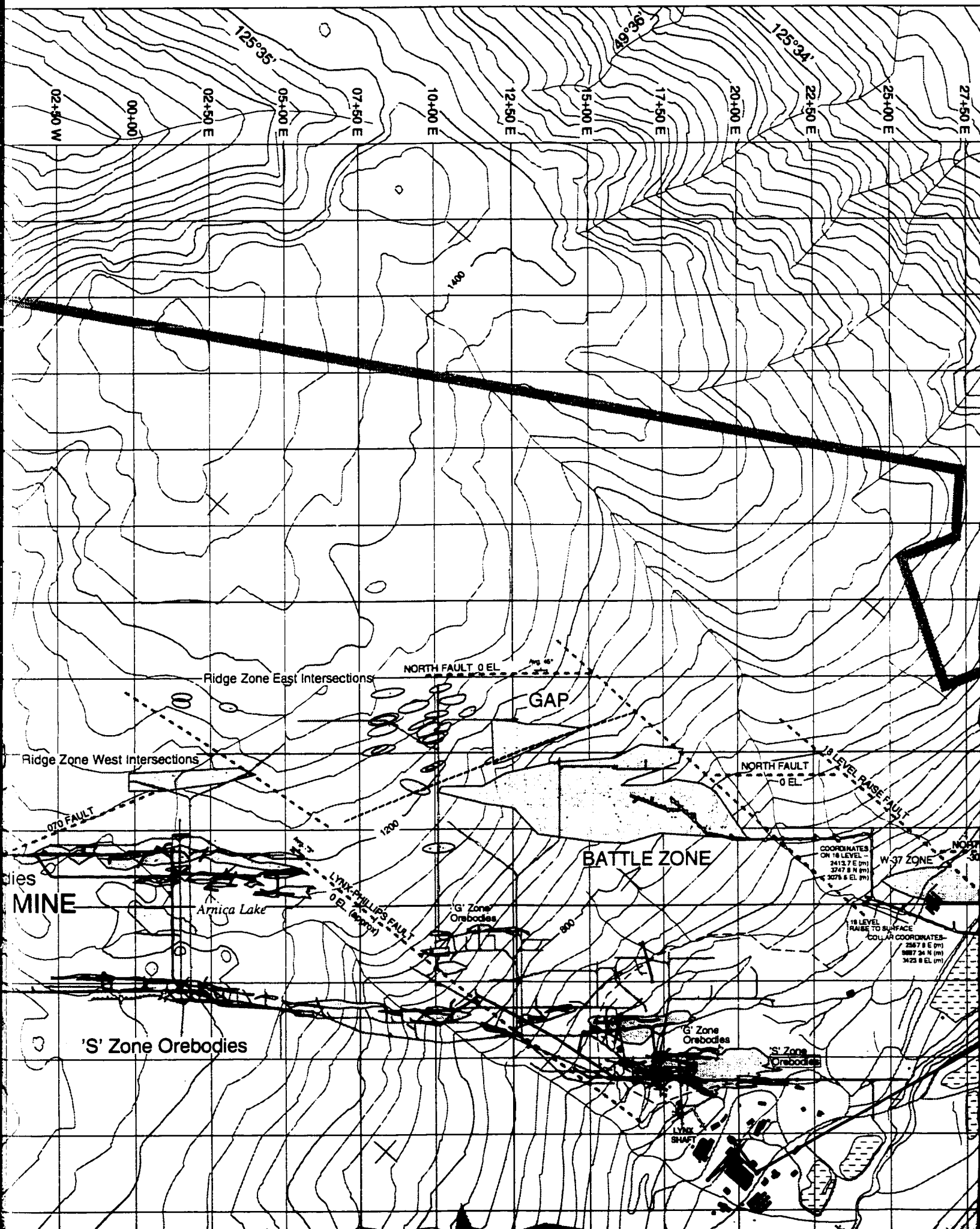
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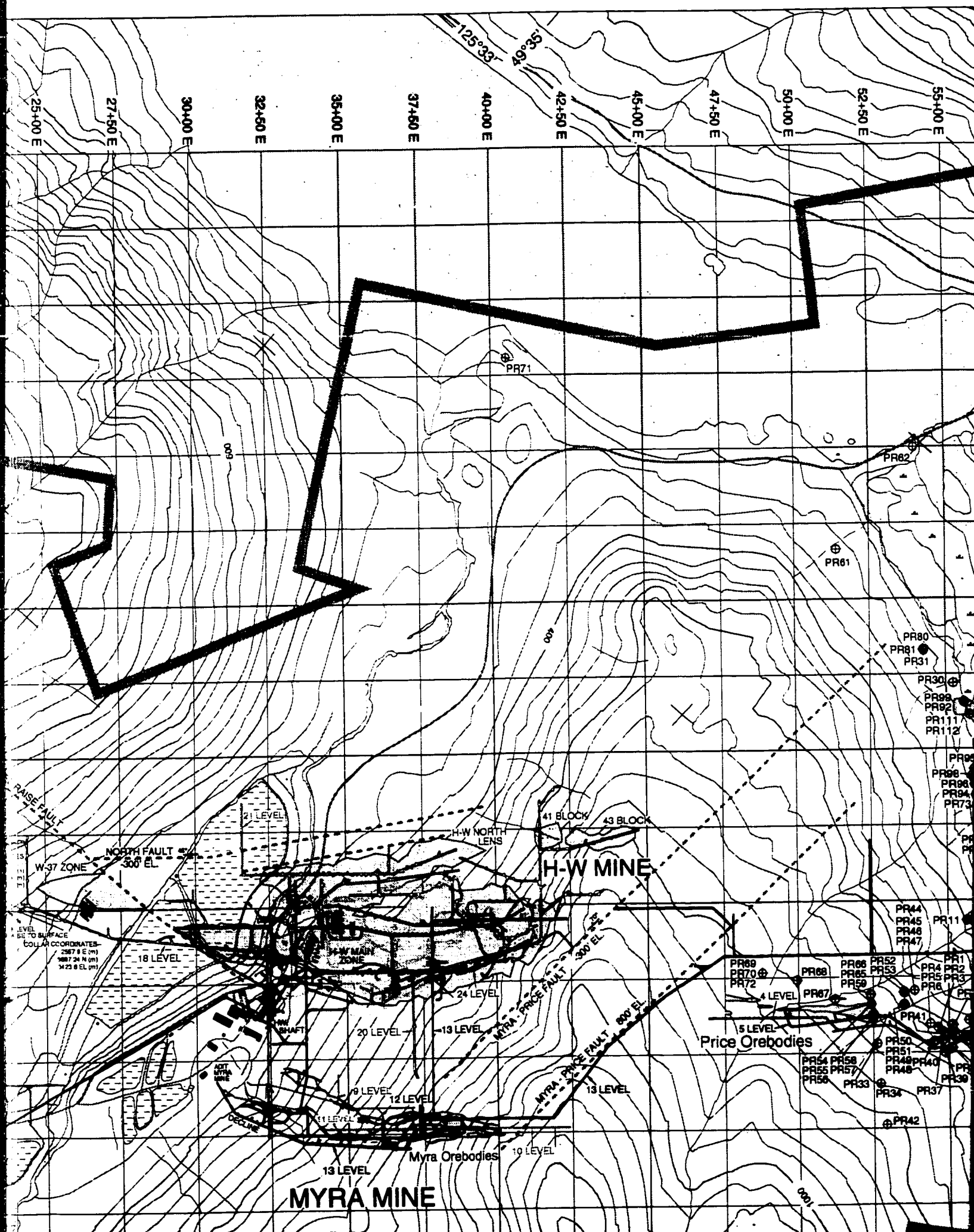
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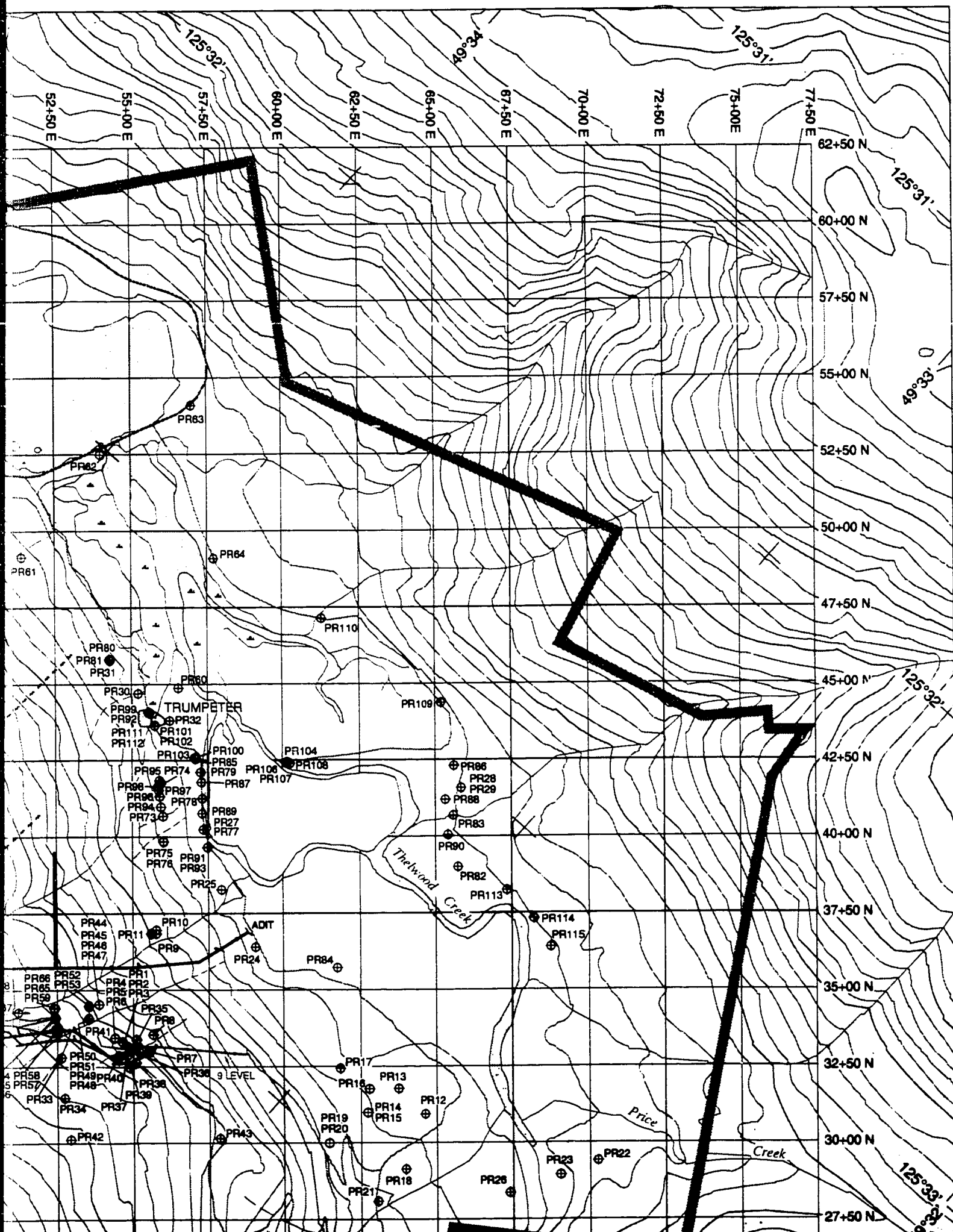
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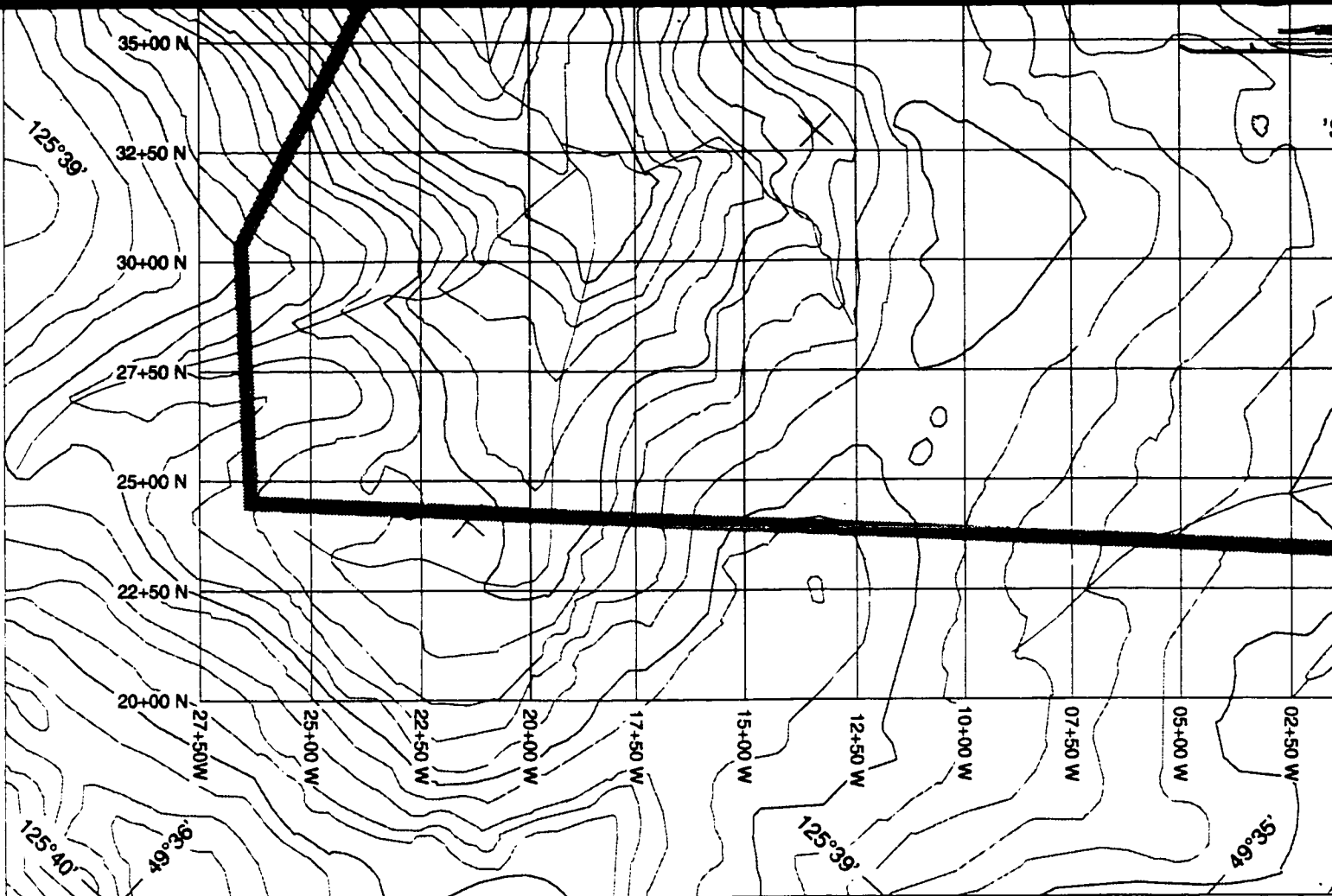
UMI











SITE PLAN MYRA FALLS MINING

4 LEVEL (Price: 626.4 m, 2055')		14 LEVEL (Lynx: 381.0 m, 1250') (Myra: 367.0 m, 1204')
5 LEVEL (Lynx: 570.5 m, 1872') (Price: 579.7 m, 1902')		15 LEVEL (Lynx: 338.3 m, 1110') (Myra: 325.2 m, 1067')
6 LEVEL (Lynx south: 539.5 m, 1770') (Lynx north: 548.6 m, 1800')		16 LEVEL (Lynx: 295.6 m, 970') (Myra: 281.9 m, 925')
8 LEVEL (Lynx: 453.0 m, 1486')		17 LEVEL (Lynx: 248.4 m, 815') (Myra: 241.4 m, 792') (Price: 238.0 m, 781')
9 LEVEL (Myra: 413.6 m, 1357') (Price: 416.1 m, 1365')		18 LEVEL (Lynx: 205.5 m, 675') (Price: 202.5 m, 667')
10 LEVEL (Lynx: 381.0 m, 1250') (Myra: 367.0 m, 1204')		19 LEVEL (Lynx: 172.5 m, 565') (Price: 170.0 m, 557')
11 LEVEL (Lynx: 338.3 m, 1110') (Myra: 325.2 m, 1067')		20 LEVEL (Lynx: 143.5 m, 465') (Price: 141.0 m, 457')
12 LEVEL (Lynx: 295.6 m, 970') (Myra: 281.9 m, 925')		21 LEVEL (Lynx: 114.5 m, 365') (Price: 112.0 m, 357')
13 LEVEL (Lynx: 248.4 m, 815') (Myra: 241.4 m, 792') (Price: 238.0 m, 781')		22 LEVEL (Lynx: 85.5 m, 265') (Price: 83.0 m, 257')
13 level decline		23 LEVEL (Lynx: 56.5 m, 165') (Price: 54.0 m, 157')
		24 LEVEL (Lynx: 27.5 m, 65') (Price: 25.0 m, 57')
		25 LEVEL (Lynx: 0.0 m, 0') (Price: 0.0 m, 0')

Claim limit

Road

Drillhole

PR34 ⊕

CONTOUR INTERVAL 40 METRES

MINE GRID IN METRES

