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The role of Redox and Spontaneous Potential in Vertical Mass Transport of Elements from Mineralization in Areas of Thick Glacial Sedimentary Cover

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THE ROLE OF REDOX AND SPONTANEOUS POTENTIAL IN VERTICAL MASS TRANSPORT OF ELEMENTS FROM MINERALIZATION IN AREAS OF THICK GLACIAL SEDIMENTARY COVER

by

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Abstract

A recent theory implicated redox-gradients in vertical transport of elements from buried mineral deposits to surface soils and predicted the formation of 'reduced chimneys' in intervening overburden. This thesis tests that theory through surface and/or subsurface investigations at six sites; two host electronically conductive sulphide mineralization and four host non-conductive chemically reduced features including three kimberlites and an H_2S-sourced 'forest ring.' Redox and spontaneous potential (SP) measurement techniques were developed and surveys carried out on surface and down-hole. Methods included: oxidation-reduction potential on groundwater and soil slurries; determination of $H_2S_{(aq)}/SO_4^{2-}{}_{(aq)}$ in groundwater and $O_{2(g)}$ and $CH_{4(g)}$ in the headspace of wells; and a hybrid redox-SP method using both Pt and non-polarizable electrodes.

The predicted 'reduced chimneys' were observed in overburden above mineralization. SP measurements demonstrate the presence of negative electrical anomalies over buried electronic conductors but *positive* responses over the non-conductors. It is proposed that strong redox gradients induce an electrical field, which results in mass transport of ions. Redox-active chemical species in a redox gradient are influenced by neighbouring species that are more electronegative on one side than the other. Redox-active polar ions and molecules should therefore exhibit a preferred orientation with their negative poles pointing in the positive redox direction, i.e. toward the neighbours with the strongest affinity for electrons. Alignment of constituent dipoles would result in a macroscopic polarity within the redox gradient and electrical anomalies that are negative at its oxidizing end. Since resistivity is finite, this electrical field should induce current in the form of an ion flux.

The theory accounts for geochemical and electrical anomalies over buried mineralization in a variety of environments. It suggests that a negative SP response should develop above a buried, reduced feature if a redox gradient above it is positive-upward. However, where a reduced chimney extends to surface, the predominant redox gradient is horizontal and oxidizing-outward, which would induce a positive-inward

electrical polarity and a positive SP response on surface above the feature. Buried electronic conductors are a special case in which the whole conductor polarizes in the positive-upward redox gradient of the shallow Earth's crust.

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Introduction

Partial extraction soil geochemical techniques are being increasingly used in mineral exploration worldwide for the detection of buried mineralization. Partial extractions are sometimes referred to as selective leach procedures because they are considered to selectively extract a particular hydromorphically transported component of elements that is weakly bound to soil particles. The techniques, therefore, provide greater sensitivity for the detection of locally derived exogenic metal sources than do the strong acid digestions that dissolve most or all of the soil sample.

Of particular interest is the trend in the last decade toward the use of partial extractions in areas of thick, young glacial overburden cover. Numerous researchers (e.g., Jackson, 1995; Bajc, 1998; Cameron et al., 2004) have reported geochemical responses in surface soils over known mineralization through fine grained glaciolacustrine sediments of up to 50 m in thickness. Partial extraction anomalies in glacial environments, as elsewhere, are most commonly reported as either apical or halo responses that are centred over mineralization, which suggests vertical transport of elements from the bedrock source. Prior to these studies, the vertical mobility of elements through glacial clays less than 10 Ka in age was considered to be restricted to 5 – 10 m (Smee, 1983). The primary dispersion mechanisms of diffusion and groundwater transport that operate in these environments are far too slow to account for the observed geochemical anomalies on surface, which suggests another mechanism is operating.

In 1998, I published a geochemical dispersion model that proposed electrochemical transport along redox gradients as an explanation for vertical element mobility and the soil geochemical anomalies observed over mineralization. That model was further developed in Hamilton (2000) and is presented here as Appendix 1. Building upon the work of Govett (1976) and Bolviken (e.g., 1979), I argued that oxidizing agents would be consumed in water saturated overburden above a reduced feature in bedrock, thereby creating a strong redox gradient away from the feature. Redox reactions occur in the gradient between reduced and oxidized species; however, because the latter are limited in the phreatic zone, there is a net outward migration of reduced species away from the bedrock source. This migration is interrupted at the water table, above which

oxidizing agents are abundant. The upward movement of reduced species, such as Fe^{2+}, followed by their oxidation, is consistent with previously observed geochemical phenomena on surface including: metal anomalies (e.g., Jackson, 1995; Bajc, 1998), acidic responses (Gleeson et al. 1988; Govett and Chork, 1977), carbonate remobilization (Smee, 1998) and halo-type responses (Clark, 1996). However, one phenomenon that was predicted by the model but which had not been reported was the development of reduced 'columns' (later 'chimneys') in water saturated overburden above the features. Reduced conditions between the buried feature and the water table were unequivocally required if 'redox gradient transport' was operating as proposed.

Another aspect of redox gradient transport is that it does not appear to conform to existing mass transport models. The general mass transfer equation, which governs the movement of mass and charge in solution, has only three terms, which are those for chemical diffusion, advection (velocity of the fluid) and electromigration (i.e., transport of ions in an electrical field). There is no redox term. In purely aqueous systems that have no wires connecting different parts of the solution, redox should not influence the movement of mass and charge, except where it influences the concentration gradient. Notwithstanding this, many geoscience authors have noted the close coincidence between changes in redox conditions and geochemical and electrical phenomena.

This thesis addresses the issue of redox gradient transport by investigating: (1) redox conditions over known mineral deposits and testing for the presence of 'reduced chimneys'; and, (2) processes that might result in the transport of elements along a redox gradient and yet be conformable with existing mass transport models.

To meet these objectives, data were collected in four field programs carried out between 2000 and 2003 by the author on behalf of the Ontario Geological Survey (OGS) and its collaborative partners. The objective of two of these studies was specifically to test my hypothesis that reduced chimneys develop over buried reduced mineralization. All four studies collected simultaneous redox and electrical field (spontaneous potential – SP) data to investigate the relationship between the two parameters.

Thesis Outline and Summary

This thesis is written as a series of three articles for publication in refereed journals. A fourth article, included as Appendix 1, is a chapter I contributed to the Handbook of Exploration Geochemistry, Volume 7 (Hamilton, 2000). Its purpose is to provide a statement of the concept of redox gradient transport, which this thesis investigates. Each chapter is self contained which results in a certain degree of unavoidable repetition, particularly in the introductions and references.

Chapter 1 describes a field investigation carried out at the Marsh Zone property, a sulphidic syenite-hosted gold deposit overlain by 20 m of clay beneath 1.5 m of peat. It is located near Matheson, Ontario. Twenty five boreholes were drilled and monitoring wells installed on two transects to investigate subsurface site conditions. New measurement techniques were developed to characterize the redox and electrical conditions on surface and in the subsurface. The methods-development focused on techniques to minimize the inherent biases that arise due to polarization of the Pt surfaces of oxidation-reduction potential (ORP) probes and Pt SP electrodes. The new protocols were then used to measure ORP on peat, unweathered clay and groundwater.

The SP data show a negative electrical response on surface above the feature, which is typical for conductive sulphides. The redox data indicate the presence of a reduced chimney in water-saturated clay above the syenite mineralization. pH Was also characterized in sediments and waters and a basic response correlates with the reduced conditions. This is accompanied by other phenomena that suggest vertical mass transport within the reduced chimney.

Chapter 2 describes a similar investigation carried out at the Cross Lake property, near Timmins Ontario, on two transects over Zn-Cu-Pb volcanogenic massive sulphide mineralization. Redox and SP measurement techniques are further developed and used down-hole in 40 monitoring wells. In addition to a negative electrical response on surface above the sulphides, the data demonstrate reduced chimneys in overburden above mineralization. Other phenomena, including 'acidic caps' over the chimneys, can be accounted for by the upward mobility of reduced metals and their subsequent oxidation.

Chapter 3 describes two other investigations. One was an OGS subsurface study at the Thorn-North 'forest ring', which occurs over an accumulation of $H_2S_{(aq)}$ in

overburden and rock. The second was from an OGS contribution to a Geological Survey of Canada Targeted Geoscience Initiative study of three kimberlites in the New Liskeard and Kirkland Lake areas of Ontario. The investigation of redox and SP at these sites in particular helped to constrain the causes of SP because no buried conductors are present to introduce secondary electrical fields. Inverse correlations were noted between redox and SP, suggesting a genetic relationship. Reduced chimneys and large-scale *positive* electrical anomalies were noted in association with the buried features.

'Redox-induced spontaneous polarization' is proposed as a mechanism responsible for ion mobility in redox gradients. Since a redox gradient also represents a gradient in electronegativity, each redox active species is influenced by neighbours that are more electronegative on one side than the other. This would result in a preferred orientation to the electrical dipoles of redox-active ions and polar molecules with their negative poles pointing in the positive redox direction. Analogous to ferroelectricity, this preferred orientation would produce a macroscopic electrical field with electrical anomalies that are negative at the oxidizing end of the redox gradient. In the groundwater environment resistivity is finite and therefore, by Ohm's Law, electrical current as an ionic flux must result. This could account for rapid mass transport, the formation of reduced chimneys and surface geochemical anomalies, and both positive and negative electrical anomalies over mineralization of various types. Where redox gradients are vertical and oxidizing-upward, a negative-upward polarity would occur and a negative SP anomaly would develop on surface. Where gradients are horizontal and reducing-inward, as in the case of a shallow reduced chimney or an outcropping porphyry sulphide, a positive-inward polarity would develop and a corresponding positive SP anomaly would develop on surface. A tabular electronic conductor in the redox gradient of the upper Earth's crust would represent a special case in which the entire ore body polarizes with a cathodic pole developing at the top, resulting in negative SP anomaly on surface. Where disseminated sulphides exist in a strong redox gradient, each sulphide grain would polarize and serial amplification of voltage would result in larger voltages than could occur over massive sulphides.

Statement of Original Contribution

All the fieldwork described in this thesis was my own or was carried out under my immediate supervision. The projects were collaborative in nature and multi-faceted but the deep subsurface studies and investigation of SP, redox, metal mobility and transport mechanisms were largely my responsibility. The ideas, theories and interpretation of data are also mine, but were subject to review by my collaborators and co-authors, who provided important editorial input and suggestions.

This thesis builds on earlier work by Govett (1976), Bolviken (1979) and Hamilton (1998). Its purpose is to test an earlier theory that mass transport occurs along redox gradients in water saturated overburden and, if evidence supports this, to investigate the process empirically and theoretically. The work required the development of methods that could measure the SP and redox contrast in overburden above buried mineral deposits relative to adjacent areas. Techniques were developed for the measurement of ORP in soil slurries collected on transects across the features of interest. The measurement of well head-space gases was used as an indicator of groundwater redox conditions, which to my knowledge had not been done before. SP techniques were developed for the measurement and differentiation of both electrical fields and redox gradients on transects across the buried features, and I was greatly aided by a publication by Timm and Moller (2001) on the same subject that was printed after my initial work. Finally, this work unequivocally demonstrates the presence of 'reduced chimneys' in at least 5 instances and infers their occurrence at 3 other sites. The chimneys had been predicted by the earlier theory and had not been previously documented over mineral deposits.

The origin of SP over mineral deposits has been debated for over 100 years, but there is no clear consensus as to why it occurs. The numerous published theories apply only to specific situations, such as SP over electronically conductive mineral deposits, and are sometimes mutually exclusive. The theory of 'redox-induced spontaneous polarization' presented in this thesis provides a reasonable explanation for the formation of SP over reduced mineral deposits in the mineral deposit environments where it is known to occur. It does not negate earlier theories but rather proposes that a number of theories developed to explain SP in specific circumstances are explaining different parts

of the same processes. For example, the theory does not preclude a permanent ferroelectric polarity in the ore body as Corry (1994) suggested but rather would fulfill the requirement that an initial transient electrical field existed that could be retained by the orebody during cooling. The theory is also compatible with the existence of electrical dipoles related to large, steeply dipping, electronically conductive ore bodies as envisioned by Sato and Mooney (1960), Govett (1976) and Bolviken (1979). Indeed, these models would be an expression of redox-induced spontaneous polarity on a massive scale with the entire orebody developing a negative-upward electrical polarity in the positive-upward redox gradient in the upper earth's crust. The "redox-gradient transport" envisioned by Hamilton (1998) and implicitly required in the models of other authors would occur but it would be the electrical field induced by the redox gradient that actually moves ions.

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CHAPTER 1

Redox, pH and SP variation over mineralization in thick glacial overburden (I): methodologies and field investigation at the Marsh Zone gold property

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Abstract

A surface and subsurface investigation of pH, oxidation-reduction potential (ORP) and spontaneous potential (SP) was carried out over sulphide-hosted gold mineralization in an area of thick and extensive glacially derived overburden. Protocols were developed to measure ORP and pH in clay slurries, peat and groundwater to test for the presence of redox and pH phenomena that were predicted to occur over mineralization. ORP protocols focused on removing memory effects caused by probe history and storage and on obtaining a reproducible measure of the ORP over mineralization relative to background areas. The results confirm the presence of distinct reduced 'columns' in clay and interstitial groundwater overlying sulphide mineralization that are in fact reduced 'curtains' that follow the trace of mineralization. These are accompanied by high pH within the reduced column, with minor lows on the flanks, and elevated H_2S and CO_2 in shallow groundwater over mineralization. Whereas the H_2S appears to have its source in bedrock mineralization, the CO_2 is likely a secondary near-surface phenomenon related to oxidation of metals in the reduced column, which produces acid and concomitant dissolution of carbonate in the clays. Wide groundwater temperature anomalies are spatially associated with mineralization. High ORP in shallow peat above mineralization may be evidence of an 'oxidized cap' over the reduced column. A minor SP response in surface peat was noted but is small in comparison to the redox field voltage. The presence of reduced columns and other features are consistent with a previously published redox-gradient transport model.

1.1 Introduction

Soil geochemical responses by partial extraction and other analytical techniques are increasingly being reported over mineralization in areas of thick glacial cover (Govett & Chork, 1977; Gleeson *et al.*, 1988; Antropova *et al.*, 1992; Jackson, 1995; Bajc, 1998; Hamilton & McClenaghan, 1998; Hamilton & Cranston, 2000; McClenaghan *et al.*, *in prep.*). Many of these responses are difficult to account for because the thickness and young age of the intervening glacial deposits require geochemical processes that operate very quickly, over just a few thousand years, over significant vertical distances. A number of authors (Govett, 1973, Govett *et al.*, 1976; Govett & Chork, 1977; Bolviken &

Logn, 1975; Smee, 1983; Tomkins, 1990; Jackson, 1995; Clark, 1996; Hamilton, 1998; Hamilton, 2000) have proposed models that involve electrochemical processes in the movement of metals upward from sulphide mineralization or other reduced geological features. Although these models are not in agreement, and are in some cases mutually exclusive of one another, they all directly or indirectly involve redox differences as the underlying energy source that promotes element transport. Their operation as proposed would result in changes in both pH and redox in the subsurface that ought to be measurable.

The most recent of the proposed transport models was that of Hamilton (1998, 2000) and is shown on Figure 1-1. Briefly, that model invokes upward transport of redox active ions through overburden along redox gradients rather than transport in a sulphide-dipole-induced electrical field. Consumption of oxidants in groundwater-saturated overburden above a reduced feature in bedrock creates a reduced environment. Between the top of the reduced feature and the water table, a vertical electrochemical gradient exists, along which reduced and oxidized mobile species migrate toward each other. Redox reactions occur between the two and, because oxidants are limited in the phreatic zone, they are preferentially consumed causing reduced species, and thereby negative charge, to propagate outward and upward. This is interrupted at the water table, above which oxidants are abundant. A consequence of this process would be dissipation of negative charge away from the reduced feature, which would allow its continued oxidation. In the case of a buried conductor, dissipation of charge away from the top of the feature is required if SP currents within the conductor are to continue. The corollary is that, where a measurable electrical field (i.e., an SP low) occurs on surface over a buried sulphide conductor entirely below the water table, dissipation of charge and concomitant mass transport away from the conductor must be occurring by a process that is at least conceptually similar to this. The net result of such a mechanism would be an upward movement through overburden of reduced species, particularly metals such as Fe^{2+}, and the development of a reduced 'column' in groundwater saturated overburden between the reduced bedrock feature and the water table.

Although hundreds of case studies of SP variation over mineralization and other features have been published since the 1950s, there has been very little work done on

redox variation in overburden over mineralization. This is partly because there are inherent problems with measuring oxidation-reduction potential (ORP) above the water table (Bartlett & James, 1995), but also because ORP probes are difficult to use and often generate unreproducible data. This paper reports a field investigation that was initiated, first to develop and test techniques for the measurement of redox and variants of SP in subsurface sediments, and secondly to measure these parameters in glacial overburden on transects across buried sulphide mineralization. This was part of a larger study, jointly carried out by the Ontario Geological Survey (OGS), the Geological Survey of Canada (GSC) and the Canadian Association of Mining Industry Research Organisations (CAMIRO). The objectives of the larger study were to test a variety of partial extraction soil geochemical techniques for their ability to detect mineralization through thick overburden and to determine the geochemical mechanisms by which elements are transported from mineralization to ground surface.

The two sites chosen for our studies are located in Ontario's Abitibi clay belt, a 20 000 km^2 area covered by Quaternary aged (*c.* 8 Ka) glaciolacustrine clays and glaciofluvial sands that generally exceed 20 m in thickness and which overlie much of the Archean-age Abitibi Greenstone belt. The 'Marsh Zone' (Fig. 1-2) is a syenite-hosted gold deposit owned by St. Andrew Goldfields Limited. The 'Cross Lake' property (Hamilton, et al., 2003, Fig. 1) is a volcanogenic massive sulphide (VMS) deposit that hosts Zn, Cu and Pb mineralization and is held by Cross Lake Minerals Limited. These two sites were chosen after field visits to about a dozen, from an initial list of about 80 sites. The selection criteria included: (1) thick (>20 m), predominantly clay overburden; (2) sulphide mineralization with little or no graphite; (3) bedrock geology well defined by diamond drilling; (4) surface terrain types representing the three most dominant in the Abitibi: clay, sand and peat; and, (5) minimal surface disturbance by exploration activities, mining or surface infrastructure (which may affect SP).

The field methodologies developed for redox, pH and surface SP and the resulting data for the Marsh Zone are reported herein. Subsurface SP methods and the more voluminous data for Cross Lake are reported in the second of this two-paper series. Both soil and groundwater geochemical sampling were carried out as part of this work but the

results will be reported elsewhere and are not dealt with here, except where they are helpful to the pH and redox discussion.

1.2 Objectives and Theoretical Approach

The objectives of the Marsh Zone and Cross Lake fieldwork were to determine the subsurface variation in redox, pH, and electrical fields in overburden above sulphide mineralization, and to determine if the geochemical transport model of Hamilton (1998, 2000), or any of the other models, is supported by the data. To do this, techniques had to first be developed that could measure these parameters in the overburden types and field environment of the Abitibi clay belt.

Spontaneous potentials are natural voltages in the earth and, as they are almost always measured using non-polarizing, half-cell type electrodes, they measure electrical fields alone and have no redox component to their voltage (Timm & Mollar, 2001). Redox voltage is caused by electrochemical differences in composition between a sample and a reference cell (a half-cell of a metal and its salt) and can only be directly measured using electrodes based on Pt or other noble metals. If the half-cell and Pt components of the electrode are close enough together, the probe can be considered to be measuring only the redox component of voltage with no contribution from any electrical field. A hybrid of the SP and redox measurement techniques, referred to here as platinum-SP (PtSP), involves the use of a stationary half-cell connected to a mobile Pt electrode (Bolviken *et al.*, 1973) that is used to measure the voltage difference between the half-cell and various points on the ground surface or down a well. This technique measures *total* voltage which is the sum of the electrical field and redox field components (Timm & Mollar, 2001).

Currently the best tool for redox measurement available to geochemists is the Pt-based ORP probe, which has serious inherent problems due to polarization of the Pt surface, slow equilibration times and 'memory' effects that make it difficult to obtain reproducible data. In addition, most ORP probes cannot be calibrated, which means that results cannot be compared between probes and sites. The PtSP method suffers from similar problems and non-polarizing, solution-based SP electrodes suffer from a whole series of different problems. A large part of the work carried out at the Marsh Zone was to develop techniques that could obtain meaningful electrical and electrochemical data in

overburden materials despite these issues. Some of the techniques described below are conceptually similar to those described by Timm & Mollar (2001) for measuring electrical and redox fields in bedrock except they are applied to overburden and on a geographically larger scale. They were also developed independently of that work, although we are indebted to those authors for their insights.

1.3 Overburden Stratigraphy and Bedrock Geology

The Marsh Zone gold deposit is hosted in a narrow, 5 m wide, vertical 'syenite' dyke that underlies a flat-lying peat bog (Fig. 1-3). The syenite (actually an albitite) contains about 10% sulphide, which is predominantly pyrite. On the site grid, two parallel cut lines transecting mineralization were investigated. Referred to as 15 east and 14 east, these lines are located 30 m apart and strike approximately north-south. Diamond drill records indicate the mineralized dyke crosses Line 15 between 15 and 20 m south, strikes *c.* 16° southeast, relative to the baseline and therefore crosses Line 14 between 5 and 10 m south. The dyke intrudes talc-chlorite schist (Fig. 1-3). A quartz-feldspar porphyry dyke occurs a few metres to the north, which is bounded on the north side by mafic metavolcanics.

The bog overlying mineralization is fairly open in its central part and sphagnum forms low spongy hummocks on surface. The water table is permanently present within 30 cm of ground surface. Hand auguring during soil sampling showed peat thickness ranging from 2 m near the centre of the bog to 0.4 m near the northern edge. Glaciolacustrine clay immediately underlies the peat (Fig. 1-3).

In February 2000, a drilling program was initiated using a CME auger/coring drill rig mounted on tracks. Eleven shallow boreholes were drilled on each line to 7.5 m depth on 400 m transects across mineralization. In all boreholes, glaciolacustrine varved clay was encountered immediately beneath the peat. The only other overburden unit encountered was clayey till, in the bottom 1 m of the northernmost well on Line 15. This suggests a shallower bedrock depth to the north, which is supported by the presence of outcrop several hundred metres to the northwest. As part of the drilling program, three deeper holes were drilled to rock on the south half of Line 15 and encountered

mineralization at 18 m south and talc-chlorite schist at 60 and 200 m south at depths of 20.5, 22.5 and 9.5 m respectively.

1.4 Overview of Field Program

Fieldwork at the Marsh Zone began in 1999 with a soil sampling program on Line 15 that involved hand-auguring and sampling of two peat depth intervals and C-horizon clay. In conjunction with this, subsamples of peat were collected for field pH determination and a surface SP survey was carried out. This was followed by a winter drilling program that involved both split-spoon sampling of clay at regular depth intervals and immediate testing of the clay for slurry ORP and pH.

Monitoring wells were installed in each hole after drilling and these consisted of 32 mm diameter, environmental-grade, internally threaded PVC pipes with machine-slotted screens. The screens and graded-silica filter packs were all finished in clay at the same interval between 6.5 and 7.8 m depth and were sealed above the filter pack with bentonite. Wells were also installed in the three holes drilled to rock on Line 15. All wells were 'developed' by pumping almost dry on several occasions to remove any fluids contaminated during the drilling process. Groundwater was later sampled and tested for pH and redox in a flow cell; *in situ* temperature, dissolved H_2S and CO_2 using field test kits; and later in the laboratory for major ion and trace element chemistry. Down-hole and surface SP and PtSP testing and direct measurement of peat and groundwater ORP were carried out during the 2000 and 2001 field seasons.

As mentioned, an integral part of the field program at the Marsh Zone involved iterative testing and development of the ORP, SP and PtSP methods, the results of which, and the methodologies that were ultimately developed, are described below under the following SP and redox method development sections. The geochemical phenomena and processes that these procedures have revealed at the Marsh Zone are described in 'Results and Discussion.'

1.5 Development of Methodologies

1.5.1 SP method development

SP protocols are well established (e.g., Burr, 1982). They involve the use of two non-polarizing electrodes, a voltmeter and a long reel of insulated copper wire. One electrode is left at a base station and the other is advanced along the line. They are connected together through the voltmeter by the reel of wire. Voltage readings are taken at each station and repeat readings can be taken as the wire is reeled back in to allow correction of any drift in the readings over the course of the survey. By convention, the negative electrode on the voltmeter is connected to the stationary pot, which allows for a negative response when the mobile electrode is passing over areas that are negatively charged relative to the ground under the stationary electrode.

In general, sulphidic ore bodies and other conductors have been shown to have negative SP responses (Sato & Mooney, 1960; Burr, 1982). Unfortunately, false anomalies can occur that seriously complicate the interpretation of SP data, the most significant of which are due to variable moisture content of the soils being measured. Counter-intuitively, positive anomalies are noted when the mobile electrode is used in moist areas and the reverse when used in very dry areas. Testing in a similar bog near the Marsh Zone showed moisture-related variability of up to 60 mV within a 1 m radius, which is higher than many mineralization-related responses. Favourable SP results have been most often reported from areas of uniform soil moisture. Where possible, these problems were minimised in the Marsh Zone and Cross Lake surveys by careful selection of measurement sites at each station that had uniform soil moisture conditions (i.e., consistently off hummocks, not in puddles, etc.).

Several types and combinations of voltmeters, electrodes and wire were tested to optimise the method for the variable terrain of the Abitibi region. The wire used must be well insulated and have sufficient thickness to withstand a drag resistance of several hundred metres through forest when being pulled out or reeled in. Approximately 500 m of 22 gauge (*c.* 1.5 mm) insulated copper wire was optimal for our surveys. The reel was geared to increase the speed of reeling and was modified in later surveys to add contact brushes. These provide a constant electrical connection with the stationary pot as the reel

spins and avoids the necessity of disconnecting the electrode each time the wire is reeled out.

Two electrode types were used at the Marsh Zone. The conventional 'pot-type' electrode has a porous asbestos base and the 'lance-type' has a sharpened lathed-oak plug at the end of a 1.5 m plastic tube that allowed it to be inserted into the peat. Both were filled with a gelled, saturated solution of $CuSO_4$ in contact with a copper rod, which was connected through a one-hole rubber stopper to the wire. The pot electrode was placed at a base station in a shaded area and the lance electrode was advanced along the line on the end of the wire and inserted into the upper 10 cm of peat at each station. The porous ends of both electrodes were soaked in a saturated $CuSO_4$ solution when not in use. The lance electrode was developed as part of this project and proved to be much more convenient as the mobile electrode.

The primary criterion for the selection of a voltmeter is its input impedance, which is the resistance to current through the voltmeter during measurement. Higher impedance means more resistance to current flow (an ideal voltmeter would allow no current flow, but in reality all voltmeters have a finite impedance). Modern digital voltmeters, used for electronic work typically have impedances ranging from several tens of kΩ to one MΩ (10^4 to 10^6 Ω), whereas pH meters have far higher impedances ranging from one to over one million GΩ (10^9 to 10^{15} Ω).

Lile (1996) measured the electrical power at variable load of several anomalous SP occurrences over sulphide mineralization in peat terrain. He placed one electrode within the anomaly and one outside it and short-circuited the two through various resistances while measuring both voltage and current. His data show no significant drop in voltage until the load resistance drops to below *c.* 15 kΩ. This suggests that a voltmeter with an impedance of 15 kΩ or greater is likely to be sufficient to measure natural potential differences in peat without much voltage loss during measurement. Most, but not all, digital voltmeters have input impedances that are this high.

For a standard SP survey using Cu-$CuSO_4$ electrodes, best results were obtained using an 'off-the-shelf' digital voltmeter with an input impedance of several 10s of kΩ (*c.* ~10^4Ω). When ultra-high impedance pH-type voltmeters were used, electromagnetic (EM) interference became a serious problem. EM interference from magnetic storms

(particularly during the summer of 2000), and possibly from radar and other sources of EM radiation, induces tiny current fluctuations in the long SP wire. A meter with impedance in the order of kΩ to one MΩ appears to generate enough load to dampen the sharp fluctuations in voltage that accompany the current induction. Meters with much higher impedance tend to measure these voltage fluctuations which appear on the SP curve as voltage noise. Longer wires produce more noise. Figure 1-4 shows this effect at the Marsh Zone and another test site in the Abitibi region during a period of high electromagnetic activity in July, 2000. Readings were taken over 1 minute intervals at increasing increments of distance using a high impedance pH-type voltmeter. The background noise clearly increases as the length of wire increases for both sites. There is also a drift toward more negative values, as exemplified by repeat data collection at 100 m on the second site at 30 and 40 min. The noise and drift are sufficiently large that an SP survey under these conditions would yield uninterpretable results.

1.5.2 Redox method development

A number of redox and pH measuring techniques were developed and applied at the Marsh Zone. During drilling, clay samples were collected and clay slurries measured for ORP and pH in the field. Groundwater samples were later taken from monitoring wells and measured for ORP, pH and other parameters. Down-hole SP surveys were also carried out. Described below are a number of protocols, developed before and during the drilling program, to deal with the inherent limitations of Pt ORP probes.

ORP probe limitations. ORP probes consist of a Pt electrode connected to a reference cell, which contains an electrolyte solution with a metallic electrode in contact with a salt of that metal. In the probes used in our experiments (Corning model 476516) the half-cell consists of Ag in contact with $AgCl_{(s)}$ and $AgCl_{(aq)}$. Electrolytic contact between the half-cell solution and the sample is maintained through a porous ceramic junction. The ORP is the voltage difference between the half cell and Pt in contact with the sample as measured with a very high impedance voltmeter. The probe and sample together represent a reversible voltaic cell. If the sample is more oxidizing than the half-cell, the Pt electrode functions as a cathode and the Ag electrode as an anode according to the reaction:

$$Ag_{(s)} + Cl^- \rightarrow AgCl_{(aq)} + e^-.$$

If the solution is more reducing than the half-cell, the Pt electrode acts as an anode and the Ag electrode a cathode and the reaction is reversed. Because Pt is considered inert, the solution can only accept or liberate electrons by respectively reducing an oxidized ion or oxidizing a reduced ion in solution or in the slurry in contact with the electrode, e.g.:

$$Fe(OH)_3 + e^- \rightarrow Fe^{2+} + 3OH^- \text{ (or the reverse).}$$

There are several problems related to the polarizable nature of Pt that complicate the use of ORP probes. During measurements, the reactions occurring at the electrode can deposit products on the surface of the Pt. In addition, Pt-oxides develop on the surface during storage (Galster, 2000). Not only do these deposits interfere with the contact between the Pt and the next sample to be measured but they also impart an electrical potential of their own. The results are memory effects and long equilibration times, especially after long-term storage or when measuring a sample with low ionic strength after one with high. The problem is so significant that, when measuring earth materials, full equilibration of the probe can take weeks (Solomin, 1965).

To deal with polarization, researchers have attempted various procedures for removing the deposits from the probe surface. These take the form of either cleaning or deoxidizing (Galster, 2000). Cleaning techniques include using acids or other caustic solutions to dissolve deposits off the probe surface. Unfortunately, this process itself will usually form oxides. Deoxidation techniques involve either the use of a reducing agent, or cathodic reduction of the oxides through the application of a negative charge to the Pt. Repeated deoxidation by these techniques can have a detrimental effect on the surface of the probe. Galster (2000) states that the only confident way to remove deposits and oxides is to polish the surface with a fine inert polishing agent. Unfortunately, the design of many commercial ORP probes does not allow for this.

ORP measurement of soil slurries. During the drilling programme, clay from split spoon samples was mixed into an approximate 1:1 slurry with distilled water and measurements for pH and ORP were made. The pH meter was calibrated at the beginning of each day, cleaned with distilled water after sample measurement and stored between samples in pH 4 buffer solution. The ORP probe required more complicated preparation because of

polarization issues. For the Marsh Zone survey a protocol was developed to depolarize the ORP probe using the sample itself. The first sample slurry of each day was repeated, the first time to depolarize and the second to obtain the readings for that sample. The second set of readings were almost invariably lower than the first. Between samples the probes were cleaned with a jet of distilled water and kept in KCl storage solution to minimise contact with air. However, dissolved oxygen in the water and KCl solution and the unavoidable contact of the probe with air between solutions resulted in some polarization. The probe was therefore allowed to depolarize in each sample for a period of 5 min, with readings being taken at 1, 2 and 5 min. The difference in the three sets of readings clearly demonstrates the importance of probe depolarization and consistent probe immersion times (Fig. 1-5).

The purpose of collecting the redox data was to obtain a *relative* measure of the redox conditions along the line. The protocol described above achieved this at the Marsh Zone, as will be shown in this paper. However, it appeared during field implementation that redox trends along transects such as those in Figure 1-5 may not have been fully developed at 5 min. To determine the appropriateness of the 5 minute equilibration times, a laboratory investigation was undertaken. Samples of clayey silt were collected at the Cross Lake site in 2001, vacuum sealed under N_2 and flash-frozen within several minutes of collection. Several weeks later in the laboratory the samples were slowly thawed and ORP was determined under N_2 using multiple probes.

Figure 1-6 shows a typical equilibration curve for four probes in the same sample. The different behaviour of the curves in the first several minutes results from differential polarization of the Pt surfaces of the probes. The longer-term drift in the readings represents equilibration of the probes over time as a potential related to the sample slurry develops on the Pt surface. Eventually this drift would end but, depending on the starting condition and pre-treatment of the probe, it could take days or even weeks to completely stabilize (Soliman, 1965). Because the probes are all referenced to Ag-AgCl half-cells, one might expect the four curves in Figure 1-6 to trend toward the same point but they do not. This is common with ORP probes because they are generally not calibrated against solutions of known voltage. The differences are due to probe idiosyncrasies that would presumably include variations in the electrode surface of the Pt or Ag, the resistance of

the porous junction, the electrical connection with the solid AgCl or to impurities in the KCl electrolyte. Regardless of the cause of these idiosyncrasies, Figure 1-6 shows the critical importance of using the same probe for a given ORP transect. This necessitates the simultaneous use of multiple probes in case one is damaged or otherwise malfunctions in the middle of a transect.

Some probe idiosyncrasies also result in slow equilibration times and can be so significant that the probe should not be used. Probes, especially if new, should be tested prior to a survey and only those with fast equilibration times and that give repeatable readings at specific immersion times in solutions of known voltage should be used. Although this is necessary, it is also expensive and may involve effectively discarding new probes.

Achieving full ORP equilibration is impossible in a field situation, and it is therefore reasonable to equilibrate for a consistent period of time as was done in the Marsh Zone study. Figure 1-6 shows that a 5 minute immersion period is about the minimum amount of time that is required to remove the worst effects of polarization and obtain a more consistent rate of equilibration. Figure 1-7 shows that the reproducibility of duplicates measured under N_2, as determined by the slope and R^2 value of the regression line, improves drastically between 30 s immersion time and 5 minute and moderately between 5 and 10 min. Between 10 and 30 minute there is almost no further improvement, which suggests the samples have reached a rate of equilibration that is related to the sample and not the initial condition of the probe surface. The optimum equilibration time under N_2 would therefore be about 10 min, however, 5 minute should yield acceptable results in most cases.

Measuring under air, as was done at the Marsh Zone, adds the further complication of oxidation of the sample during measurement. Tests as part of the same laboratory investigation showed that many slurries measured under air began to oxidize between 5 and 10 minute after mixing and by 30 minute their ORPs had increased by several hundred millivolts. Duplicate measurements after two days showed that entire samples can oxidize and increase in ORP by up to 600 mV if sample bags are opened under air, even if they are closed immediately afterward. Therefore in a field setting,

where samples will be measured under air, 5 minute of probe immersion appears to be the best compromise between minimising oxidation and allowing sufficient depolarization.

Groundwater ORP. Shallow groundwater in the Abitibi region has a considerably lower ionic strength than does a typical clay slurry and therefore initial polarization of the ORP probe can have an even more detrimental effect on groundwater measurements. It was determined, during ORP testing of groundwater at the Marsh Zone, that very long initial depolarization times in the sample were required to prepare the probe for analysis. However, once the probe was depolarized, many samples could be analysed with only several minutes of equilibration provided they were analysed in short succession.

Figure 1-8 shows results from two transects of shallow wells along Line 15 at the Marsh Zone. ORP measurements were taken in a flow cell at the wellhead on water pumped from the bottom of the well screen. An initial north to south transect was followed immediately by a return transect from south to north. The probe depolarized throughout the entire southward transect in water from successive shallow wells and only reached a constant rate of equilibration by about the time it was completed. On the return transect, the 1 to 2 minute of probe contact with air between wells resulted in about 20 mV of polarization that masked the signal for the first 2 minute of immersion. By 3 minute the probe was sufficiently equilibrated to reveal an anomaly over mineralization.

Another depolarization approach that proved successful involved pumping water from the first well on the line into the flow cell and leaving the probe in it to depolarize for about an hour. The flow cell was left in a bag that had been thoroughly purged with N_2 to remove air. The first two or three wells on the line would then be repeated at the beginning of the traverse to ensure reproducible readings. Both these methods of depolarization were successful because the redox chemistry of the shallow well water is fairly consistent and therefore the magnitude and direction of polarization of the Pt was also consistent. However, in an earlier survey, the deep well water was inadvertently measured in the middle of the transect and this *negatively* polarized the probe for at least the following two wells. This demonstrates that long equilibration times on every sample are required when testing water except where a system has been devised that ensures consistent redox media with short intervals between samples.

ORP of saturated peat. As the peat at the Marsh Zone is fully saturated, it represents a good medium for the measurement of ORP. Large samples (c. 1 kg) were collected from about 0.5 m depth along Line 15, placed in sealed plastic bags and kept in coolers. The samples were then measured for ORP within 24 hours of collection by inserting the probe into the sample, squeezing the bag to remove gases and recording measurements after 1, 2 and 5 minute of probe immersion.

1.6 Results and Discussion

1.6.1 Subsurface redox, pH and related parameters

The results of ORP and pH analysis of unoxidized clays collected during the drill programme from below the peat are shown in Figure 1-9. On Line 15 a 'column' , or 'chimney' of reduced clay is apparent over mineralization, accompanied by a pH high in the overlying peat, sampled at 50 cm depth (an equipment malfunction resulted in unusable pH data for clay slurries on Line 15). The pH high corresponds well with the position and strength of redox negativity in the underlying reduced column. On Line 14, a reduced column is also apparent over mineralization but is much more subdued, perhaps because no samples were collected directly over mineralization. The subsurface clay pH on Line 14 shows an excellent correlation between high pH and reduced areas.

The presence of these reduced columns over sulphide mineralization is consistent with the model of Hamilton (1998, 2000) but they are the first to be documented by field studies. More accurately this is a reduced 'curtain' that follows the trace of mineralization and appears as a column only in cross-section. Lithological units with contrasting redox properties were also postulated to show a response and apparently do on both lines at the Marsh Zone. As shown in Figure 1-9, mafic metavolcanic rocks appear to have a more reduced response than the talc-chlorite schist, presumably due to differing redox properties. Although the effect of lithology on ORP is by no means conclusive, there are no surface features or overburden conditions present that could account for this ORP shift from north to south.

The correlation between reduced ORP and basic pH conditions is interpreted to result from the suppression of background oxidation that occurs due to near-surface weathering processes in the clay. Although slow, oxidation processes that would result in the oxidation of reduced metals probably occur in the upper few metres of the glacial clay and one of the products would be H^+: $Fe^{2+} + ½O_2 + 2H_2O \Rightarrow Fe(OH)_3 + H^+$. In the subsurface profile, areas that are more reduced have less metal oxidation occurring and therefore less H^+ production, which results in an inverse correlation between pH and redox. This would be particularly acute within the reduced column where the background oxidation would be most strongly suppressed. The presence of increased amounts of reduced species in the reduced column would also provide an opportunity for enhanced oxidation at its flanks where it comes into contact with the more oxidized background redox regime (Hamilton, 2000). Enhanced oxidation is supported by a pH low immediately adjacent to, and on either side of, the reduced column in the peat pH data for Line 15 and the uppermost clay data for Line 14 (Fig. 1-9).

Figure 1-10 shows the pH and ORP of well water along Lines 14 and 15. On both lines ORP decreases over mineralization and the response on Line 15 is much stronger, probably for the same reason as with the slurry ORPs. Although in no way remarkable, there is also a slight pH increase over mineralization on both lines with slight decreases on either side. ORP and pH in groundwater are much less reliable than in slurries because of the lower ionic strength of the groundwater solutions. Also, the exsolution from groundwater of dissolved gases such as CO_2 and H_2S and the oxidation of metals or H_2S can affect the pH of well water, particularly if the water had been standing in the well for any length of time.

Figure 1-11 shows H_2S and CO_2 in groundwater from shallow wells for both lines and for the deep wells on Line 15. H_2S shows elevated concentrations in shallow well water over mineralization on both lines, with a background of <0.03 mg l^{-1} and a peak concentration over mineralization of 0.1 mg l^{-1}. As expected, the deep well data show a higher background of up to 0.5 mg l^{-1} but they also show a far higher peak of 7 mg l^{-1} from the well finished in the mineralization. CO_2 also shows peaks in the shallow well data over mineralization and, although it has a slightly higher background in bedrock,

there are *lower* concentrations in groundwater from mineralization than in groundwater from the shallow overburden above it.

These data suggest that the dissolved gases are related to the presence of mineralization but, whereas the H_2S appears to originate from it, the source of CO_2 must be shallower and may be related to a secondary process. H^+ from the oxidation of H_2S or metals may result in minor carbonate dissolution (the clays contain about 20% carbonate) and CO_2 production in the general vicinity of the reduced column (Hamilton, 2000). Diffusion of dissolved CO_2 resulting from this process might cause a generally higher concentration in near-surface groundwater over mineralization than in adjacent areas. An alternate explanation is input of CO_2 from biological activity. Redox boundaries such as occur in association with the reduced column are excellent sources of metabolic energy for bacteria. Enhanced microbial activity by metal- or sulphide-oxidizing bacteria could result in the increased biogenic CO_2 production. Carbon isotope studies are being considered as a way of determining the CO_2 source. Elevated CO_2 in groundwater over mineralization has also been observed at other sites in the Abitibi Region as part of this study. Soil gas CO_2 anomalies have been noted over mineralization for many years (e.g., Lovell *et al.*, 1983; McCarthy *et al.*, 1986).

Figure 1-12 presents the in-well temperature for June 2001 and July 2002 showing wide temperature peaks over, but not perfectly centred on, mineralization. There are a number of possible reasons for these broad peaks over mineralization including solar warming in the more open part of the bog, and therefore a causal relationship between the temperature peak and mineralization can neither be established nor ruled out. These data are shown because other data for sites, soon to be published, also show temperature anomalies that are spatially related to mineralization and in particular, to subsurface reduced columns.

1.6.2 Surface redox and pH

Figure 1-13 shows the pH and ORP of peat sampled at *c.* 40 cm depth along Line 15. Again, there is a strong inverse correlation between pH and redox. Similar to the pH data for slightly deeper peat samples (Fig. 1-9) there is a pH low flanking the underlying reduced column on both sides and a rise over mineralization. This corresponds to an

opposite response in the ORP showing an apparently oxidized area immediately over and flanking the reduced column. This oxidized 'cap' may result from the deposition of the products of oxidation reactions (e.g., oxidized metals) at the top and flanks of the reduced column. A similar feature has been observed at other sites above the water table.

1.6.3 Surface SP

Results of an SP survey carried out on surface peat in July 1999 are shown in Figure 1-14. A -7 mV drift was removed from the raw data and a regression line plotted through the resulting data in order to remove the south-north increasing trend in the raw data. Relative to background, the residual SP shows a minor response of about 5 mV over mineralization. In thin (unsaturated) overburden over sulphides, Burr (1982) reports sulphides can be expected to provide a surface response of up to 350 mV. Logn and Bolviken (1974) measured much higher maxima of up to 800 mV for a very large subcropping pyrite deposit. A response of 5 mV is therefore extremely low, as might be expected over a deposit containing only 10% sulphides and overlain by more than 20 m of fully saturated clay and peat. The weak response also shows that the electrical field associated with the mineralization is very small relative to the redox field.

1.7 Summary and Conclusions

Successful use of ORP probes to delineate redox responses in overburden or groundwater above mineralization requires protocols to depolarize the probe prior to use. In this study, probes were successfully depolarized using the samples themselves and brought to a stage in the equilibration curve that can reasonably be attributed to equilibration with the sample rather than remnant polarization due to probe storage or probe history. When measuring ORP on clay slurries in the field, 5 minute of equilibration appears to the optimal compromise between allowing sufficient time for depolarization and minimising sample oxidation in air. The lower ionic strength of groundwater requires longer initial depolarization times than for clay slurries, when measuring the first sample. Several hours of immersion in the first sample followed by 5 minute in each subsequent groundwater sample measured produced acceptable results,

provided samples were measured in close succession. Alternatively, the groundwater in every well on the line was measured and then re-measured on a return traverse.

ORP results for clay slurries and groundwater show a strongly reduced area over mineralization, consistent with the model of Hamilton (1998, 2000), which takes the form of a reduced 'column' in cross-section or 'curtain' in three dimensions. This column extends downward from the base of the peat, into the clay, to at least 6 m depth and is inferred to continue down through overburden to mineralization and probably upward into the peat. In general, the ORP inversely correlates with pH, particularly in the vicinity of the reduced column. This is postulated to be due to the suppression of metal and sulphide oxidation in the more reduced parts of overburden, thereby suppressing H^+ production. Dissolved H_2S and CO_2 in shallow groundwater are elevated above mineralization. Measurements on groundwater extracted from three wells in bedrock suggest that mineralization is the source of the H_2S whereas the source of CO_2 is shallower. Given the spatial relationship between the CO_2 high and mineralization, it appears to be a secondary process involving carbonate dissolution near the flanks and top of the reduced column where reduced metals are oxidizing. Alternatively, it may be biogenic CO_2 from enhanced microbiological activity near the sharp redox boundaries associated with the reduced column.

A wide positive ORP response occurs in shallow peat that shows a minor decrease immediately over mineralization. Again, the ORP data inversely correlate with pH. The positive ORP response may indicate an oxidized 'cap' caused by the deposition of the products of metal oxidation above and adjacent to the reduced column. A minor SP response on surface over mineralization indicates a minor electrical field associated with the sulphide conductor. The 5 mV SP response, however, is very small compared with the redox response of several hundred millivolts, measured in the underlying clay. Most of these features spatially associated with the reduced column are genetically related to it as is further discussed in the second of this two paper series (Hamilton et al., 2003).

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Chapter 1 Figures

Figure captions

Fig. 1-1. The progressive modification of redox-equipotential lines in saturated overburden overlying a reduced feature in bedrock. Reduced species flow lines depict the movement of negative charge-carrying species such as Fe^{2+}, $S_2O_3^{2-}$ and Co^{2+}. Positive charge-carrying ions such as UO_2^{2+}, MoO_4^{2-}, SO_4^{2-} and dissolved oxygen radicals have similar flow lines but in the opposite direction (modified from Hamilton, 2000; after Hamilton, 1998).

Fig. 1-2. Location of Marsh Zone field area within Ontario.

Fig. 1-3. Overburden stratigraphy and bedrock geology of Line 15 at the Marsh Zone. Scant information on bedrock topography exists from 20 to 200 north.

Fig. 1-4.. SP versus distance at two sites in the Abitibi region during a period of high electromagnetic interference. Readings were taken on both sites in July, 2000 and were recorded manually over 1-min. intervals using an ultra-high impedance pH-type voltmeter.

Fig. 1-5. ORP of clay slurries from 3 m depth on a transect across mineralization after 1, 2 and 5 min. of probe immersion.

Fig. 1-6. Equilibration curves for four ORP probes in a clay slurry. Different behavior of the probes in the first 5 minute is due to Pt memory effects resulting from different probe

histories. Data for probes 1 and 5 were recorded using a datalogger. Data for probes 6 and 3 were recorded manually.

Fig. 1-7. Reproducibility of slurry ORPs of lab duplicate clay samples measured under N_2 after various periods of probe immersion, from 30 sec. to 30 min. Axes are graded in mV.

Fig. 1-8. The effect of sample immersion time on probe depolarization during groundwater ORP measurement. The survey required the entire north to south transect to depolarize the probes. Only on the return transect is a response apparent over mineralization.

Fig. 1-9. Subsurface pH and ORP of clay slurries after 5 minute probe immersion. Equipment malfunctions rendered Line 15 clay slurry pH data unusable so pH data for overlying peat are shown instead. Horizontal scale is distance (m). Black dots represent locations of unoxidized clay samples from below peat. The white dots at 200 north are oxidized clay samples that were not used in the ORP kriging . Line 15 bedrock geology is shown. Line 14 geology is similar but is not precisely known (QFP = quartz-feldspar porphyry).

Fig. 1-10. ORP and pH of groundwater. Samples were measured in a flow-cell after 1 minute of equilibration for pH and 3 minute for ORP. Prior to ORP measurement on each line, an initial depolarizing traverse measured the ORP on every well on a line then each well was re-tested once probes had depolarized.

Fig. 1-11. H_2S and CO_2 dissolved in groundwater at Marsh Zone. H2S detection limit was 0.01 $mg \cdot l^{-1}$.

Fig. 1-12. In-well temperature of groundwater at the Marsh Zone for June, 2001 and July, 2002.

Fig. 1-13. pH and ORP of shallow peat (c. 40 cm depth), Line 15, Marsh Zone.

Fig. 1-14. SP in surface peat (5 cm depth), Line 15, Marsh Zone.

Figure 1-1. Redox gradients over a reduced feature in bedrock.

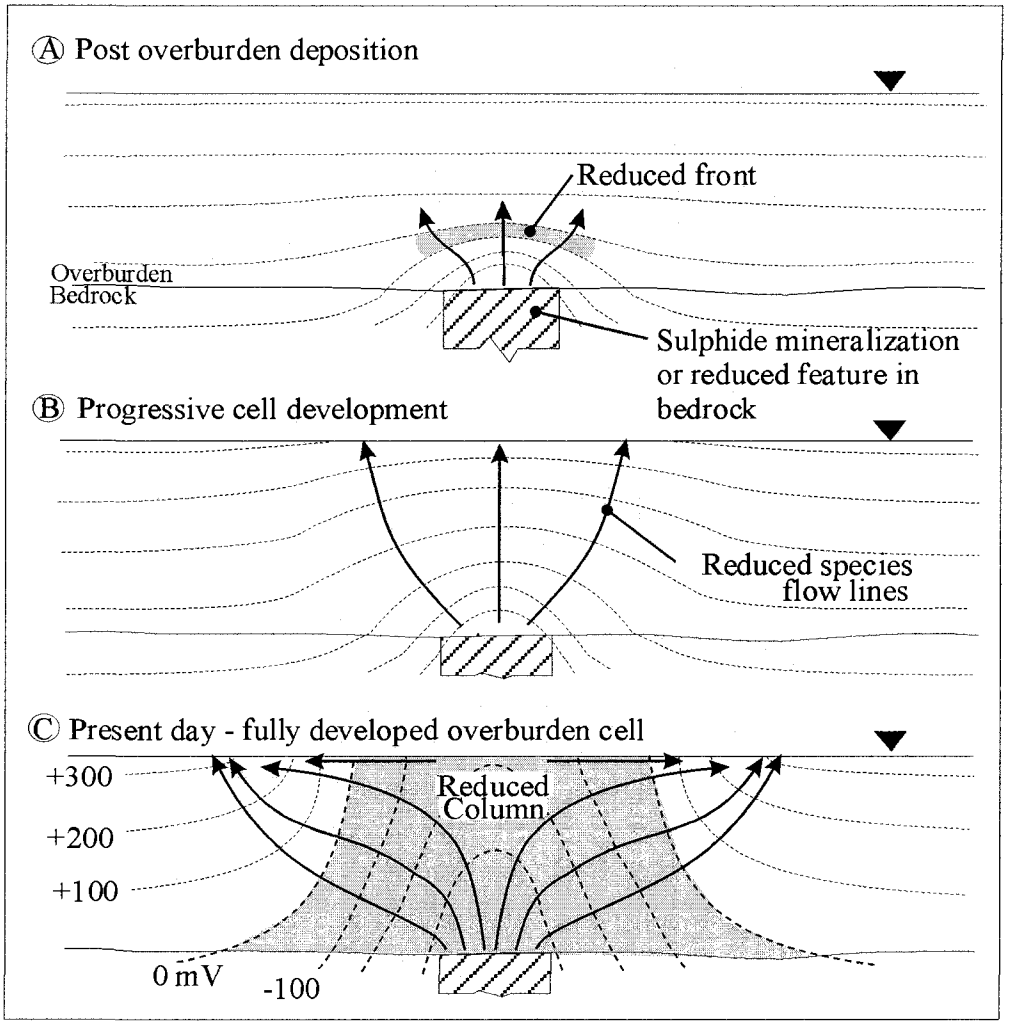


Figure 1-2. Location of the Marsh Zone

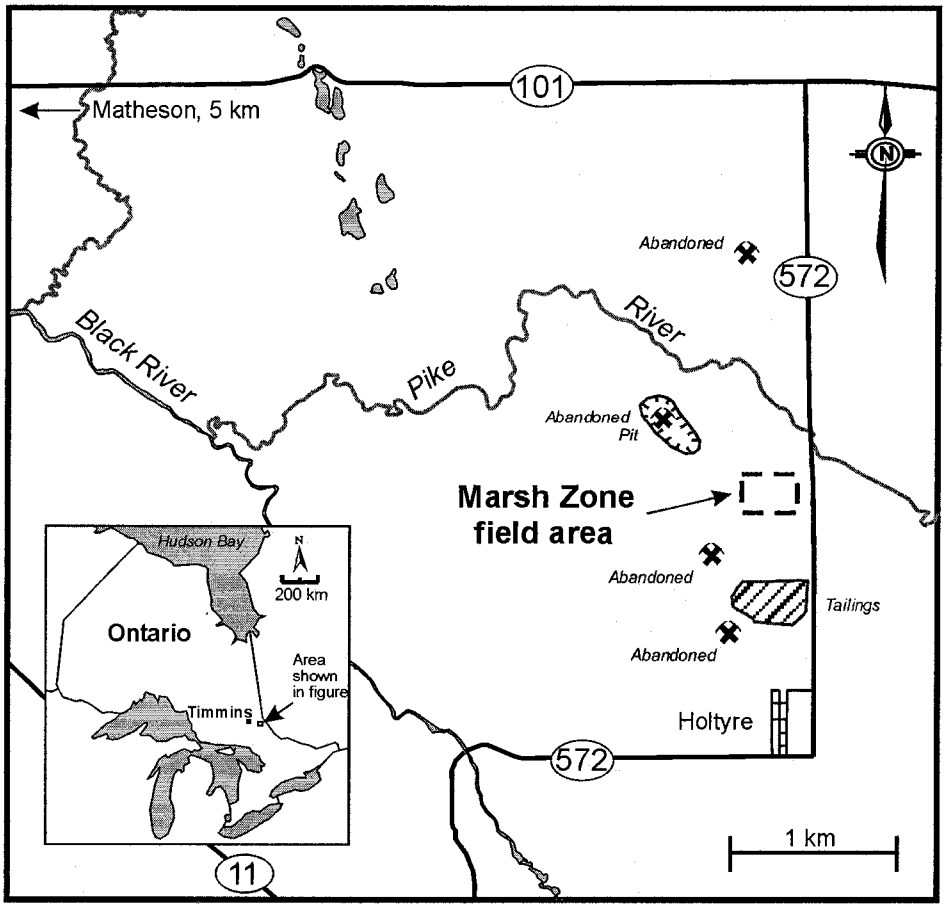


Figure 1-3. Overburden stratigraphy and bedrock geology, Marsh Zone

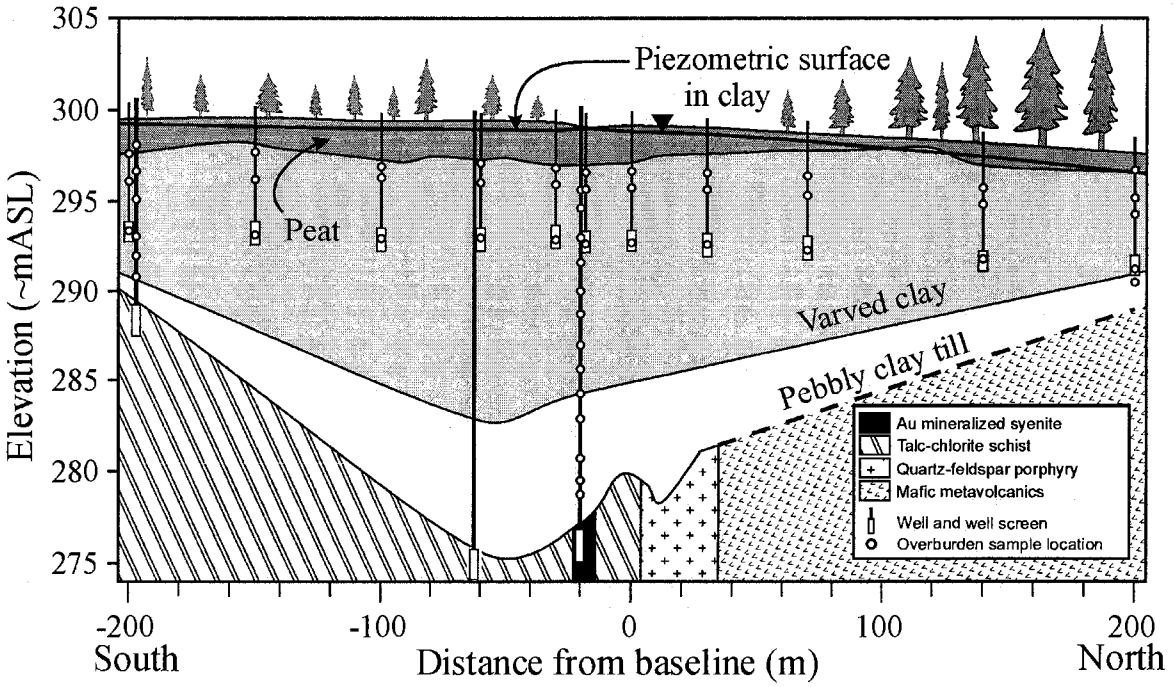


Figure 1-4. SP variation in background areas.

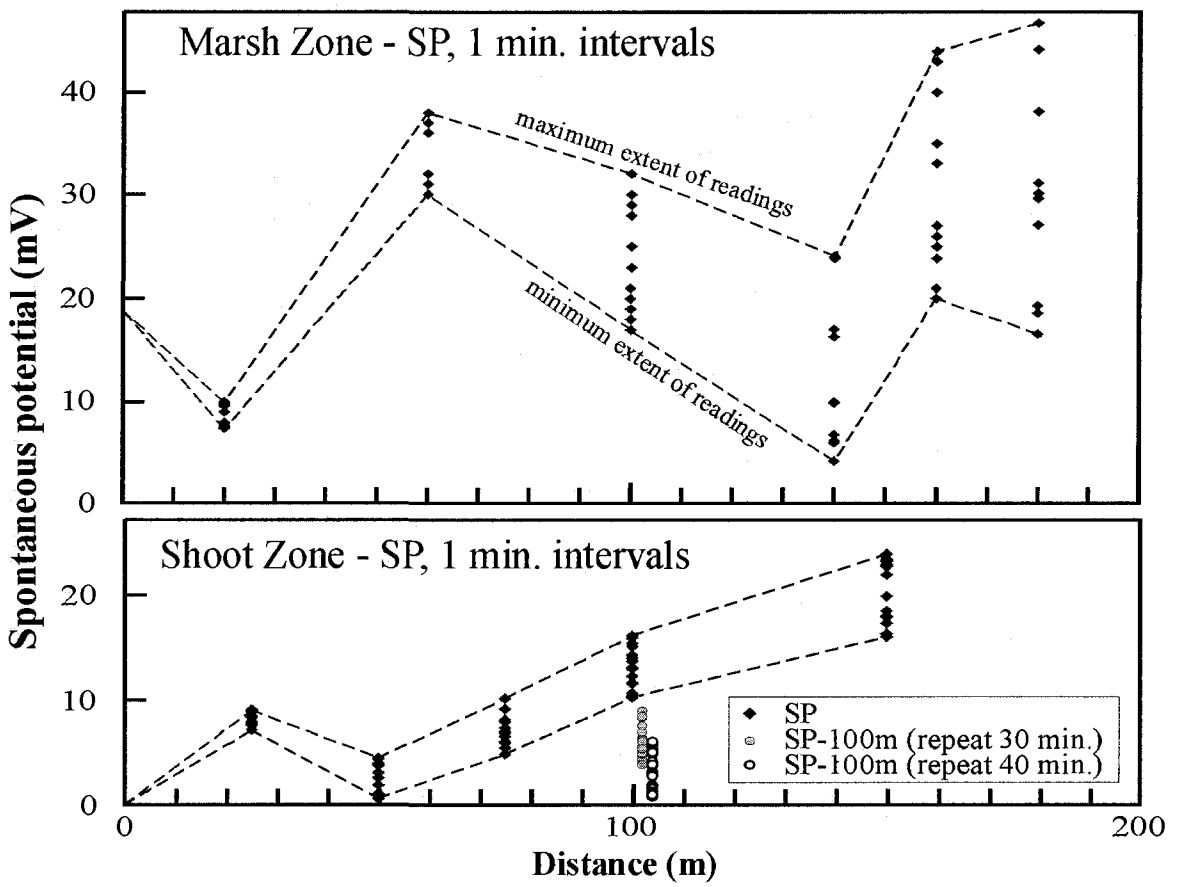


Figure 1-5. Effect of time on probe ORP probe equilibration.

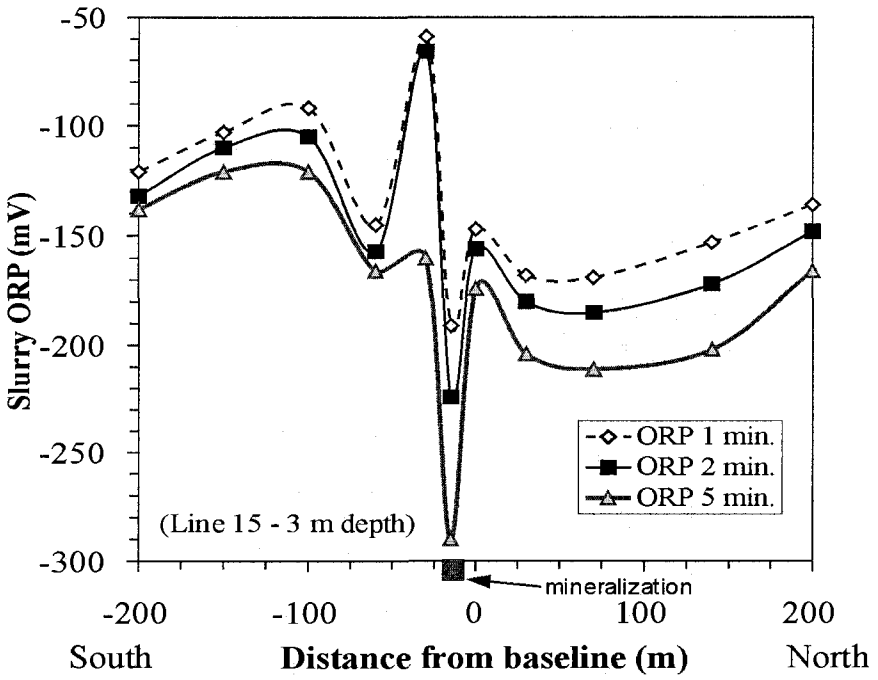


Figure 1-6. Different behavior of 4 ORP probes in the same clay slurry.

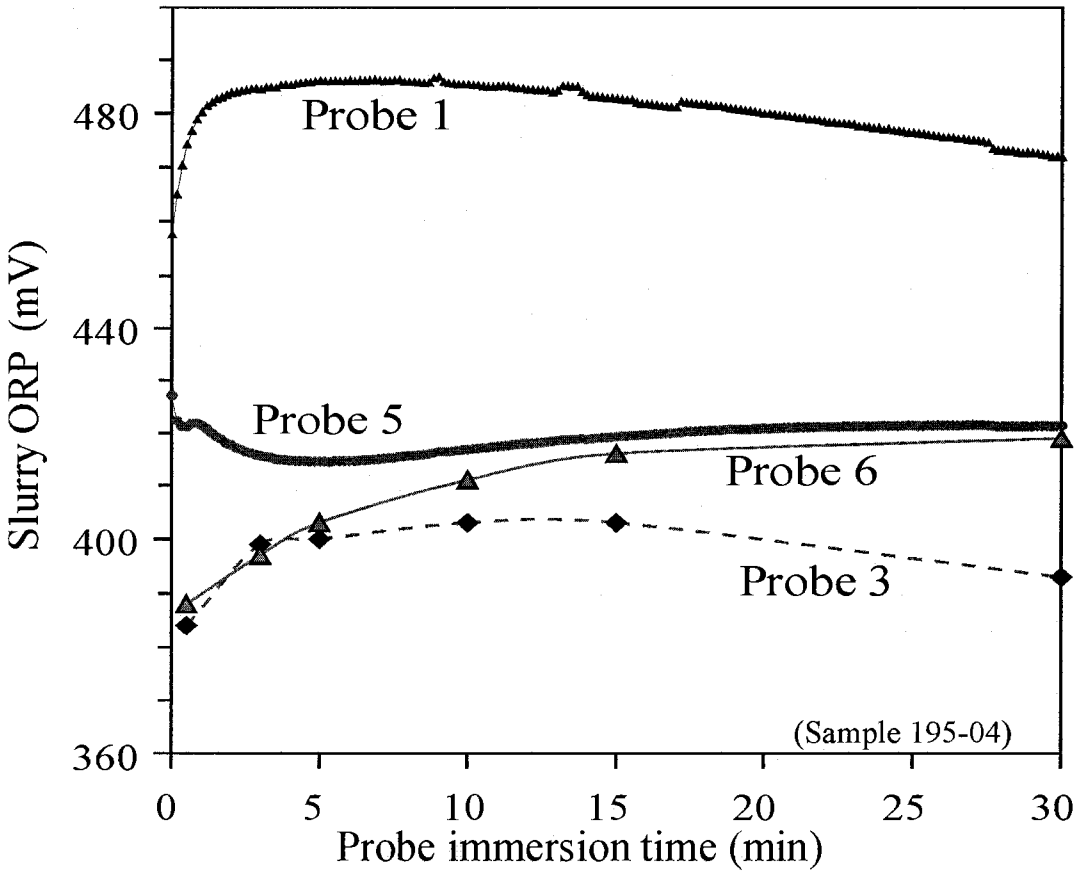


Figure 1-7. Reproducibility of lab duplicates measuring slurry ORP.

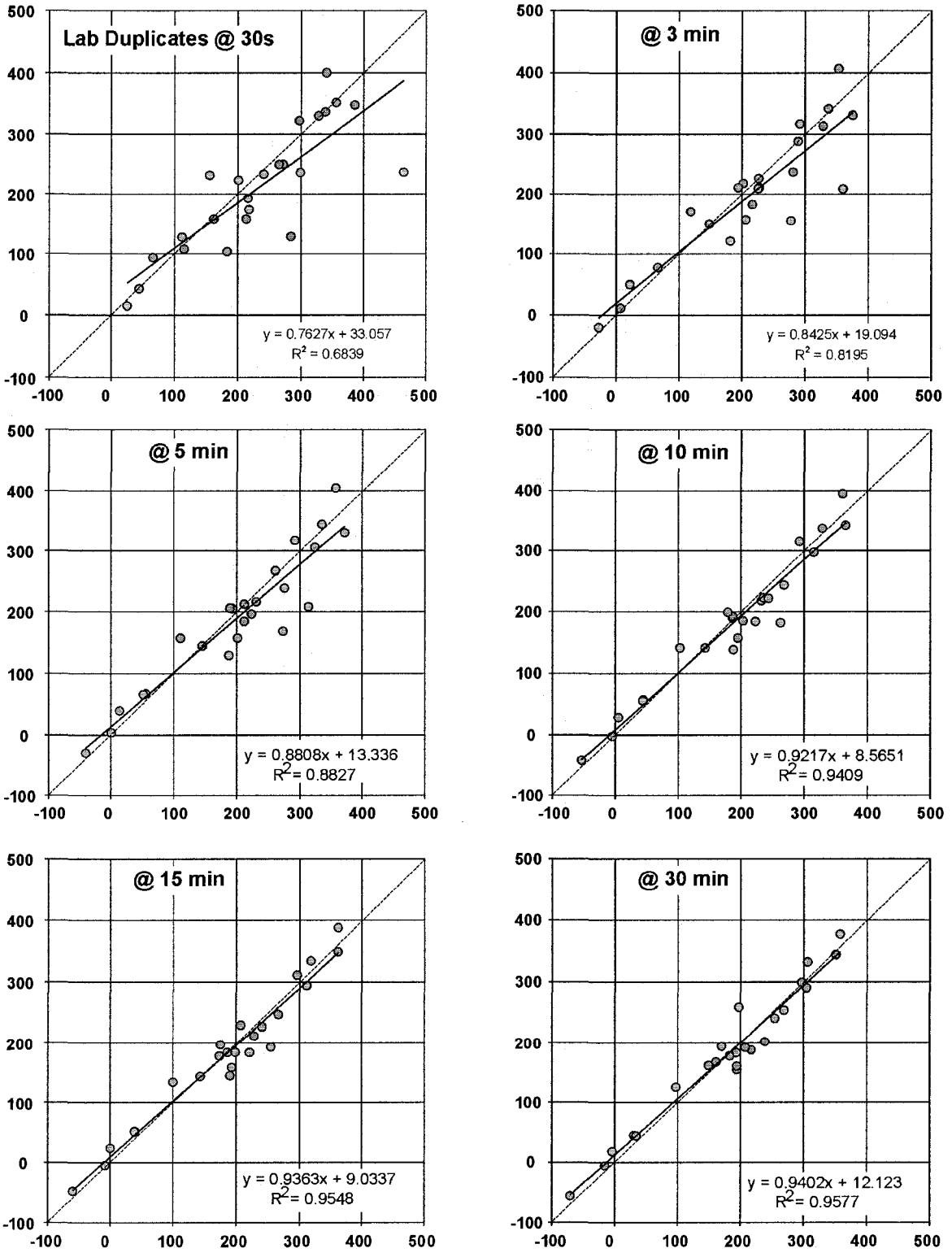


Figure 1-8. Probe depolarization during measurement of groundwater ORP.

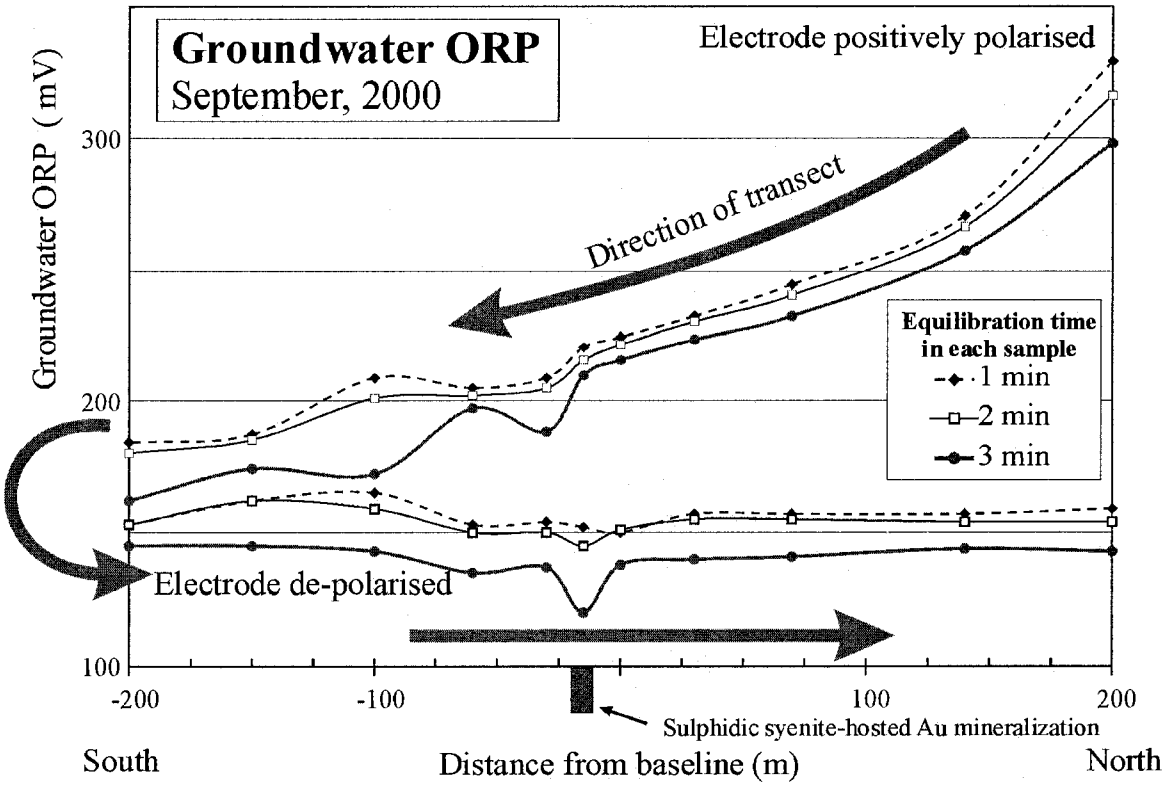


Figure 1-9. ORP and pH of sediments overlying mineralization at the Marsh Zone.

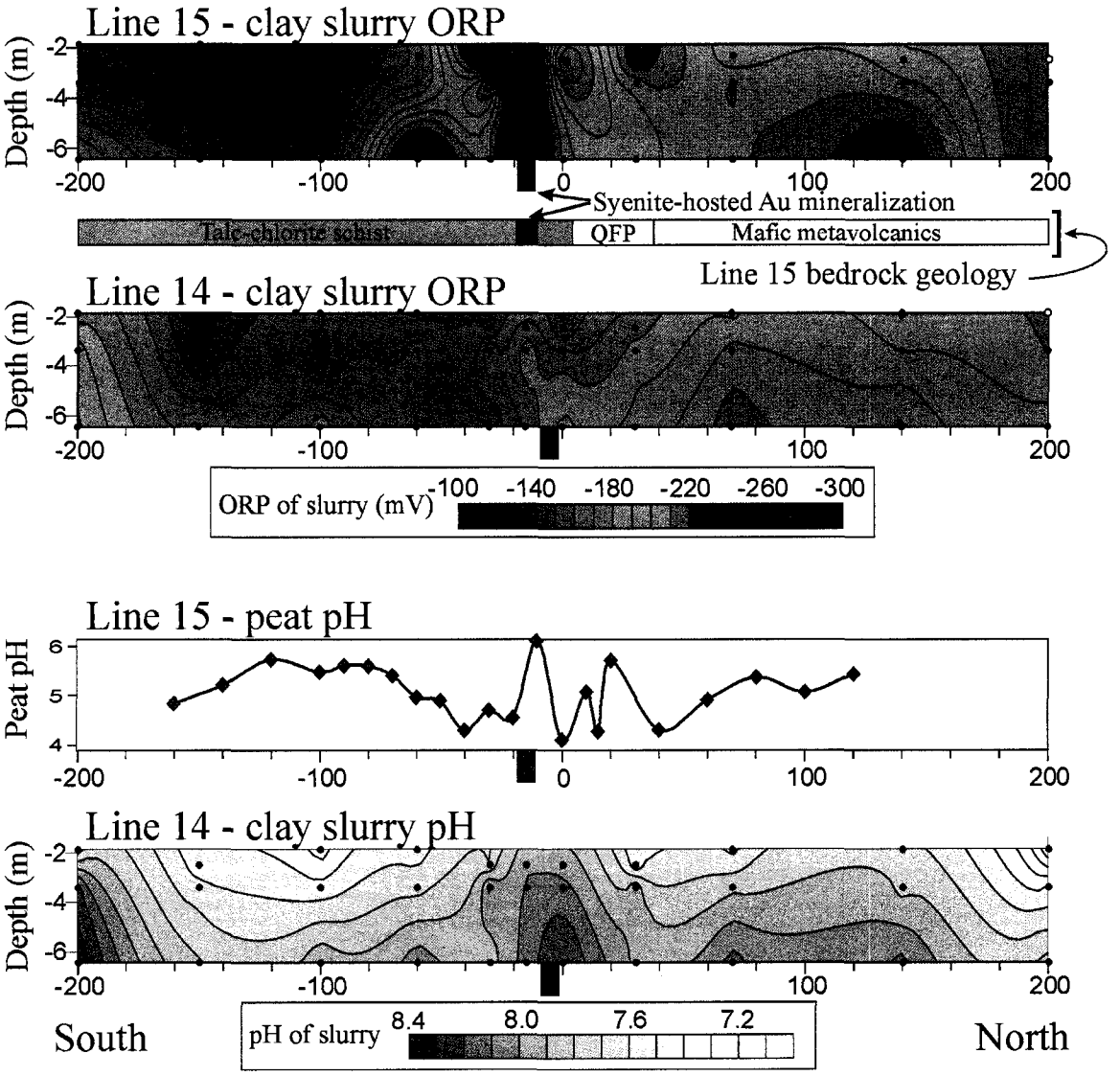


Figure 1-10. ORP and pH of groundwater.

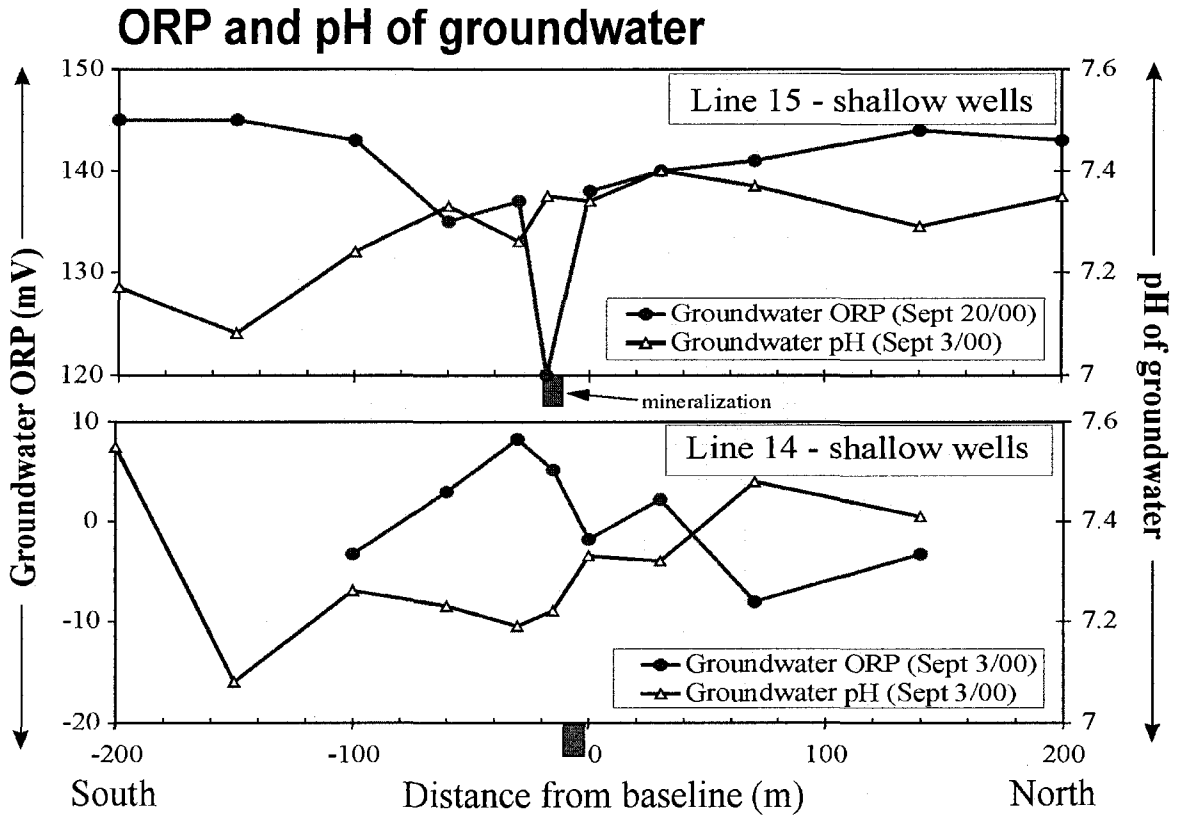


Figure 1-11. H_2S and CO_2 Dissolved in groundwater.

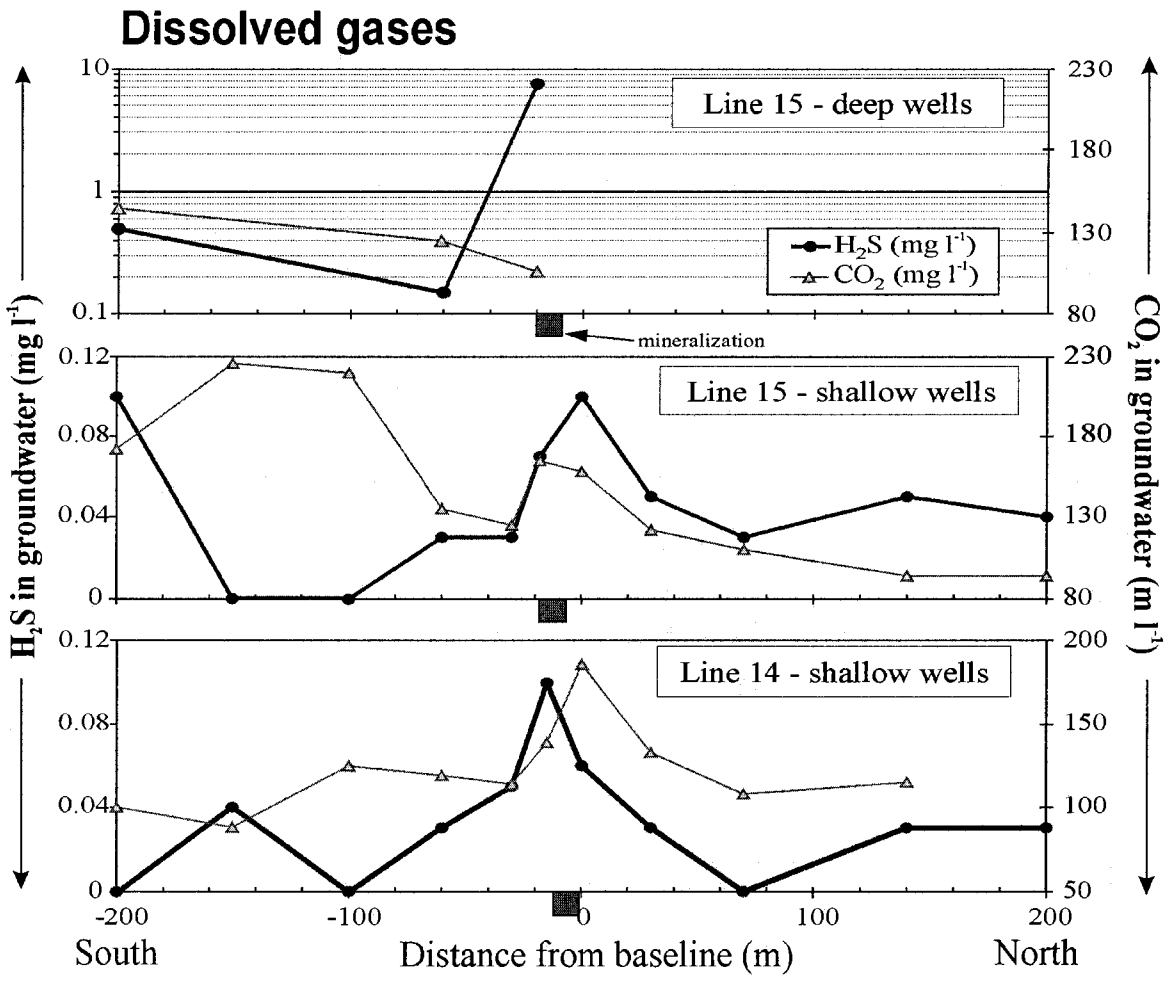


Figure 1-12. Temperature of groundwater.

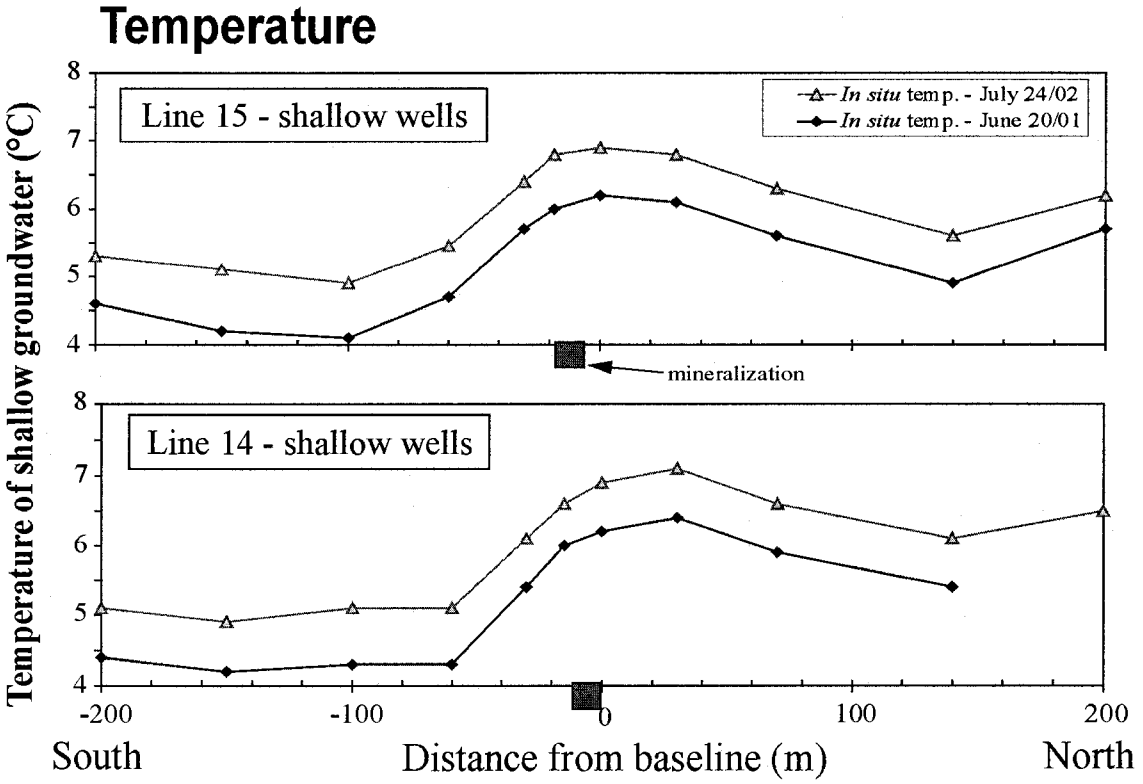


Figure 1-13. ORP and pH of saturated peat.

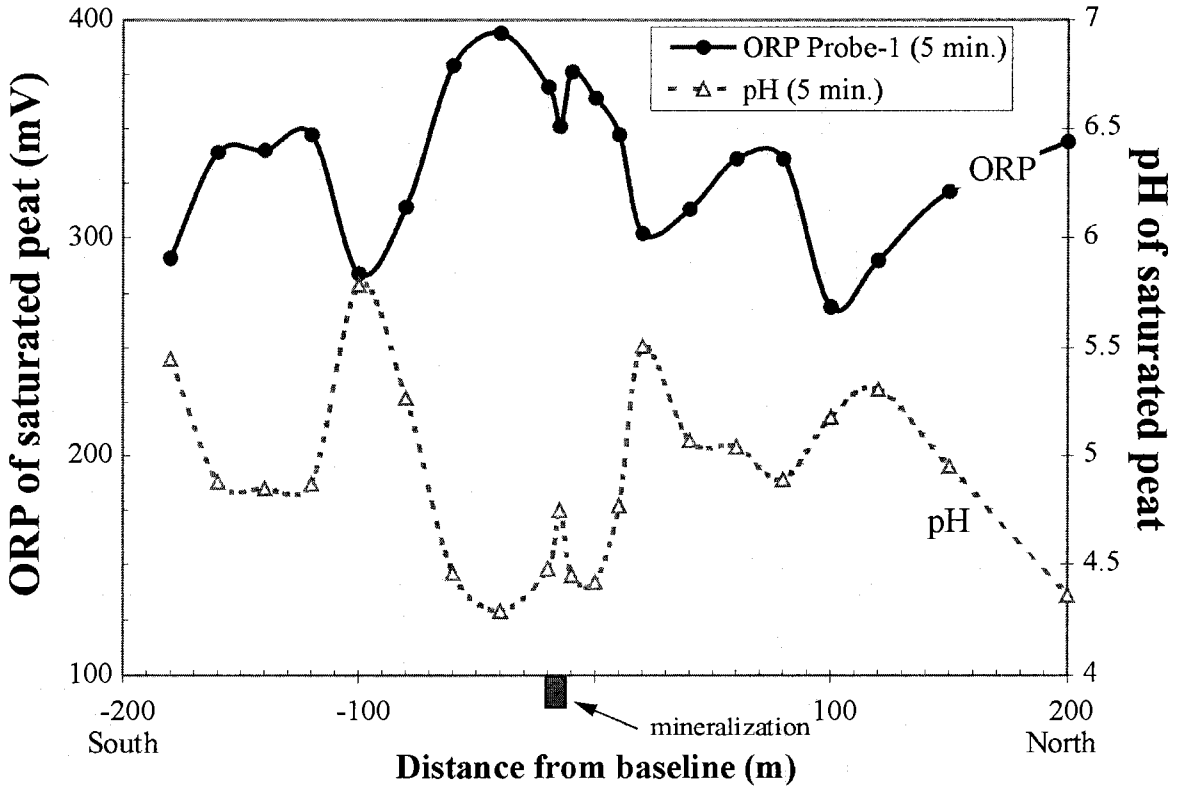
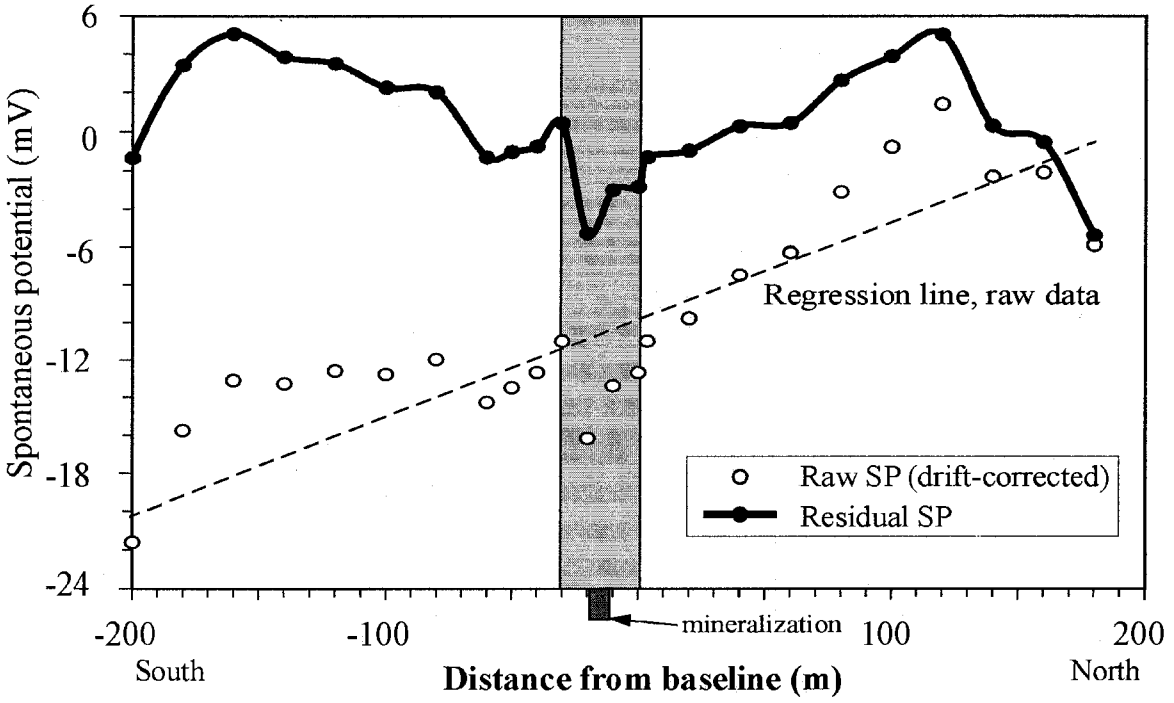


Figure 1-14. SP in surface peats



CHAPTER 2

Redox, pH and SP variation over mineralization in thick glacial overburden (II): field investigations at Cross Lake VMS property

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Manuscript published in Geochemistry Exploration Environment Analysis:

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Abstract

An investigation of surface and subsurface redox and electrical field conditions was carried out over a volcanogenic massive sulphide (VMS) deposit in thick glacial clay and sand terrain of the Abitibi clay belt of northeastern, Ontario. Thirty-seven boreholes were drilled to 9 m depth on two lines crossing the strike of mineralization and were completed in either sand or clay. An additional three were drilled from 30 to 50 m and completed in bedrock. Monitoring wells were installed in all holes and groundwater was later sampled. A variety of oxidation-reduction potential (ORP) and spontaneous potential (SP) techniques were used, the methodologies for which were introduced earlier and are further developed here. The best definition of redox conditions was obtained by ORP measurement of clay and sand slurries from split-spoon samples collected and analysed during the drilling program. Related techniques included groundwater ORP and down-hole platinum-SP (PtSP) testing, the latter measuring total potential field, which is the sum of the electrical and electrochemical components of voltage. Although the performance of the methods differed, the results consistently show chemically reduced areas (reduced 'columns') in the phreatic zone above mineralization with overlying acidic 'caps' in the vadose zone. Other features noted over mineralization include carbonate remobilization, partial extraction metal anomalies in shallow soils, CO_2 enrichment in groundwater, and elevated groundwater temperature. These varied features are related and provide evidence for upward transport of reduced species from mineralization. They agree well with phenomena predicted in a previously published redox-gradient transport model.

SP was measured, both down-hole and on surface, and shows a weakly negative electrical field response over mineralization. This response is small in comparison to the redox response and is interpreted to occur because, in addition to being oxidizable, the sulphide is also conductive and SP currents within it produce a small electrical field. It is postulated that oxidizable but non-conductive features such as sphalerite, would also produce a reduced column but without an electrical field, whereas, conductive, non-

oxidizable features such as graphite would produce an electrical field but with little or no redox response.

2.1 Introduction

This paper describes an investigation into spontaneous potential (SP), pH, and redox variation in thick, glacially derived overburden above volcanogenic massive sulphide (VMS) mineralization at the Cross Lake property, near Timmins, Ontario (Fig. 2-1). It is the second of two papers presenting studies over mineralization in thick, glacial overburden environments in this area of the Abitibi clay belt. The first (Hamilton *et al.* 2004) described oxidation-reduction potential (ORP) and SP measurement methodology and its application to clay and peat overlying sulphidic syenite-hosted Au mineralization at the 'Marsh Zone' property, 50 km east of Cross Lake (Hamilton *et al.* 2004, Fig. 2-2) The present paper describes further developments of the methodology as well as the results obtained at Cross Lake.

Fieldwork at Cross Lake included a drilling program on two lines, down-hole overburden sampling, pH and ORP measurement of clay and sand slurries, monitoring well installation, subsequent groundwater sampling, and surface and down-hole SP measurements of several types.

The Marsh Zone and Cross Lake projects are part of a larger study, jointly carried out by the Ontario Geological Survey (OGS), the Geological Survey of Canada (GSC) and the Canadian Association of Mining Industry Research Organisations (CAMIRO). The objectives of the larger study were to test a variety of partial extraction soil geochemical techniques for their ability to detect mineralization through thick overburden and to determine the geochemical mechanisms by which elements are transported from mineralization to ground surface. The soil sampling and partial extraction analysis studies were carried out in conjunction with the work described here but will be presented in later papers.

2.2 Background and Approach

Theories by a number of authors (see Hamilton *et al.* 2004) propose electrochemical transport of metals and other species away from orebodies. The proposed

processes should produce a measurable effect on redox, pH and electrical field conditions in overburden above the deposit and, in the model of Hamilton (1998, 2000), should produce a reduced 'column' or 'chimney' in groundwater saturated overburden above the orebody. Hamilton *et al.* (2004) reported the presence of reduced columns over sulphidic Au mineralization at the Marsh Zone along with a number of spatially related geochemical features such as CO_2 and H_2S anomalies, pH responses and temperature anomalies. Hamilton (2000) proposed that features such as these and others that are often reported over mineralization, such as soil carbonate anomalies and metal zonation, could be accounted for by the presence of a reduced column (Fig. 2-2). Where a reduced column comes in contact with the water table, oxidation reactions must constantly occur. A product of oxidation of reduced metals will be H^+ and if carbonate is present in the overburden it will be dissolved near the flanks of, and above, the reduced column and reprecipitated in adjacent areas where the pH is higher. The result would be carbonate depletions and CO_2 enrichments over and adjacent to the reduced column and carbonate enrichments flanking it. Oxygen consumption in the vadose zone (if present) would produce soil gas O_2 depletions. In addition to the oxidation and precipitation of reduced metals, the very presence of a zoned pH/redox feature in overburden would necessarily produced elemental anomalies on surface, which would be controlled by the pH/redox stability of individual elements. Figure 2-2 shows a very wide reduced feature and a stronger geochemical response at the flanks of the feature where redox gradients would be highest. A narrow reduced chimney, such as occurred at the Marsh Zone, would more closely approximate a redox point-source and produce more apical responses for parameters such as pH, and CO_2.

The purpose of our work at both the Marsh Zone and Cross Lake was to measure these effects in areas of thick, glacially derived overburden and to determine which, if any of the proposed transport mechanisms are supported by the data. This first required methods to measure redox conditions in clay, sand and peat that specifically addressed the problem of ORP probe polarization.

ORP probes have Pt surfaces that retain a 'memory' of the redox conditions encountered during storage and previous sample measurement (Galster 2000). Removal of this memory effect is crucial to achieving reproducible results. As part of the first

phase of this study (Hamilton *et al.* 2004) the ORP of clay slurries was measured from specific depths on transects across mineralization at the Marsh Zone. The protocol at the Marsh Zone involved depolarizing the ORP probes using the samples themselves. Repeat readings of the first sample at the beginning of each day and a 5 minute period of readings in each subsequent clay slurry sample provided sufficient time for probes to depolarize. When measuring groundwater ORP, much longer depolarization times were required because of the lower ionic strength and lower concentrations of redox-active species in groundwater relative to the clay slurry. In the case of groundwater, probes were depolarized by immersion in water from the first well for several hours prior to the survey or by measuring ORP in groundwater at every well along the line and then remeasuring it on the return traverse.

Both the groundwater and clay slurry ORP data from the Marsh Zone showed distinctly reduced areas over mineralization. In the third dimension the reduced area appears as a reduced 'curtain' in overburden above the trace of mineralization. In cross-section it appears as a 'column' as predicted by previously published models (Hamilton 1998, 2000). The groundwater samples were collected from the single-point well screen locations, therefore the data are one-dimensional and the reduced areas appear as lows on ORP versus distance line plots.

SP measurements were carried out on surface peat over the Marsh Zone mineralization and a weak anomaly was noted. The SP signal was interpreted to be a weak electrical field related to electrical currents in the 10% conductive pyrite associated with the Au-mineralization. This 5 to 10 mV SP response is small in relation to the several hundred millivolt redox response.

2.3 Site Conditions

2.3.1 Bedrock geology

The Cross Lake site is located in Sheraton township *c.* 40 km SE of Timmins and 10 km east of Nighthawk Lake (Fig. 2-1). The property sits on the eastern flank of the Kettle Lakes Esker and overburden thickness varies from 30 to over 50 m. The area is densely wooded with mixed birch, poplar, spruce and some pine. Prior to our visits there

had been extensive diamond drilling by Cross Lake Minerals Ltd. The good drill coverage and thick clay and sand sequences over mineralization make this an excellent case-study area for thick-overburden geochemical methods.

Figure 2-3 shows a generalized geological plan-view with the surface projection of known mineralization at Cross Lake and the position of the two cut lines, Lines 6 and 40, along which surface soil samples as well as drill holes for this study are located. Line 6 extends from 0 to 800 m south, and Line 40 extends from 1100 to 1800 m south.

The dominantly felsic pyroclastic volcanic rocks that host the VMS mineralization at Cross Lake dip steeply SE at *c.* 65° and strike NE - SW. The stratigraphic package (Fig. 2-4) has not been overturned and the units from footwall to hangingwall comprise:

- Footwall 'tiger-stripe' intermediate to felsic tuff with rhythmically alternating bands of chloritic to sericitic alteration;
- Main Cross Lake felsic tuff hosting the sulphide mineralization and consisting of strongly sericite-altered tuff, lapilli tuff and chert. The mineralization occurs as massive sulphide in the upper part of the unit;
- Hangingwall breccia containing angular tuff and rhyolite fragments ranging in size from a few centimetres to over 2 m; and,
- Crystal Tuff overlies the altered units.

The mineralization-hosting sericite-altered tuff and silica exhalite has been fractured and the interstitial pore space filled with sulphides. The sulphides in order of abundance are pyrite, honey-coloured (iron deficient) sphalerite, chalcopyrite and galena.

The cross-sections of Lines 6 and 40 (Fig. 2-4) show the position of three 'deep' boreholes drilled as part of this project by the OGS. One of these holes confirmed the presence of moderately high grade mineralization at 200 south on Line 6 with several percent sphalerite, minor chalcopyrite and over 10% total sulphides. Another borehole on Line 40 intersected mineralization at 1417 south but the mineralization was of much lower grade and was estimated to contain less than 1% sphalerite, no visible chalcopyrite, and less than 10% total sulphides. Diamond drill hole records show that on Line 40 the deeper mineralization is higher grade.

Based on the diamond drill hole observations, the projected subcrop of mineralization on Line 40 is between 1400 and 1420 south and on Line 6, between about 180 and 220 south. On both cross-sections, the subcrop of mineralization is positioned as precisely as the data allow and is probably accurate to within +/- 10 m.

2.3.2 Quaternary geology and soils

A thick sequence of Quaternary glacial sediments directly overlies bedrock at Cross Lake. Till was deposited between the last glacial maximum and deglaciation (*c.* 20 to 10 ka) and overlies bedrock on parts of Line 40. At Cross Lake, bedrock and till are overlain by glaciolacustrine sediments, including sand, silt and clay, deposited in glacial Lake Ojibway during deglaciation between 10 and 8 ka, on the flanks of the SE- trending Kettle Lakes esker (Fig. 2-1). The two lines being studied at Cross Lake were chosen for sampling because they represent two terrains typical of the Abitibi clay belt. Line 6 has mostly unsaturated clay and silt at surface along its length except in depressions, where it is occasionally saturated. Line 40 has sand on surface along most of its length, which is seasonally wet at surface on the northern third of the line and dry along the rest.

The Quaternary stratigraphy on site is specifically known from the three OGS holes drilled to bedrock and from a total of 37 auger holes drilled to 9 m depth on the two lines and in background areas. On Line 6 (Fig. 2-4), it consists almost entirely of varved clays with silt laminae (averaging 4:1 clay:silt). Several small sand seams were noted in the varves. OGS borehole No. 2 extended below this and encountered varved silt (> 4:1 silt:clay) from 11.5 m to bedrock, which was encountered at 29 m. The lateral extent of this silt unit is not known and its presence was not noted in any of the shallow wells.

On Line 40 (Fig. 2-4) eolian-reworked shallow glaciolacustrine sands are exposed on surface in the northern two-thirds of the line. A paleo-beach ridge of this material forms a 5m topographic high at 1400 south. The sands grade downward below *c.* 5 m into rhythmically clay-laminated sand (typically 10:1 sand:clay). The laminae are usually only a few millimetres thick at first but range up to several centimetres in thickness with increasing depth in the north part of the line. Below 15 m, varved clay and silt (*c.* 4:1) occurs to about 25 m depth. Below the clay, oversaturated very fine to fine silty sand was

encountered that extends almost to bedrock, which was encountered at 51 m depth at 1417 south and 45 m depth at 1725 south. Both deep holes on Line 40 encountered about 1.5 m of bouldery silty sand till immediately overlying bedrock.

Soil forming processes have been active since deglaciation and podzolic and gleysolic soils, as defined by Agriculture Canada Expert Committee on Soil Survey (1987), have formed. On Line 40, podzolic soils formed on sandy glaciofluvial sediments, while on Line 6, gleysolic soils formed on silty clay glaciolacustrine sediments. The soils generally consist of, from surface downward: humus (H), dark brown organic-rich mineral soil (Ah), light grey elluviated mineral soil (Ae), and orangey brown illuvial mineral horizon (B) containing accumulations of iron and aluminum.

The water table is within 4 m of surface across the area investigated and therefore the mineralization is fully saturated within the entire study area.

2.4 Overview of Field Program

Fieldwork began in 1999 with SP and pH surveys along the two lines. SP was carried out using conventional Cu-$CuSO_4$ pot-type electrodes on surveys that totalled 800 m on Line 6 and 700 m on Line 40. A soil-sampling program followed that included humus, B-horizon and depth specific sampling for partial extraction geochemistry. At that time, subsamples of humus and B-horizon were taken, kept in a cooler and analysed for pH in the field within one day of sampling. In 2000, a second round of sampling was carried out on a tighter spacing over mineralization. Partial extraction analysis on the 1999 and 2000 samples, but particularly in the latter samples, shows distinct anomalies in ore-forming elements on surface. A detailed discussion of the soil geochemical results is presented in Cameron *et al.* (2004).

In 2000, using an auger drill, 15 shallow boreholes were drilled on Line 6, 18 on Line 40, and 4 background holes away from both lines, all to a depth of 9 m (except one at 1400 south on Line 40, which was extended an extra 3 m). The three holes that were drilled to bedrock used large-diameter (PQ-sized) mud rotary drilling equipment. Four split-spoon samples were taken in each shallow hole at consistent depths. In the three deep holes, near-continuous sampling was carried out from surface through overburden and into bedrock. The samples were tested for ORP and pH in the field and later analysed

for a large suite of elements after aqua regia digestion. After overburden sampling, a monitoring well was installed in each borehole from which groundwater was later sampled and tested for dissolved gases (CO_2 and H_2S), *in situ* temperature, ORP, pH, metals and anions.

A series of down-hole SP tests were made in the monitoring wells on both lines. SP was carried out using both non-polarizable and Pt electrodes and the results are discussed below. The partial extraction chemistry of overburden samples and the chemistry of groundwater will be reported elsewhere and are only discussed here to assist in the discussion of the ORP and pH results.

2.5 Methods Development

2.5.1 Soil and groundwater ORP and pH methods

Methodologies for the ORP and pH measurement of clay slurries at the Marsh Zone were described in detail in Hamilton *et al.* (2004). Briefly, the procedure involves split-spoon sampling of the clay with a geotechnical auger-rig; storage of the sample in a polyethylene bag for a period of up to one hour; mixing the clay into an approximate 1:1 slurry with distilled water, and measurement of ORP and pH after 1, 2 and 5 minute of probe immersion.

For the slurry measurements at Cross Lake, this methodology was modified slightly. A reducing pre-treatment solution was used to pre-polarize the probe in an attempt to improve response times and provide a consistent starting potential from which the probes would equilibrate. At the beginning of each day, ORP probes were soaked for several minutes in a commercially available acidic ferrous-sulphate pre-treatment solution (Hanna Catalogue No. 1230). Just prior to each measurement the probes were again soaked for a specific period. They were then rinsed thoroughly with a jet of distilled water and immediately immersed in the sample. Measurements were taken at 1, 2 and 5 minute as they had been in the Marsh Zone study. Figure 2-5A shows the difference in average response time for a probe that was soaked for 30 s in the pre-treatment solution versus the same probe (P1) with no treatment. The untreated measurements were taken on a total of 82 samples from Line 40 and the measurements

with the treated probe on 65 samples from Line 6. When the probe was pre-treated, it responded three times faster between the 1 and 2 minute readings and five times faster between the 1 and 5 minute readings. The response rate for the untreated probe was so slow that the Line 40 data for that probe (P1) could not be used.

Figure 2-5B shows a similar test using another probe (P3) that was treated for 30 s on the 82 samples from Line 40 and for 60 s on the 65 samples from Line 6. The results show comparatively little difference between the average response rates (an increase of only about 40% during both time intervals), with the extra 30 s of probe immersion. However, the presence of ferric deposits was noted on this probe, suggesting over-treatment. Our protocol has since been modified to soak the probe for several minute at the beginning of each sample run and for only several seconds prior to measurement on each sample.

The ORP measurements on groundwater were made without pre-treatment, partly because of the difficulty of pretreating the probe in a flowcell but also because of concerns that the high ionic strength solution would over-polarize the probes and result in long equilibration times.

The well screens on Line 6 are all finished in clay/silt and have extremely slow recovery rates. In the first groundwater sampling and groundwater ORP survey, wells were pumped down and allowed to recover for several days prior to sampling. As a result, the actual sample medium was standing well water that had time to both degas volatiles such as CO_2 and absorb O_2. This is far from ideal and the usual way of preventing this is the time consuming and expensive procedure of using an inflatable packer. Our compromise approach involved pumping down the well, purging the headspace from bottom to top with N_2 and immediately capping the well with a vapour lock to prevent air exchange in the headspace as the water level recovers. This procedure minimised oxidation and reduced degasing by promoting similar vapour pressures in the headspace as in the recovering well water.

Figure 2-6 shows groundwater ORP and pH measured on two occasions on Line 6. In both cases, ORP probe polarization was significant, with most of the wells on the first traverse being affected, and three wells being affected on the second. We attribute the improved probe equilibration in the 2002 data to our soaking the probe for 24 hours in

the second well on the line prior to that survey. This may have had the unintended consequence of allowing oxidation of solutes in the well water because the wires prevented re-installation of the vapour lock, hence the higher ORP in that well.

In 2002, the wells were vapour-locked and in 2000 they were not. Figure 2-6 shows that the vapour locks were effective in several ways. First, the magnitude of the ORP is far lower in the second survey, suggesting the vapour locks were effective in reducing oxidation of aqueous species. Secondly, in the September 2000 survey, there is a distinct peak in ORP, which is contrary to the other types of ORP and SP data. Slurry ORP and PtSP data (discussed later) show a response that is similar to the 2002 survey, i.e., two peaks on the edge of the anomaly that flank a dip in the centre. The position of this dip coincides with the most positive ORP response over mineralization in the 1999 data. The peak in the earlier data, and the much higher ORPs, are interpreted to be due to oxidation of the reduced species present in the stagnant well water, the products of which are themselves oxidizing agents and impart a higher ORP to the groundwater.

An even more obvious manifestation of the effectiveness of vapour locks is the pH data (Fig. 2-6). As mentioned, groundwater pH in this environment is subject to change once the water enters the well, especially during well recovery. CO_2 degassing will raise the pH whereas oxidation of metals or H_2S will lower it. Different groundwater chemistry and differential rates of recovery in the various wells (i.e., water level recovery after purging) will promote or impede these processes and the result may be unintelligible pH data such as those collected in 2000. When vapour locks were used in 2002, pH determined on groundwater from the same wells showed more consistent results with a pH low over mineralization and a more uniform background pH. The latter pH data are more consistent with other types of pH data collected.

ORP measurement and groundwater sampling on Line 40 was simpler because the well screens were finished in sand, or clay with sand seams, and the water levels recovered as they were pumped. With the exception of the last two or three wells on the north end of the line, none of the wells could be pumped dry and therefore representative groundwater samples could be collected without the use of vapour locks. As discussed in Hamilton *et al.* (2004), the purpose of collecting the redox data is to obtain a *relative* measure of the redox conditions along the line. It is important to note that these

techniques did not result in a stabilized reading, nor was this intended. Complete equilibration of the probes would take so long that the technique could not be used in the field. Therefore, the ORP readings obtained by these techniques can only be compared with other readings taken using the same technique, equilibration times and ORP probe.

2.5.2 SP and PtSP methods

The surface SP methodology used at Cross Lake was similar to that described in detail in Hamilton *et al.* (2004) for the Marsh Zone. It involved using one stationary, non-polarizing, Cu-$CuSO_4$ electrode and one similar mobile electrode connected by a long reel of wire. Electrical-field voltages were measured between the two as the mobile electrode was advanced along the line.

Unlike SP, platinum SP (PtSP) measures a total field, which is the sum of the redox voltage and the electrical field voltage. Variants of PtSP were described by Bolviken *et al.* (1973), who used it down-hole, and Timm and Moller (2001), who used it on an outcrop scale on rock to demonstrate the relationship between SP, ORP and total field. The OGS has been experimenting with PtSP for a number of years (Hamilton and McClenaghan 1998). Initially, in 1998, short Pt wire electrodes were permanently fixed to the outside of PVC pipes that were either installed as monitoring wells in overburden up to 30 m deep, or forced down into soft clay to depths of up to 10 m. The use of permanently fixed Pt electrodes was partially successful for delineating redox trends in overburden along transects (Hamilton and Cranston 2000) but there were serious problems due to the voltage idiosyncrasies of the various electrodes. These problems are inherent to Pt electrodes and result from differences in the Pt surface of each electrode and the 'memory effects' of other redox active compounds that have come into contact with the probe surfaces. It was anticipated that long equilibration times after installation would diminish these problems but additional issues arose, related to probe emplacement and the effectiveness of the probe contact with the overburden materials that further complicated the voltage readings.

It was determined that the only solution that mitigated these problems was to use the same Pt electrode for every measurement on a given transect. Methodologies were also required that would ensure good probe contact with the overburden materials and

that would depolarize the Pt surface and remove memory effects prior to each measurement.

Preliminary PtSP surveys were carried out at the Marsh Zone and more comprehensive surveys at Cross Lake. Two approaches were used; the first involved contacting saturated peat, in which case the mobile electrode was attached to a pole and inserted into the peat; the second involved contacting groundwater, where the electrode was attached to a reel and lowered down a well into the well screen. As there was very little peat at Cross Lake, only down-hole measurements were taken there.

The down-hole PtSP probes were depolarized by immersion in one of the first wells on the line or a background well for a period of at least two hours prior to the survey. Figure 2-7 shows the initial down-hole PtSP survey carried out at the Marsh Zone that involved measuring the PtSP, after 1 minute of probe immersion, in each of the wells along the line and then retesting each well on the return traverse. Two deep wells, finished in bedrock, were inadvertently measured in the middle of the survey and the high H_2S concentrations (up to 7.5 mg l^{-1}) in these wells *negatively* polarized the probe. This polarization lasted throughout the measurement of at least the three subsequent shallow wells. It is also clear that 1 minute of probe immersion was insufficient to obtain a full response because the dip in the PtSP readings over mineralization is insignificant in comparison to the groundwater and clay-slurry ORP responses (Hamilton *et al.* 2004, Figs 9 & 10), whereas they should have been similar.

Figure 2-8 is a schematic diagram showing the down-hole SP-related measurements taken down wells on Line 6. The method is similar to that employed by Timm and Moller (2001) but in our case, has been applied to groundwater instead of rock and on a geographically larger scale. The measurements were taken in the well screen (*c.* 8 m depth) and included: PtSP, which measures total field and used a mobile Pt electrode against a stationary Cu-$CuSO_4$ electrode; SP, which measures electrical field and used a mobile Cu-$CuSO_4$ electrode against the stationary Cu-$CuSO_4$ electrode; and $ORP_{(Cu\text{-}CuSO4)}$, which measured the voltage between the Pt and Cu-$CuSO_4$ down-hole electrodes and therefore represents an ORP referenced to a Cu-$CuSO_4$ half-cell. ORP measurements were also taken at the same time in a flow-cell using a commercial ORP probe with a Ag-AgCl reference cell.

Figure 2-9 shows the results of the down-hole measurements on Line 6. Soaking the electrode in the upper 2 m of groundwater in the second well on the line for 24 hours prior to the survey reduced, but did not eliminate, the positive polarization of the probe. This initial polarization is attributed to oxygenation of the water that occurred because the vapour lock could not be reinstalled with the probe immersed in the well. This interpretation is supported by the higher ORP, measured at the same time (using a commercial probe), of water from the second well (Fig. 2-6) relative to the adjacent wells.

Both the SP and the PtSP show a dip over mineralization demonstrating the presence of both an electrical field and a redox response. As it should, the calculated ORP obtained by subtracting SP from PtSP shows a very good correlation with the measured $ORP_{(Cu\text{-}CuSO4)}$. The two profiles are not identical because the Pt electrode continued to equilibrate somewhat after the PtSP readings and the voltage had changed slightly by the time the $ORP_{(Cu\text{-}CuSO4)}$ data were acquired. As was noted at the Marsh Zone, the SP contribution to the total field related to the mineralization is very small in comparison to the redox contribution.

2.6 Results and Discussion

2.6.1 Clay slurry ORP and pH on borehole samples

The results of pH and ORP determinations on clay slurries from borehole samples along Line 6 are shown in Figure 2-10. A distinct reduced 'column' is apparent, centred on 200 south. It occurs below, and terminates at, the water table and continues below the depth of investigation and presumably down to bedrock mineralization. A wider and less intensely reduced area is apparent to the north over the less mineralized parts of the lapilli tuff. Another reduced area can be seen at 350 south, the cause of which is still unknown. Above the water table, each reduced area is 'capped' by areas of lower pH, the intensity of which correlates with the strength of the underlying redox negativity.

Line 40 (Fig. 2-11) also shows a reduced area over mineralization, centred on about 1435, but which is much wider and more diffuse than occurs in the clay on Line 6. The subcrop of mineralization at 1417 is low grade but higher grade sulphides occur

down dip and approximately beneath the reduced area. The low-grade subcropping mineralization is similar in composition to the background sulphide composition in the lapilli tuff, which also shows a reduced area over it. It is perhaps significant that an unexplained slightly more reduced area at 1620 occurs roughly on strike with the unexplained response at 350 on Line 6, further suggesting the ORP is responding to bedrock lithology. As on Line 6, an acidic area above the water table caps the reduced zone over mineralization.

Along most of Line 40, and particularly to the south, the oxidized zone extends considerably below the water table, in contrast to Line 6, where it is largely restricted to the vadose zone. This is due to greater penetration of dissolved O_2 in the sands than in the clays resulting in a deeper weathering front. This oxidized trend decreases toward the north in the more clay-rich sands where lower ORP is accompanied by higher pH. Within this general trend, a slightly acidic zone occurs over the lapilli tuff unit, as it does on Line 6, but appears much less significant due mostly to the wider pH colour scale used in Figure 2-11. An important feature to note about both cross-sections is that the reduced column has a deep origin and becomes more apparent with increasing depth away from O_2, whereas the pH response is a surface phenomenon that fades rapidly with increasing depth.

2.6.2 ORP, pH and related parameters in groundwater

Figure 2-12 shows the groundwater ORP and pH measurements for Line 40. Figure 2-6 shows the ORP and pH data for the vapour-locked wells on Line 6, which are more precise than the earlier data from the non-vapour locked wells, also shown. As discussed above, initial ORP probe polarization was a problem and the depolarization trends on both lines are apparent. On Line 6 the response over mineralization takes the form of two flanking highs with a dip in the middle. On Line 40 there are two flanking highs widely straddling a distinct low over the mineralization. One or the other of these two patterns is characteristic of ORP and PtSP responses over mineralization and have been noted repeatedly in the Marsh Zone and Cross Lake data.

The cause of the flanking high ORP on either side of the ore zone probably relates to the ability of the Pt probe to measure labile oxidized metals better than it can measure

dissolved O_2. The primary oxidizing agent in the shallow subsurface is O_2 but Pt electrodes measure its potential very poorly (Krauskopf 1979). In contrast, Pt electrodes measure metallic redox couples such as Fe^{2+}/Fe^{3+} well. ORP measurements in the vadose zone and unsaturated soils are notoriously inaccurate (Bartlett & James 1995) because the lesser oxidizing agents such as Fe^{3+} are better measured than the far more important O_2, resulting in an inaccurate representation of the total availability of oxidizing versus reduced species (i.e., the Eh). The characteristic pattern of twin peaks flanking the low (or dip) is therefore attributed to an area with reduced metals in the centre and oxidized metals at the flanks that are themselves the product of oxidation. As it is presumed that O_2 is being consumed in the flanking areas, these areas must be actually more reducing than the adjacent areas outside the reduced column. They show an apparently higher ORP because of the higher concentrations of oxidized metals that are labile with respect to the Pt probe. This demonstrates, yet again, the poor state of development of redox measurement techniques. Inadequate though it is, the Pt electrode is currently the best tool available to geochemists for the measurement of mixed redox potentials.

Another way to approximate the total availability of oxidizing agents in the shallow phreatic zone would be with accurate measurements of dissolved O_2 in interstitial groundwater. This could best be accomplished with a packer system and O_2 determination by Winkler titration, but would also require a different well design. The existing wells have screens finished at a specific depth from surface. To properly determine the concentrations of dissolved O_2, either multi-level wells or single-level wells finished at a specific depth from the *water table* would be required. A consistent distance from the vadose zone is required because in homogenous clays, this is the most important control on the availability of O_2 and inconsistency might mask any O_2 depletion over mineralization. Although dissolved O_2 measurements were not made on groundwater, depletions are likely to occur in the reduced column based on the ORP data. Dissolved CO_2 measurements were made (Fig. 2-13) and are elevated over mineralization on Line 6 and on Line 40. The CO_2 response over mineralization on Line 40 is partly obscured by a doubling of the CO_2 concentration (from 25 to 50 ppm) in the confined portion of the aquifer on the northern third of the line.

A similar approach is to determine the O_2 concentrations in overlying vadose zone soil gas. O_2 depletions and CO_2 enrichments have, for many years, been known to occur over buried sulphide mineralization (e.g., Lovell *et al.* 1983). Although they are to be presented elsewhere, soil gas data collected at Cross Lake show O_2 depletions and CO_2 enrichments over mineralization on both lines.

The pH response on Line 6 (Fig. 2-13) shows a distinct low over mineralization with moderate to large increases at the flanks. The pattern is less obvious on Line 40 due to the CO_2-related pH low on the northern third of the line. In the unconfined sand aquifer to the south, as on Line 6, the pH response is centred over mineralization, is the lowest pH on the unconfined portion of the transect, and roughly corresponds with the centre of the ORP response in both groundwater and clay/sand slurries. The pH low is attributed to the production of acid by oxidation of reduced metals where the reduced column meets dissolved O_2 in or near the vadose zone. The acid, in turn, dissolves some of the abundant carbonate in the deeper clays and sands and creates a CO_2 anomaly. Oxidation reactions consuming O_2 in both the vadose zone above, and the shallow phreatic zone within, the reduced column accounts for the observed O_2 depletions in soil gas on these lines.

2.6.3 Down-hole PtSP and SP

Despite continuing problems with initial probe polarization, the PtSP surveys showed responses over mineralization. Figure 2-9 shows the PtSP and SP data for Line 6 collected on wells that had been purged and vapour-locked. PtSP decreases over mineralization, however the trend is partly obscured by the depolarization trend. The SP low, measured at the same time, is not affected by the polarization and indicates that an electrical field is present, in addition to the redox response. A stronger PtSP response occurs on Line 40 (Fig. 2-14) despite a depolarization trend that encompasses most of the transect. When a regression line is plotted through the data and the trend removed, the residual data show a more apparent negative response over mineralization but of fairly low magnitude.

2.6.4 Surface SP, pH and carbonate

SP of surface soil was determined on both lines prior to drilling and the results are shown in Figure 2-14. An SP low is apparent over mineralization on both lines, indicating an electrical field detectable at surface. The response is probably related to spontaneous potential currents within the sulphide conductor and is minor compared with the redox response as measured by the subsurface ORP on clay and sand slurries. The SP measurements were originally made to aid in determining the presence or absence of reduced columns (Hamilton and Cranston, 2000). However, work by Timm and Moller (2001) suggests that there is not necessarily any relationship between redox phenomena and electrical fields measured by SP. The apparent relationship between the two at both Cross Lake and the Marsh Zone is coincidental due to sulphide minerals being both conductive and oxidizable. Had the feature been non-conductive but oxidizable, such as sphalerite alone, it is postulated that the reduced column would still have been present (Hamilton 2000) but the electrical field would not have been. Conversely, had it been conductive but non-oxidizable, such as barren graphite, it is postulated that the electrical field would have been present but the reduced column would have been absent, or nearly absent.

Acidic pH occurs in soils over mineralization on Line 6 and to a lesser extent on Line 40 (Fig. 2-15). As is usual, the pH signal in B-horizon soil is uniformly less acidic than in the humus on both lines and it also shows a more distinct low over mineralization (2000 sampling). The 2000 sampling, although limited in extent, had a higher sample density and showed a much stronger response over mineralization on Line 6. Disturbed ground over the mineralization on Line 40 resulted in poor sample coverage in the 1999 sampling. The 2000 sampling compensated for this by sampling parallel to but 15 m east of the line. The results show a low over mineralization but sample coverage does not extend far enough into background to be definitive.

Carbonate in B-horizon soils, as determined by the Leco Furnace method, is nearly absent (median *c.* 0.05%) along most of both lines due to surface weathering of the primary carbonate minerals in the clay and sand. The obvious exceptions are on Line 6 where two anomalous areas flank the mineralization and are interpreted as parts of a 'rabbit-ear' anomaly. The sample medium on Line 6 was clay and silt that had an original

carbonate content of *c.* 20%, based on unweathered samples from depth, and contains acid-reactive carbonates below, at 0.6 to 0.8 m depth. Because the carbonate 'rabbit-ears' closely flank the acidic zone, they most likely result from remobilization of the primary carbonate below the acidic zone that is then redeposited in the flanking areas where pH is higher (Hamilton 2000). Smee (1998) described a process similar to this over a porphyry Au deposit in Nevada. On Line 40, the original carbonate content of sand sediments was lower than the silt and clay sediments on Line 6. The depth at which acid reactive carbonate occurs was greater than the 1.5 m depth of surface investigation, which makes lateral carbonate deposition much less likely.

2.6.5 Groundwater temperature

On Line 40 a strong, 1.5°C, temperature high occurs in groundwater over the subcrop of mineralization (Fig. 2-16) and to a lesser extent over the approximate subcrop of the felsic lapilli tuff. A smaller and more variable response occurs over the mineralization on Line 6. As there are topographic changes and some vegetation-cover changes over mineralization, it was first thought that the responses might be due to preferential solar warming of the wells in the areas near mineralization. Repeat measurements in January, when the average daily high temperature was -15°C, determined that this could not be the case. Temperature highs also occur in groundwater overlying mineralization at the Marsh Zone but are wider and less distinct. Although these data are not conclusive, one explanation for the temperature highs may be the exothermic oxidation of species in the vicinity of the reduced column.

2.7 Summary and Conclusions

Of the variety of techniques evaluated for delineating ORP and pH trends over mineralization, the measurements on slurries of Quaternary overburden samples were by far the most informative. Groundwater ORP and down-hole PtSP both suffered from significant problems due to Pt electrode polarization and the relatively low ionic strength of groundwater. All the techniques, however, showed evidence of the same phenomena, namely reduced 'columns' in saturated overburden materials above mineralization that

are overlain by acidic areas, which are best developed in the vadose zone and shallow groundwaters and diminish rapidly with depth below the water table.

The presence of the acidic zones above the reduced columns has important implications. H^+ is the most mobile and one of the most reactive of aqueous species and its continued presence over the reduced columns in this high-rainfall, high-carbonate environment indicates a continuous source. The only likely source of H^+ is metal oxidation reactions, and therefore there must be an ongoing, upward movement of reduced metals to resupply the oxidation process and maintain the pH anomaly.

There is close similarity between phenomena predicted by the model (Fig. 2-2) and actual observations at Cross Lake, including: reduced columns, acidic caps, metal deposition (not presented here), CO_2 enrichments, O_2 depletions and carbonate remobilization. CO_2 enrichments were measured in groundwater and, although $O_{2(aq)}$ was not measured, depletions are suggested by the ORP data. O_2 depletions and CO_2 enrichments in vadose-zone soil gas and flanking carbonate anomalies were also identified at Cross Lake and will be the subject of a later publication. The groundwater temperature anomalies were not predicted but may be due to the exothermic oxidation of metals in the near-surface. Many of these features were also observed at the Marsh Zone (Hamilton *et al.* 2004). The presence of negative SP responses over the deeply buried and fully saturated sulphide conductors at both the Marsh Zone and Cross Lake indicates an electrical field associated with current movement in the sulphide conductors, which supports the model. The small SP electrical field noted over mineralization on both lines at Cross Lake is similar to one observed over the sulphide mineralization at the Marsh Zone. Also similar is its very small magnitude relative to the ORP field delineated by the slurry measurements. On both sites, on all three lines where both were measured, the subsurface redox field exceeds the electrical field by about an order of magnitude.

2.8 Acknowledgements

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Chapter 2 Figures

Figure captions

Fig. 2-1. Location of the Cross Lake study area within Ontario and in relation to the Kettle Lakes Esker.

Fig. 2-2. The development of geochemical anomalies directly and indirectly related to electrochemical processes (modified after Hamilton, 2000).

Fig. 2-3. Plan view of the generalized bedrock geology, location of Lines 40-west and 6-southeast and OGS wells. The trace of mineralization includes the surface projection of known mineralization and therefore cannot be used to obtain the position of mineralization subcropping beneath overburden. Grid units are metres (source: Cross Lake Minerals, modified).

Fig. 2-4. Geological cross sections along Lines 40 west and 6 southeast. Bedrock information is derived from diamond drill-hole records and nearby cross sections provided by Cross Lake Minerals Limited (1999), and also from three boreholes drilled to several metres into rock by the OGS. Overburden information is derived from the three deep holes and 37 9-m deep shallow holes drilled by the OGS on or near the two lines.

Fig. 2-5. (A) Average responses in mV for a probe (P1) treated for 30 s in a reducing pre-treatment solution versus the same probe when not treated.
(B) Average responses in mV for a probe (P3) treated for 1 minute in a reducing pre-treatment solution versus the same probe treated for 30 s.

Fig. 2-6. The effect of vapour locks on groundwater ORP and pH of recovering well water on Line 6. Measurements on both dates were taken several days after pumping-down the wells. In July 2002, each headspace was purged with N_2 and vapour locks were installed immediately afterward.

Fig. 2-7. Preliminary testing of the down-hole PtSP method at Marsh Zone. Inadvertent testing of one of the deep wells in the middle of the transect and subsequent negative polarization of the electrode demonstrates the susceptibility of Pt probes to memory effects that can render the resulting data useless.

Fig. 2-8. Schematic diagram showing the measurement techniques for, and relationship between SP, ORP and PtSP. Each voltage measurement is taken independently with the other two circuits disconnected.

Fig. 2-9. SP and ORP parameters from wells on Line 6, Cross Lake: (A) SP (=electrical field) and PtSP (=total field) were measured between a surface base station and probes lowered down each well in succession. (B) The redox-field component of voltage was determined by subtracting the SP from the PtSP and agrees well with the down-hole CuSO4ORP as measured between the down-hole Pt and $CuSO_4$ probes.

Fig. 2-10. ORP and pH in the uppermost 10 m of overburden on Line 6. Horizontal scale is in m.

Fig. 2-11. ORP and pH in uppermost 10 m of overburden on Line 40. Horizontal scale is in m. Dashed bar under plot between 1400 and 1500 represents higher grade sulphide mineralization at depth. The dashed water level represents a piezometric surface (confined aquifer); the solid water level represents a water table (unconfined aquifer).

Fig. 2-12. Groundwater ORP and pH on Line 40. Vapour locks were not required because the fast rate of recovery allowed sampling immediately after purging.

Fig. 2-13. Dissolved CO_2, determined by titration, and pH in groundwater at Cross Lake. Only the Line 6 pH data were collected from vapour-locked wells.

Fig. 2-14. Down-hole PtSP data for Line 40 showing the median of 2 second readings between 4.5 and 5 minute after probe immersion. The probe was polarized during measurement of most of the wells on the line as seen by the northward-decreasing trend in the data. Removing the trend by plotting the residual shows a clearer dip over mineralization and over the lapilli tuff unit to the north. Down-hole Cu-$CuSO_4$ SP data were not collected for this line.

Fig. 2-15. Surface spontaneous potential and pH of surface soils and $\%CO_3$ in B-horizon soil on Lines 6 and 40. Note different vertical scales used for Line 6 versus Line 40 data.

Fig. 2-16. Groundwater temperatures on three occasions for Lines 40 and 6. Measurements were taken in situ with a down-hole temperature probe lowered into the well screen to c. 9 m depth. Several wells were frozen during the January, 2002 survey and temperature in these wells could not be determined.

Figure 2-1. Location of the Cross Lake study area.

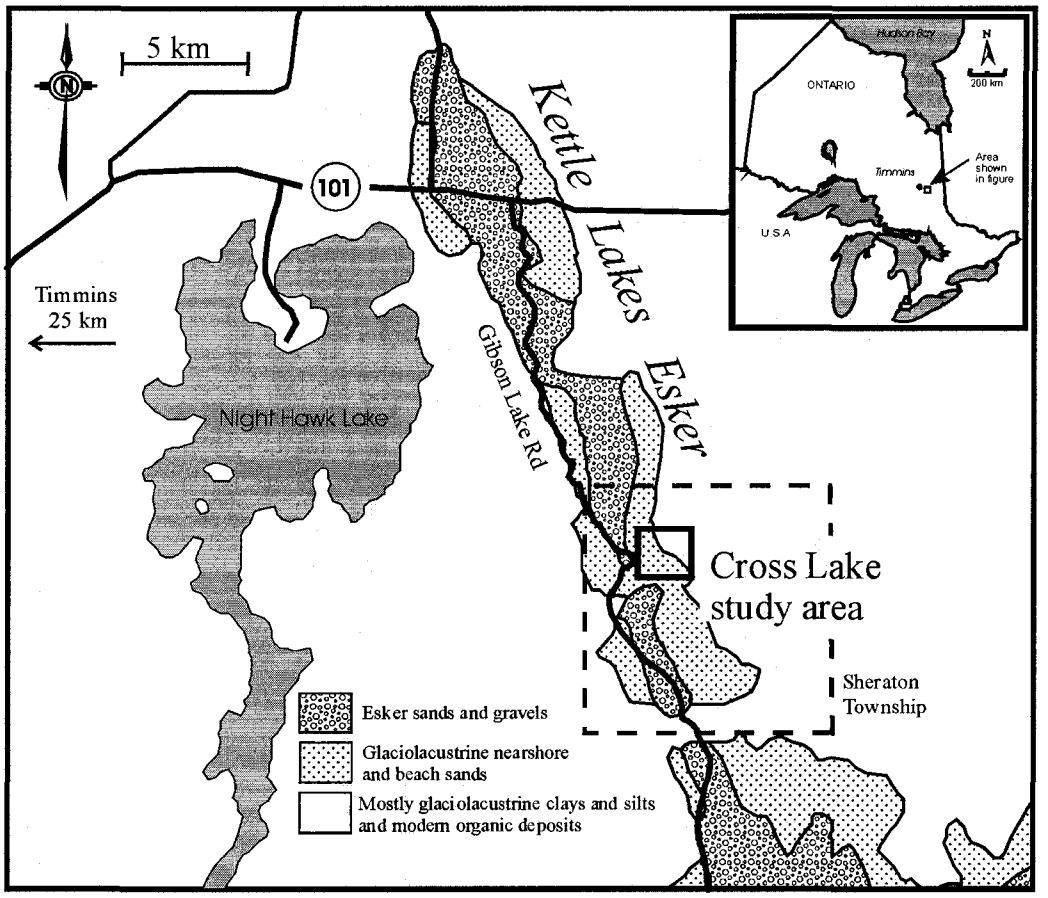


Figure 2-2. Geochemical anomalies due to electrochemical processes.

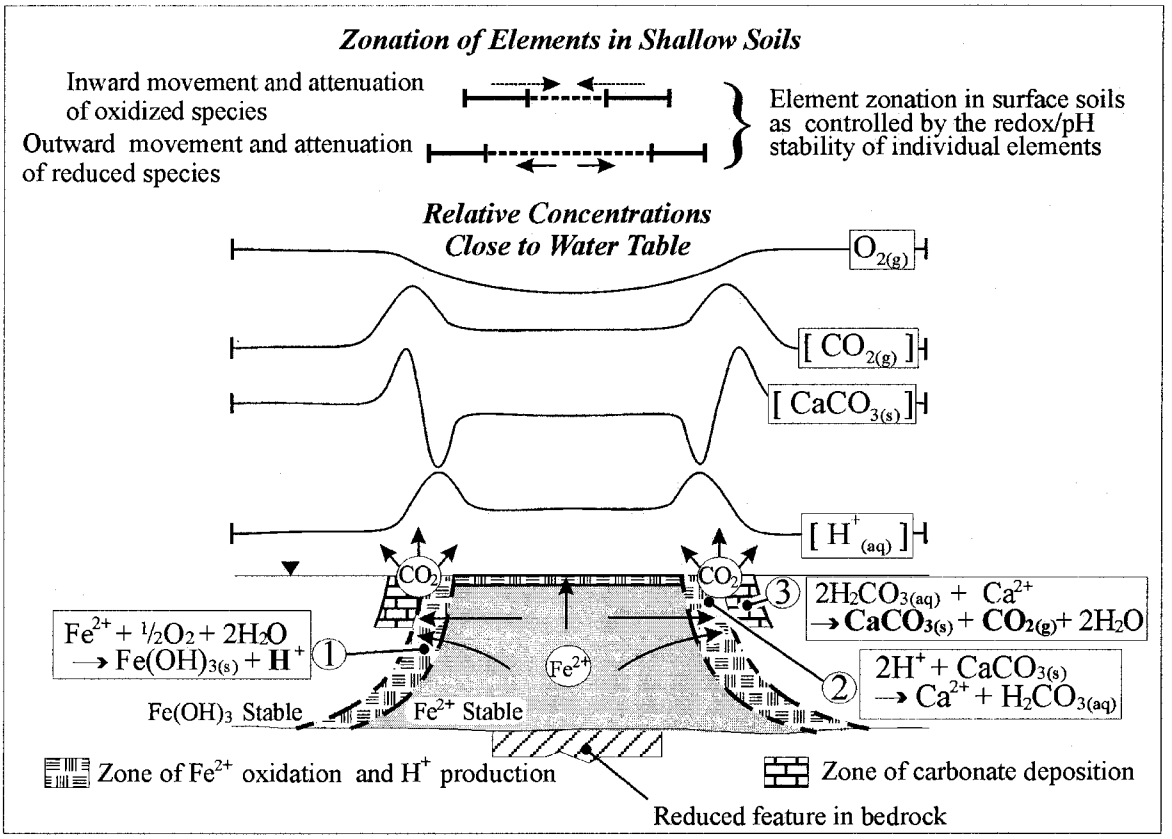


Figure 2-3. Generalized bedrock geology, Cross Lake.

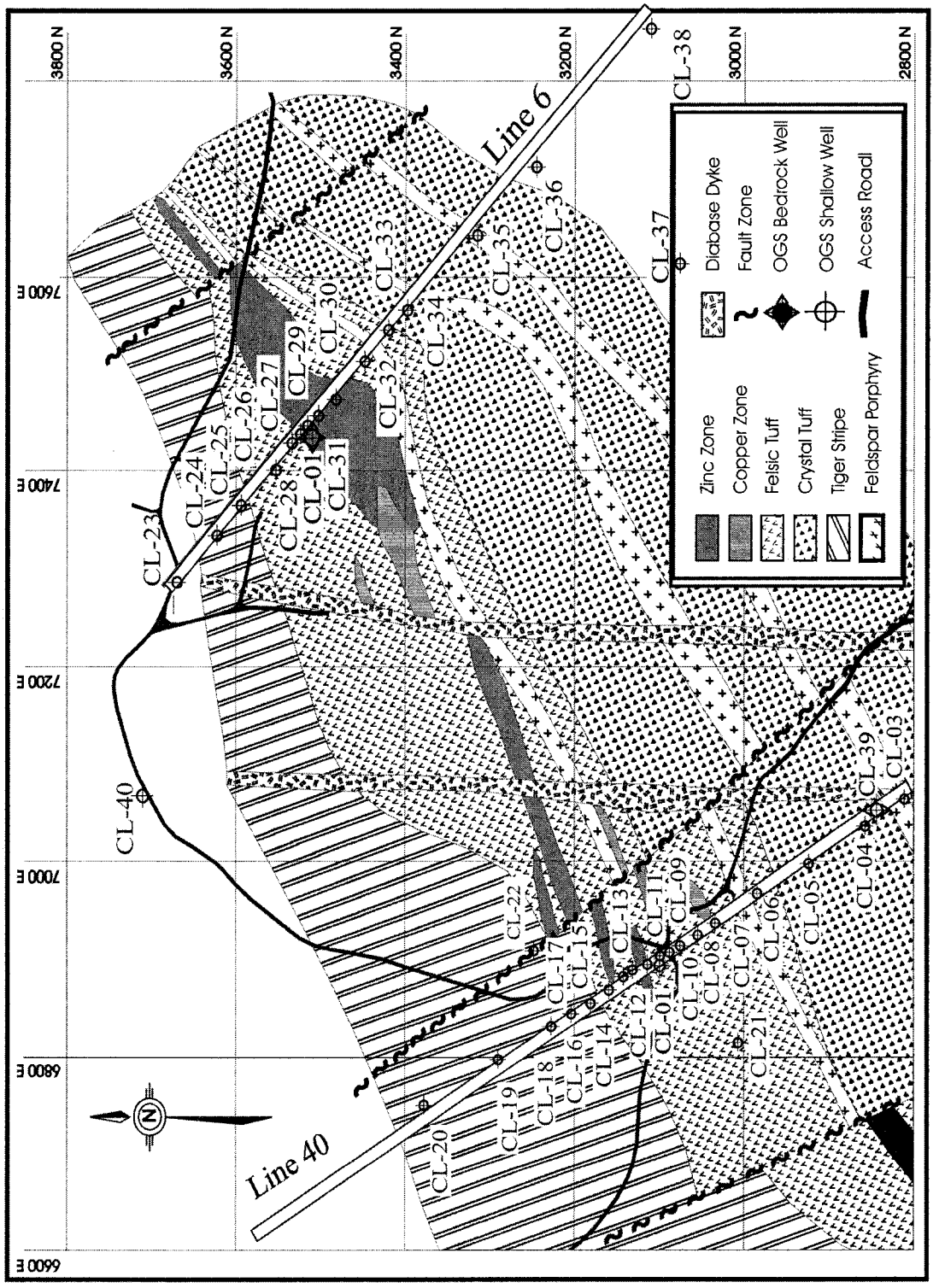


Figure 2-4. Generalized cross sections, Lines 6SE and 40W.

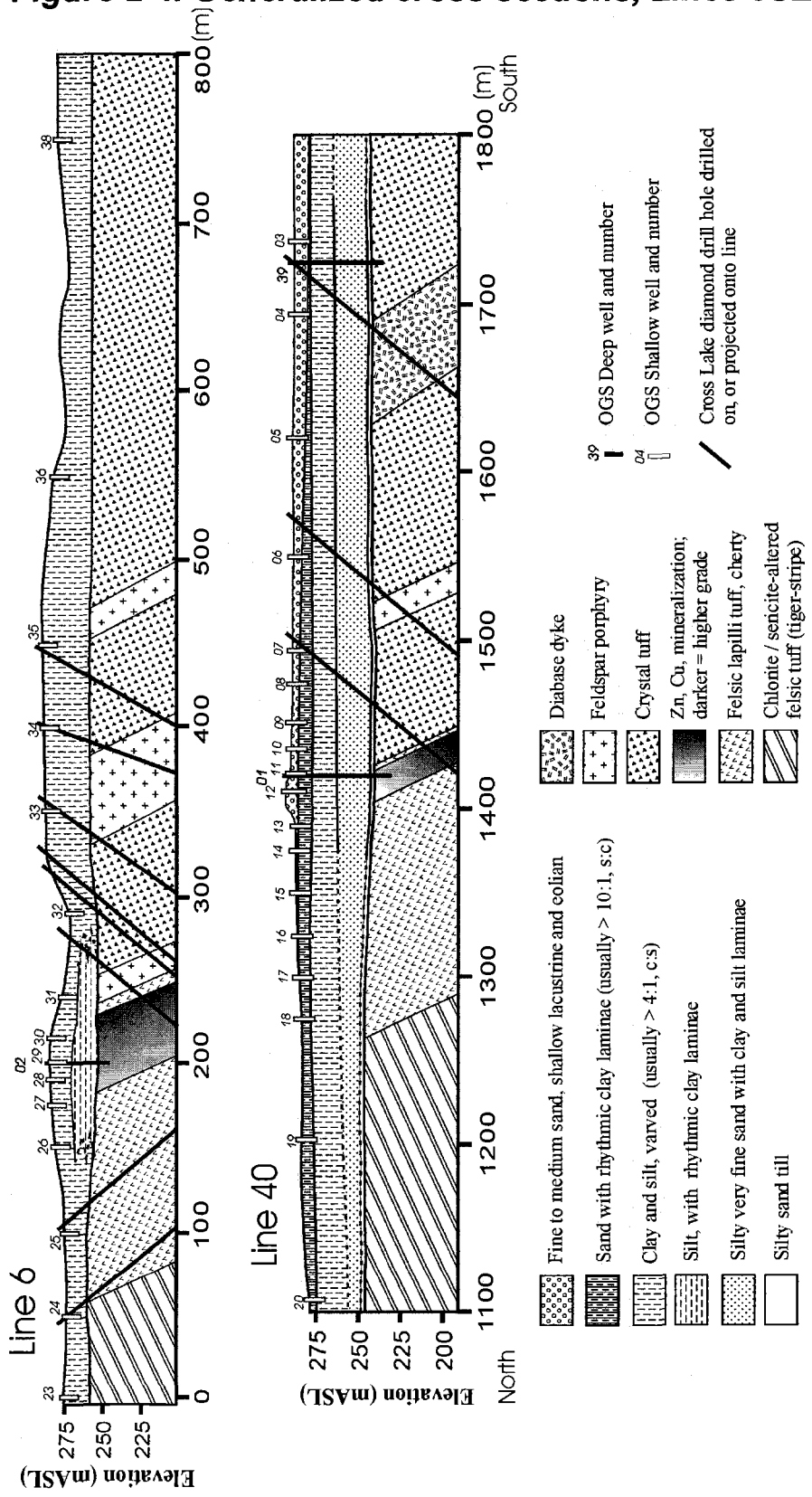


Figure 2-5. The effect of pre-treatment solution on ORP probe response time.

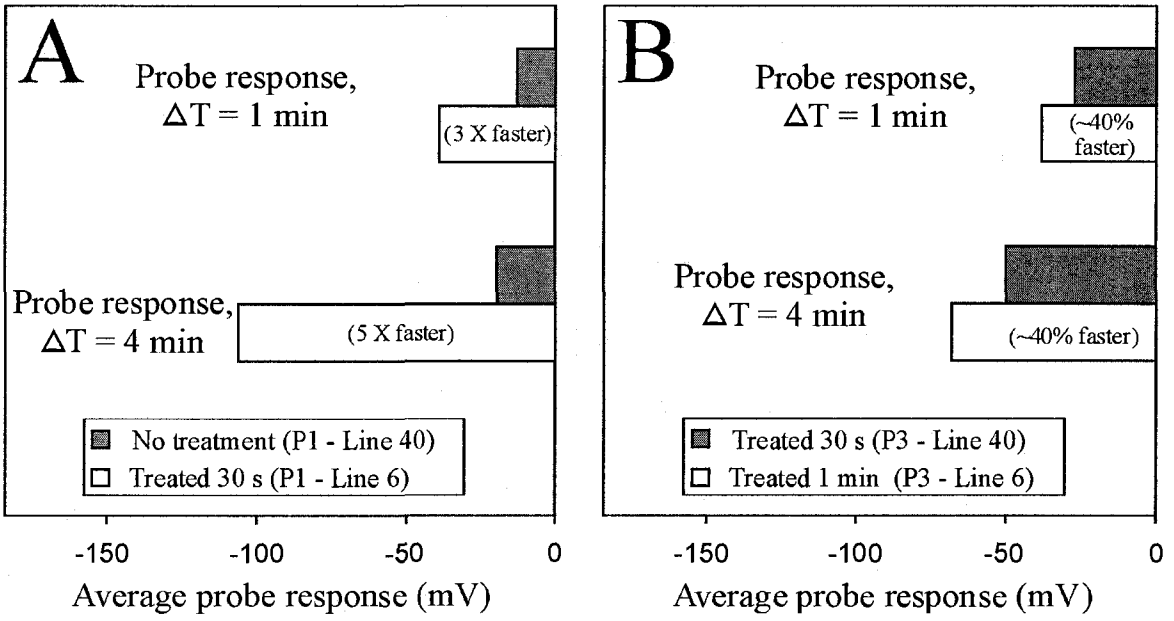


Figure 2-6. The effect of $N_{2(g)}$ purging and vapour locks on groundwater ORP & pH.

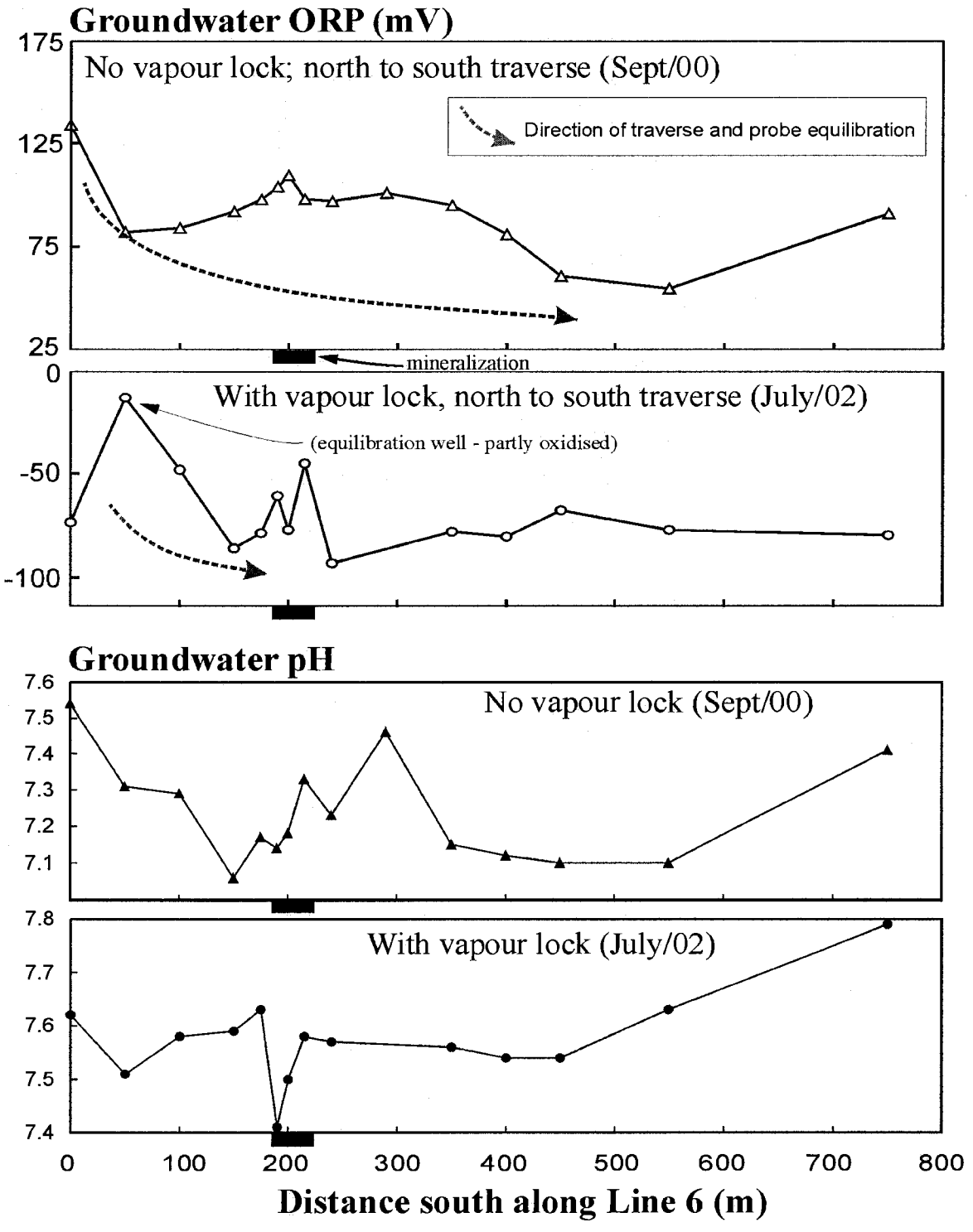


Figure 2-7. Preliminary testing of the down-hole PtSP method at Marsh Zone.

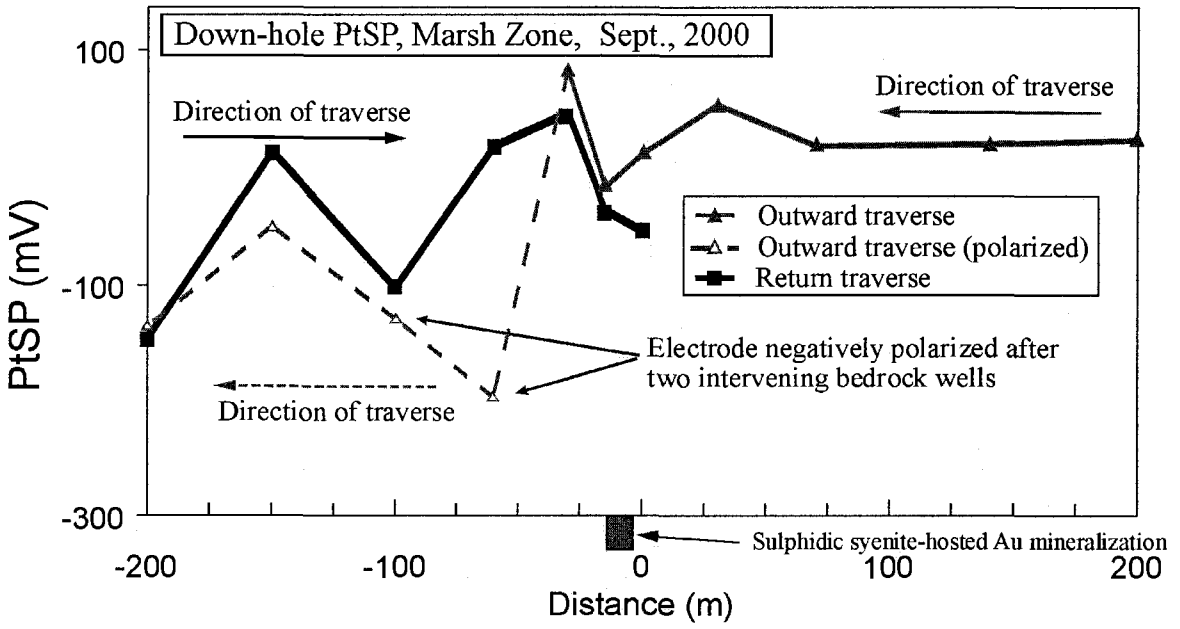


Figure 2-8. The down-hole SP / PtSP / ORP methodology.

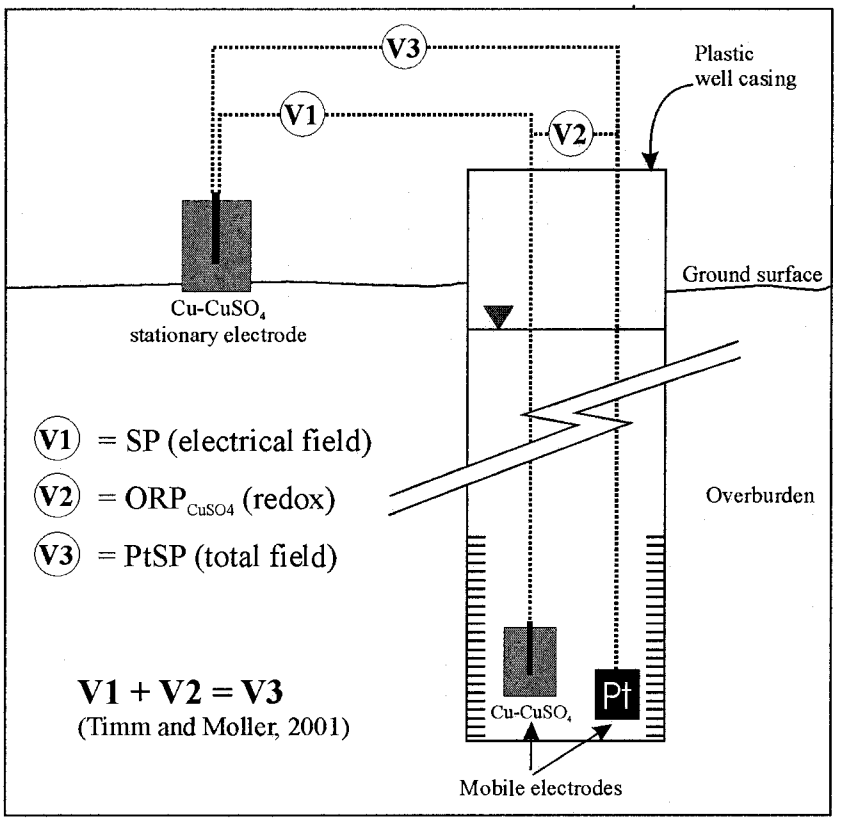


Figure 2-9. SP, PtSP, $ORP_{(measured)}$ and $ORP_{(calculated)}$ at Cross Lake, Line 6.

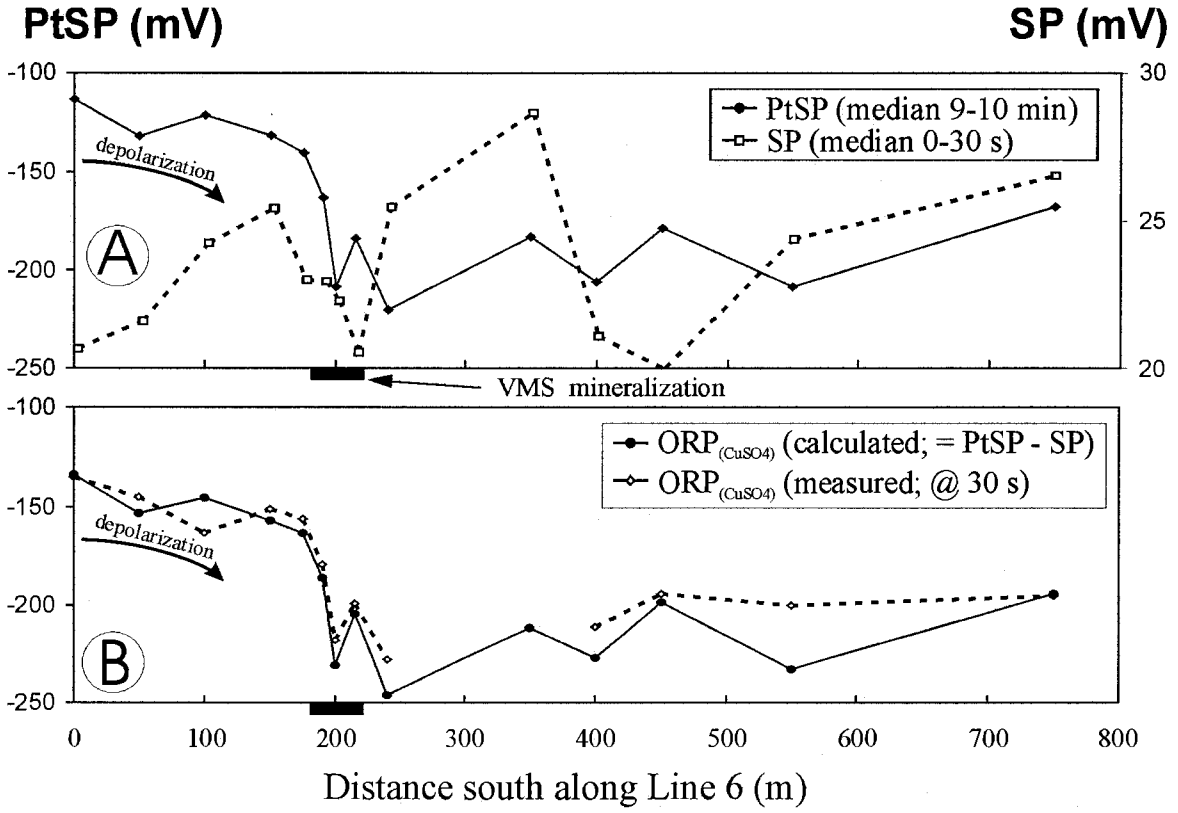


Figure 2-10. ORP and pH of sediments overlying mineralization, Line 6.

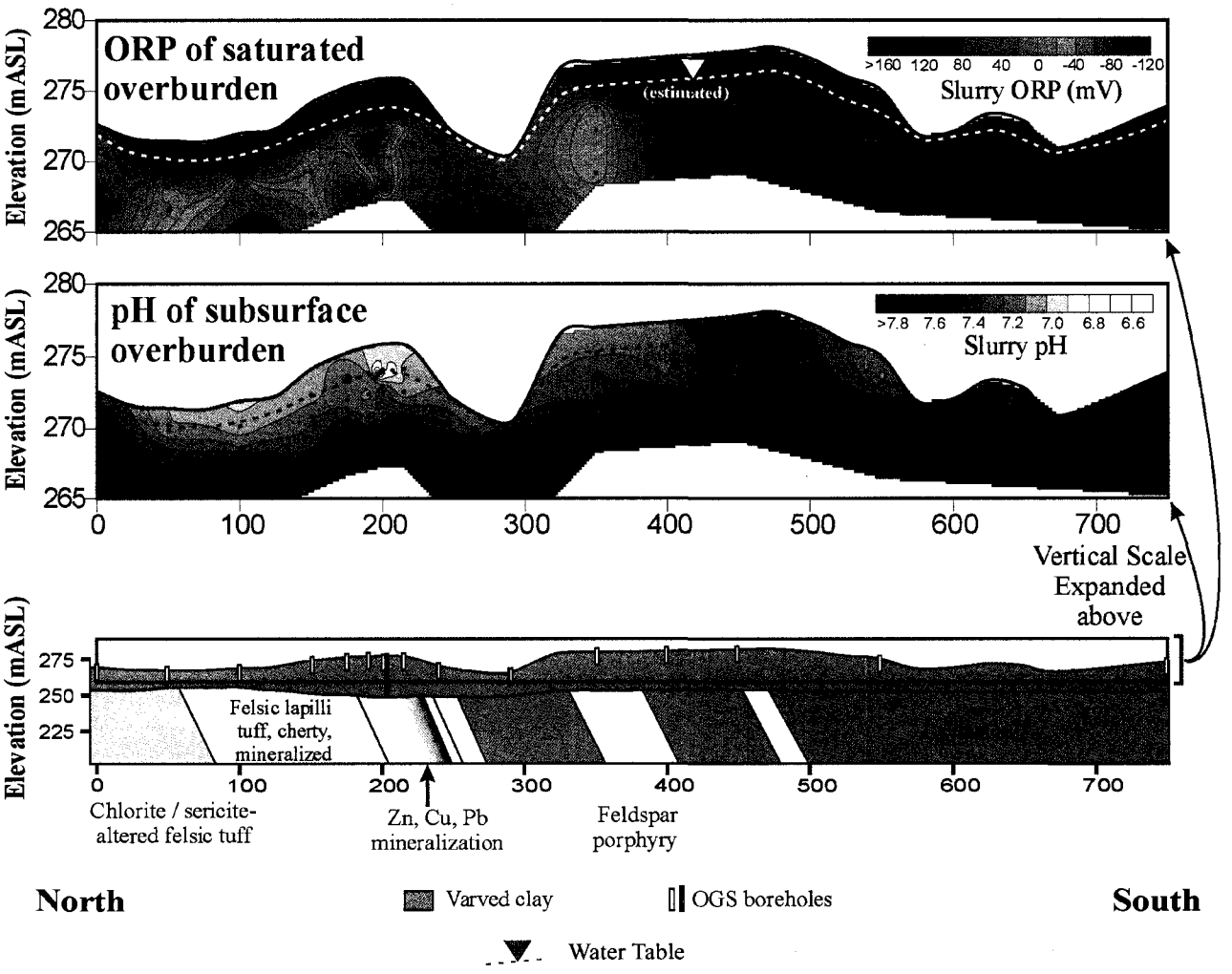


Figure 2-11. ORP and pH of sediments overlying mineralization, Line 40.

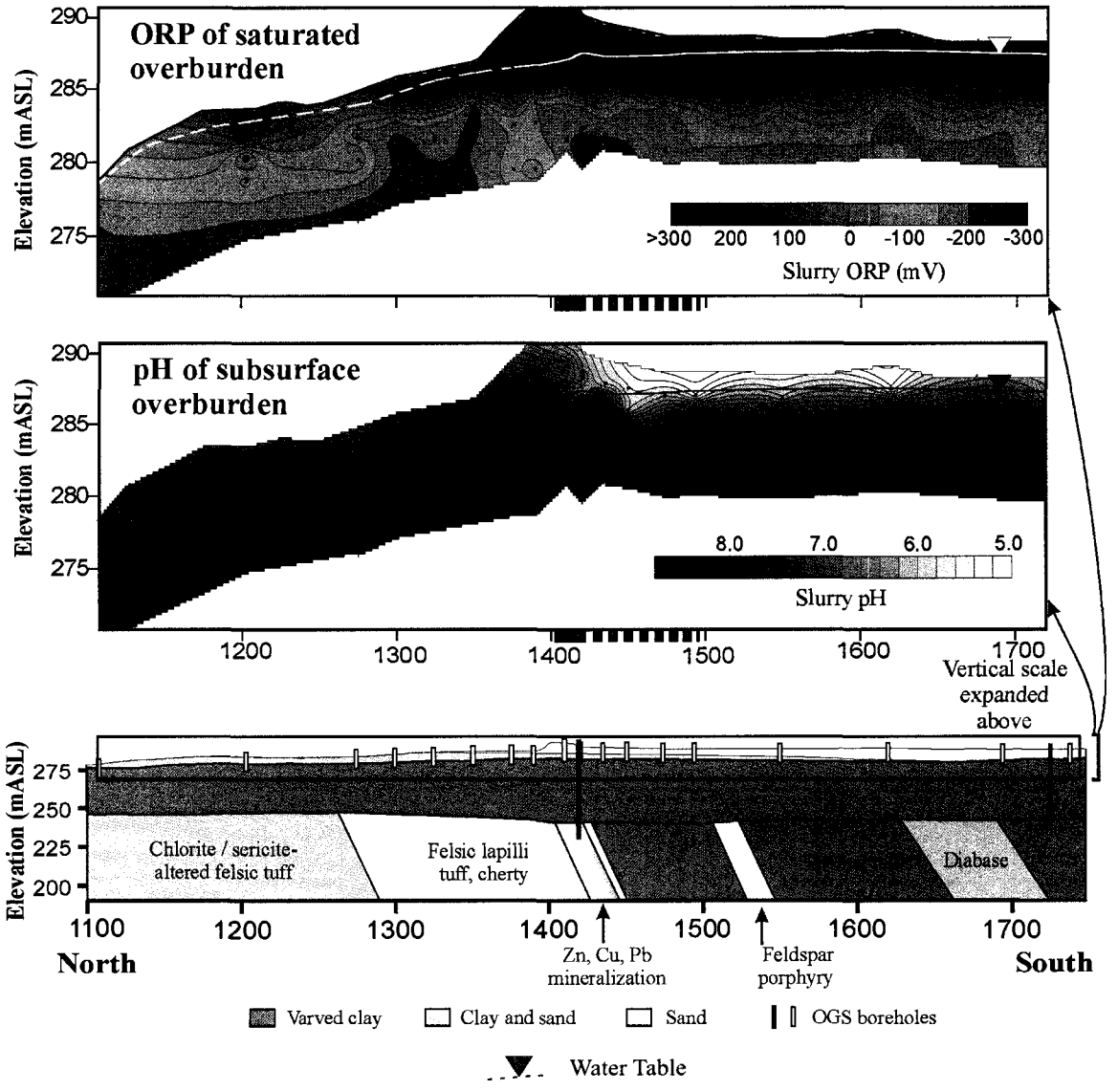


Figure 2-12. Groundwater ORP and pH on Line 40.

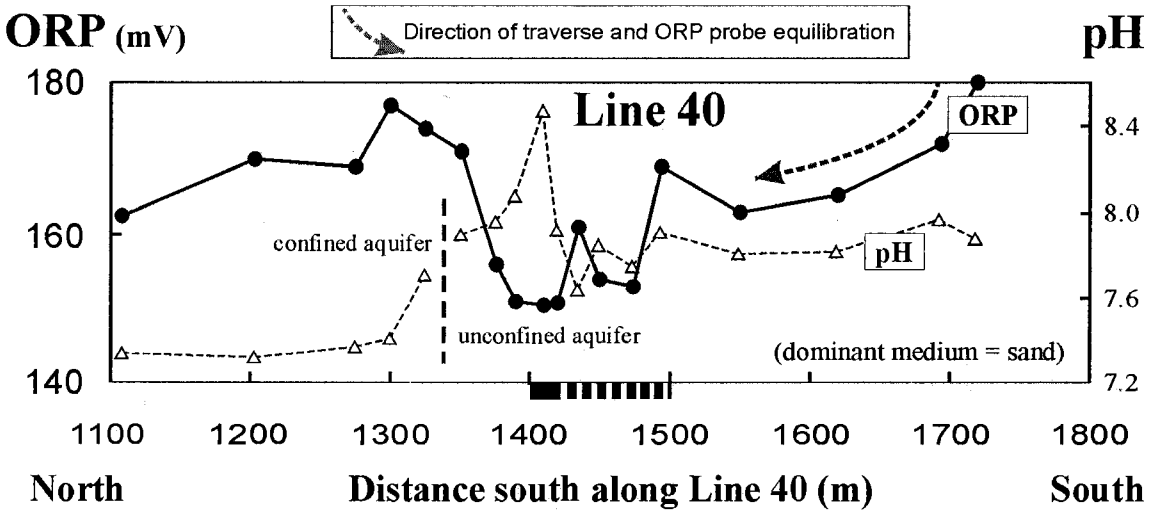


Figure 2-13. pH And dissolved CO_2 of groundwater.

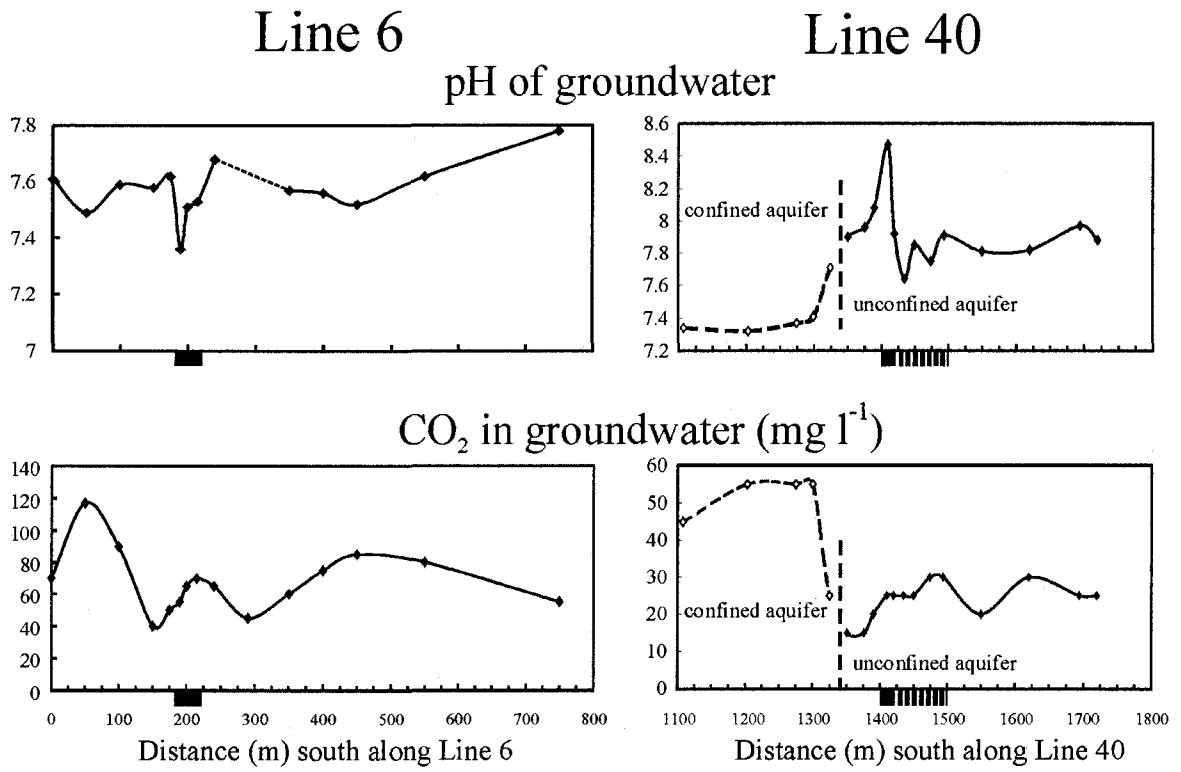


Figure 2-14. Down-hole PtSP data for Line 40.

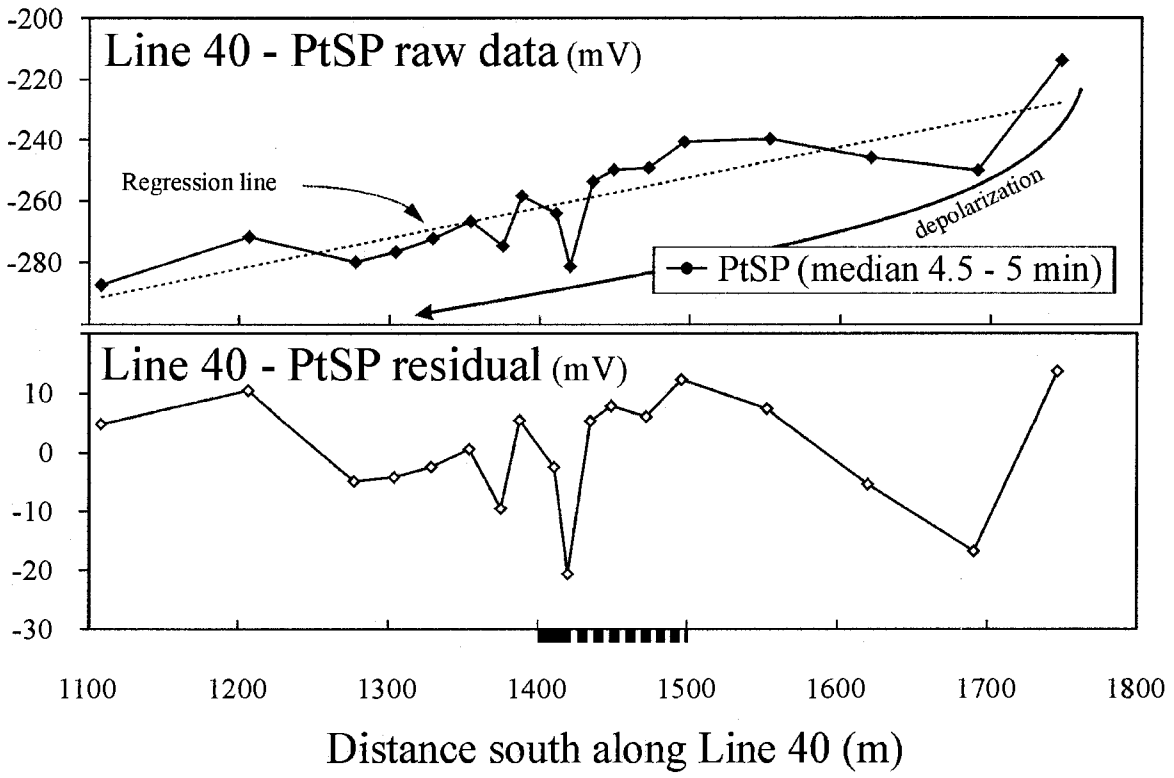


Figure 2-15. Surface SP and pH and carbonate content of surface soils, Cross Lake.

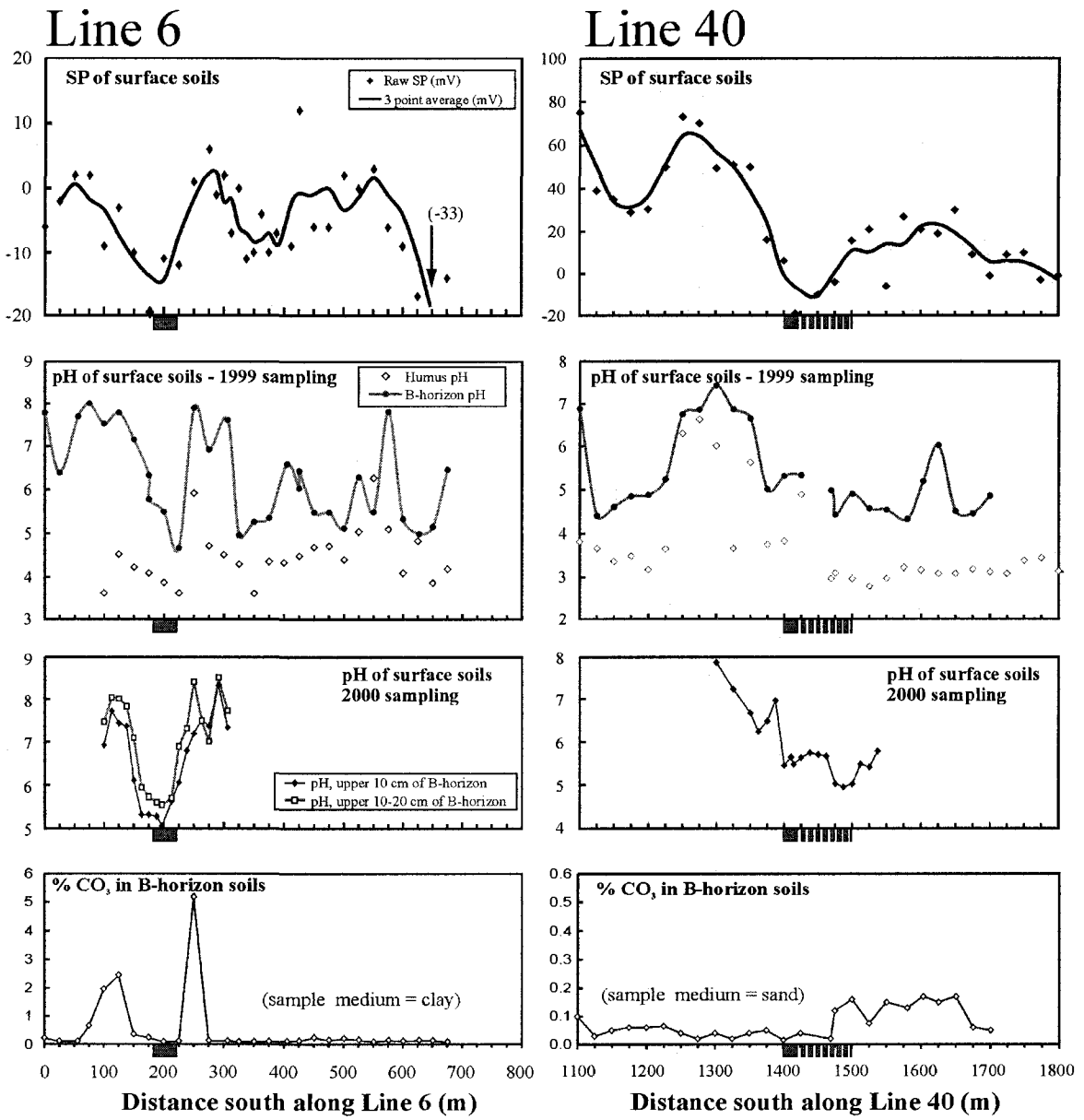
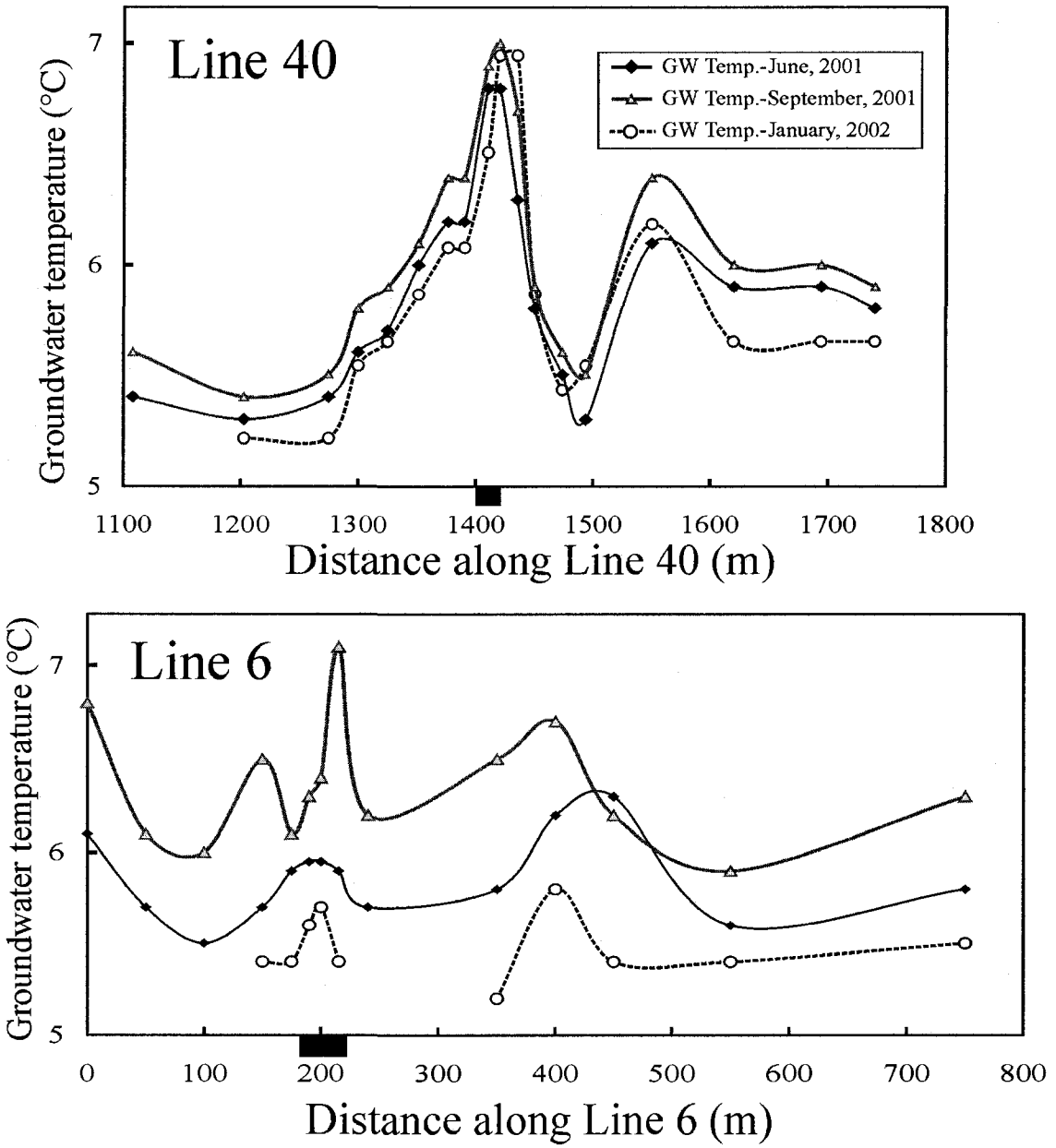


Figure 2-16. Groundwater temperature, Cross Lake.



CHAPTER 3

Redox-induced spontaneous polarization as a cause of electrical and geochemical anomalies over mineral deposits

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Abstract

The origin of spontaneous potential (SP) anomalies above concealed metallic ore bodies has been debated for over 150 years. To evaluate the causes of SP, we examined reduced, but non-electronically conductive, features including three kimberlites and a localized accumulation of H_2S in a 'forest ring.' Reduced 'chimneys' were observed in water-saturated overburden across the features, with corresponding *positive* electrical anomalies on surface. We suggest that the electrical fields and associated SP form in response to strong redox gradients. Since the dipole electrical fields of ions and polar molecules overlap throughout a redox gradient each redox-active ion is influenced on one side by more, and the other side less, electronegative neighbours. The lowest energy orientation of ionic dipoles would be with their negative poles pointing toward neighbouring ions with the stronger affinity for electrons, i.e., toward the oxidizing end of the redox gradient. A preferred orientation of constituent dipoles would impart a macroscopic electrical polarity to the whole redox gradient and produce electrical (i.e., SP) anomalies that are negative at the oxidizing end of the gradient and positive at the reducing end. Where disseminated sulphides occur in a strong redox gradient, countless sulphide grains would similarly polarize and serial amplification of their overlapping dipoles could result in much larger SP voltage than is theoretically possible for massive sulphides.

Redox-induced spontaneous polarization is similar to ferroelectric alignment of electrical dipoles in solids but occurs in an aqueous medium and therefore would constitute an electrical field in a medium of finite resistivity. Electrical current would result, comprising a flux of ions. This process could account for the positive SP responses we observed, the negative responses reported over buried conductors and buried disseminated porphyry sulphide deposits and the geochemical anomalies associated with such features.

3.1 Introduction

Spontaneous potential (SP) anomalies have been documented in a variety of settings and in some cases their causes are well understood. Examples include electrokinetic coupling (streaming potentials) produced by geothermal fields (Corwin and

Hoover, 1979; Apostolopoulos et al. 1997) and active volcanoes (Hashimoto and Tanaka, 1995). In contrast, SP anomalies have been reported above ore bodies for over 150 years but their cause remains a subject of debate (e.g., Vagshal and Belyaev, 2001).

SP responses over buried sulphide mineralization usually take the form of negative voltage excursions measured between a stationary electrode located away from mineralization and a mobile electrode that is advanced across it. The magnitude of the SP response on surface is influenced by a number of factors including the mineralogy, the geometry of the ore deposit with respect to the water table and its texture (i.e., massive or disseminated). Negative responses up to about 350 mV are common for massive sulphides whereas graphite yields somewhat greater voltages (Sato and Mooney, 1960). Much larger SP anomalies have been reported in association with porphyry-type deposits (Corry, 1985) and high sulphidation gold deposits (Goldie, 2002). Surface geochemical anomalies have been reported in close spatial association with SP over ore deposits and many authors have attributed these to electrochemical processes (e.g., Govett, 1973, 1976; Bolviken and Logn, 1975; Smee, 1983; Bajc, 1998; Hamilton, 1998).

Some published models account for SP in specific cases, such as the electrical dipole models developed to explain negative surface responses over steeply dipping metallic ore bodies (Schlumberger and Schlumberger, 1922; Sato and Mooney, 1960; Thornber, 1975; Bolviken and Logn, 1975; Govett, 1976). So far, no single model can satisfactorily account for SP and related phenomena in all mineral deposit environments where they occur. In particular, there is no adequate explanation for SP responses over non-electronically conductive features, such as buried disseminated sulphides and petroleum reservoirs. In order to better understand the relationship between redox and electrical fields, studies were carried out at four sites over features that are reduced but not conductors of electrons. Such features are useful in understanding the cause of the SP phenomena because the presence of electrical fields in the absence of electronic conductors constrains possible processes that may result in SP.

3.2 Study Areas

3.2.1 Locations

Three of the four sites studied (Fig. 3-1) are buried kimberlites, two (B-30 & A-4) occurring in the Kirkland Lake kimberlite field and the other (95-2) in the New Liskeard field of northeastern Ontario. The fourth is a "forest ring". Forest rings are peculiar circular outlines that occur in boreal forests of northern Canada (Veillette and Giroux, 1999; Giroux et al., 2001), which are commonly hundreds of metres in diameter and centred on accumulations of chemically reduced substances in overburden or rock (Hamilton, 2000b; Hamilton and Cranston, 2000). They are static and their circular outlines are visible due to a change in vegetation at the rims of the rings. More than 1500 forest rings have been identified in northern Ontario (Hamilton et al. 2004c). For the purposes of this study they are excellent sites to investigate the effects of strong redox gradients at shallow depths. The "Thorn-North" ring was selected because it has been studied in the greatest detail. It is also the only site that is known to be centred on an H_2S-source; the others investigated so far occur over accumulations of CH_4 (Hamilton et al. 2004c).

3.2.2 Bedrock geology and overburden stratigraphy

Thorn-North forest ring

The Thorn-North ring (Fig. 3-2) is approximately 580 m in diameter and occurs in a heavily forested area of glacial sediments, approximately 30 m in thickness, on the western margin of an esker. Fifty four boreholes were drilled in overburden on transects across the ring and monitoring wells were installed (Fig. 3-2). Overburden at the depth of the well screens (7 m) changes abruptly near the centre of the ring from glaciolacustrine clay and clay till in the west to esker sands in the east (Fig. 3-2). The esker is draped by a 1 – 2 m thick oxidized clay unit to the eastern extent of the sampled line. This is overlain by thin sand and overlying discontinuous peat with a typical combined thickness of less than 1 m. An ephemeral perched water table occurs above the clay in this area. In an area to the southwest affecting the 6 wells on the southwest axis and 4 on the extremity of the

west axis, this deeper clay is overlain by lacustrine sand of 3 – 6 m in thickness. Peat cover above the clays west of the esker boundary is typically 1 m and locally as much as 2 m in thickness. Generally no peat occurs above the lacustrine sand.

Bedrock inside the ring was examined in two boreholes (Fig. 3-2). The more easterly of these encountered a quartz-feldspar porphyry with minor (<2%) disseminated sulphide that was predominantly pyrite and the other encountered intensely sheared quartz-feldspar porphyry. A third borehole was drilled approximately 75 m west of the ring and intersected gabbroic rocks with very minor pyrite.

Kimberlites

Surface conditions at B-30 and A4 are moist with discontinuous peat along most of each transect and black-spruce dominated forest cover. Surface soils at 95-2 are drier podzols with pine forest cover. Sader et al. (2003) describes the stratigraphy of glacial sediments in the three sites based on boreholes. All three kimberlites are covered by about 50 m of glacial sediments composed predominantly of glaciofluvial sand overlying sandy till. Basal till thickness at A4 and 95-2 is approximately 10 m and at B-30 varies between 5 and 10 m and is underlain by several metres of weathered kimberlite.

The kimberlites at the B-30 and A4 sites are Late Jurassic in age and intrude Archean mafic to intermediate volcanic rocks. The kimberlite at both sites contains xenoliths of Archean and Paleozoic carbonate rocks that once covered the Archean rocks but which have since been eroded off. The age of the 95-2 kimberlite has not been determined but other kimberlites in the New Liskeard field range in age from Late Jurassic to Early Cretaceous. The 95-2 kimberlite intrudes Proterozoic siltstone of the Huronian Supergroup (Brummer et al. 1992) and contains xenoliths of these sedimentary rocks and the underlying Archean gneissic rocks. The distribution of buried kimberlite on the three sites is delineated by ground magnetic surveys and a number of vertical boreholes. The boundary on the eastern edge of A4 kimberlite is somewhat uncertain due to sparse boreholes in the area and an ambiguous geophysical signal.

3.3 Data Acquisition

3.3.1 Drilling, monitoring well installation and soil sampling

Drilling at the Thorn-North site was carried out using a track-mounted CME drilling rig and 0.2 m (8") diameter hollow-stem augers. Small 32 mm (1¼") diameter plastic monitoring wells were installed in each borehole following the methods reported in Hamilton et al. (2004a). In each of the shallow wells, a single screened groundwater sampling interval was installed within a graded silica filter-pack at a depth of 6.4 m (21') to 7.6 m (25') and sealed above with bentonite. The depth to static water level in the wells varies from 1-2 m in the west to 3-4 m in the eastern wells. During drilling, soil was sampled at several intervals using a split spoon.

At each of the kimberlite sites soils were sampled using a hand-auger at a consistent depth 10 to 20 cm. At the B-30 site, organic peat and B-horizon were both present at this depth interval at various points along the transect and they were collected separately. Samples were sealed in air-tight plastic bags, purged with $N_{2(g)}$ and then frozen for transport to the laboratory.

3.3.2 Spontaneous potential

At the Thorn-North site, down-hole SP surveys were conducted by lowering two electrodes into the screened portion of plastic monitoring wells (Fig. 3-3) and measuring voltage using a high impedance voltmeter against a base station electrode on surface. One of the down-hole electrodes consisted of a 20 cm Pt wire wrapped around a plastic core. The second was a small non-polarizing Cu-$CuSO_4$ half-cell electrode similar to that normally used in surface SP surveys. Careful use of these electrodes allows simultaneous determination of electrical field, total field and redox data as described in Timm and Moller (2001). Immediately prior to the commencement of measurements, the Pt electrode was pre-polarized by immersing it in an acidic ferrous-sulphate pre-treatment solution (Hanna Part No. 1230) for 30 seconds, which reduces the oxidizing memory effect acquired during storage (Hamilton et al. 2004b). In each borehole, measurements were made first with the Cu-$CuSO_4$ electrode followed by the Pt electrode after 1 minute of probe immersion and these are respectively referred to as the SP and "PtSP"

measurements. Measurements were made on the first well of each traverse and then consecutively in each shallow well on that traverse without interruption. The base station electrode was located near the zero metre point where the north-south and east-west lines cross and consisted of a standard Cu-$CuSO_4$ ceramic pot-type electrode.

Similar equipment and protocols were used in surface measurement of electrical and total fields over kimberlites except the electrodes were mounted on sharpened lances that were jabbed into the soft soils at each site. The Pt electrode was mounted in a shallow transverse groove on the end of a wooden lance. The Cu-$CuSO_4$ electrode was mounted on the end of a long polycarbonate tube with the electrode half-cell located at the bottom end. Electrolytic contact between the interior of the latter electrode and the soils was accomplished with a sharpened oak plug that was soaked in a saturated solution of $CuSO_4$ when not in use. The Pt lance was jabbed into moist peat or surface soils at the site 24 hours prior to the survey to allow depolarization of the Pt. Measurements were then taken between a stationary Cu-$CuSO_4$ electrode at a base station and each mobile electrode as they were advanced across the feature and inserted into the soils at each station.

The 'redox field' parameter (Fig. 3-3) was obtained for the forest ring and kimberlite sites by subtracting the SP from the PtSP measurements. Redox by this method is equivalent to ORP using a Cu-$CuSO_4$ reference cell except the cell remains stationary while the Pt electrode is moved from site to site. When measuring groundwater, this method minimizes some of the variability in the data caused by the reference junction encountering solutions of different ionic strength or temperature. When measuring soils it reduces variability due to the junction contacting soils of differing grain size and moisture content.

3.3.3 Oxidation-reduction potential of soils and groundwater

Oxidation-reduction potential (ORP) of groundwater was measured using commercial probes (Corning Model No. 476513) with internal Ag-AgCl reference cells and a pH/mV meter. Prior to ORP measurement, the water level in each well was pumped-down and allowed to recover over several days. On a second occasion, the pumping was followed by purging of the headspace with $N_{2(g)}$ and the installation of

vapour locks to prevent oxidation of the slowly recovering waters. Before the start of each traverse, ORP probes were depolarized in water from one of the wells to be tested for a period of 1 hour. Throughout this period ORP values dropped steadily by approximately 200 mV as the probes lost the oxidizing polarity that they had acquired during probe storage. The measurement at each well started with the transfer of water from the screened portion of the well using a peristaltic pump to a flow cell containing two ORP probes and a temperature probe. Readings were taken at 1, 2 and 3 minutes after probe immersion and the latter values are reported here. On each traverse, ORP was measured at the first well and then successively and continuously at each well along that line until all wells had been tested.

At Thorn-North, soil-slurry ORP measurements were made on samples collected during the drilling program from uniform depth intervals. Samples were taken with a split-spoon, kept in a sealed plastic bag and analyzed within an hour of collection. The measurements were made after immersion of the probes for 5 minutes in a prepared slurry (1:1 by volume of soil and water). Polarization of the probe during overnight storage in air was reduced by repeating the measurements on the first sample at the beginning of each day. The first set of readings invariably showed higher ORP than the second and the latter set was recorded as the ORP for that site. The method resulted in a good reproducibility from 25 duplicate pairs with a coefficient of determination (R^2 value) of 0.883 for the regression line (Hamilton et al. 2004a).

The soil slurry method was also used on surface soil samples from the three kimberlite sites. Several weeks after collection, the samples that had been frozen after collection were slowly thawed in the laboratory and tested for slurry-ORP under a $N_{2(g)}$ atmosphere.

3.3.4 Limitations of Pt-based electrodes.

PtSP, soil slurry ORP and groundwater ORP measurements rely on Pt electrodes to measure redox or total field. It is well known that Pt electrodes do not necessarily provide quantitatively reliable redox data for geological materials (Lu and Macnae, 1998), partly because of the polarizing memory effect that Pt electrodes acquire during sampling and storage (Hamilton et al., 2004a). This contributes to the excessively long

times that Pt-based probes can require to equilibrate with geological materials (Solomin, 1965). In our study, it is the redox *contrast* between the target and background areas that is important and full equilibration of the Pt electrodes was neither attempted nor achieved.

Noble metal-based electrodes can provide reliable results when measuring metallic redox couples such as Fe^{2+} / Fe^{3+} but are not ideal for measuring systems in which $O_{2(g)}$ contributes significantly to mixed potentials such as water-unsaturated (vadose zone) environments (Bartlett and James, 1995). However, noble metal-based probes are currently the only instrumental technique for measuring mixed potentials in the field and therefore they were used in this study. The results of these methods at the Thorn-North site were verified by additional redox-indicating parameters, which are described below.

3.3.5 Sulphur species in groundwater

The oxidation state and concentration of dissolved sulphur species are indicative of groundwater redox conditions. The presence of $H_2S_{(aq)}$ directly reflects reducing conditions in groundwater samples. Concentrations of $SO_4^{2-}{}_{(aq)}$ that exceed the local background of several mg/l most likely indicate a nearby source of reduced sulphur since crystalline Precambrian Shield rocks and overburden in this part of Ontario have few minerals containing SO_4^{2-}.

The amount of $H_2S_{(aq)}$ in groundwater at the Thorn-North site were measured using field colorimetry. The test kit used (Hach No. 2238-01) can determine total sulphide in the range of 0.01 to 11.25 mg/l with a precision of 0.01 mg/l. The low turbidity of the samples suggests the sulphide species are all dissolved (i.e., H_2S, HS^- or S^{2-}). The $SO_4^{2-}{}_{(aq)}$ concentrations were determined in the laboratory using an ion chromatograph (Dionex DX300) with a detection limit of 0.01 mg/l.

In this case, Eh values cannot be obtained using the Nernst equation and the S^{2-}/S^{6+} ratio because the two parameters were measured on samples collected on different dates.

3.3.6 Gases in well headspace

The measured concentrations of $O_{2(g)}$ and $CH_{4(g)}$ in the well headspace are additional indicators of redox conditions in the wells. After pumping-down of water levels, the consumption of $O_{2(g)}$ in the headspace provides an approximation of the availability of reducing agents in the recovering waters. Methane is commonly produced under anoxic conditions by methanogenic bacteria and is highly reactive to form water and CO_2 under oxidizing condition. Its presence can therefore provide an indication of bacteriological activity and reducing conditions.

The concentrations of $O_{2(g)}$ and $CH_{4(g)}$ were measured in the vapour headspace of wells using an Eagle Portable Multi-Gas meter after water levels in the wells had been pumped-down and allowed to recover. The $O_{2(g)}$ measurement, by the electrochemical cell method, has an accuracy of ±5% of full scale and a resolution of 0.1%. The methane concentration is derived from a measurement of total combustible gases by Pt catalysis, calibrated to methane, and has an overall accuracy of ±5% of full scale and a resolution of 5 ppm. The measurement involved removing the well cap, inserting a tube 50 – 100 cm into the headspace of the well and, as the pump inside the instrument withdraws the gases, respectively recording the minima and maxima of the $O_{2(g)}$ and $CH_{4(g)}$ readings.

3.4 Results of Field Investigation

3.4.1 Redox-indicating parameters

Thorn-North forest ring

All the redox-indicating parameters at the Thorn-North site show a negative redox response from the outside to the inside of the ring, although no single parameter shows this at all ring edges. The ORP measurements on groundwater (Fig. 3-4A) show a sharp decline on transects from the outside to the inside of the ring on east, west and southwest edges. There are too few wells on the northeast boundary to assess the response and reliable groundwater ORP data for groundwater do not exist for the north-south line.

Soil slurry ORP data collected at 2 m depth (Fig. 3-4B) show a sharp decrease as the boundary is transected from outside to inside, except on the east edge. Higher values

of slurry ORP beginning just east of +100 m on the west-east line are from the thin oxidized clay unit that drapes the esker. As mentioned, unsaturated sand underlies this clay unit and some or all of these samples may have been from the vadose zone. The north-south transect shows 'edge effects' at the ring boundaries which take the form of lows with minor flanking highs. These are similar in morphology to 'rabbit-ear' responses in soil geochemistry over buried mineral deposits that have been attributed to electrochemical processes (Govett, 1976; Govett and Chork, 1977).

$H_2S_{(aq)}$ data for the east-west and southwest-northeast lines (Fig. 3-4C) show higher concentrations inside the ring and a sharp drop at the boundary. In the two bedrock wells (Fig. 3-2), very high $H_2S_{(aq)}$ concentrations of 11.0 and 2.25 mg/l were recorded for the central and easterly bedrock wells. Very low $SO_4^{2-}{}_{(aq)}$ concentrations of 7.3 and <0.01 mg/l, were respectively recorded for these same wells. Most or all of the detectable $SO_4^{2-}{}_{(aq)}$ in water from the central well likely resulted from oxidation of its $H_2S_{(aq)}$ between collection of the sample and laboratory analysis, suggesting groundwater in bedrock is extremely reduced. $SO_4^{2-}{}_{(aq)}$ in groundwater from the overburden wells shows elevated concentrations across the ring, particularly from clay on the north, south and west axes (Fig 3-4C). SO_4^{2-} shows very high spikes in concentration at the edges near the east, southwest and northeast boundaries, precisely where H_2S concentrations drop. This indicates a very abrupt transition from a reduced regime inside the ring to an oxidized regime outside.

The $O_{2(g)}$ content (Fig. 3-4D) in the head space of wells is lower inside the ring relative to outside, particularly for wells with screens finished in clay. A substantial depletion occurs at the ring edges, especially in clay on the south, west and southwest boundaries of the ring and to a lesser extent on the north boundary. $CH_{4(g)}$ in the well headspace is generally low inside and outside the ring but shows spikes in concentration at the ring boundaries (Fig. 3-4D) which suggests increased microbial activity in these areas.

Kimberlites

The surface ORP measurements at the kimberlite sites (Fig. 3-5A) were subject to all the limitations of Pt-based probes but they were adequate to demonstrate the *relative*

redox response over the kimberlites. The redox of soils on all three sites shows spiky lows over the kimberlites. From our experience, a spiky redox response is common in shallow soils due to non-uniform oxidation of the sediments, biological processes and variable moisture and organic content.

3.4.2 SP and PtSP

Thorn-North forest ring

Down-hole SP data for the Thorn-North ring are shown in Figure 3-6. The redox-field data show generally lower values inside the ring and negative excursions on the inside boundaries, which are consistent with other redox-related parameters. This is particularly evident to the north, west and east. The response is unclear to the south because the Pt electrode became negatively polarized in the third well from the south, which affected the data in the southernmost two wells. This problem was also observed with groundwater ORP but not in the soil-slurry ORP data, which suggests it may have been due to organic contamination in the well during or after installation.

The SP data on both traverses show *positive* excursions over the ring that correlate well with the negative redox anomaly across the ring. The only exception is a single value in a well located at +150 m on the east-west traverse. This well occurs at the boundary between clays to the west and sand to the east and its more negative response may be due to other factors such as streaming potentials related to water flow near the boundary.

Kimberlites

The redox field data (Fig. 3-5B) show lower values over the B-30 and A4 kimberlites than adjacent areas. They show similar variations to those of the direct ORP measurements on soil slurries but with much less site to site variability. This is partly due to the stationary reference junction encountering no grainsize and moisture variability. It may also result from the PtSP probe being inserted slightly deeper (ca. 10 cm) than the redox sample interval and the fact that it is an in situ measurement that disturbs the soils less. The redox low at A4 in these data is offset from the area underlain by kimberlite and this may be due to the imprecisely known boundary of the kimberlite. At 95-2, a redox

low is not clearly defined in the redox field data, perhaps due to poorer contact between the Pt electrode and the drier soils encountered at this site.

The electrical field response over the kimberlites shows two significant trends. First, there are low magnitude *positive* excursions, which correspond well with the negative excursions in oxidation potential over the kimberlite. Second, there is a general reverse correlation between the redox and SP, particularly in the areas denoted on the Figure 3-5B with the letters A to H.

3.5 Discussion

3.5.1 Redox response - kimberlites

Kimberlite magmas are considered to be oxidizing (Kopylova and Caro, 2004) relative to other mantle-derived magmas but in the near-surface environment the weathering of kimberlites develops profoundly reducing environments. Serpentinization of ultramafic rocks, including kimberlites, commonly produces CH_4 and H_2 from CO_2 and water (*e.g.,* Barnes et al. 1978; Sleep et al., 2004). The recent work by Sader et al. (*in press*) confirms the highly reducing nature of waters from the 95-2 and A4 kimberlite bedrock where Eh values were respectively measured as low as -114 and -536 mV (referenced to the standard hydrogen electrode). At B-30 in 1999 we measured an Eh of -199 mV in the only borehole available for sampling. In addition $H_{2(g)}$ was detected in gas samples collected from a number of boreholes at 95-2 and A4 (Sader et al. 2004). This suggests that waters in at least parts of the kimberlites are sufficiently reducing to exceed the lower limits of water stability.

On surface, the measured and/or calculated ORP (i.e., SP – PtSP) show a negative redox anomaly in soils over the 3 kimberlites relative to background areas. These redox lows in surface materials overlying the very reducing groundwater in bedrock suggest the presence of 'reduced chimneys' in overburden above the kimberlites similar to those observed above metallic sulphide deposits (Hamilton et al. 2004a & b).

3.5.2 Redox response – Thorn-North forest ring

The sharp decrease in redox on the inside edge of the Thorn-North ring is manifest by different combinations of redox-sensitive parameters on each of the 6 transects crossing the ring edge. In this area, the complex stratigraphy, including sand (aquifer), oxidized clay/silt and reduced clay/silt, controls the redox reactions occurring at each ring edge. This, in turn, affects which measurement parameters will be effective in detecting a redox response in a particular environment. For example, on the east line, H_2S/SO_4^{2-} measured in groundwater collected from a depth of 7 m revealed a sharp transition from reducing inside to oxidizing conditions outside the ring, whereas soil slurries of oxidized clay from 2 m depth did not. This is because the latter medium contains ferric iron, due to weathering, and this dominates the ORP response both inside and outside the ring.

At Thorn-North, the data indicate very reducing conditions in bedrock, caused by high concentrations of $H_2S_{(aq)}$. Much lower but still significant concentrations of $H_2S_{(aq)}$ are measured in the shallow groundwater inside the ring, which drop-off precipitously at the ring edge on the 4 transects where it was measured. These are coincident with high concentrations of $SO_4^{2-}{}_{(aq)}$ across the ring, particularly in the clays. The provenance of $SO_4^{2-}{}_{(aq)}$ due to shallow oxidation of depth-derived $H_2S_{(aq)}$ is supported by the high $H_2S_{(aq)}$ concentrations in rock and the SO_4^{2-}/ H_2S molar ratios in groundwater, which average 821 in the shallow clays within the ring but less than 0.12 in bedrock. The latter is an over representation since the measured $SO_4^{2-}{}_{(aq)}$ includes some derived from oxidation of $H_2S_{(aq)}$ in the sample between collection and analysis.

The very high spikes in $SO_4^{2-}{}_{(aq)}$ at the ring edges occur mostly in sand dominated environments on the east and northeast and where sand immediately overlies clay in the southwest. As noted, these $SO_4^{2-}{}_{(aq)}$ spikes occur precisely where the $H_2S_{(aq)}$ drops off, indicating a change from a reduced to an oxidized regime. SO_4^{2-}/ H_2S molar ratios averaging 1380 in groundwater on the inside of these three edges increase by at least a factor of 10 over the 10 m distance to the next well outward, $H_2S_{(aq)}$ drops to below the 0.01 mg/l. detection limit.

The data suggest that H_2S is fluxing upward in the middle of the ring, and outward at the edges, where it encounters $O_{2(aq)}$ and oxidizes. The very high molar ratios

of SO_4^{2-}/ H_2S in the shallow clays and particularly in the sands at the ring edges are a conundrum because they indicate the reactants are in flux, by an as yet unspecified mechanism, but the products are building-up rather than fluxing away by the same process.

The observed variation in redox-sensitive parameters demonstrate the chemically reducing conditions inside the ring and the strong redox gradients at the edges, although a detailed discussion of the redox chemistry of the Thorn-North site and the origins of the ring itself is beyond the scope of this paper. The oxidation potential within the ring increases outward by several hundred mV over less than the 10 m separating one well from the next. The boundary appears to be near vertical and occurs to a depth of at least 7 m. Therefore, the forest ring is a visual manifestation of a large, circular 'reduced chimney' in overburden, although the origin of the H_2S accumulation in rock upon which it is sourced is not currently known.

3.5.3 Electrical field response – all sites

At all four sites studied, the electrical field shows a reverse correlation with redox. This is observed over hundreds of metres along transects across the buried features but also occurs on a smaller scale over metres to 10s of metres in areas where redox changes rapidly. This is particularly well recorded at the ring edges (Fig. 3-6) where, coincident with the sharp redox gradients, is a small negative excursion or 'ripple' in the electrical field.

The reverse relationship between redox and electrical field appears to be contrary to mass transfer models. The movement of mass and charge in solutions is governed by the general mass transfer equation (Bockris and Reddy, 1970):

Eq. 1.

$$J_{(j)} = -\left\{\frac{zF}{RT} D_j C_j \frac{\partial \phi}{\partial x}\right\} - \left\{D_j \frac{\partial C_j}{\partial x}\right\} - \left\{C_j \frac{K}{n} \cdot \frac{\partial H}{\partial x}\right\}$$

Where:

j = species "j"
D = Diffusion coefficient
C = Concentration
z = valence (of j)
F = Faraday's constant
R = ideal gas constant
T = temperature
ϕ = Voltage (electrical field)
K = hydraulic conductivity
H = hydraulic pressure
n = porosity (of porous medium)
J_j = flux of species "j" in the x direction

Equation 1 has only three terms, shown in parentheses, which are respectively those for electromigration, diffusion and velocity of the fluid. In our case, the Darcian equation for groundwater velocity has been substituted in the velocity term and for simplicity "j" is considered to be conservative (i.e., not reactive along its path). As such, only three generalized types of mass transport can occur in an aqueous medium: (1) transport of charged species in an electrical field, i.e., a gradient of electrostatic potential; (2) diffusion along a concentration gradient; and, (3) physical movement of the fluid, e.g., advection along a pressure gradient. The equation contains no redox term and requires:

1. except for its effect on the concentration gradient, oxidation state in a solution does not influence the movement of mass and charge; and,
2. there should be no direct relationship between redox voltage (chemical potential) and electrical field voltage, provided the system is purely aqueous, i.e., provided there are no wires to connect areas of the solution that have different redox properties.

The features being studied do not contain significant quantities of metallic or semimetallic phases and as such do not exhibit electronic conduction. Therefore there ought to be no electrical field associated with these features and no relationship between the significant changes in redox and the measured SP. However, this is in contrast with the observed relationship between these two parameters and the positive SP response.

3.5.4 The origins of spontaneous potential

Previous models

A variety of dipole-conductor models have been proposed to explain SP anomalies over steeply dipping electronically conductive mineral deposits (e.g., Schlumberger and Schlumberger, 1922; Sato and Mooney, 1960; Bolviken and Logn, 1975; Thornber, 1975; Govett, 1976; Hamilton, 1998). Differences in oxidation potential in the groundwater environment between the top and bottom of the conductor cause it to polarize with a negative (cathodic) pole in the shallow oxidized environment and a positive (anodic) pole at depth. Electrons from deeper reducing agents move upward

along the conductor to reduce shallow oxidizing agents. Return current in the surrounding groundwater electrolyte occurs as an ionic flux, which yields geochemical anomalies in near-surface soils (Govett, 1973, 1976; Bolviken and Logn, 1975; Smee, 1983). However the dipole models cannot account for the large SP responses reported over disseminated sulphides and oxide caps (Burr, 1982; Corry, 1985; Goldie, 2002) or over other reduced and non-electronically conductive features such as oil reservoirs (Campbell, 1960; Pirson, 1981) and dissolved hydrocarbon plumes in groundwater (Nyquist and Corry, 2002).

Corry (1994) suggested that a permanent ferroelectric polarity exists in sulphide ore bodies. Ferroelectricity is a property of some solids whereby the electrical dipoles of constituent molecules have a preferred alignment, which imparts a macroscopic electrical polarity to the whole solid. A permanent ferroelectric polarity would require that an initial electrical field existed to be retained by the ore minerals as they cooled to below their Currie temperature. If a permanent ferroelectric polarity were responsible for the widely reported negative SP responses over mineralization, it follows that such pre-existing electrical fields must almost always occur in the vicinity of cooling ore deposits and have a negative upward vector. However, since electrical fields associated with ferroelectric solids are static, as the sole mechanism for SP this explanation would preclude net mass and charge transport and geochemical anomalies associated with SP anomalies.

A third proposed explanation for negative SP responses over mineral deposits argues against the presence of an electrical field and suggests that the responses are caused by the lower oxidation potential encountered in soils over the ore zone by the mobile SP electrode relative to the stationary electrode located in a more oxidized background area (Corry, 1985). This model was applied to both disseminated and massive sulphides. It was later used to explain negative SP responses over dissolved hydrocarbon plumes in shallow aquifers (Nyquist and Corry, 2002).

However, despite the support of other authors who suggested changes in oxidation potential can contribute directly to SP responses (e.g., Veder, 1981; Bolviken and Logn, 1975; Govett, 1976; Hamilton, 2000a), Timm and Moller (2001) demonstrated that SP responses obtained using non-polarizing electrodes result only from differences in electrical potential (i.e., electrical field voltage) and are not affected by changes in

oxidation potential of soils contacting the electrode. They also showed that total field, which is the sum of the electrical and chemical components of voltage, can be measured in moist environments using a noble-metal based mobile electrode and a stationary non-polarizing electrode (Fig. 3-3). This is supported by the observation (Corwin and Hoover, 1979) that chemical potentials in soils add biases of only several 10s of mV when using non-polarizing electrodes (due to contamination of the electrolyte), whereas they can add biases of hundreds of mV when using bare metallic electrodes (Schlumberger, 1920). Timm and Moller's (2001) methodology was reproduced with similar results on a geographically larger scale by Hamilton et al. (2004b).

At the Yanacocha high-sulphidation gold deposit in Peru, Goldie (2002) documented very large negative SP responses, exceeding several volts, above oxidized silicified units with high apparent resistivity. These units represent the supergene oxidized zones, 200 to 500 m in thickness, which overlie the primary disseminated sulphides. There is no apparent relationship between topography and SP. He notes that no model can satisfactorily account for such large SP responses, but suggested several contributing factors to the SP including downward movement of waters in the porous silica units. However, this explanation is not consistent with the insignificant differences in SP response between the wet and dry seasons.

Redox –induced spontaneous polarization

The mineral deposit environments described above represent areas where redox anomalies are accompanied by an electrical field. Even the SP responses over a relatively redox-inert graphite conductor have a redox association since the dipole model suggests graphite can act as a short-circuit route for electrons from deep reducing agents to shallower oxidizing agents.

A redox gradient represents a gradient in electronegativity, and therefore the electrical dipoles of some ions and polar molecules should exhibit a preferred orientation (Fig. 3-7). Species that are capable or nearly capable of redox reaction in the local pH/Eh regime (referred to as 'redox active') will be influenced by the dipole electrical fields of neighbouring ions that are on one side more, and the other side less electronegative. The lowest-energy rest state of the dipoles of redox active species would therefore be with

their negative poles pointing in the positive redox direction, i.e., toward the neighbour that has the strongest affinity for electrons. The result of a preferred orientation of ionic and molecular dipoles would be a macroscopic electrical polarity to the redox gradient as a whole. This induces electrical (i.e., SP) anomalies that are negative at the oxidizing end of the redox gradient and positive at the reducing end. In the specific case of disseminated sulphides in a redox gradient, individual sulphide grains would polarize and serial amplification of many grain-dipoles would result in SP voltages that are much larger than the maximum voltages expected from a massive sulphide deposit (Sato and Mooney, 1960).

In an areal sense, reduced chimneys over kimberlites and forest rings represent roughly circular, negative redox anomalies. According to the model of redox-induced spontaneous polarization (Fig. 3-7), the horizontal, negative-inward redox gradients would induce a positive-inward electrical field and an overall positive SP anomaly on surface (Fig. 3-8A), as has been observed.

Other redox anomalies with presumed horizontal, negative inward redox gradients have been described in association with positive SP anomalies. Reduced chimneys have been reported in strata overlying oil and gas deposits (Pirson, 1981; Tomkins, 1990; Saunders et al. 1999; R.W. Klusman, pers. comm., 2004) as have surface SP responses above oil fields (positive – Campbell, 1960; negative – Pirson, 1981). In a case where porphyry sulphides *outcrop* a rare positive SP deflection was noted on surface relative to adjacent areas by Corry (1985). Whether a negative redox anomaly exhibits a positive or negative electrical field response would depend on whether the predominant redox gradient over the feature is horizontal or vertical, respectively. In young glacial sediments with a high water table (Fig. 3-8A), the reduced chimneys reach almost to surface and therefore the redox gradient is horizontal and the electrical response is positive (the small "ripples" in the electrical field response at the edges of the Thorn-North ring may be due to the intensity of the redox gradients there imposing locally stronger but complementary electrical fields on the larger trend). Where a reduced feature is deeply buried it would exhibit a vertical, positive upward redox gradient that would induce a negative electrical anomaly on surface (Fig. 3-8B). An example would be the negative SP anomalies reported over buried porphyry sulphides (Corry, 1985).

In the case of a buried disseminated sulphide body with a supergene oxidized enrichment zone, such as the shallow part of the Yanacocha deposit, the redox gradients are positive upward and unusually strong due to juxtaposition of the positive redox anomaly of the oxidized zone with the immediately underlying sulphide zone. The strong positive upward redox gradients at the interface create a negative-upward electrical field and a large negative SP anomaly on surface (Fig. 3-8C). The very high voltages observed at Yanicocha would result from serial amplification of the voltage by countless sulphide grain-dipoles in the very strong redox gradient near the sulphide/oxide interface.

The proposed interpretation of redox-induced spontaneous polarization is compatible with the previous electrical dipole models of Schlumberger and Schlumberger (1922), Sato and Mooney (1960), Bolviken and Logn (1975), Govett (1976) and others. The large-scale dipole developed around a buried, steeply dipping electronic conductor would represent a special case of redox-induced spontaneous polarization in which the entire conductor polarizes (Fig. 3-8D). The conductor develops a negative upward electrical polarity in the positive-upward redox gradient in the upper earth's crust (Bolviken, 1979) causing a negative SP anomaly on surface.

3.5.5 The origin of geochemical anomalies

Geochemical anomalies in soil can be the result of dispersion from mineralization by several mechanisms, including transport in an electrical field (Govett, 1973, 1976; Bolviken and Logn, 1975; Smee, 1983). Apical or single-peak anomalies can form by any dispersion process but halo or 'rabbit-ear' (Govett, 1973) responses, which comprise two peaks straddling mineralization, have most often been attributed to electrochemical processes. Halo-responses were observed at the Thorn-North site in $SO_4^{2-}{}_{(aq)}$ (for wells in sand) and $O_{2(g)}$ depletion / $CH_{4(g)}$ enrichment in well headspace. Apical anomalies were noted in $H_2S_{(aq)}$ and $SO_4^{2-}{}_{(aq)}$ (for wells in clay).

Redox-induced spontaneous polarization as proposed would constitute an electrical field in a medium of finite resistivity, which by Ohm's Law, would necessitate electrical current. In the groundwater environment this must occur as a flux of ions that includes the redox-active ions that constitute the redox gradient. For such a process to be

in steady state, both a continuous source and sink of reducing agents (i.e., a source of oxidizers) are required.

At Thorn-North, groundwaters have near neutral pH and contain $HS^-_{(aq)}$ as the predominant dissolved sulphur, which will move as a negative charge-carrier outward in the electrical field, encounter $O_{2(aq)}$ at the edges and oxidize to form $SO_4^{2-}{}_{(aq)}$. At the ring edge, both the redox gradient and the resultant electrical field fall off sharply, which limits the outward dispersion of $SO_4^{2-}{}_{(aq)}$ and accounts for the high ratio of $SO_4^{2-}{}_{(aq)}$ / $H_2S_{(aq)}$ here. A vertical redox gradient also exists across the ring, which serves to induce the upward movement of $HS^-_{(aq)}$. Once it oxidizes near surface, the low permeability of the clays, coupled with the diminished redox and electrical fields, would limit the dispersion of the $SO_4^{2-}{}_{(aq)}$ products and an apical anomaly across the ring would result.

3.6 Conclusions

The Thorn-North forest ring and the reduced chimneys over the three kimberlites are examples of discrete, negative redox anomalies in shallow earth materials with no nearby electronic conductors. They exhibit horizontal, inwardly-reducing redox gradients around their circumference and *positive* electrical field anomalies on surface across the features as measured using non-polarizing electrodes. We propose that the positive electrical responses over these features are due to positive-inward *electrical* polarity to the redox-active ions that constitute the redox gradient. Redox-induced spontaneous polarization results from a preferred orientation of redox-active ions and polar molecules within the redox gradient such that the negative ends of the dipoles point in the positive (oxidizing) redox direction, toward the neighbouring species with the higher affinity for electrons. The resulting macroscopic electrical field is analogous to ferroelectricity except that it occurs in an aqueous medium and some of its constituent species are therefore free to move within the induced electrical field.

Redox-induced spontaneous polarization, can account for SP responses reported in a variety of geological settings. Whether an SP response on surface above a reduced feature is negative or positive depends on the orientation of the redox gradient. Most buried reduced features produce vertical, positive upward redox gradients and would induce a negative-upward polarization and negative SP responses on surface. These

would be particularly strong where disseminated sulphides exist within a strong redox gradient because individual sulphide grains would polarize and stacking of the grains would produce in-series voltage amplification and much higher SP voltage than is possible over massive sulphides.

Where buried reduced features outcrop or where a reduced chimney above the feature reaches the surface (as observed in our study), the redox gradients would be largely horizontal and negative inward, inducing a positive inward electrical polarity and a positive SP response on surface.

The dipole electrical field around a steeply dipping metallic conductor is a special case of redox-induced spontaneous polarization, in which the entire conductor polarizes in the positive upward redox gradient of the earth, generating a negative-upward electrical anomaly above the conductor. Therefore the proposed model is compatible with pre-existing dipole models by Schlumberger and Schlumberger (1922), Sato and Mooney (1960), Bolviken and Logn (1975), Govett (1976) and others.

The proposed model also supports Corry's (1994) argument that a net electrical polarity occurs within some orebodies and is responsible for an SP phenomenon, except the polarity would be transient and induced by the redox gradient. Such a process does not preclude a permanent ferroelectric polarity in the ore minerals but rather would fulfill the requirement of a pre-existing negative upward electrical field, a remnant of which is retained by the orebody during cooling.

The electrical field resulting from redox-induced spontaneous polarization would induce electrochemical transport of ions and result in geochemical anomalies that are partly indicative of ore composition. It can therefore account for both apical and 'rabbit-ear'-type geochemical anomalies in soils above buried mineral deposits. However, positive charge carriers would move in the opposite direction and may also be deposited in surface soils and therefore not all elemental anomalies would indicate ore composition. Redox-active ions that constitute the redox gradient would also be mobilized by this mechanism and this would serve to maintain the gradient as these ions are constantly attenuated by redox reactions.

Natural redox reactions are frequent sources of metabolic energy for bacteria. The methane spikes at the edge of the Thorn-North ring are suggestive of increased microbial

populations occupying areas where the redox gradient is highest. The proposed process would be enormously beneficial to autotrophic organisms because it results in a converging flux of oxidizing and reducing agents, which are primary metabolic nutrients for these types of bacteria.

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Chapter 3 Figures

Figure captions

Fig. 3-1. Location of study sites within Ontario.

Fig. 3-2. Locations of monitoring wells at the Thorn-North forest-ring site. The thick white line shows the western boundary of esker sands as defined by drilling and air photo interpretation. Thick grey lines are drill roads and define the sampling transects. Position of wells relative to each other is accurate to within a few centimetres. Georeferencing of air photo is accurate to +/- 10 m. Grid units are in metres and the projection is NAD 1983, UTM Zone 17N (Ontario Ministry of Natural Resources air photo number 91-4826-64-86).

Fig. 3-3. Schematic diagram showing the measurement of spontaneous potential using a Cu-$CuSO_4$ electrode (SP), total field using a Pt electrode (PtSP) and oxidation-reduction potential using a stationary Cu-$CuSO_4$ reference electrode. The 'redox field' parameter, discussed in the text was obtained by subtracting the SP from the PtSP (from Hamilton, 2004b).

Fig. 3-4. Redox-sensitive parameters in well water and gas at Thorn-North forest ring. Green box shows the extents of the forest ring and yellow margins shows the position of the whitish rim that delineates the ring edge. 4(A) Groundwater ORP measured in a flow cell on well water extracted after pumping-down water levels and then: (i) purging the headspace with $N_{2(g)}$, adding vapour locks and allowing 4 days of water level recovery; and (ii) not purging and allowing 2 weeks of water level recovery. 4(B) ORP measurement on a 1:1 distilled water / soil slurry on samples collected during drilling with a split-spoon and analyzed within 1 hour of sampling from a depth of ca. 2 m. 4(C) $H_2S_{(aq)}$, measured in the field, and $SO4^{2-}{}_{(aq)}$ measured in the laboratory on groundwater extracted from the wells. 4(D) $O_{2(g)}$ and $CH_{4(g)}$ measured in the vapour headspace of wells several weeks after pumping-down water levels and capping the wells.

Fig. 3-5. Redox and SP data for surface soils at three kimberlites shown in Fig. 3-1. 5(A) shows ORP for soil slurries measured in the laboratory after field preservation. Samples were collected at a consistent depth of 10 to 20 cm both organic soils (peat) mineral soil (predominantly B-horizon sands) were encountered. Raw data are shown as points and a thin line and a 3 point moving average is shown as a thick line. 5(B) shows surface SP and redox-field parameters, which are related to one another as shown in Fig. 3-3. Grey boxes show the approximate extents of the kimberlites. Letter designations on Fig 5B show areas where redox and electrical field vary inversely.

Fig. 3-6. Down-hole SP and 'redox field' for the east-west and north-south transects of the Thorn-North ring. Electrical field and 'redox field' parameters are related to one another as shown in Fig. 3-3. A negative electrode polarization was acquired in the 3rd most southerly well probably as a result of contaminants introduced during drilling. This also negatively biased values in the remaining 2 wells to the south.

Fig. 3-7. A schematic diagram showing the formation of redox-induced spontaneous polarization in a medium with a redox gradient. (A) No electrical field is produced in a medium that exhibits no redox gradient because ionic dipoles have no preferred orientation. (B) Redox-active ions in a redox gradient are influenced by neighbouring species that are on the one side more and the other side less electronegative. This should result in a preferred orientation to their ionic dipoles with negative poles pointing in the positive redox direction, i.e., toward the neighbours with the strongest affinity for electrons. (C) The polarization of constituent dipoles would result in a macroscopic electrical polarity to the medium within the entire redox gradient with a negative electrical anomaly at the oxidizing end of the gradient and a positive anomaly at the reducing end. In most cases this redox gradient is positive-upward, which would result in a negative SP anomaly should result on surface above the feature.

Fig. 3-8. Schematic diagram showing several variations of redox-induced spontaneous polarization. Where a reduced, non-electronically conductive feature outcrops (Fig. 3-

8A) horizontal, negative inward redox gradients would predominate, yielding a positive SP response on surface with flanking lows. Above a buried reduced feature (Fig. 3-8B), redox gradients would be vertical and positive upward, which would yield a negative SP response on surface. A buried disseminated sulphide body with an oxidized cap (Fig. 3-8C) would have an intense vertical redox gradient and sulphide grains exposed to it would themselves polarize. Serial amplification of the voltage of multiple sulphide grains would result in larger SP voltages than would be typical with massive sulphides. A buried, steeply dipping electronic conductor (Fig. 8D) is a special case in which the electrical field results from the redox-induced polarization of the whole conductor and produces a negative SP anomaly on surface.

Figure 3-1. Study areas.

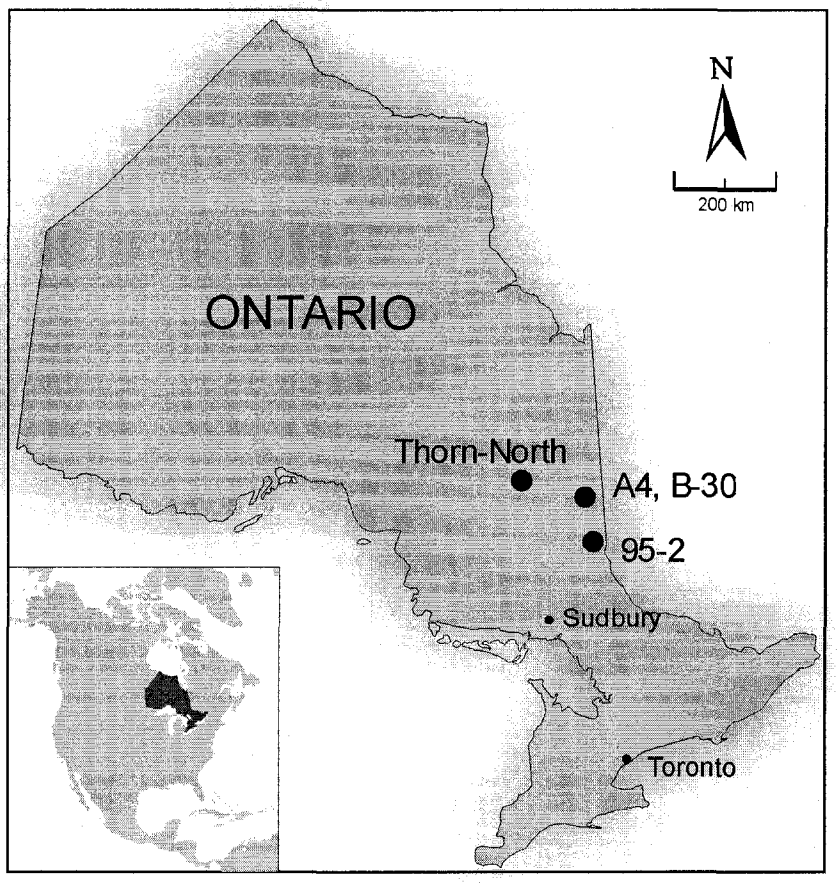


Figure 3-2. Monitoring well locations, Thorn-North forest-ring.

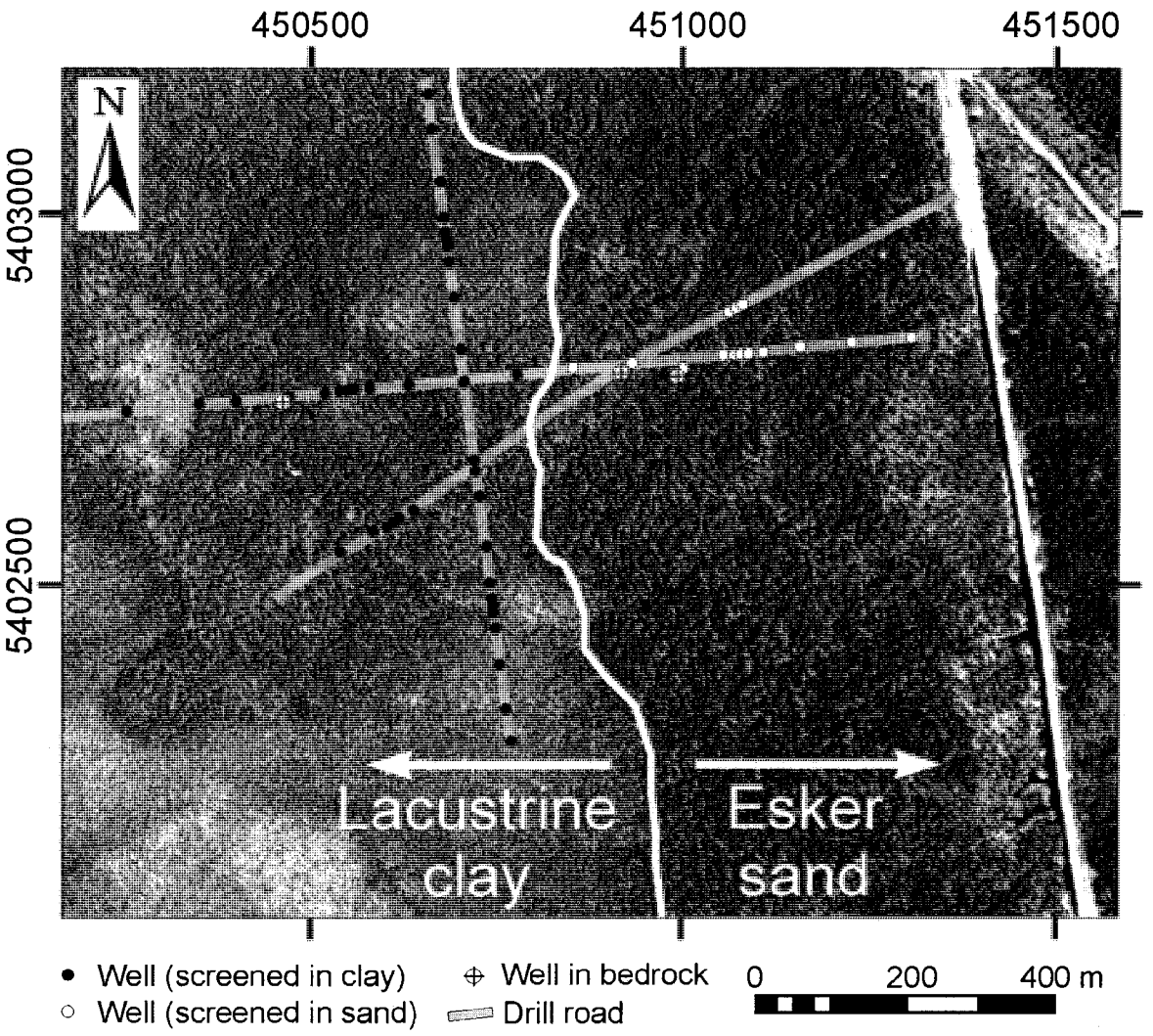


Figure 3-3. The down-hole SP / PtSP / ORP methodology.

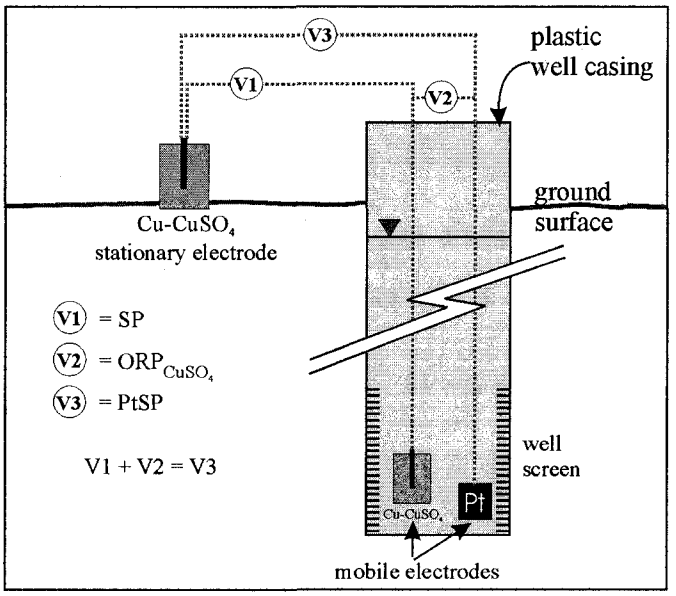


Figure 3-4. Redox-sensitive parameters in well water and gas, Thorn-North.

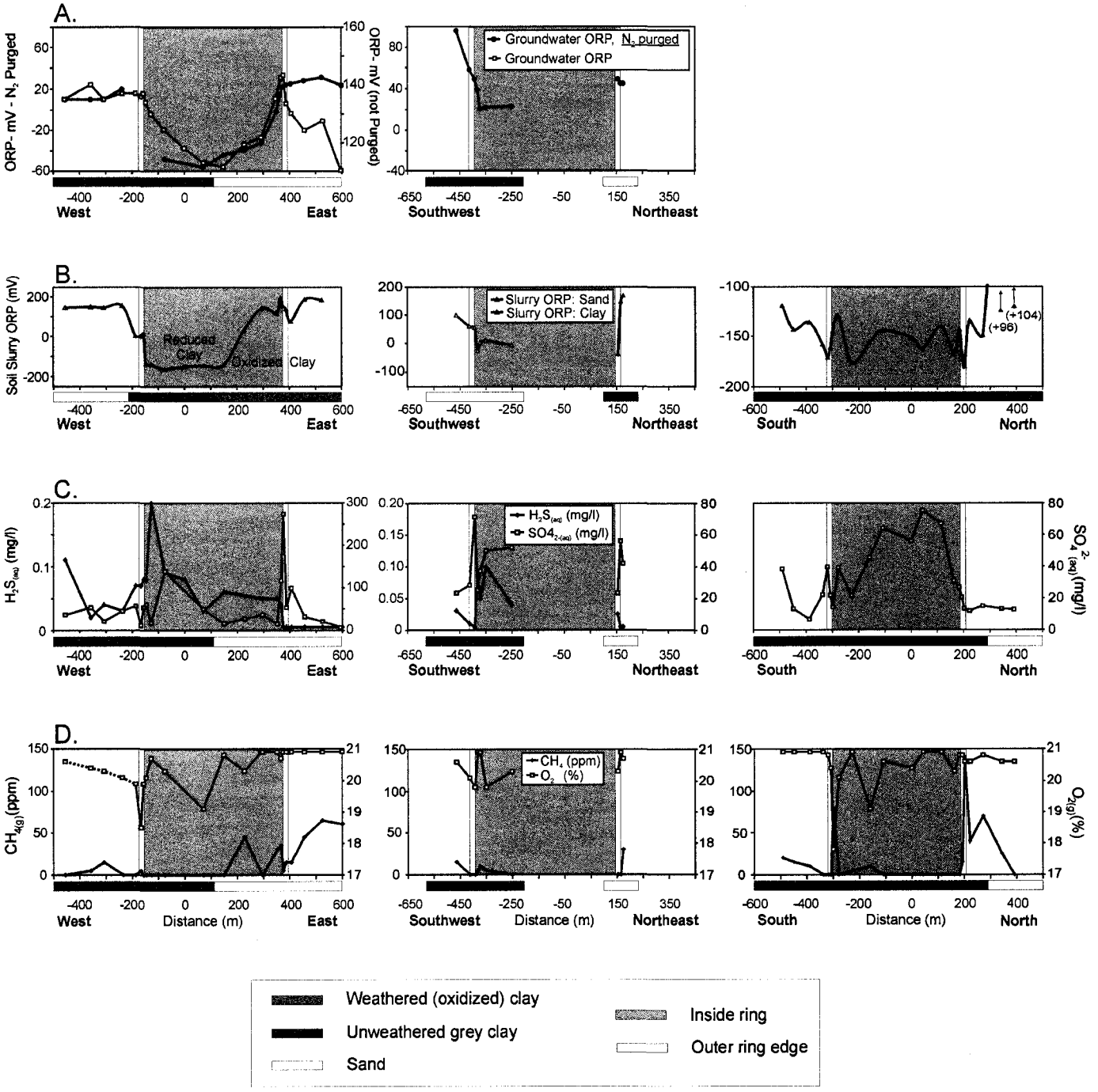


Figure 3-5. Redox and SP data for surface soils at three kimberlites

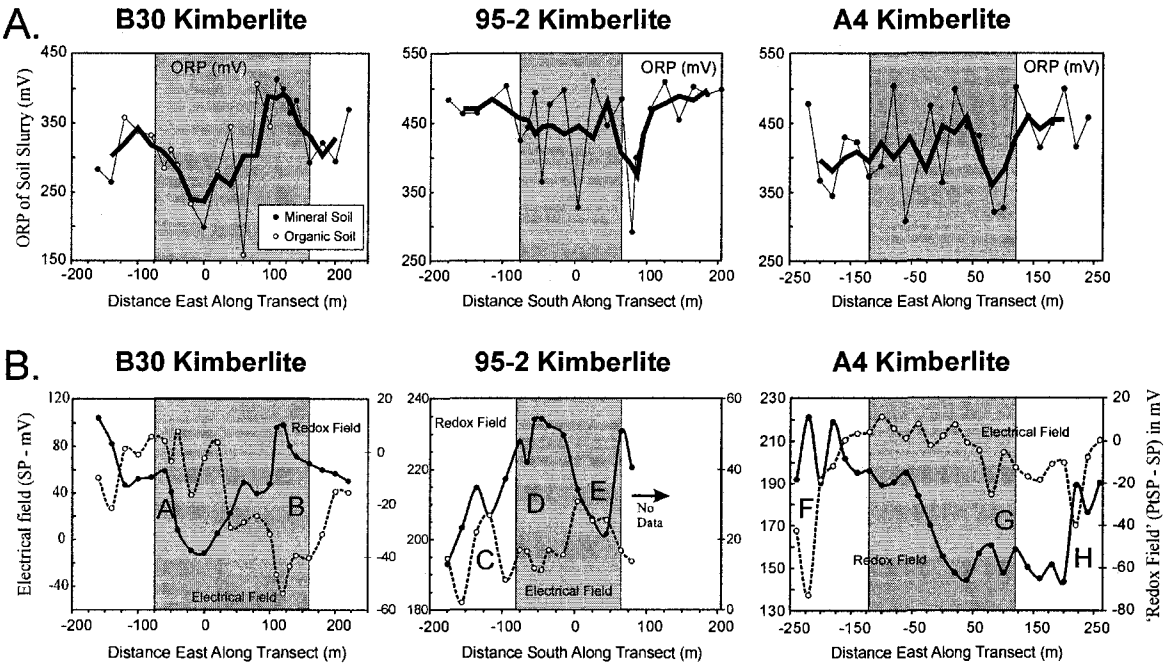


Figure 3-6. Down-hole SP and 'redox field', Thorn-North ring

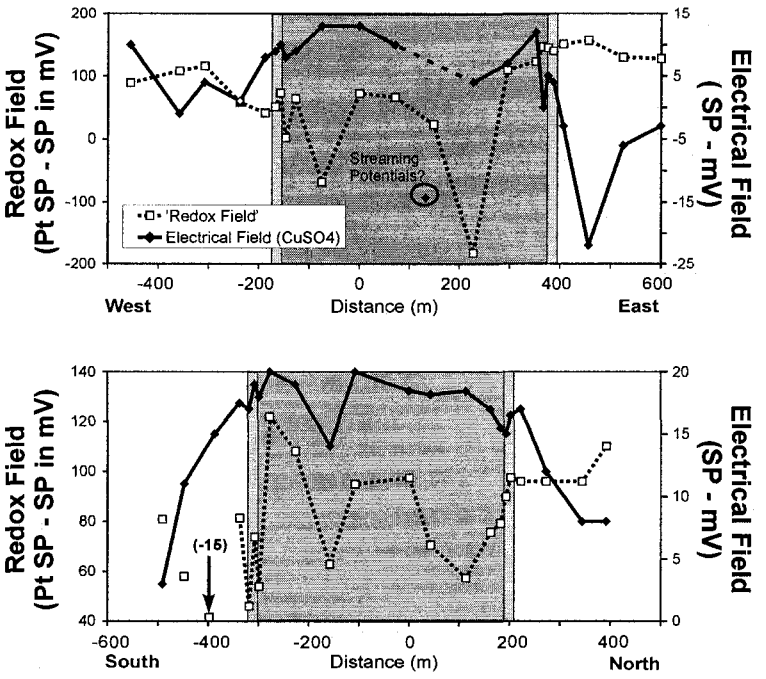


Figure 3-7. Redox-induced spontaneous polarization schematic.

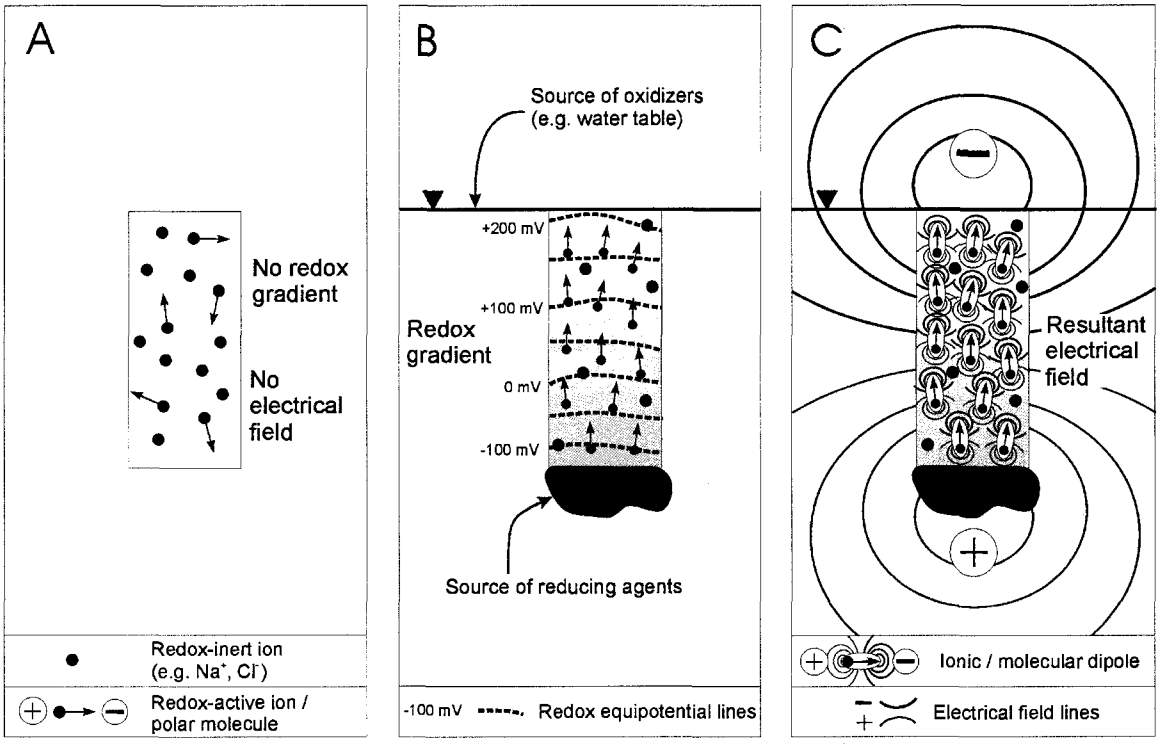
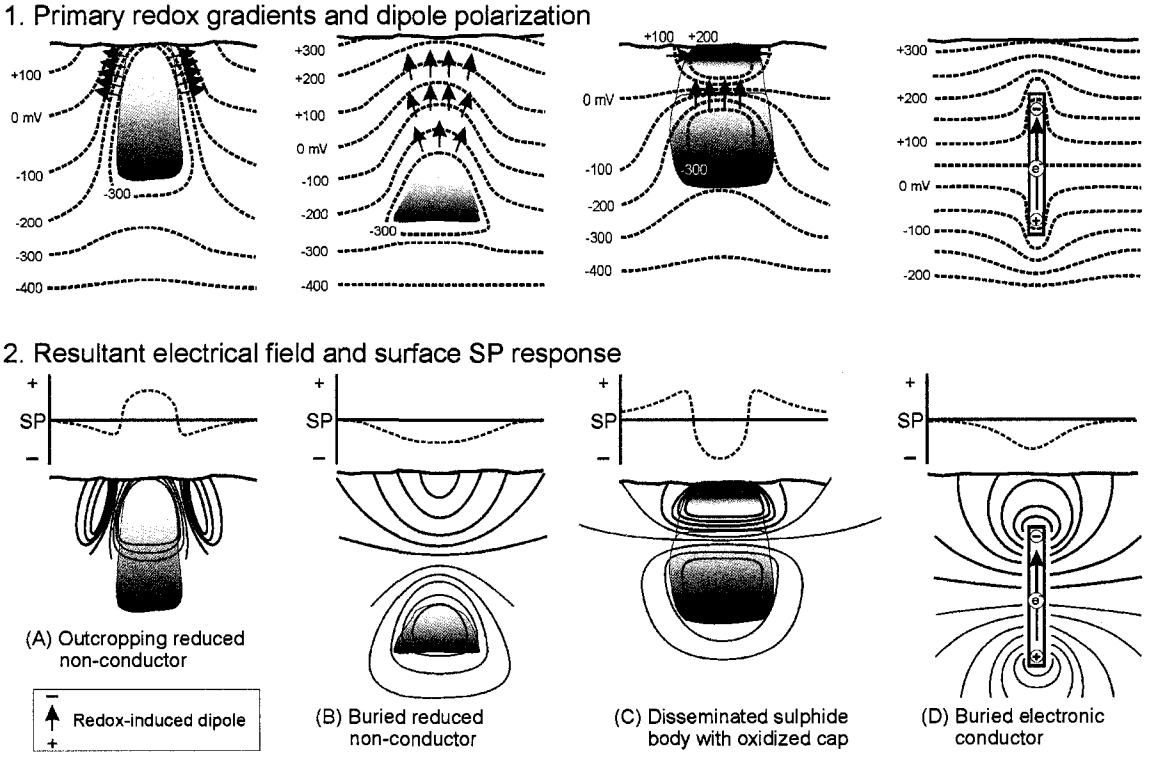


Figure 3-8. Variations of redox-induced spontaneous polarization



Appendix 1

Spontaneous potentials and electrochemical cells

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A1.1 Introduction

Selective leach techniques have become popular in mineral exploration for the treatment of geochemical soil samples. Their popularity stems from the fact that they are considered to extract selectively a particular hydromorphically-transported component of metals in the sample and, as such, show better anomaly-to-background contrasts than do conventional strong acid digestions which dissolve most of the chemical matrix of the soil.

A number of case studies have been published involving selective leaching of samples taken over known mineralization. It is apparent from this work that these techniques have some capability to detect a geochemical response due to mineralization and other geological features, through a significant thickness of rock or overburden. What is less apparent, however, is the transport mechanism that moves elements to surface from the source. Recent work in Quaternary glaciated terrain (Bajc, 1998; Jackson, 1995; Hamilton and McClenaghan 1998) has shown selective leach anomalies, apparently related to bedrock features, above as much as 45 m of overburden sediments. The young age (<10 Ka) and thickness of these deposits require that, at least in glacial environments, a very fast transport mechanism operate.

During the weathering process, elements can disperse from source mineralization by a variety of chemical processes. For reasons discussed below, electrochemical processes are increasingly thought to be the primary transport mechanism in environments of thick, young, exotic (i.e., transported) overburden. They are also likely to operate in other environments, but their dominance as a transport mechanism is less certain. This chapters presents the principles behind electrochemical mass transport and discusses the role of natural electrogeochemical processes in the formation of selective leach and conventional geochemical soil anomalies.

A1.2 Geochemical Transport Mechanisms

Transport processes resulting from the chemical weathering of mineralization involve the dispersion of elements down gradients of one kind or another, including chemical, temperature, piezometric (both gaseous and aqueous) and electrochemical

gradients. These mechanisms have been invoked as components of the numerous transport and dispersion concepts that have been used by researchers to account for soil geochemical anomalies overlying mineralization. The models used in the past can be grouped broadly into those that rely on: (1) diffusion; (2) advective groundwater transport; (3) gaseous transport; and, (4) electrochemical transport. Combinations of these are also possible.

A1.2.1 Diffusion

Diffusion along concentration gradients has been named as a possible cause for observed soil anomalies over mineralization (Govett and Chork, 1977; Smee, 1979, 1983). Smee (1979) calculated diffusion rates and total diffusion distances for a number of ions through glaciolacustrine clay for an 8000-year period. The calculations were based on measured parameters or reasonable approximations. None of the ions was calculated to travel more than 10m, with the exception of H^+, which would have traveled 28 m. Smee (1979) concluded that diffusion was too slow to account for soil anomalies in Quaternary glacial units thicker than 5 m. Whereas anomalies spatially related to mineralization have been noted overlying thicknesses up to 45 m of young glacial sediments.

H^+ and other ions are likely to be the product of oxidation of mineralization, which requires the downward diffusion of oxygen. This would decrease the speed of the process by limiting the formation of ions at the bedrock surface and thereby limiting the development of a concentration gradient between bedrock and ground surface. This further precludes chemical diffusion as a major contributor to the formation of selective leach anomalies in thick, young, exotic overburden. Diffusion becomes a more likely transport mechanism with increasing age and/or decreasing thickness of the overlying material.

A1.2.2 Advective groundwater transport

Bolviken and Logn (1975) and Smee (1983) include groundwater transport as a possible mechanism for element dispersion from mineralization. Webber (1975) pointed to the much higher potential migration rate of groundwater as compared with that of

diffusion or electrochemical transport and concluded that advective groundwater transport is likely to be the more important dispersion mechanism.

Groundwater transport may indeed disperse large quantities of elements but in stratified geological materials it tends to do so laterally. This is particularly true with respect to stratified glacial overburden, including glaciolacustrine varved clays, for which horizontal hydraulic conductivities are typically orders of magnitude higher than those that occur in the vertical direction (Freeze and Cherry, 1979). This results in horizontal groundwater flow being favoured over vertical by a similar factor.

Selective leach anomalies that have been attributed to bedrock features are most commonly reported as either apical (single peak) or rabbit-ear (twin peak) anomalies lying almost directly over the feature. If groundwater transport were a significant contributor to the mobility of the elements involved, one would expect anomalies occurring down a long dispersal plume in the down-gradient direction of groundwater flow. This has not been reported in surface soils. Furthermore, selective leach anomalies are often noted in surface soils far above the water table. Since groundwater obviously could not play a significant role in the formation of many of these anomalies, it is reasonable to conclude that it plays a relatively minor role in the formation of selective leach anomalies as a whole.

A1.2.3 Gaseous transport

The measurement of soil gases has been used to identify the presence of mineralization by a number of workers (e.g., Lovell et al., 1983; McCarthy et al., 1986). Gaseous transport of metals and/or other species has been suggested as a possible mechanism in the development of soil geochemical anomalies (Clark, 1997; Smee, 1998). Case studies in support of gaseous transport are largely cited from arid or semi-arid areas where the water table exists 10s to 100s of metres below ground surface. Large scale and rapid gas transport in these environments is plausible because of the very thick vadose (unsaturated) zone. Gases in the phreatic zone (i.e., below the water table) in the zone of meteoric groundwater (envisioned here as the zone where lithostatic load adds nothing to the fluid pressure) typically exist in dissolved form and therefore their transport occurs largely by diffusion or groundwater advection.

Some authors have suggested a gaseous transport mechanism below the water table in which gaseous carriers move metals in a separate gas phase (Clark, 1997). This is extremely unlikely. In the vadose zone, gases can exist in gaseous phase at partial pressures that are considerably below atmospheric pressure. This is not the case below the water table where the sum of partial pressures of all dissolved gases must exceed the fluid pressure for a separate gas phase to exist. By definition the "water table" in a saturated geological medium is the point at which the fluid pressure is exactly equal to atmospheric pressure (Freeze and Cherry, 1979). Below the water table, the fluid pressure exceeds the vapour pressure and, above it, the vapour pressure exceeds the fluid pressure. In the zone of meteoric groundwater, gases typically only exist as a vapour phase below the water table in the following circumstances:

1. In extremely sluggish groundwater flow environments e.g., as methane pockets in shale where the gas is in pressure-equilibrium with surrounding groundwater and where the only dispersion mechanism is diffusion;
2. in environments where the fluid pressure is decreasing i.e., where groundwater is moving up, such as occurs at discharge zones; and,
3. in environments where the vapour pressure is increasing or at least being maintained by ongoing processes at a continuously high level, i.e., where gas is being actively generated or being supplied from below.

Scenarios 1 and 2 can be ruled out because, as mentioned, neither diffusion nor groundwater discharge can account for the majority of selective leach anomalies. If scenario 3 were applicable as a transport mechanism for metals and gases below the water table, a large source of gas would be necessary. If it were applicable as a cause of rabbit-ear anomalies in all environments, a large source of gas would be necessary at every mineral deposit that produces such anomalies. It follows, therefore, that the source of gas must be genetically associated with the weathering of the mineral deposit. Finally, if a separate gas phase were present, it would require that gas be generated at mineralization in high enough concentrations to partition into a vapour phase. If it did not, its rate of diffusion of elements from mineralization would be in a similar range with that of other dissolved species, which is far too slow to account for many of the anomalies noted in thick, young glacial terrain.

Elevated CO_2 has been shown to be coincident with rabbit-ear metal anomalies over mineralization in arid terrain and will be used as an example. For any gas in equilibrium with water, the concentration of that gas in solution is proportional to total pressure. At a depth of 30 m below the water table and assuming CO_2 is the dominant dissolved gas phase, the partial pressure required to exsolve CO_2 would be about 4 atmospheres, which is an extremely high concentration (exceeding the pCO_2 of soft drinks). Concentrations exceeding 1 atmosphere are very rare in natural meteoric groundwater and usually only occur in thermal springs and spring discharges along seismically active faults (Barnes et al., 1978, Hamilton et al., 1990). Concentrations this high in areas of abundant carbonate would dissolve vast quantities of carbonate, which would re-precipitate when the CO_2 degasses from near-surface groundwater. The general lack of such deposits in association with rabbit-ear anomalies over conductors suggests that transport of elements by CO_2 or CO_2-saturated groundwater cannot be responsible for many of the reported selective leach anomalies.

It is difficult to conceive of any naturally occurring gas other than CO_2 that could be called upon to transport metals or other species from sulphide mineralization as a widespread process. Similarly, other gases would also require high concentrations to exsolve as depth and hydrostatic pressure increase, and are therefore unlikely to be responsible for transport of metals below the water table. Furthermore, in stratified geological environments, gases do not typically move straight up but are trapped by zones of fine-grained sediments. As such, gases below the water table are likely to be dispersed by groundwater and are not expected to form tight, well centred, anomalies immediately over mineralization, nor slightly offset rabbit-ear anomalies, which often show a depletion over mineralization. Carbon dioxide and elevated carbonate content in soils has been used to account for rabbit-ear anomalies in arid environments but have been attributed to direct oxidation of sulphide (Smee, 1998) in what is presumably an unsaturated environment. These anomalies are further discussed below (Section 6.0).

A1.2.4 Electrochemical transport

Characteristic element dispersion patterns have long been recognized over mineralization at certain sulphide deposits and other electronic conductors in bedrock.

These patterns include apical anomalies overlying mineralization or rabbit-ear anomalies that flank mineralization. Anomalous parameters reported include H^+, organic carbon, electrical conductivity and metals. Many authors (e.g., Govett, 1973, 1976; Govett and Chork, 1977; Bolviken and Logn, 1975; Smee, 1983; Govett et al., 1984; Clark, 1996; Jackson, 1995; Bajc, 1998; Hamilton, 1998; Hamilton and McClenaghan, 1998) have attributed these patterns to electrochemical processes.

Although the electrochemical transport models presented in the literature are sometimes conflicting, most are based on the same underlying idea. The conduction of electrons upward, along mineralization, from deep, more chemically-reducing areas results in anomalous electrochemical gradients in the surrounding country rock and overlying overburden. The movement of mass and charge in the form of ions results in the development of geochemical anomalies in the overlying overburden. Different names have been attached to this process including geobattery, oxygen concentration cell, natural galvanic corrosion, oxidation cell and natural voltaic cell.

The primary appeal of using electrochemical transport to explain selective leach anomalies is that it can account for their development in almost any environment, including thick, young, exotic drift. The rate of movement of charged species in an electrochemical field can far exceed that of chemical diffusion, provided the gradient is high enough. Hamilton (1998) determined theoretical transport times through 30 m of clay along a realistic electrochemical gradient to be less than 2000 years for most species. The presence of clay confining units, groundwater flow or saturated/unsaturated conditions should not impede the movement of charge provided an electrochemical gradient exists through overburden as a whole.

All four of the mechanisms described above probably operate to some degree at every site where mineralization is buried and it is possible that any one of them could dominate in selected environments. However, the first three are precluded as major contributors to transport in thick, water saturated Quaternary glacial environments. Since selective leach anomalies are now commonly reported in glacial terrain, electrochemical processes are likely to dominate in at least this environment.

A1.3 Voltaic Cells

Since various authors have referred to the electrochemical mechanism occurring around ore-bodies as a geobattery or natural voltaic cell, it is appropriate to introduce the concept of voltaic cells. Voltaic cells are man-made electrical circuits in which the impetus for current flow comes directly from the chemical energy of partially-separated reactants within the cell. All batteries are voltaic cells.

The basic components of a voltaic cell are a wire, two electrodes and two partially-separated solutions. When the electrodes are placed in their respective solutions and the wire is used to connect them, a spontaneous flow of electrons occurs in the wire from one electrode to the other. The impetus for current flow comes from the difference between the oxidation potentials of the electrodes and the solutions, or between the electrodes and themselves, or between the two solutions in which the electrodes are immersed. A chemical redox reaction occurs between these separated species such that the oxidation half of the reaction occurs in one solution and the reduction half occurs in the other. The partial separation of the solution can be accomplished by a membrane or a salt bridge, which allows an electrolytic connection but does not allow a general mixing of the two solutions. Within the cell, electrical current moves in the form of free electrons in the wire and as ions in the electrolyte.

At the electrodes, ions or neutral species change their oxidation state and either accept from, or discharge electrons into, the electrodes. At the anode, electrons are discharged into the electrodes by conversion of the metallic electrode materials to a positively- charged ion or by conversion of a negatively-charged species to a neutral species or gas or ion with a higher oxidation state. At the cathode electrons are usually discharged into solution by either conversion of a positively-charged ion to a neutral species or gas or by conversion of a neutral species to an anion with a lower oxidation state. In all voltaic cells, there must be reduction of species at the cathode and oxidation at the anode and ions must be discharged, or attenuated, or both, at the electrodes. In order to maintain electrical neutrality the creation of an ion at an electrode must be accompanied by the simultaneous removal of an oppositely-charged ion at the other electrode. To prevent local charge imbalances this process also requires the net migration

of ions away from the electrode at which they are liberated into solution and toward the electrode at which they are attenuated.

In general, anions move toward the anode and cations toward the cathode, and therefore charge can be carried by reduced anions toward the anode and oxidized cations toward the cathode (Hamilton, 1998). However, it is actually the movement of negative and positive charge that results in electrical current between the electrodes and, in some cases, reduced cations can move toward and deposit negative charge at the anode or oxidized anions can move toward and deposit positive charge at the cathode. Examples of this include the movement of Fe^{2+} toward an anode where it loses an electron to become Fe^{3+} and the movement of $Ag(CN)_2^-$ toward a cathode where it is reduced to $Ag_{(s)}$. This apparently paradoxical process of cations moving toward an anode, and anions toward a cathode arises because, in addition to electrical attractive forces acting upon charged species, diffusive forces also play a role according to the Nernst-Planck flux equation (Bockris and Reddy, 1970, p. 398). As charge-carrying species are consumed there is a strong diffusive gradient toward the electrode that results in their movement. There are many species, both positive and negative to which these forces of opposite attraction can apply, but iron species are probably the most significant from a geological point of view.

Figure A-1 shows an example of a voltaic cell. A zinc electrode is immersed in a solution of NaCl and a copper electrode in a solution of $CuCl_2$ with a semi-permeable membrane separating the two solutions. If a wire connects the two electrodes, electrons flow spontaneously from the zinc electrode to the copper electrode because Cu^{2+} is a stronger oxidizing agent than $Zn_{(s)}$. At the copper cathode, Cu^{2+} in the solution is reduced to $Cu_{(s)}$ by electrons that are the product of the simultaneous oxidation of $Zn_{(s)}$ to Zn^{2+} at the zinc anode. The difference in oxidation potential of the two metals results in a differential of approximately 1.10 volts between the two electrodes (assuming equal concentrations of Cu^{2+} and Zn^{2+}). Across the membrane, Cl^- ions must move toward or Na^+ ions away from the anode to redress the loss of negative charge from solution around it and the gain in negative charge around the cathode. In this particular cell, there is a net increase in ionic strength around the anode and a decrease around the cathode. The redox reaction would still occur without the membrane but in the absence of a physical

separation of the solutions, $Cu_{(s)}$ would plate-out on the surface of the zinc electrode and no current would flow through the wire.

An electrolytic cell is similar to a voltaic cell except the electrochemical reactions involved do not occur spontaneously but require the input of current from an external source. Wires connected to each end of a battery and submerged in a suitable electrolyte can represent an electrochemical cell. As with voltaic cells, the creation and/or removal of ions at the electrodes facilitates the transfer of current into and out of solution. If the electrolytes in solution are redox-inert within the stability field of water (e.g., Na^+ and Cl^-) and the voltage is over 1.2 volts, the hydrolysis of water may transfer current at the electrodes:

-at the anode: $\frac{1}{2}\ H_20 \Rightarrow H^+ + \frac{1}{4}O_{2(g)} + e^-$

-at the cathode: $H^+ + e^- \Rightarrow \frac{1}{2}\ H_{2(g)}$

Hydrogen ions are created at the anode and removed at the cathode and during the process oxygen and hydrogen gases are produced at the respective electrodes. If the voltage of the cell is significantly below 1.2 volts then water cannot be hydrolysed. If the electrodes are inert and there are no redox-active electrolytes (i.e., those that cannot change their oxidation state and thereby accept or lose electrons at the electrodes) in solution then virtually no current will flow in the cell.

Many voltaic cells can act as electrolytic cells if a power source is used to reverse the direction of spontaneous electron flow. A lead storage battery, for instance, is a voltaic cell when discharging and an electrolytic cell when being recharged. The two types of cell also differ in a number of other ways. The most fundamental difference is that in a voltaic cell conditions are more chemically reducing around the anode than around the cathode whereas in the electrolytic cell the situation is reversed (Figure A-2). Electrons are "pulled" into solution at the cathode of a voltaic cell by the oxidizing agents in solution whereas they are "pushed" in at the cathode of an electrolytic cell by an external power source. Another difference is the nature of their electrical fields within the electrolyte. In the electrolytic cell, the electrical field is applied; if the current is turned off, the field will dissipate. In most voltaic cells, either the oxidants or reductants or both are dissolved species in separate solutions. As such, the potential field between the two electrodes is not applied but is semi-permanent and results from the differences in

oxidation potential between species in solution, or between these and the electrode materials. Allowing the flow of current between the two electrodes will modify the shape of equipotential lines in the field but does not create the field.

Table A-1 shows the standard electrode potentials of a number of redox half-reactions. Tables of standard voltages can give an approximate idea of the likelihood of redox reactions to occur spontaneously. Standard voltages are a measure of the oxidation potential of half reactions measured against that of the H^+–H_2 half cell. Any reducing agent in the centre column is capable of spontaneously reducing any oxidizing agent in the left-hand column that is lower in the table. Standard voltages are usually calculated for 25° C and assume molar concentrations of all species in solution and partial pressures of 1 atmosphere of all gases involved in the reaction. Concentration changes of up to several orders of magnitude and temperature changes up to several 10s of degrees Celsius have relatively small effect on the voltages in a given reaction. The effect of concentration can be calculated using the Nernst Equation. For the reaction:

$$aA + bB \Rightarrow cC + dD$$

The Nernst equation takes the following form (at 25° C):

$$E = E^0 - \{0.0591/n\} \bullet \log_{10}\{([C]^c \bullet [D]^d)/([A]^a \bullet [B]^b)\}$$

Where E = reaction voltage; E^0 = standard electrode potential of the reaction; and n = number of electrons involved in the redox reaction.

The Nernst equation demonstrates that a change in concentration of the species involved in the reaction does not change the final voltage if the concentrations of all species change by a similar factor. For example, a hundred-fold dilution of the species involved in the Cu-Zn reaction to 0.01 molar still produces 1.10 volts because the ratio of $[Zn^{2+}]/[Cu^{2+}]$ is the same. It takes very large changes in the ratio to change voltage significantly and therefore, it is often acceptable to use standard voltages to qualitatively predict the spontaneity of a reaction. However, a problem arises with the application of this principle in the case of natural reactions that involve either H^+ or OH^-. In nature, a molar concentration of either H^+ or OH^- is exceptionally high relative to a molar concentration of many of the other species that they are likely to react with. As such, the standard conditions used in the determination of standard electrode potentials result in an

exaggeration of the potential concentrations of H^+ and OH^- relative to many other naturally-occurring reactants.

The results of this are particularly apparent when considering the half-reactions involving the oxidation of Cl^- to more oxidized forms such as ClO^-, ClO_3^- and ClO_4^-. Since these substances are above the $O_2 - H_2O$ half reaction (Table A-1), it appears that they are less oxidizing than oxygen. This suggests that dissolved oxygen is capable of spontaneously oxidizing Cl^- and producing $HClO^-$, ClO_3^- and ultimately ClO_4^-. In fact, this is not the case within the chemical realm of natural waters. The only naturally-occurring form of chlorine within the Eh-pH regime of shallow terrestrial waters is Cl^- (Stumm and Morgan, 1970, pg. 320). The confusion results from the over statement of the concentrations of reactants in this equation that is inherent with standard electrode potentials. In this case, the concentration of OH^- is overstated by at least three orders of magnitude, since the upper limit of pH in terrestrial waters is about 11 (Bass Becking et al., 1960). pO_2 is overstated by a factor of five, since the maximum pO_2 in the groundwater environment is the same as the mole ratio of oxygen in the atmosphere, which is about 0.2.

Notwithstanding this, provided the user is aware of these problems, Table A-1 can be useful in the estimation of the approximate voltages of natural reactions. In addition, it can be used to show the range of reactions that could occur in nature and that might be responsible for spontaneous potential currents in the Earth. In the terrestrial environment, materials such as Cl_2 or $Fe_{(s)}$, that are capable of oxidizing or reducing water to O_2 or H_2 respectively, rarely occur in large quantities. Therefore, reducing agents that occur in half-reactions on Table A-1 above the H^+-H_2 reaction and oxidizing agents that occur below the O_2-H_2O reactions are not likely to participate in natural voltaic cells.

In the preceding and following discussions, the effect of kinetics and rate-limiting factors on redox reactions has largely been ignored. Electrode potentials have been treated as the sole factor that will determine whether one reaction is favoured over another. In reality, there are many processes that affect rates of reaction, such as diffusion of species across phase boundaries, high resistance to current flow between electrodes and solution, high activation energies and slow intermediate reactions. Such processes may result in one reaction being favoured over another that has a much higher reaction

potential or in a negligible reaction rate for reactions that might otherwise occur according to their electrode potentials. In the Earth, it is more justifiable to make extrapolations from thermodynamic data than it would be in a sterile laboratory setting because of the ubiquitous occurrence of biological catalysis. In nature, thermodynamic reactions that can occur typically do occur because organisms have developed systems for "piggybacking" on these reactions to obtain metabolic energy from them. Examples abound of biologically mediated reactions in nature that have reaction rates that are orders of magnitude faster than they would have had in a sterile laboratory setting. As a result, in a very general sense, kinetic inhibitors to thermodynamic reactions tend to be minimised in natural environments relative to the laboratory.

A1.4 Spontaneous Potentials in Earth Materials

The existence of spontaneous potentials in the Earth has been known for at least 150 years and their measurement has been used systematically in the search for buried ore deposits since the 1920s (Parasnis, 1979). Spontaneous or "self" potentials (SP) are natural voltage differences between two points in the earth that result in electrical currents in earth materials. They arise largely because of differences in the oxidation-reduction (redox) potential of earth materials.

Spontaneous potentials are useful in mineral exploration because SP anomalies are often associated with electronically-conductive mineralization. The vast majority of these anomalies are negative over mineralization relative to surrounding terrain, which suggests that mineralization acts as a source or conduit of electrons (Sato and Mooney, 1960). Burr (1982) reports that sulphide mineralization in Canada produces negative anomalies of up to 350 mV and that anomalies over 450 mV are usually due to the presence of graphite, which is a far better conductor of electrons. These ranges are in contrast to typical background variations of only a few millivolts to a few tens of millivolts where mineralization is absent (Parasnis, 1973). In thick overburden the contrast between anomalies and background readings decreases to the extent that 100 m or more of overburden can render the SP response due to bedrock features too weak to interpret (Lang, 1956).

A1.4.1 Measurement of spontaneous potential

Theoretically, SP can be measured in two ways. One way involves the use of an oxidation-reduction potential (ORP) meter on samples of Earth materials taken from two areas; the measurement should provide voltage differences that approximate the spontaneous potential between the two areas. An ORP probe, in contact with a moist sample, represents a reversible voltaic cell. The probe is connected to a millivolt meter that can measure the voltage difference between the sample and a half-cell such as Ag-AgCl, which is usually located inside the probe. An inert metal, usually platinum, on the outside of the probe serves as an electrode in direct contact with the sample. A semi-permeable junction of porous glass or ceramic maintains electrolytic contact between the sample and the half-cell. If the sample is more reducing than the Ag-AgCl half-cell (standard electrode potential = 222 mV) then the platinum wire behaves as an anode and accepts electrons from the sample. Inside the probe, electrons are simultaneously provided to Ag^{+} to form $Ag_{(s)}$ on the Ag electrode. If the solution is more oxidizing than the Ag-AgCl half-cell, the platinum behaves as a cathode and the reverse reaction occurs inside the probe. Thus, the ORP readings on the millivolt meter represent a relative voltage difference between the half-cell and the sample. If desired, the Eh of the solution can be obtained from these results by adding to the readings, the voltage difference between the reference cell and the standard hydrogen electrode.

In practice, ORP probes have inherent limitations that often render this approach to SP measurement unworkable. Because platinum is effectively inert, the gain or loss of electrons on the electrode surface necessitates the attenuation of ions from the sample by their conversion to neutral species or to charged species of a higher or lower oxidation state. For the readings to be reproducible, one or more reversible redox-couple such as Fe^{2+} / Fe^{3+}, HS^{-} / SO_4^{2-} or Cu^{2+} / Cu^{+} must be present in solution near the electrode. Since not all redox-active solutions contain such reversible redox couples (Drever, 1982), ORP probes may not always provide reproducible or accurate results (Bartlett and James, 1995). A related problem occurs due to the build-up of deposits on the platinum during these reactions leading to memory effects in the probe when testing other solutions. This causes long-term drift in the readings, particularly when testing a sample of low ionic strength after one with high ionic strength. Furthermore, many natural redox couples have

slow rates of reaction, which also result in slow response and instrument drift during ORP measurement. Consequently, ORP probes are often used to obtain a qualitative idea of the redox composition of waters or sediments but are seldom used to obtain quantitative SP measurements between two areas.

By far the most common way to measure SP is to use a millivolt meter connected between two non-polarising electrodes placed at different points on the ground. A measured voltage difference would usually equal the spontaneous potential between the two points. Non-polarizing electrodes are important because they must be equally capable of receiving and discharging electrons. The type that is almost invariably used for SP surveys is the Cu-$CuSO_4$ electrode. It consists of a copper rod in contact with a saturated solution of $CuSO_4$ that is in electrolytic contact with the ground. The latter contact is accomplished through the use of a wet membrane of asbestos or porous ceramic. If the ground at point "A" is more reducing than at point "B" (Figure A-3), it will have the capability of providing negative charge. Across the membrane of the electrode at "A", anions move up from the ground and/or cations down. Inside the electrode, electrons are provided to the copper by oxidation of $Cu_{(s)}$ to $Cu^{2+}_{(aq)}$. At point "B", which is relatively oxidizing, there will be a tendency for negative charge to discharge into the ground and positive charge into the electrode by the conversion of $Cu^{2+}_{(aq)}$ to $Cu_{(s)}$ at the surface of the copper, and a corresponding migration of cations up through the membrane and anions down through the membrane. There is, therefore, an electrical potential difference between the two areas that is measurable with the millivolt meter and which would result in current in the wire if a direct connection were made.

An important interference often encountered during the measurement of SP using Cu-$CuSO_4$ electrodes occurs due to variable moisture conditions. These can cause false anomalies, which can seriously complicate the interpretation of the survey, especially thick overburden. Wet areas have often been observed to cause high positive readings relative to adjacent areas (e.g., Parasnis, 1979; Burr, 1982). This is perhaps counterintuitive because it appears to imply that wet soils are more oxidizing than unsaturated soils. Burr (1982) attributed higher SP readings in swamps and wet soil to pH effects. Eh, and therefore SP, have a general pH dependency because many natural redox reactions involve hydrolysis. For example, for the half-reactions that involve either the

oxidation or reduction of water, a decrease of 1 pH unit will result in an increase in the Eh of the reaction by approximately 60 mV. Therefore, the higher Eh of peat and moist humus layers is consistent with the fact that these materials are usually more acidic than are mineral soils. Lower electrode-ground resistance has also been noted in moist areas and in humus soil layers relative to underlying mineral soils and has been suggested as a possible contributor to moisture-related anomalies (R.Chaplain, pers. comm., 1998). Streaming potentials as a result of groundwater discharge in low-lying areas has also been suggested as a possible source of SP (Dobrin and Savit, 1988) and could therefore be a source of false anomalies in low-lying areas. Streaming potentials are generated by the movement of water through a porous medium that is capable of ion exchange such as clay or oxides on sand.

Other factors that can affect SP surveys tend to be less significant than the problems due to moisture. Magnetic storms (Burr, 1982), radar and other electromagnetic radiation can cause induction in the long SP wire, particularly when it is fully extended. Telluric currents, which are global-scale electrical currents in the Earth induced by the Earth's magnetic field, could conceivably affect SP surveys but typically result in SP difference of only a few millivolts per kilometre.

The use of SP surveys as an exploration tool has waned since the 1950s with the increasing sophistication of other electrical geophysical techniques such as induced potential (IP) and ground resistivity. Part of the reason is that the interpretation of these non-passive techniques is easier because electrical and electronics theory can be applied. Since the causes of natural SP above mineralization are still widely misunderstood (Hamilton, 1998), the interpretation of the results of SP surveys is difficult.

A1.4.2 Sources of spontaneous potential

All moist Earth materials contain redox-active species such as $O_{2(aq)}$, Fe^{2+}, HS^-, OH^- and H^+, which impart a bulk redox capacity, or Eh if measured against the H^+-H_2 half-cell, to the soil or groundwater. The variable chemical composition of overburden, groundwater and rock therefore results in variable redox capacity which, in turn, results in spontaneous potential voltages and currents between different points in the Earth. The multitude of potential processes that affect the composition of Earth materials and might

thereby affect redox processes could be divided into primary lithological and surficial processes.

Primary lithological processes are defined as all those that contribute to the variable composition of rock. They result in specific lithologies and mineral accumulations in various places in the upper crust. The mineral assemblages in these materials can impart a redox potential to the groundwater/rock matrix with which they are in contact and can result in a characteristic redox signature for various rock types and mineral accumulations. For example, the presence of large amounts of gypsum in carbonate rock can fix the equilibrium Eh of the groundwater/rock environment to no lower than approximately -275 mV, which is the Eh of the SO_4^{2-} - HS^- half cell (at pH 8 and using certain other assumptions; Garrels and Christ, 1965, p. 215). In this environment, species that can impart a lower Eh are unlikely to be present because most of the reducing agents capable of reducing SO_4^{2-} to HS^- would already have been consumed. However, the Eh can be greater than -275 mV because SO_4^{2-} is the only geologically important sulphur species in oxidized environments (Krauskopf, 1979), where its redox behaviour is relatively inert (Bartlett and James, 1995), and therefore it adds little to the redox-buffering of oxidized systems.

Processes such as these can occur due to mineral assemblages or dissolved species in many other rock types. In unweathered pyritic rocks, Eh is typically maintained below the sulphide oxidation half-cell. Ferrous olivines and clinopyroxenes in ultramafic rocks undergoing weathering can produce very reducing conditions that approach the limits of water stability (around -400 mV at pH 11; Barnes et al., 1978). The presence of dissolved oxygen in oxygenated terrestrial waters typically maintains Eh at a fairly high empirically-observed level of over 200 mV. The empirical limit is used because there is no perfect correlation between dissolved oxygen concentration and Eh, probably due to the myriad biological and inorganic processes that involve oxygen. There is, however, a general relationship between the presence of dissolved oxygen and high Eh to the extent that most oxygenated terrestrial waters are found to have an Eh of between 200 and 400 mV. The upper limit of geologically observed Eh is around 800 mV and the theoretical electrical potential of oxygen is higher still at 1000 mV at pH 4.0 (Figure A-4).

The presence of water itself restricts the Eh of aqueous systems to a well-defined stability field. Figure A-4 shows the theoretical and empirical stability fields for water in natural environments. As shown in Table A-1, reducing agents that are more reducing than $H_{2(g)}$ rarely exist in the shallow terrestrial environment because their oxidation by abundant water would have occurred long ago. However, as crustal thickness increases, water and other volatile fluids are excluded from the geological environment and this allows more reduced Eh conditions. The mineral assemblages of rocks formed in these environments often reflect their low-Eh origins. The rare production of $H_{2(gas)}$ due to the reduction of water by minerals has been noted in groundwater interacting with ophiolite sequences (Barnes et al., 1978; Clark, 1987), and demonstrates the very reducing nature of some rocks that form in water-poor environments. Groundwater from kimberlites (author's unpublished data) shows Eh and pH conditions that also border the lower limits of water stability.

This process of mineral-water reactions fixing the Eh of groundwater is loosely referred to as redox buffering (Drever, 1982). However, the slow rates of reaction of many redox processes rarely result in mineral-water solutions that approach chemical equilibrium as do most pH buffering reactions. Consequently, most natural redox processes are in a state of disequilibrium and therefore one can only generalise about the outcome of most redox-buffering processes. Non-equilibrium kinetics play a major role in almost all natural redox processes, especially those involving oxygen, the most geologically important oxidizing agent.

Surficial processes that affect the redox composition of Earth materials include: weathering, drainage, groundwater movement, mechanical mixing and dispersion of rock material, soil formation, the accumulation of organic material and biological processes. There is an almost unlimited number of ways these factors can combine to affect the composition of Earth materials and therefore to affect local redox conditions. However, the processes that are most likely to locally affect redox can be simplified.

The principal oxidizing agent on earth is free oxygen ($O_{2(g)}$), for which the only significant terrestrial source is plant photosynthesis. The only appreciable source of oxygen to the geological subsurface is the atmosphere, which contains 21% oxygen. Since redox variability in shallow Earth materials cannot be due to variations in the

primary source of oxidizing agents, it must be due to: (1) kinetic processes which limit the transfer of oxygen into the subsurface; and/or, (2) processes that control the consumption of oxygen (i.e., that control the availability of reducing agents)

The primary limitations on the transfer of oxygen into the subsurface are its solubility in water and its slow rate of aqueous diffusion. In the fully-saturated groundwater environment below the water table, the concentration of oxygen has an upper limit from which it can only decrease. Its solubility limits the concentration to a maximum of about 10 ppm at 25°C. In contrast; the maximum concentration of gaseous oxygen in the vadose zone is limited only by its molar ratio in the atmosphere and can therefore reach 210,000 ppm. This enormous disparity demonstrates why moisture content is the single most important factor controlling the availability of oxygen in a geological environment (it also demonstrates why subaqueous disposal of sulphidic mine tailings is so effective in preventing their oxidation). In many subsurface environments, the water table represents a sharp redox boundary between abundant oxidizing agents above and abundant reducing agents below. This is particularly true in young, exotic overburden.

Most of the other surficial factors controlling local redox conditions involve processes that control the availability of reducing agents. Chief amongst these is the accumulation of organic matter. All forms of organic matter are reducing relative to oxygen and most can be oxidized fairly quickly in Earth materials by microorganisms. As such, the oxidation of organic matter is one of the primary consumers of oxygen in the shallow subsurface. Typically, higher concentrations of organic matter in soils lead to more reducing conditions, particularly in saturated environments. Also important is the lability (i.e., availability to microorganisms as a source of metabolic energy) of the organic matter. Well-humified peat would not be as chemically reducing as methanogenic organic muck collected from a perpetually submerged portion of a bog because the former has already undergone oxidation of its most labile organic components.

The other major consumer of oxygen in the shallow subsurface is the oxidation or weathering of mineral matter and particularly, of metallic sulphides. Areas of unusually active weathering, due either to larger accumulations or to more reactive minerals, would

typically result in an enhanced consumption of oxidizing agents relative to surrounding areas and to more negative redox conditions. The dispersion of the dissolved products of weathering, such as Fe^{2+}, can affect redox conditions at some distance from the source.

All forms of mechanical dispersion of rock material can affect the availability of reducing agents. Continental glaciation results in the widespread deposition of relatively unoxidized rock, till, clay and other drift materials over vast areas. Different deposit types (e.g., sand, clay) resulting in different permeabilities in transported materials can also lead to higher or lower water tables and variable rates of percolation of oxygenated groundwater. This can result in a poorer availability of oxidizing agents in fine-grained deposits as compared to coarse-grained material. Generally, in older terrain with deep weathering profiles, such as laterite, there is a greater availability of oxidizing agents in shallow areas because most reducing agents have already been consumed.

Finally, both temperature and pH variations can also affect redox reactions. Significant horizontal temperature variations in the earth are rare over short distances but vertical temperature gradients are ubiquitous. However, the effect of temperature on Eh is fairly small and, since vertical geothermal gradients are locally quite uniform, their effects on redox reactions will not be considered here. On the other hand, pH does vary significantly over short distances. Redox reactions that involve either H^+ or OH^- in either the reactants or product will be affected by pH and this is the case in many, though not all, natural redox reactions.

Surficial and bedrock processes control the local balance of oxidizing versus reducing agents in the shallow subsurface. The result, in young surficial environments, is an electrochemically inhomogeneous shallow subsurface with local redox gradients almost everywhere. These represent fields of electrical potential (SPs) between the local sources of oxidizing and reducing agents and along which ions will have a tendency to move. This movement of redox-active ions is consistent with the universal tendency of chemical systems to approach maximum entropy. In the long term, and therefore in older deposits, it results in increasing local homogenization of redox conditions in the shallow subsurface and a tendency for local conditions to approach the larger redox trend that overprints all redox processes, i.e., the redox stratification of the earth's crust.

A1.4.3 Redox stratification in the earth

An upward increasing redox stratification exists in the Earth's crust (Bass Becking et al., 1960; Bolviken and Logn, 1975). This redox field results from the process of oxygen re-supply by the atmosphere overriding the general tendency toward redox homogeneity (maximum entropy) and establishing of an overall vertical gradient between the oxygenated surface and mineralogical reducing agents deep in bedrock. Subject to the limitations described, the upper limit of this Eh field is fixed by the electrical potential of oxygen at the lowest geologically reasonable pH (around +1000 mV – Figure A-4). The lower limit is usually considered to be the lower limit of water stability at the highest geologically reasonable pH (around -400 mV – Figure A-4). Indeed, rocks from the lower crust and upper mantle appear to have formed in Eh environments that are at or slightly below the Eh stability field of water. This 1400 mV spread represents the maximum potential redox differences to be expected due to naturally occurring redox-active substances in the Earth's crust. It is consistent with the fact that the vast majority of spontaneous potential measurements, which are below 1500 mV (Sato and Mooney, 1960).

Almost any natural redox-active substance that can exist in the Eh stability field of water could potentially contribute to this redox gradient. Natural terrestrial materials more oxidizing than oxygen are virtually non-existent and consequently natural redox reactions that oxidize oxygen in water to O_2 typically do not occur. Oxidizing agents are therefore likely to be restricted to oxygen and electrochemically-weaker oxidative species such as Fe^{3+}, Mn^{4+}, SO_4^{2-}. Geological materials more reducing than water do exist but the natural reduction of hydrogen in water is rare in the zone of meteoric groundwater and occurs only under exceptional circumstances (e.g., Barnes et al., 1978; Clark, 1987). As a result, reducing agents are likely to be less reducing than $H_{2(g)}$ and could include reduced aqueous sulphur species (e.g., HS^-); reduced sulphide minerals (e.g., pyrrhotite); mafic or ultramafic minerals (e.g., ferrous olivines and pyroxenes) or their dissolved products, and hydrogenous organic matter.

An electrochemical gradient such as occurs in the Earth's crust represents a field of electrical potential in an electrolyte. This gradient induces the movement of ions (Figure A-5) and results in an electrolytic charge transfer between deep and shallow areas

(Bolviken and Logn, 1975; Hamilton, 1998). Negative charge-carrying redox active ions tend to move upward toward more oxidizing Eh conditions and positive charge-carrying ions tend to move downward toward a more reducing environment. The ion migration is analogous to movement of charge-carrying ions toward the electrodes of a voltaic cell.

In order for charge transfer to occur, ion movement must be accompanied by redox reactions that attenuate some or all of the migrated species. All of the charge-carrying species would have a particular Eh range within which they are stable in groundwater, and a particular Eh limit beyond which they are likely to become attenuated and thereby pass on charge to other species (Figure A-5). As such, the reactions that transfer charge from the migrating ions are likely to occur all down the gradient from deep in the crust to ground surface. The movement of redox inert species such as Na^+ and Cl^- is also likely to occur in the Earth's redox field, as it does in a voltaic cell to prevent local charge imbalances. However, this movement is in response to the migration of redox-active species and the resultant redox reactions and therefore does not cause the transfer of electrical charge but rather results from it (Hamilton, 1998).

This electrical current that is inferred to exist between shallow and deep areas in the Earth's crust must be subtle but ubiquitous. The upward movement of negative charge is a kinetic process and counteracts, to some extent, the continuous supply of oxidizing agents to the shallow subsurface from the atmosphere. However, deep weathering profiles in arid environments in which the majority of mineralogical reducing agents have been consumed suggests that this process is not static but favours the long-term consumption of mineralogical reducing agents.

A1.5 Spontaneous Potential Cells

A1.5.1 Ohms Law in the development of cells

Current density at low voltages in an electrical medium is governed by Ohm's Law:

$$E = r \cdot j;$$

where E is electrical field strength, or voltage gradient, in V/m; r is resistivity, or electrical resistance per unit length of medium, ohm•m; and j is current density, or

electrical current per unit cross-sectional area, in amps/m^2. This simple equation states that in an electrical field, current density will increase if either the voltage gradient or the electrical conductivity (i.e., the inverse of resistivity) increases within the medium.

The term cell, when used in a laboratory electrochemical context refers to a system through which electrical current passes and which has two connectable electrodes immersed in an electrolytic conductor. In a voltaic cell, electronic current is spontaneous and therefore, to induce current through the wire joining the electrodes, there must be physical separation of oxidizing and reducing agents in the solution. The redox field in the Earth represents an electrolyte within which there is vertical separation of oxidizing and reducing agents. For the purpose of the following discussion an SP cell is defined here as a natural system that induces the spontaneous, long-term flow of electrical current in a focused area within the earth, i.e., the current flux has to be anomalous with respect to background current.

Although there must be constant ionic current in the Earth's redox field, cells as just defined can only develop due to major inhomogeneities in either the electrical conductivity of Earth materials or the SP gradient in a particular area. Indeed the development of earth cells of this type is entirely predictable by Ohm's law. If an area of increased electrical conductivity occurs across an otherwise uniform voltage gradient, an increase in current density in that zone must also occur. As discussed below, a vertically-oriented geological conductor crossing horizontal redox equipotential lines in the Earth is one example of such a system. Likewise if an area of increased voltage gradient occurs in a medium of uniform electrical conductivity, an increase in current density must also occur. Examples of this type of cell are also discussed below.

The term conductor, when used in a geological context usually refers to electronically conductive or semi-conductive materials in bedrock, such as graphite or metallic sulphide mineralization. These substances do conduct electricity far better than low-porosity silicate or carbonate bedrock. However, they are typically poorer conductors than most groundwater saturated overburden. Part of the reason that this fact is not widely recognized among geologists is that the electrically conductive properties of groundwater and bedrock have typically been expressed in inverse ways. The electrical conductivity of groundwater is most commonly reported in conductivity units whereas

the conductive properties of bedrock are reported in resistivity units. Table A-2 shows the electrical conductivities of some typical groundwaters and those of a number of common bedrock materials converted from their usual resistivity units. It is evident that, very few common bedrock conductors begin to approach the electrical conductivity of most groundwater. Overburden is usually more electrically conductive than the groundwater within it because of the additional conductivity imparted by clay minerals and oxide surfaces (Keller and Frischknecht, 1966). This demonstrates that the electrical conductivity of overburden far exceeds that of low-porosity bedrock and usually also exceeds that of most bedrock "conductors".

A1.5.2 Cells associated with electronic conductors in bedrock

Geobatteries centred on electronically conductive, steeply dipping mineralization have been described for many years and most geologists are aware of their existence. However, several widely referenced geochemical models developed to account for SP cells in the Earth were based on a fundamental false premise. The problems stem from the fact that most authors (e.g., Bolviken and Logn, 1975; Govett, 1976; Sivenas and Beales, 1982; Smee, 1983; Clark, 1997), inadvertently or otherwise, saw the conductor itself as the voltaic cell. This led to models involving self-polarising conductors that generated their own electrical field within the Earth's redox field (Fig. A--6). When considering the conductor and the earth electrolyte as a whole, the result was an electrolytic cell, not a voltaic cell. Hamilton (1998) provided an in-depth treatment of the theoretical problems with some of these models.

There are two models for the development of SP cells around electronically-conductive mineralization that are considered here to be theoretically sound. They are the reactive groundwater model and the reactive conductor model. Each developed separately for different geological environments and in neither case do the authors address both sets of processes when developing their models. However, they are in no way mutually exclusive and probably represent end-members of the types of cells that can occur around conductive ore bodies.

Sato and Mooney (1960) proposed a reactive groundwater model for the development of SP cells that, in effect, put to rest several decades of debate on the origins

of negative SP centres over conductive mineralization. They carried out a critical review of existing hypotheses and used geophysical theory to establish a mechanism that accounted for the commonly-observed spontaneous potential phenomena around single-phase mineralogical conductors. The greater oxidation potential in the near-surface groundwater-bedrock environment relative to the deep environment was postulated to result in upward movement of electrons through conductive mineralization (Figure A-7). At the surface of the conductor, oxidation of reducing agents in deeper areas provides electrons to the conductor, allowing the simultaneous reduction of oxidizing agents in shallower areas where electrons are received from the conductor. For a single-phase conductor, oxidation or reduction of the electronic conductor itself does not contribute directly to the process that results in spontaneous potential currents, i.e., does not contribute to the remote transfer of electrons from one area of the conductor to another. If the conductor were the reducing agent it would oxidize in its upper part, where oxidizing agents are more abundant, negative current would not move along its length from depth and there would be no resulting spontaneous-potential phenomena associated with the conductor. Oxidation of the conductor takes place as a local detached redox phenomenon that does not contribute directly to spontaneous-potentials.

The movement of electrical current along the conductor necessitates the mass transport of ions in groundwater to, or away from, the electrodes to deposit charge and/or to prevent local charge imbalances caused by the production or deposition of charged species. In general there will be a migration, from surrounding areas, of positive charge toward (i.e., negative charge away from) the upper part of the conductor and negative charge toward (i.e., positive charge away from) the lower part of the conductor.

Thus, the conductor functions as both the electrodes and the wire in a natural voltaic cell connecting the cathodic part of the conductor near surface with the anodic part in the deeper environment. The reactants are solid-phase and dissolved constituents in the low-Eh and high-Eh environments that respectively surround the anode and cathode. The difference in oxidation potential of the reactants arises from the ubiquitous redox gradient that exists in the Earth's crust. The conductor provides a less resistive route to upward flow of negative current from depth and concentrates the background current, thereby short-circuiting the redox field. The conductor and redox field combined

represent the voltaic cell; without the redox field, there would be no reactants; and without the conductor there would be no focusing of current and hence, no cell.

The consumption of oxidizing agents around the upper part of the conductor results in more reducing conditions immediately around the top of the conductor than occurs in adjacent areas (Hamilton, 1998). Likewise, locally-anomalous oxidized conditions develop around the bottom of the conductor because of the consumption of reducing agents. However, conditions can never become as reducing at the top of the conductor as they are at the lower end or all current would cease. The result of the process is to modify the shape of the redox field around the conductor (Figure A-7). This also modifies the lines of current flux since, in isotropic media, current moves perpendicular to lines of equal potential.

The specific redox half reactions that result in current flow through the conductor are of less importance than their aggregate effect on voltage. The stability field of water restricts the overall voltage of the cell to less than 1500 millivolts. Redox reactions involving the reduction or oxidation of water, such as occur in most electrolytic cells, are unlikely to be part of the SP charge-transfer mechanism despite contrary statements by some authors (Bolviken and Logn, 1975; Sivenas and Beales, 1982; Clark, 1997).

Electrochemical cells after the model of Sato and Mooney (1960) develop due to zones of anomalously high electrical conductivity in Earth materials in what would otherwise be a roughly uniform vertical redox gradient. The issue of the conductor being electronically conductive is, perhaps, a red herring. A zone of fault gouge made up of water-saturated rock flour and phylosilicates could conceivably have a very high electrolytic electrical conductivity, especially relative to surrounding poorly-fractured rock. This should also develop a significant electrical current within it, provided an upward-increasing redox gradient also exists.

Two hidden assumptions implicit in the model of Sato and Mooney (1960) are: (1) that the conductor consists of a single phase such as graphite or pyrite; and, (2) that oxidation of the conductor would result in its conversion to a non-conductive phase. Thornber (1975) presented a model in which the conductor itself is the reducing agent, which is in apparent contrast to the model of Sato and Mooney (1960). However, the reactive conductor model is based on the presence of one oxidized and at least one

reduced phase, both of which are electronically conductive. Such scenarios have been noted in terrain with deep weathering profiles due to the phase conversion of reduced sulphide minerals to a more oxidized form.

A sulphide body containing pyrrhotite in its lower part and pyrite in its upper is an example of such a cell (Figure A-8). Pyrrhotite at the boundary between the two phases oxidizes to form pyrite, which remains electronically conductive. Electrons liberated into the sulphide mineralization move up toward the more oxidizing environment and allow the reduction of oxidizing agents in the area surrounding the upper part of the conductor. The anodic half-reaction at the pyrrhotite/pyrite interface is (Thornber, 1975):

$$Fe_7S_8 \Rightarrow 4FeS_2 + 3Fe^{2+} + 6e^-$$

Electrons pass into the conductor and positive charge into the groundwater environment in the form of Fe^{2+}. For every mole of pyrrhotite oxidized at the anode, 3 moles of Fe^{2+} are released into the groundwater electrolyte. Groundwater around the anode acts merely as an electrolyte that accepts positive charge from the sulphide anode. The redox potential of groundwater in contact with the anode does not directly affect the process but must be sufficiently low to prevent the oxidation of Fe^{2+} to Fe^{3+}. If it were not, the groundwater would directly oxidize the pyrrhotite or even the pyrite, there would be no separation of oxidizing and reducing agents and hence no SP cell.

At the upper, cathodic end of the cell, groundwater has a similar role in the SP process to its role in the reactive groundwater model; i.e., it provides oxidizing agents that consume negative charge originating from the conductor. Therefore, the movement of ions should be similar to that occurring around the top of the reactive groundwater model. At the anodic pyrite/pyrrhotite interface, Fe^{2+} moves away carrying charge upward along the increasing redox gradient and presumably oxidizes forming a gossan when it reaches the water table. It is unlikely that Fe^{2+}, generated at the anode would migrate toward the cathode in any redox-active role. There are two reasons for this. First, in the groundwater environment, Fe^{2+} is redox-inert with respect to reduction and only by oxidation can it pass on charge. Secondly, the cathode, like the anode, must be at least as reducing as Fe^{2+}, otherwise the sulphide would be locally oxidized in its upper end and no SP phenomenon would result.

The pyrrhotite-to-pyrite reaction is just one example of a process that could generate such a cell. Another is pentlandite to violarite (Thornber, 1975) and there are many other possibilities. The differentiation of a sulphide into oxidized and reduced phases in the upper and lower portions respectively is, in itself, a product of the operation of this type of cell. If subjected to long term oxidation, a deep pyrrhotite body will slowly oxidize to pyrite as the pyrrhotite/pyrite boundary progresses downward. These cells therefore require a deep weathering profile where: (1) there has been abundant time for the oxidized/reduced sulphide front to migrate downward; and, (2) most species in the bedrock/groundwater environment surrounding the conductor that are more reducing than the reduced species (e.g., pyrrhotite) have already been consumed. As such, one would expect the development of cells such as these in old geological terrain but not in younger terrain such as continentally-glaciated areas. However, the reactive groundwater and reactive conductor models may be end members and probably both operate to some degree wherever conductor-based cells occur.

A1.5.3 Cells in the absence of electronic conductors

Virtually all discussion in mineral exploration regarding SP cells and associated electrochemical phenomena assumes the presence of an electronic conductor. There has been little discussion of voltaic cells that involve no electronic conduction, but these cells undoubtedly exist. The nervous systems and muscles of organisms use the transfer of purely ionic current with no electronic conduction. Spontaneous potentials in the absence of electronic conductors have long been recognized in the petroleum industry and result from salinity and redox differences between strata. The presence of spontaneous potentials has also been noted in relatively thick overburden overlying mineralization in the absence of an overburden conductor of electrons (Burr, 1982). Since electrons cannot move freely in an electrolyte solution, many of these cases must involve electrochemical cells of sorts in which current is transferred exclusively in the form of ions.

Two types of SP cells have been postulated to develop in media with presumably homogenous resistivity. These are SP cells over bedrock mineralization and deep-hydrocarbon based cells in bedrock. These cells are not centred on zones of elevated electrical conductivity but rather on zones of elevated SP (voltage) gradient.

In both the reactive groundwater and reactive sulphide models, the impetus for electronic current flow in mineralization comes from the redox differential between the oxidized groundwater environment surrounding the upper part of the conductor and reducing agents in contact with its lower part. The upward movement of electrons consumes oxidizing agents in basal overburden and results in the development of a negative redox anisotropy in groundwater-saturated basal overburden over mineralization relative to the surrounding overburden over country rock. whilst electronic current continues, there must be continual outward dissipation of negative charge into surrounding overburden; otherwise the build-up of reducing conditions around the top of the conductor would eliminate the voltage differential and current would cease. Once solid-phase oxidizing agents are consumed, this dissipation of negative charge must take place by the outward migration of reduced ions away from, or the inward migration of oxidized ionic species toward, the cathode. This process is necessarily coupled with oxidation-reduction reactions, occurring between the top surface of the conductor and the water table, that involve both reduced and oxidized species. The dissipation of negative charge away from the conductor is accomplished as the oxidation states of reduced species change during this process, resulting in dissolved, gaseous or precipitated products that have a higher redox potential than the reduced reactants.

Figure A-9 provides a hypothetical example of the possible outcome of this process in young, exotic sediments. Figure A-9a depicts a fine-grained glacial material, shortly after deposition, in which a background redox differential of 150 mV exists between groundwater at the water table and in basal overburden units. An electronically-conductive, steeply dipping mineral deposit occurs in bedrock. More reducing conditions immediately above the conductor result in a redox differential of 300 mV between the top of mineralization and the water table. Spontaneous potential contrasts exceeding 150 mV between conductive mineralization and adjacent rock have often been reported (e.g., Pflug et al., 1996; Bolviken and Logn, 1975).

At the time of overburden deposition, a very strong vertical redox gradient exists just above the bedrock conductor along which ions would have a tendency to move. The outward movement of reduced ions such as HS^-, Fe^{2+} or $S_2O_3^{2-}$ result in the migration of a reduced front away from mineralization. At the front, reduced ions come in contact with

oxidizing agents and redox reactions would take place, thereby dissipating negative charge away from the conductor. Once the front reaches the water table, a reduced column will have developed in the groundwater-saturated overburden above mineralization.

If the capacity for electrical current in the conductor was high, the production of reduced species might exceed the capacity of the unsaturated zone above the column to provide oxygen across the water table phase boundary. In this case, the column would probably widen out. As it widens, the surface area exposed to oxidizing agents along the entire reducing front increases. Once the column diameter was sufficiently large, the capability of the water table phase boundary and surrounding overburden to provide oxidizing agents equals that of the conductor to provide negative charge. The supply of oxidizing and reducing agents would therefore be balanced and a steady-state kinetic equilibrium is established between the two processes within the cell. The equipotential lines around the column above the conductor cease to move outward and their previously-horizontal configuration becomes nearly vertical in the vicinity of the reduced column. The end result would be a permanent Eh anisotropy in overburden between the conductor and the water table due to the upward propagation of the redox anisotropy from the bedrock surface. In the fully-developed column (Figure. A-9b), electrical current must become focused at the flanks of the column because the SP gradient is stronger in that direction than it would be in the vertical direction.

For every electron passed upward along the conductor, a corresponding amount of reduced species must move away from, or oxidized species move toward, the conductor. This continual migration of redox-active species must be coupled with redox reactions in order to transfer charge. If redox equipotential lines are totally static, the production of reduced species at the conductor must be accompanied by the simultaneous consumption of reduced species somewhere between bedrock and the water table. This would result in the almost instantaneous transfer of electrical current despite the much longer time required for mass transport of reduced species to the ground surface (see discussion on ion mobility, below).

There are many redox-active ions that could potentially carry charge including abundant reduced anionic sulphur species and ferrous iron. The migration of cations and

anions occurs simultaneously and must be exactly balanced, after accounting for precipitation and other fixation reactions, in order to maintain macroscopic charge balance in all parts of the groundwater environment. The migration of redox-inert ions (such as Na^+ and Cl^-) may play a role in maintaining charge balance in some part of the cell.

The model just described was proposed by Hamilton (1998) to account for selective leach geochemical anomalies over conductive mineralization in high-water table Quaternary glaciated terrain. It should, however, be applicable in most overburden environments that meet the main criterion for the development of such a cell, i.e., that overly a redox anisotropy on the bedrock surface. The presence of any geological unit that is strongly reducing relative to surrounding rock should result in an overburden cell. Indeed, the association of reduced bodies with field data that suggest electrochemical activity has been made in the past (Clark, 1996, 1997). Potential reduced sources of such cells are discussed in this appendix.

Since at least the late 1970s, very large-scale, low voltage SP current fluxes have been thought to occur in close association with petroleum reservoirs. Pirson (1981) attributed these to the reducing action of hydrocarbons in seepage areas above petroleum reservoirs. All petroleum reservoirs have overlying seepage areas of varying size, as evidenced by drill cuttings. These areas are attributed to the movement of fluids (mainly water) carrying trace amounts of hydrocarbons upward through microfractures in the shale as part of the early compaction process and later due to lithostatic pressure. Core logging technology and experimentation (Tomkins, 1990) has revealed that these areas are strongly reducing due to the cracking of long-chain hydrocarbons by natural zeolites in the shale. This creates around most reservoirs an envolope or bag of negative charge that extends over a hundred metres above and a few metres below the petroleum-bearing horizons (Tomkins, 1990).

Pirson (1981) provided core-log evidence that large-scale electrical gradients are established between the reduced zone above the reservoir and the more oxidized zone in the shallow subsurface and referred to the process as a "redox cell". Tomkins (1990) further developed this model by reviewing many of the commonly-associated physical features of petroleum reservoirs and unifying them into a single model based on a central

redox-cell overlying the reservoir. Such physical features include areas of darker surface discolouration relative to the more oxidized plain surrounding the oil zone, metal anomalies in a halo around the petroleum zone, magnetite and magnetic sulphide mineralization above the zone, calcareous cementation above the reservoir and uranium deposits flanking it. He also attributed leakage of gases such as CO_2, He and Rn to redox processes but did not clearly indicate how these related to the cell. Tompkins (1990) considered current in these oil reservoir-based cells to be maintained by ongoing seepage and cracking processes. He cites other sources as having determined that depletion of the petroleum reservoir results in a reversal of hydrostatic gradients above the reservoir that cuts off the upward seepage of hydrocarbons and effectively "shuts off" current flow.

This redox cell of Pirson (1981) and Tomkins (1990) has sources of oxidizing and reducing agents that are separated in space and also has a zone of apparently elevated current between the two sources, although, to the author's knowledge, this current cannot be measured directly. Despite the enormous scale (kilometres in depth), this clearly represents an SP cell of the type based on an area of elevated voltage gradient, not increased electrical conductivity. Their model implicitly assumes an upward increasing redox gradient in place above the petroleum reservoir, along which negatively charged species move.

The redox environment in the country rock surrounding the reservoir is likely to be less reducing than the reservoir itself; otherwise there would be no redox differential and no cell could develop. It must, however, be significantly more reducing than ground surface or current from the reservoir would not flow up but rather laterally outward. Since the lower limit of the aqueous redox field in the Earth is limited only by the redox stability of water, the downward decreasing redox field should re-establish itself at some point below the reservoir. This scenario should produce equipotential lines and ionic current patterns similar to those shown on Figure A-10. It should be possible for both anionic and cationic species to move upward along this gradient provided they carry negative charge. Figure A-10 is hypothetical and it should be noted that the ionic current configuration is not similar to that of Pirson (1981, Figures 13 & 14), nor is the equipotential line distribution the same as what he inferred. Tomkins (1990, Figure 1) showed no equipotential lines and no current flow lines.

A1.5.4 Field evidence for the presence of cells

The four models of SP cells described above were developed independently in different disciplines of Earth science for different reasons. However, they all address field evidence that is best explained with electrochemical interpretations. The model of Sato and Mooney (1960) was developed to resolve many conflicting theories in the geophysical community as to the origin of spontaneous potential phenomena occurring over conductive sulphide deposits and graphite. The model of Thornber (1975) was developed based partly on mineralogical evidence from supergene enriched nickel deposits to: (1) better understand the process of supergene enrichment; and (2) improve exploration techniques for this type of deposit. The model of Hamilton (1998) was developed to account for selective leach geochemical anomalies that occur over gold and base metal deposits in thick (>30m), young (~8 Ka), water saturated glacial deposits that could not be accounted for by any other transport mechanism. The model of Pirson (1981) and Tomkins (1990) was developed to link together, in a single genetic model, observed geochemical and geophysical phenomena that had been known for many years to occur over petroleum reservoirs. All four of these models involve a redox cell localised over a geological source of reducing agents.

"Rabbit-ear" anomalies has been attributed to electrochemical processes and were first recognized over conductive mineralization in shallow glacial overburden environments (Govett 1973, 1976; Bolviken and Logn, 1975; Govett and Chork, 1977; Nuutilainen and Peuraniemi, 1977; Smee, 1983). They have since been recognized over much thicker glacial overburden (Jackson, 1995; McClenaghan et al., 1997; Bajc, 1998). They also occur in temperate non-glacial and tropical areas and are very commonly reported in arid to semi-arid environments (e.g., Govett et al. 1984, Govett and Atherden, 1987; Clark, 1996, 1997; Smee, 1998). Where rabbit-ear anomalies are reported, usually apical anomalies of other elements are noted also. Anomalies in metals are most commonly reported because it is usual to determine metal concentrations in mineral exploration surveys. However, where H^+, electrical conductivity and anions have been measured these parameters have often been found to have similar anomalous patterns. Apical and rabbit-ear patterns are almost invariably centred directly over mineralization or other geological features such as faults (Clark, 1997; Bajc, 1998).

Where corresponding SP data are available at sites, rabbit-ear anomalies usually correlate with central SP lows over mineralization (Bolviken and Logn, 1975; Govett, 1976; Govett and Chork, 1977; Smee, 1983; Hamilton and McClenaghan, 1998). Until recently, the third-dimensional shape of such SP anomalies was not known and this led to various interpretations of current flow-patterns and ion movement. A recent cross-sectional study (Hamilton and McClenaghan, 1998) involved down-hole SP in thick (30m) glacial overburden overlain by a peat-bog and underlain by graphitic-argillite hosted gold mineralization. The results show equipotential lines and inferred ion flow patterns that closely follow the model of Hamilton (1998) and that correlate with apical and rabbit-ear geochemical anomalies in shallow groundwater and peat. It was concluded that these cells should occur wherever the presence of conductive mineralization results in redox anomalies on the bedrock surface.

Part of the reason overburden cells such as these have not been recognized in the past might be that they would be extremely difficult to detect in the vadose zone. Much higher contrasts are expected between redox conditions inside and outside the column below the water table than would occur above the water table where oxidizing agents are abundant and far more mobile. As such, the cells would develop best in areas of high water table and in these areas SP surveys have traditionally not been carried out because of false anomalies that occur due to variable moisture content and pH. This is not to suggest that the cells cannot exist in the unsaturated zone; they are just likely to be subtler. The presence of SP lows on surface above mineralization in areas of thick unsaturated zone (Parasnis, 1979; Burr, 1982; Govett et al. 1984) suggests that oxidizing agents are consumed and that cells, as defined above, can also exist in the unsaturated zone.

There is abundant field evidence for the existence of SP cells over petroleum reservoirs. Indeed this evidence itself was used to find petroleum reservoirs for almost 100 years before the cells were recognized. It includes gaseous and liquid hydrocarbon seeps, paraffin deposits, halo-type metal anomalies, iron and manganese deposition, carbonate cementation, hard drilling areas, magnetic anomalies (associated with magnetite mineralization) and uranium concentrations (Tomkins, 1990).

A1.6 Geochemical Response to Spontaneous Cells

A1.6.1 Ion mobility

One of the problems with the understanding of surface selective leach anomalies is their development in thick, young deposits. Glacial materials in Canada only 8000 years old have well developed surface anomalies spatially associated with underlying mineralization. As argued above, diffusion, gaseous carriers and advective groundwater transport can be ruled out as the primary transport mechanisms in these environments because they are too slow to account for most anomalies. The rate of movement of charged species in an electrical field, however, can far exceed the rate of other dispersion mechanisms. Ionic migration rates in an electric field are described by the equation (Webber, 1975; Glasstone and Lewis, 1960):

$$s = (\lambda_+/F) \bullet (V/d);$$

where:

s = ion velocity

λ_+ = ion conductance

F = Faraday's constant (96500 Coulombs)

V = potential difference

d = distance.

Ion conductance is specific to species. Most major ions have similar ionic conductance ranging between about 50 and 70 ($ohms^{-1} \bullet cm^2$), although H^+ has an ionic conductance of 350 $ohms^{-1} \bullet cm^2$, the highest of any ion. Figure A-11 shows theoretical ion migration distances as a function of overburden thickness for H^+ and a hypothetical anion, X^-, with $\lambda_+ = 60$. A voltage difference of 300 mV is used. Eh of this magnitude and greater is not uncommon between mineralization and ground surface (Bolviken and Logn, 1975; Pflug et al., 1996; Hamilton and McClenaghan, 1998). Figure A-11 shows that since glaciation, H^+ and other ions have had ample time to migrate through 30 m of non-reactive saturated overburden along an electrochemical gradient. Voltage differences as low as 10 mV for H^+ and 60 mV for X^- would be sufficient to move these species through a 30 m thick electrolyte in 8000 years.

The calculation shown above assumes that groundwater behaves as a perfect electrolyte and that only the ions in question are present in solution to carry charge. In fact, there are many geochemical processes that could occur between bedrock and ground surface that would affect the migration rate. For charge to be transferred between mineralization and ground surface, it is not necessary that individual ions move the entire distance. As a given ion moves upward along the redox gradient, it may move beyond its pH-Eh stability range and oxidize (Fig. A-5) thereby passing on its charge to another species. If the new species carries negative charge it will also migrate upward, ultimately passing on charge itself possibly by reaction with dissolved oxygen radicals at surface. Sharply-defined Eh zones within the overburden stratigraphy would tend to promote the replacement of charge carrying ions with others. An actively flowing and oxygenated aquifer, for example, might force a change in the charge carrier to a less reduced species, or might short circuit the cell altogether so that the cell would operate between mineralization and the base of the aquifer instead of to ground surface. The water table is also a sharp redox boundary and will almost certainly force changes in the species that carry charge.

A series of processes that involve the electrical double layer on clay and oxide surfaces could limit the rate of mass-transport of ions to the surface. Electro-filtration is the exclusion of some ions during their transport through double-layer media. Electro-filtration may limit the movement of certain ions though thick overburden thereby slowing the whole charge transfer process. Ion exchange and sorption are also double-layer processes that could reduce the rate of mass and charge transfer. Ion exchange of a redox-active ion in solution for a redox inert ion will effectively stop the transfer of charge at that exchange site and could exchange the migrating species that originated from mineralization with ones that originated in overburden. This could slow down both mass and charge transfer until a significant proportion of the sorption or exchange sites are occupied by redox-active species. It should be noted, however, that double-layer processes limiting mass transfer are also likely to limit charge transfer. The commonly-reported surface selective leach anomalies in thick overburden above mineralization are evidence that charge transfer does occur, even in young deposits. Therefore, it appears

that double-layer processes are not major inhibitors to the development of SP cells in overburden.

Not all geochemical processes in overburden will necessary slow down mass transport and charge transfer. Groundwater in overburden above mineralization may have higher ionic strength than that in surrounding areas due to the attraction of ions to, and/or generation of ions in, the reduced column. As such, there may be an area of increased electrical conductivity within the cell that should enhance current flow. Furthermore, clay surfaces impart a significant electrical conductivity to groundwater in overburden (which, incidentally, is also a double-layer process) and this might also enhance current relative to that which would occur in a pure electrolyte.

A1.6.2 Geochemical anomalies

The issue of replacement of the charge carrier as just described is extremely important to the use of selective leach procedures for geochemical exploration, particularly in younger terrain. In older geological terrain, the process may have operated for long enough to inundate the overburden with elements and species transported from depth and to give the overburden an elemental signature that is partially reflective of that of bedrock. In younger terrain, however, the charge could have just as easily been transported by exotic species liberated from overburden materials and, as such, surface anomalies would be partially or wholly reflective of the geochemistry of overburden. In general there has been insufficient research into the issue of mass transfer between bedrock and ground surface by electrochemical processes. Therefore, despite the paramount importance of this issue to exploration geochemistry, it is not considered further here. Rather, attention is given to the theoretical development of surface geochemical anomalies above a reduced feature in bedrock and does not address the issue of where the ions that form the anomaly actually came from.

The four types of redox cells described in this paper should have similar surface geochemical phenomena associated with them because they share similar ionic flow patterns in the uppermost portion of the cells. They are all based on a reduced feature as a source of negative charge and the oxygenated surface as the ultimate source of positive charge and they all must involve transfer of ionic current between the two sources. The

result will be a general outward movement of ions that are capable of transporting negative charge, such as Fe^{2+}, Co^{2+}, Cu^{+}, HS^{-} and $S_2O_3^{2-}$, and an inward movement of ions that are capable of transporting positive charge, such as UO_2^{2+}, MoO_4^{2-}, VO_4^{3-}, SeO_4^{2-}, AsO_4^{3-}, SO_4^{2-} and dissolved oxygen radicals. The final transfer of negative charge at the top of the cells involves redox reactions that, in many cases, attenuate the transported reduced species into the solid phase thereby forming geochemical anomalies.

One outcome of the migration of ions from one redox region into another should be a zonation of elements in relation to the reduced column. Element zonation is a reported feature of selective leach anomalies (Clark, 1996). Zonation could occur due to a variety of processes the most important of which would be progressive deposition of redox-active species as they migrate into or out of the reduced column. The migration paths of reduced versus oxidized ions are predictable provided the current flow patterns can be inferred and therefore, if the redox behaviour of a particular ion is also known, the shape of anomalies can also be inferred.

Two of the factors that should control where mobile elements are deposited in relation to the reduced column are: (1) the Eh at which a redox active species will convert to a species of a different oxidation state; and, (2) the mobility of the new species. For example, inward migrating species that are highly oxidizing and show low mobility in reducing environments, such as UO_2^{2+}, are expected to become reduced early and form anomalies at the outermost edges of the reduced column (Fig. A-12A). At the other extreme, inward migrating, weakly oxidizing species that can show high mobility in reducing environments, such as SO_4^{2-}, would not become reduced until they reached the inner part of the column and even then might not form anomalies in soils because of their high mobility. Similar but opposite processes occur with reduced species in the outward direction.

One of the more important reduced species capable of forming anomalies in soils is Fe^{2+}. Both the abundance and the secondary processes associated with iron reactions suggest that Fe^{2+} will have a major impact on the geochemistry of surface soils. It is moderately strongly reducing and has very low mobility, It is therefore expected to form anomalies at the redox front near the inner edge of the reduced column. When most reduced metals (and, in particular, Fe^{2+}) oxidize, they hydrolyse to form insoluble metal

hydroxides. In the process, large amounts of acid are generated (Figure A-12B). H^+ anomalies are commonly reported in association with rabbit-ear anomalies over mineralization. In the phreatic zone H^+ is most likely to be generated, not by the downward diffusion of oxygen and the oxidation of the sulphide itself, as in the past had always been assumed, but by the upward transport of reduced iron along an electrochemical gradient to oxidizing agents at the redox front (i.e., the reducing agents are brought to the oxidizing agents rather than the other way around). Secondary process related to iron oxidation may be CO_2 production in areas where carbonate is present (Figure A-12B). Acid produced at the edge of the reduced column by Fe^{2+} oxidation should produce dissolved CO_2 as H_2CO_3 (Figure A-12B) by dissolution of carbonate in rock or overburden material. In adjacent areas near or above the water table, dissolved CO_2 can degas causing carbonate supersaturation and deposition. From here, CO_2 and carbonate-charged soil moisture could also disperse upward through the unsaturated zone by capillary action. As moisture evaporates, near-surface CO_2 would degas and carbonate would precipitate, forming both soil carbonate and CO_2 gas anomalies (Smee, 1998). Smee (1998) attributed rabbit-ear anomalies in Ca, Mg, Sr, and possibly also Au and As to their transport in bicarbonate complexes and their precipitation in shallow soils due to processes such as these occurring in the unsaturated zone.

The thousands of possible redox reactions that facilitate charge transfer away from the reduced source could result in a net loss of cations or anions from solution in the vicinity of some reactions. As such, the movement of redox-inert species is likely to be continuously occurring from one part of the overburden electrolyte to another in order to compensate for local charge imbalances. However, it is difficult to predict the transport paths of these ions because their movement depends on the specific nature of the reactions occurring at a given site. Empirical observation is probably the most viable method for determining the behaviour of a redox-inert species. Clark (1996) reports an empirically-observed oxidation suite of elements that often occur as rabbit-ear anomalies flanking ore deposits and include Cl, Br, I, As, Sb, Mo, W, Re, Se, Te, V, U and Th. Most of the elements in this suite are far more mobile in oxidized than reduced forms and as such probably migrate inward to form reduction anomalies (notwithstanding the name applied to the suite). However, several elements are likely to be mobile as redox-inert

species (e.g., Cl, Br, I) or perhaps as ligands in metallic complexes, and therefore their movement may be a secondary result of other species migrating and subsequent reactions occurring inside and outside the column.

A1.7 Conclusions

Despite the different origins of the four SP cell models described in this chapter, their underlying principles are similar and can be summarised as follows. Within the redox field of the Earth, Ohm's Law suggests that a cell will form if either the redox gradient or electrical conductivity is anomalously high with respect to that of surrounding Earth materials. An Earth cell is defined as an area of spontaneously elevated electrical current between two separated sources of oxidizing and reducing agents. Resulting similarities in the geochemical surface expression of the cells would include: a reduced SP centre above the cell; the outward movement of negatively charged ions; the inward movement of positively charged ions; and, an element dispersion pattern that is characteristic of a redox cell. The most typical anomaly morphologies are the centred rabbit-ear and apical patterns which are often coincident in several elements.

Thus, the primary criterion for development of a cell is the existence of a buried reduced feature. Such feature of potential economic interest include the following:

- Conductive sulphide mineralization.
- Non-conductive but oxidizable sulphide mineralization (eg. sphalerite)
- Ultramafic dikes, diatremes and flows, Including komatiites, kimberlites and lamprophyres.
- Geological contacts between two units with strong redox contrast such as carbonatite and granite
- Shear-zones containing fault gouge
- Graphitic-hosted gold mineralization.
- Bitumen, coal or natural gas seeps.

There are, however, a considerable number of sources of reducing agents that are of no economic significance. These include the following:

- Barren sulphide mineralization

- Geological contacts between two units with strong redox contrast such as diabase and granite
- Minor barren graphite horizons
- Methane pockets in shale or overburden.
- Gas hydrates

The study of electrochemical cell processes that result in surface geochemical anomalies is still in its infancy. Many apparently unrelated geochemical processes and phenomena occurring over chemically-reduced geological features may prove to be directly or indirectly related to electrochemical processes. Although electro-geochemical techniques have enormous potential, a great deal of additional work must be done if geochemical mapping over deeply buried features is to be a reliable technique yielding easily interpretable data. The most pressing issues is to determine mass transport rates from bedrock, whether a near-surface signature due to bedrock is possible within the age period of young deposits, and whether the replacement of charge carriers between bedrock and ground surface results in spurious overburden-related anomalies. Another important issue is the understanding of the specifics of mass and charge transfer from the reduced source to the groundwater environment.

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Appendix 1 Figures and Tables

Figure captions

Fig. A-1. An example of a voltaic cell spontaneously generating current in a wire. The impetus for electron movement in the wire comes from difference in oxidation potential between $Zn_{(s)}$ and Cu^{2+}. $Zn_{(s)}$, the reducing agent, gives up electrons at the anode to become Zn^{2+}. Cu^{2+}, the oxidizing agent, acquires electrons at the cathode and plates-out on the copper electrode as $Cu_{(s)}$ (from Hamilton, 1998).

Fig. A-2. Differences in oxidation potential around the electrodes in electrolytic versus voltaic cells (from Hamilton, 1998).

Fig. A-3. Non-polarizing Cu-$CuSO_4$ electrodes for measurement of spontaneous potentials in surface materials. If the ground at "A" is more reducing than at "B", negative current will flow through the wire between the two points (from Hamilton, 1998).

Fig. A-4. The theoretical and empirical stability fields for water (after Bass Becking et al., 1960).

Fig. A-5. The inferred mechanism of charge transfer in the Earth's redox field. The redox gradient induced the movement of ions toward the environment in which they are able to transfer charge. Ions move only within a certain Eh-regime, at the limit of which they pass on charge to other species through redox reactions (modified after Bolviken and Logn, 1975).

Fig. A-6. Diagram showing the equipotential-line and ionic current flow-line distribution around an electronic conductor in bedrock after the model of Govett (1973) and Bolviken and Logn (1975) (from Govett et al. 1976).

Fig. A-7. An interpretation of the equipotential and ionic current flow lines around a single-phase sulphide ore body in a uniform redox field. After the model of Sato and Mooney, 1960 (from Hamilton, 1998). Equipotential lines are labelled to depict an upward increasing gradient and are not intended to be an actual representation of the earth field.

Fig. A-8. An interpretation of the equipotential and ionic current flow lines around a two-phase sulphide body (pyrite/pyrrhotite) after the model of Thornber (1975) (modified after Thornber, 1975). The purpose of the labelled equipotential lines is as per Fig. A-7.

Fig. A-9. The progressive modification of redox-equipotential lines in glacial overburden overlying an electronic conductor in bedrock. The impetus for ion movement comes from the strong redox gradient between the bedrock conductor and ground surface. Flow lines depict only the movement of negative charge-carrying species. Positive charge carrying species would have an equal and opposite flowpath.

Fig. A-10. An interpretation of the equipotential and ionic current flow lines around an oil reservoir after the model of Pirson (1981) and Tompkins (1990). The purpose of the labelled equipotential lines is as per Fig. A-7.

Fig. A-11. Theoretical ion migration time as a function of overburden thickness for H^+ and a hypothetical anion, X^-, under the influence of a potential difference of 300 mV.

Fig. A-12. The development of anomalies that are: (A) directly related to electrochemical processes; and, (B) related to secondary processes occurring as a result of mobility and attenuation of ferrous iron.

Figure A-1. Example of a voltaic cell.

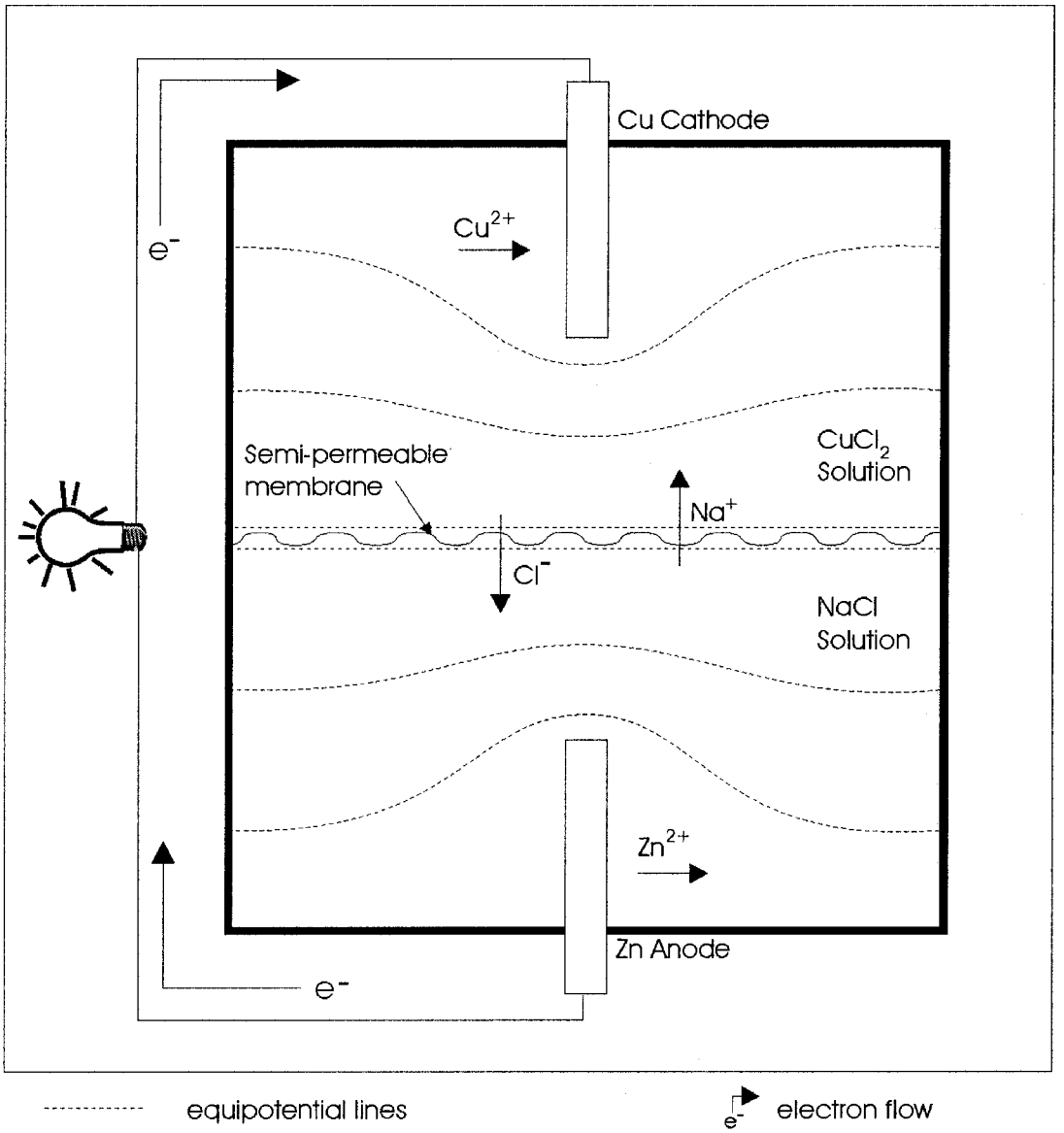


Figure A-2. ORP around the electrodes of an electrolytic vs. a voltaic cell.

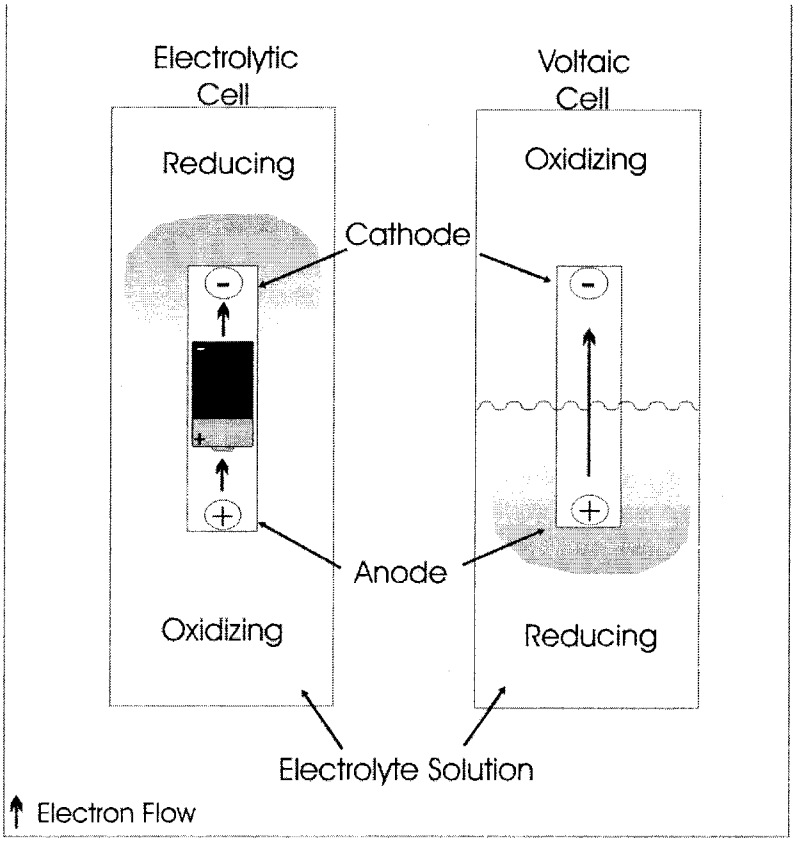


Figure A-3. Measurement of SP with non-polarizing Cu-$CuSO_4$ electrodes

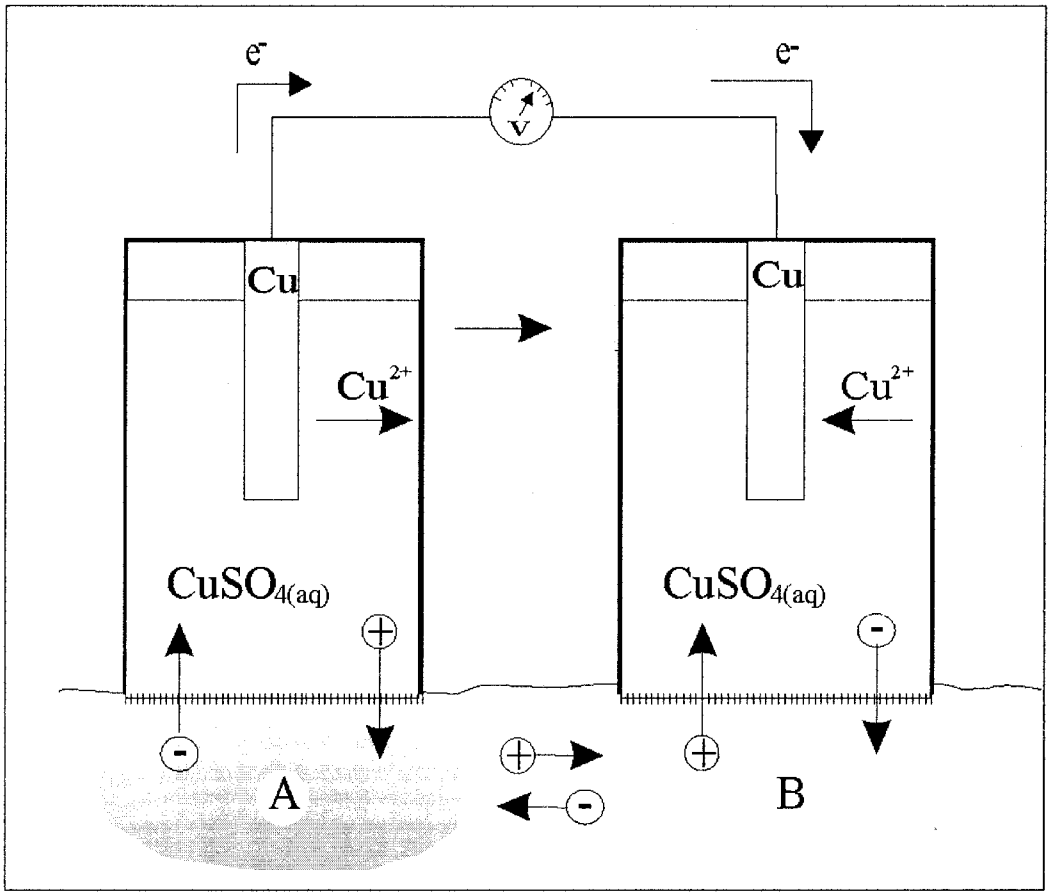


Figure A-4. The theoretical and empirical stability fields for water.

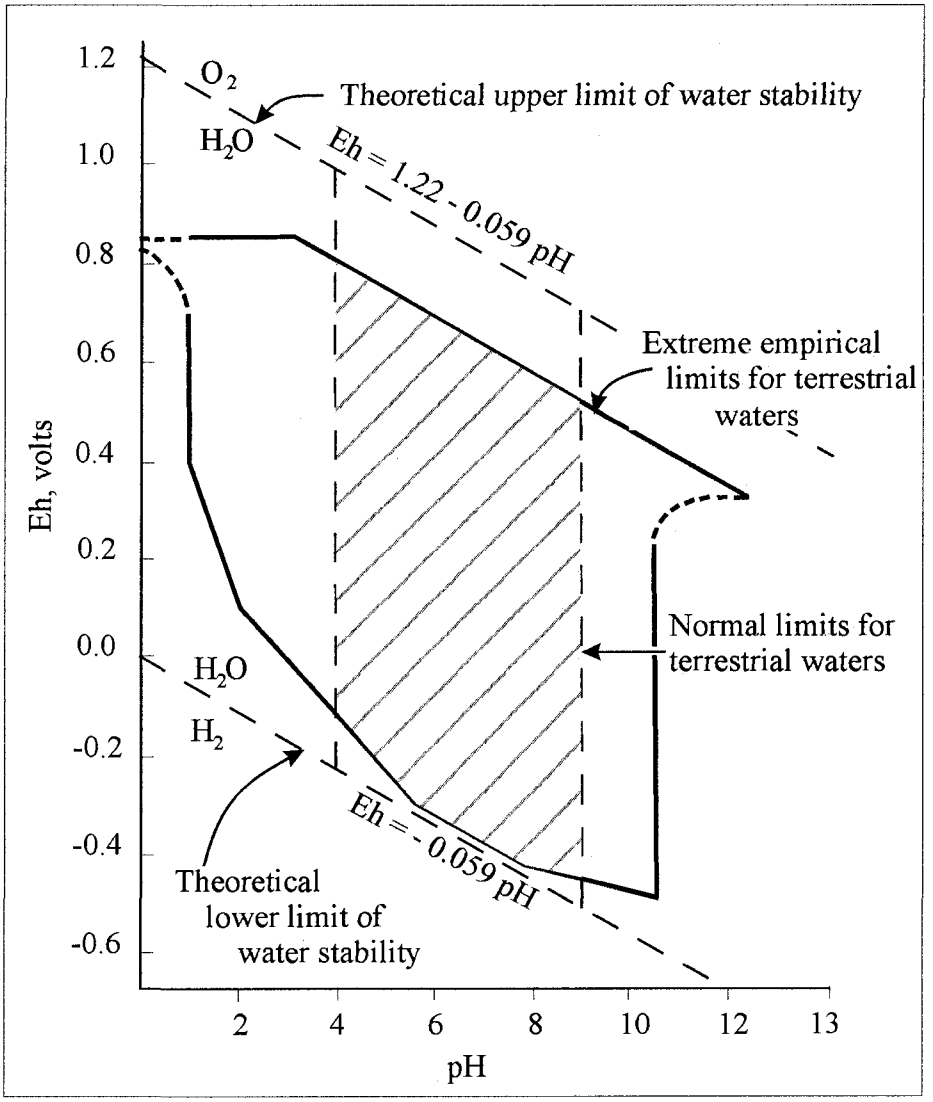
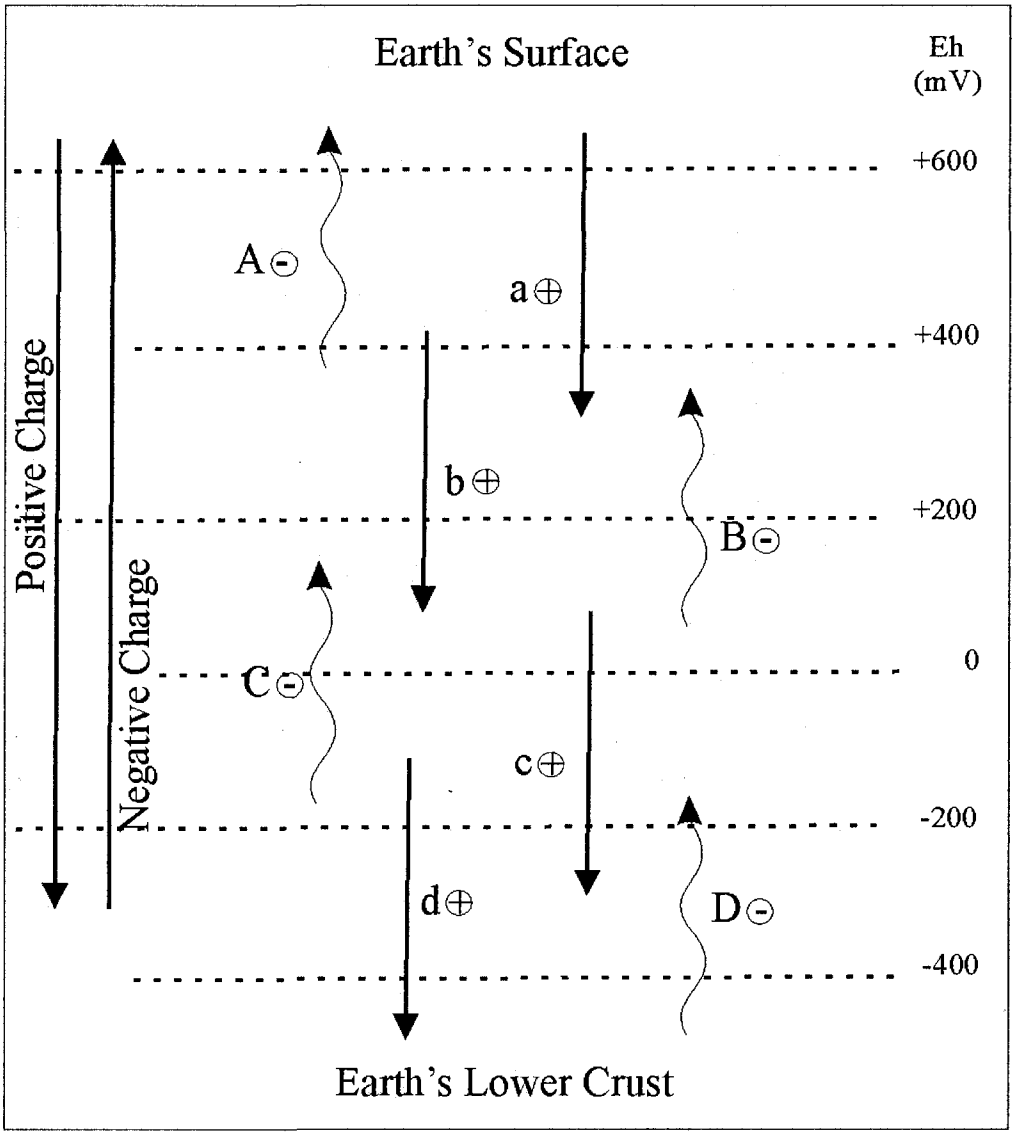


Figure A-5. Inferred mechanism of charge transfer in the Earth's redox field



Increasing Eh

$H_{2(g)} < d\oplus < c\oplus < b\oplus < a\oplus < O_2$ Positive Charge Carriers

$H_{2(g)} < D\ominus < C\ominus < B\ominus < A\ominus < O_2$ Negative Charge Carriers

Figure A-6. Govett model of the dipole electrical field around a conductor.

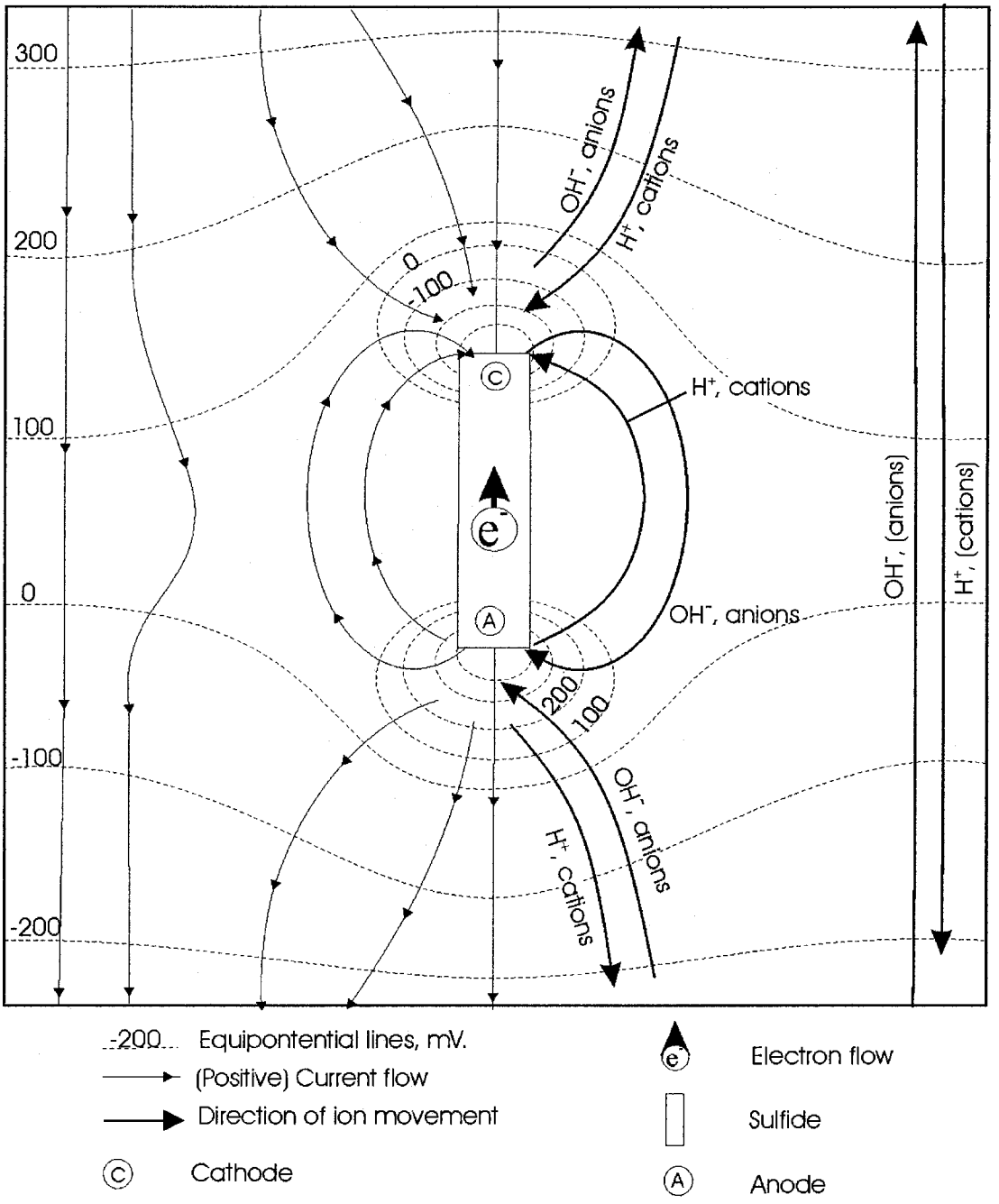


Figure A-7. Electrical field around a single-phase sulphide conductor in a redox field.

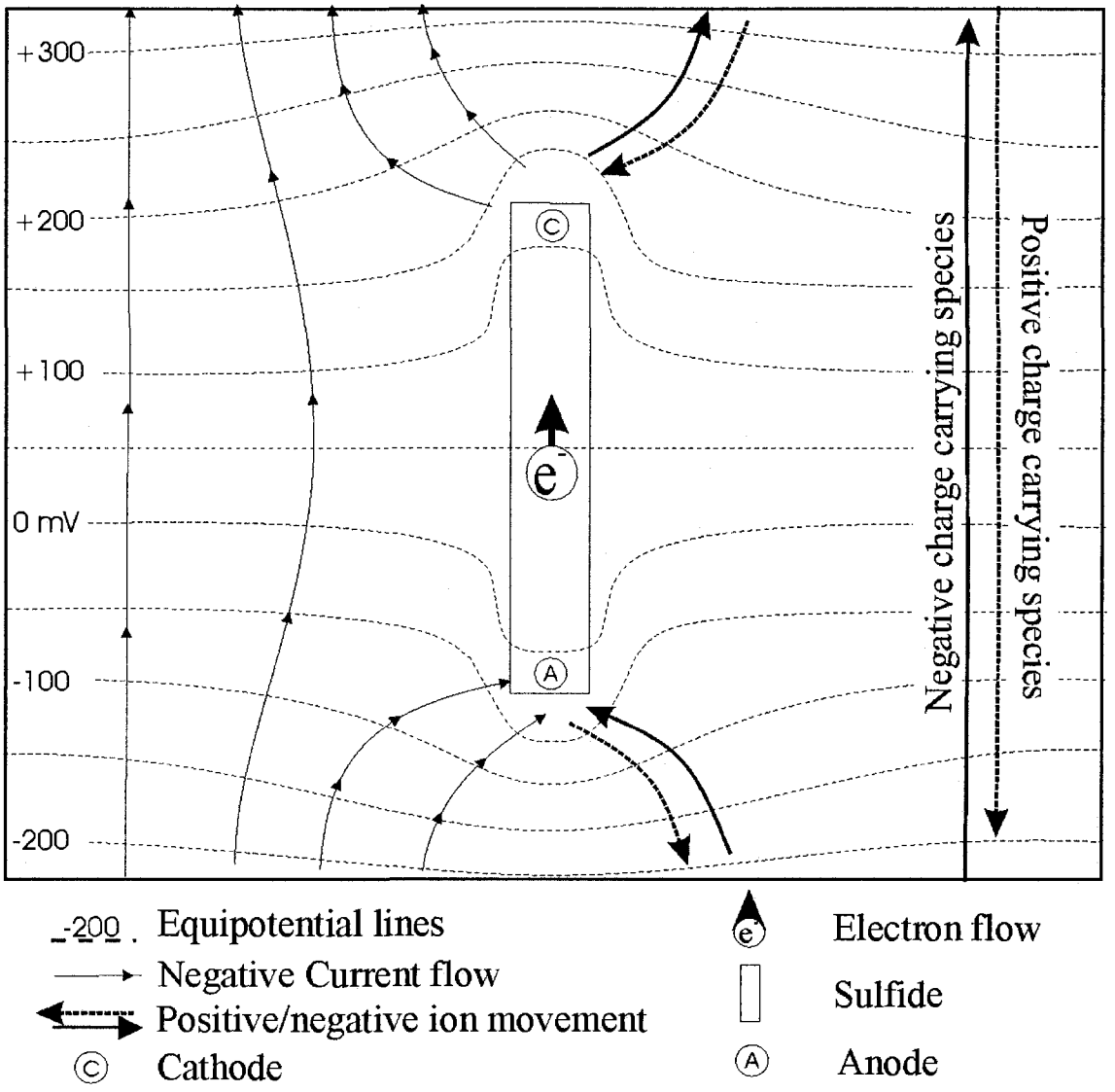


Figure A-8 Electrical field around a two-phase sulphide conductor.

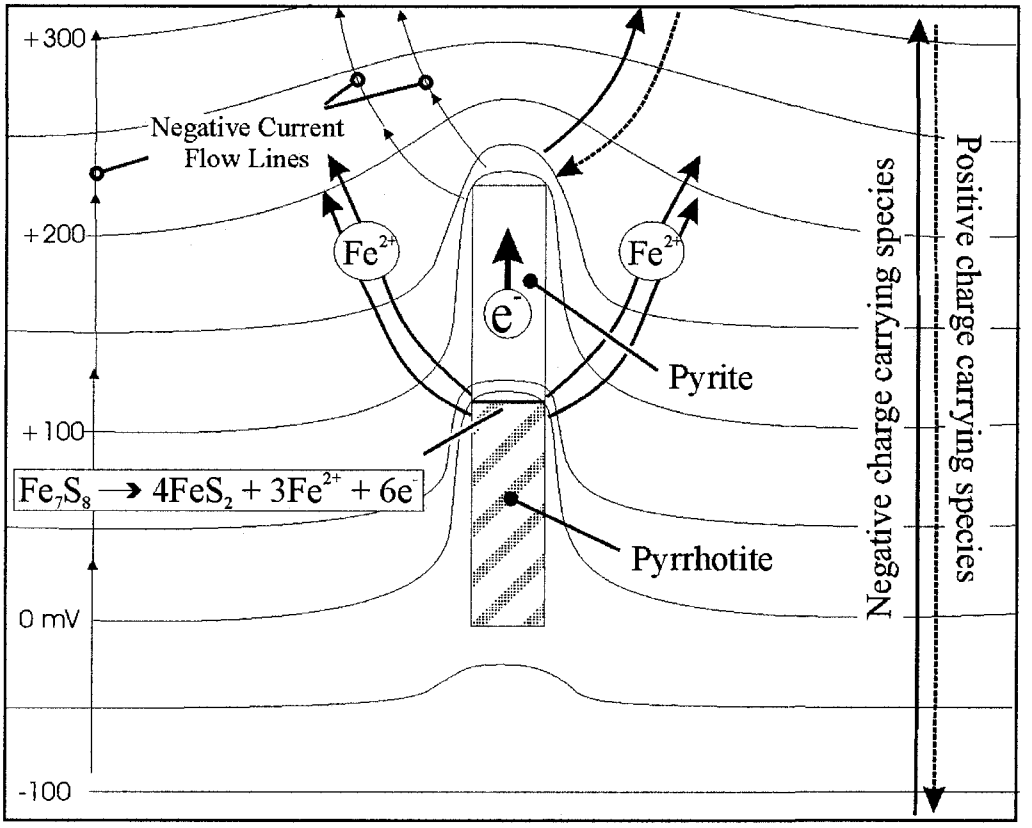


Figure A-9. Redox-gradient transport in glacial overburden above mineralization.

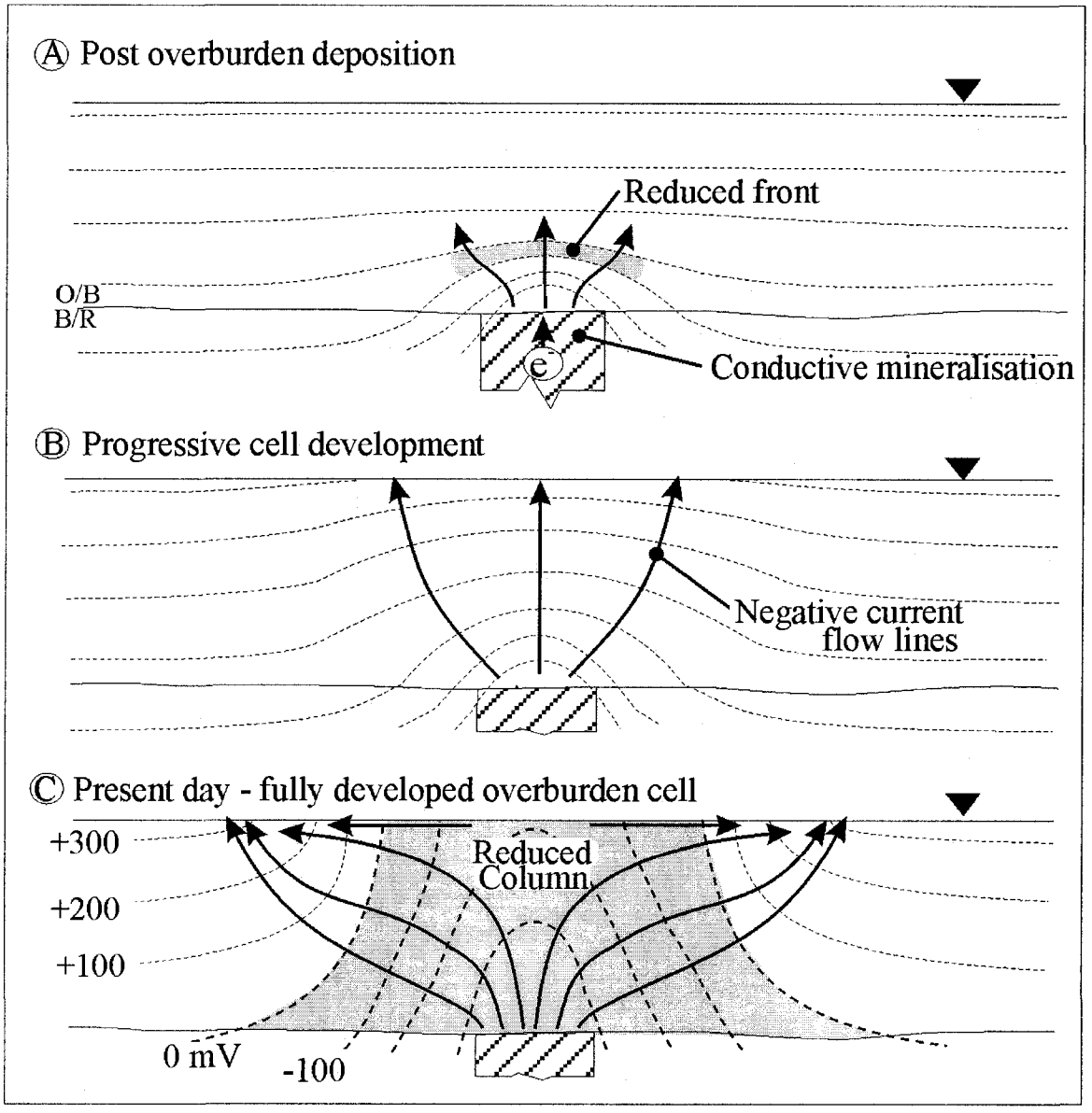


Figure A-10. Electrical field around an oil reservoir.

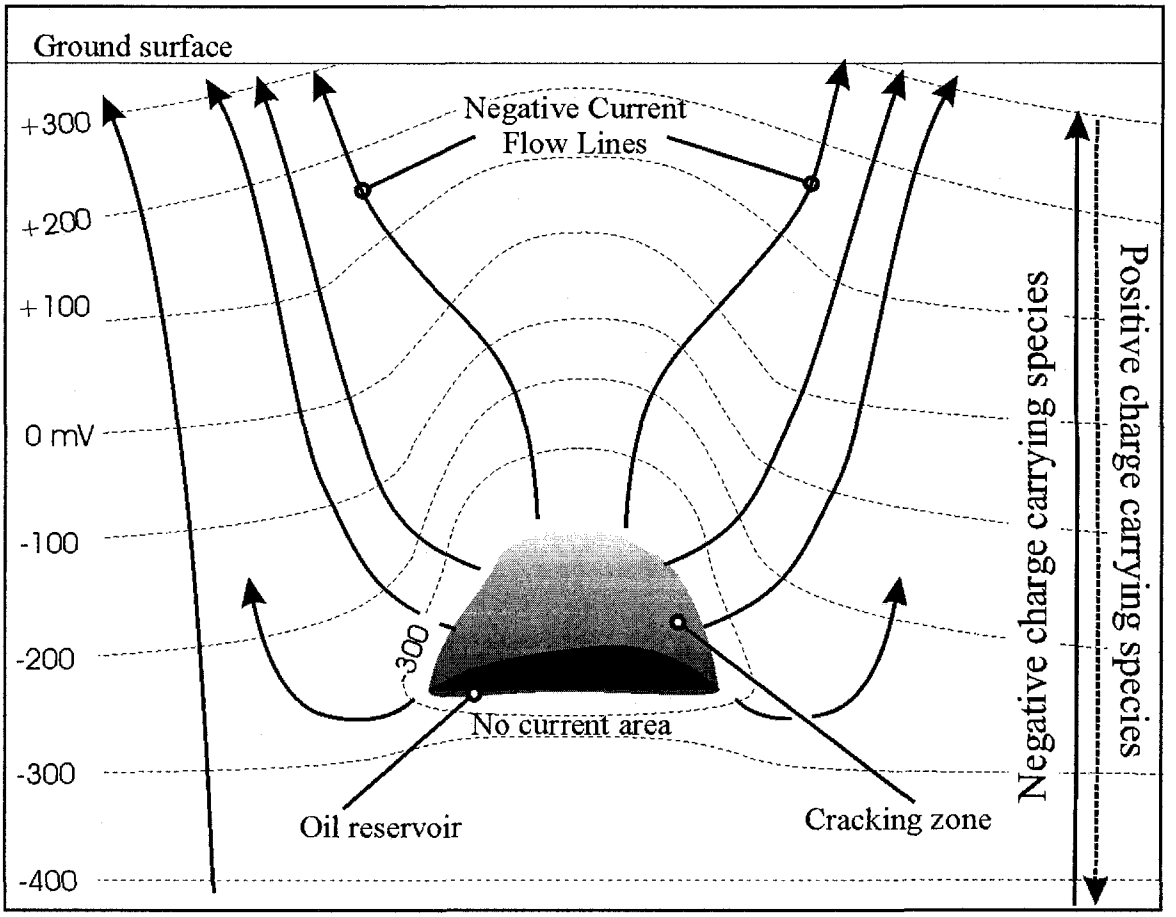


Figure A-11. Ion migration time as a function of overburden thickness.

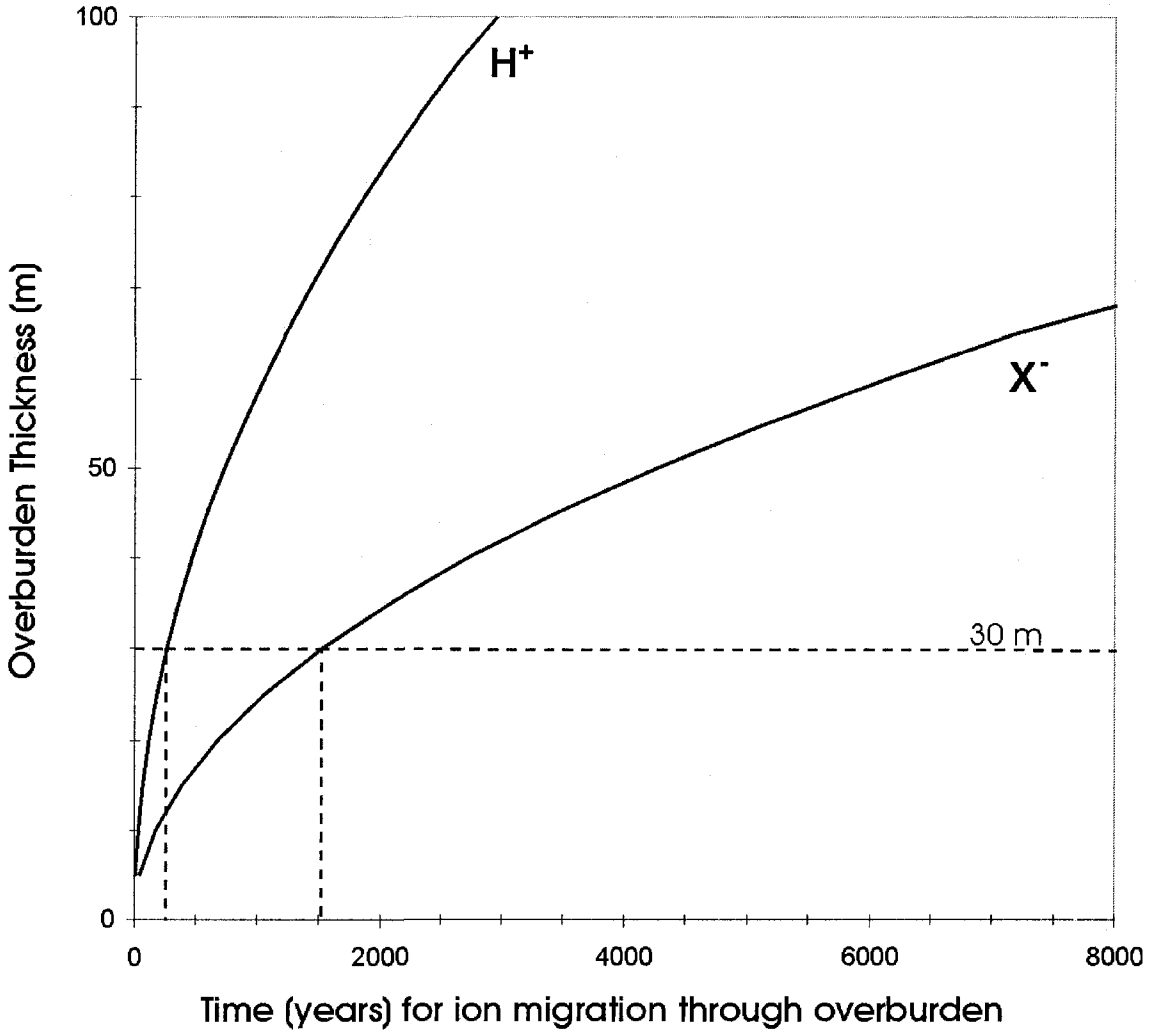


Figure A-12. The development of geochemical anomalies over a reduced column.

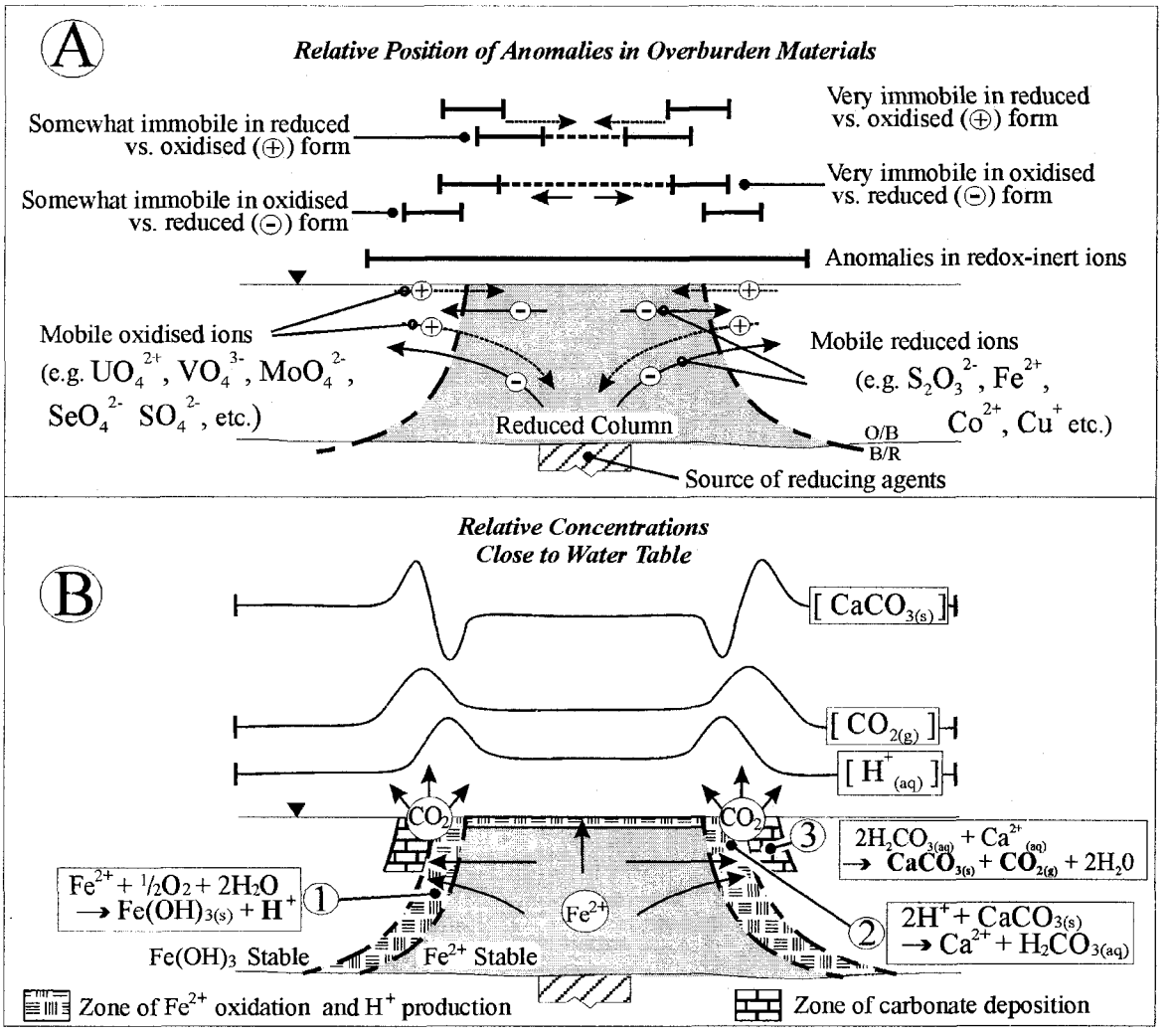


Table A-1. List of standard potentials

Oxidizing Agent		Reducing Agent	E^0_{red} (V)
$Al^{3+}(aq) + 3\ e^-$	$\Rightarrow$	$Al(s)$	-1.66
$Zn^{2+}(aq) + 2\ e^-$	$\Rightarrow$	$Zn(s)$	-0.76
$Fe^{2+}(aq) + 2\ e^-$	$\Rightarrow$	$Fe(s)$	-0.44
$Pb^{2+}(aq) + 2\ e^-$	$\Rightarrow$	$Pb(s)$	-0.13
$2\ H^+(aq) + 2\ e^-$	**$\Rightarrow$**	**$H_2(g)$**	**0.00**
$S(s) + 2\ H^+(aq) + 2\ e^-$	$\Rightarrow$	$H_2S(aq)$	0.14
$Cu^{2+}(aq) + e^-$	$\Rightarrow$	$Cu^+(aq)$	0.15
$SO_4^{2-}(aq) + H^+(aq) + 8\ e^-$	$\Rightarrow$	$S^{2-} + 4\ H_2O$	0.16
$SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^-$	$\Rightarrow$	H_2SO_3	0.17
$SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^-$	$\Rightarrow$	$SO_2(g) + 2\ H_2O$	0.20
$Cu^{2+}(aq) + e^-$	$\Rightarrow$	$Cu(s)$	0.34
$ClO_4^-(aq) + H_2O + 2\ e^-$	$\Rightarrow$	$ClO_3^-(aq) + 2\ OH^-(aq)$	0.36
$H_2SO_3(aq) + 4\ H^+(aq) + 4\ e^-$	$\Rightarrow$	$S + 3\ H_2O$	0.45
$ClO_3^-(aq) + 3\ H_2O + 6\ e^-$	$\Rightarrow$	$Cl^-(aq) + 6\ OH^-(aq)$	0.62
$Fe^{3+}(aq) + e^-$	$\Rightarrow$	$Fe^{3+}(aq)$	0.77
$Ag^+(aq) + e^-$	$\Rightarrow$	$Ag(s)$	0.80
$ClO^-(aq) + H_2O + 2\ e^-$	$\Rightarrow$	$Cl^-(aq) + 2\ OH^-(aq)$	0.89
$O_2(g) + 4\ H^+(aq) + 4\ e^-$	**$\Rightarrow$**	**$2\ H_2O$**	**1.23**
$Cl_2(g) + 2\ e^-$	$\Rightarrow$	$2\ Cl^-(aq)$	1.36
$ClO_3^-(aq) + 4\ H^+(aq) + 4\ e^-$	$\Rightarrow$	$\frac{1}{2}\ Cl_2(g) + 4\ H_2O$	1.47
$Au^{3+}(aq) + 3\ e^-$	$\Rightarrow$	$Au(s)$	1.50

Table A-2. Resistivities converted to conductivities

Electrical Conductivity of Groundwater in Various Geological Units: Shoot Zone Gold Property, Northwestern Ontario

Unit	n	Electrical Conductivity (μS/cm) -- range --	-- average --
Groundwater – Peat	3	297 – 347	328
Groundwater – Glaciolacustrine Clay	7	357 – 714	508
Groundwater – Sand Aquifer	23	138 – 558	387
Groundwater – Glacial Till	7	254 – 536	417
Groundwater – Crystalline Rock	15	159 – 581	370

Electrical Conductivity of Various Bedrock "Conductors", Converted from Resitivity Units (Keller and Frischknecht, 1966)

Conductors	Electrical Conductivity (μS/cm) -- range --			-- geometric mean --
Arsenopyrite	0.33	–	5	1.3
Chalcopyrite	0.011	–	0.67	0.086
Native Copper	330	–	8300	1700
Graphite (parallel to cleavage)	100	–	280	167
Galena	0.0011	–	15	0.13
Magnetite			1.9	1.9
Marcasite	0.00067	–	0.10	0.0082
Molybdenite	0.000013	–	0.00083	0.00011
Pyrrhotite	0.63	–	50	5.6
Pyrite	0.00017	–	0.083	0.0037
Pyrolusite	0.0000033	–	0.014	0.00022
Sphalerite ("non-conductive")	0.0000000083	–	0.037	0.000018