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# MARINE GEOCHEMICAL CYCLE

# OF

# STRONTIUM

by

Moire Anne Wadleigh

A thesis submitted to the School of Graduate Studies in partial fulfillment of the requirements for the degree of M.Sc in Geology

UNIVERSITY OF OTTAWA

OTTAWA, CANADA, 1982

"All streams flow into the sea,
yet the sea is never full.
To the place the streams come from,
there they return again."

Ecclesiastes 1:7

ABSTRACT

The 39 largest Canadian rivers (by discharge) were sampled at or near confluence with oceans during different flow regimes. The samples were analyzed for elemental Sr, Ca, Cl, total dissolved solids (T.D.S.) and the $^{87}Sr/^{86}Sr$ isotopic ratio. In addition, the geology of the river drainage basins was compiled from geological maps.

The data demonstrate a fundamental control by bedrock of river water chemistry. Multivariate statistical analysis (Q and R mode factor analysis) facilitated the classification of the Canadian rivers into three groups representing a two endmember series. Endmember 1 or group 1 is characterized by rivers with high concentrations of T.D.S., Ca and Sr, low Sr/Ca ratios and low $^{87}Sr/^{86}Sr$ ratios. From the drainage basin geology, these rivers were identified as "sedimentary". Endmember 2 or group 3 is characterized by rivers with low concentrations of T.D.S., Ca and Sr, higher Sr/Ca ratios and high $^{87}Sr/^{86}Sr$ ratios. These rivers were identified as "Shield" type. Group 2 rivers are of intermediate type; chemically similar to group 3 but isotopically similar to group 1.

A weighed mean $^{87}Sr/^{86}Sr$ ratio for continental runoff was calculated to be .7111 on the basis of the 39 largest rivers. This value is less radiogenic than the published estimates (.716 - .720), but is supported by analyses on two major world rivers, the Amazon and the Mississippi.

Seawater, a medium capable of integrating the fluxes of Sr from various sources (with different $^{87}Sr/^{86}Sr$ ratios) has an $^{87}Sr/^{86}Sr$ ratio of .709. It must therefore be a mixture of radiogenic continental Sr and Sr from a complementary, non-radiogenic source. Oceanic basalts can provide the required non-radiogenic Sr reservoir as seawater-basalt interaction is known to increase the radiogenic $^{87}Sr$ component in basalts.

The new value for continental $^{87}Sr/^{86}Sr$ sets an upper limit of 23% on the oceanic basalt (mantle) contribution to the isotopic ratio of seawater.

RÉSUMÉ :

Les 39 plus grandes rivières du Canada (par débit) ont été échantilloné en amont de leurs estuaires, pendant différent régimes. Les échantillons ont étés analysés pour Sr, Ca, Cl, solides dissous et la proportion isotopique $^{87}Sr/^{86}Sr$. En plus, la géologie des bassins hydrologiques a été compilé a partir de cartes géologiques.

Les résultats démontrent le contrôle fondamental de géologie sur la chimie des eaux fluviales. Les rivières Canadiennes ont été classifié en trois groupes a l'aide d'une analyse statistique a variable multiple. Ces groupes forment une série à deux membres-finis. Le premier membre-fini ou groupe 1 est characterisé par les rivières qui ont une concentration élevée de solides dissous, Ca, Sr, des rapports Sr/Ca bas et des rapports $^{87}Sr/^{86}Sr$ qui sont bas. A partir de la géologie des bassins hydrologiques ces rivières ont été identifié comme étant "sedimentaires". Le deuxième membre-fini ou groupe 3 est characterisé par des rivières qui ont de basses concentrations de solides dissous, Ca et Sr, des rapports Sr/Ca plus hauts et des rapports $^{87}Sr/^{86}Sr$ élevés. Ces rivières ont été identifié comme étant des types "Bouclier". Les rivières de groupe 2 sont du genre intermediare; semblable chimiquement au groupe 3 mais semblable du point de vue isotopique au groupe 1.

Un rapport $^{87}Sr/^{86}Sr$ moyen, pesé, pour l'écoulement continental a donné .7111 basé sur les 39 plus grandes rivières. Cette valeur est moins radiogenique que l'estimé précédent (.716-.720) mais est confirmé par les analyses de deux rivières majeurs mondiales, l'Amazon et le Mississippi.

L'eau de mer, un milieu capable d'integrer les fluxes de Sr de plusiers sources (avec rapports $^{87}Sr/^{86}Sr$ différents) a un rapport $^{87}Sr/^{86}Sr$ de .709. L'eau de mer doit donc être un mélange de Sr radiogenique continental et de Sr qui provient d'une source complementaire non-radiogenique. Les basaltes océaniques peuvent possiblement êtres le réservoir de Sr non-radiogenique qui est requis puisque la pénétration de l'eau de mer augmente la concentration de $^{87}Sr$ dans les basaltes.

La nouvelle valeur pour $^{87}Sr/^{86}Sr$ continental définit une limite supérieure de 23% sur la contribution du basalte océanique (manteau) à la proportion isotopique de l'eau de mer.

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# 1. INTRODUCTION

## 1.1 Purpose of Research

Strontium, with a concentration of 8 ppm and an isotopic ratio of .7091 is a major dissolved species in seawater (Compston and Pidgeon, 1962; Turekian, 1964; Faure et al, 1967; Veizer and Compston, 1974). It is homogeneously distributed throughout the oceans because of its long apparent residence time ($10^6$ years) compared to the mixing rate ($10^3$ years) of the oceans (Goldberg, 1963; Broecker, 1963; Veizer and Compston, 1974; Brass and Turekian, 1974). Seawater is capable of integrating fluxes of Sr from various sources (of widely differing $^{87}Sr/^{86}Sr$ ratios) and is therefore a medium which monitors variations in the intensities of such fluxes (Wickman, 1948).

The current estimate for the $^{87}Sr/^{86}Sr$ ratio of continental runoff is between .716 - .720 (Veizer and Compston, 1974; Spooner, 1976; Brass, 1976). This value is considerably more radiogenic than that of present-day ocean water. Consequently, seawater Sr should be a mixture of Sr from a radiogenic, continental source and a complementary, non-radiogenic source.

From plate tectonic and heat flow considerations it is evident that oceanic basalts produced at spreading centres interact with circulating heated seawater. The $^{87}Sr/^{86}Sr$ ratios of these basalts are .7025 - .7035 (Hoffman and Hart,

1978) and consequently Sr derived from this source could be the required non-radiogenic component. According to Spooner (1976), hydrothermal seawater-basalt interaction is the only geochemical process which could counteract the effect of adding isotopically heavier Sr from continental areas to the oceans (Fig. 1.1).

Balance calculations and modelling, utilizing the above estimates, suggest that the ratio of oceanic (basaltic) vs. continental flux of Sr into modern oceans should be between 60:40 and 25:35 (the missing 40% in the latter case assigned to recycled limestone Sr) (Brevart and Allègre, 1977). If, however, the continental crust is not as radiogenic as generally believed (DePaolo, 1979), the proposed magnitude of the mantle flux of Sr could be reduced considerably (Veizer, in press). The latter alternative is favoured also by Turekian (1977), who argued against a significant contribution from seafloor basalts to the $^{87}Sr/^{86}Sr$ composition of seawater.

Evaluation of the magnitude of the hydrothermal flux of Sr from mid-oceanic ridges is essential because of its role in the marine geochemical cycle. Knowing the $^{87}Sr/^{86}Sr$ ratios of the fluxes to the oceans, the relative proportions of Sr from each source can be calculated as follows:

$$^{87}Sr/^{86}Sr_{CR}\ (x) + {}^{87}Sr/^{86}Sr_{OB}\ (1 - x) = {}^{87}Sr/^{86}Sr_{SW},$$

where CR= continental runoff, OB= oceanic basalts, SW=

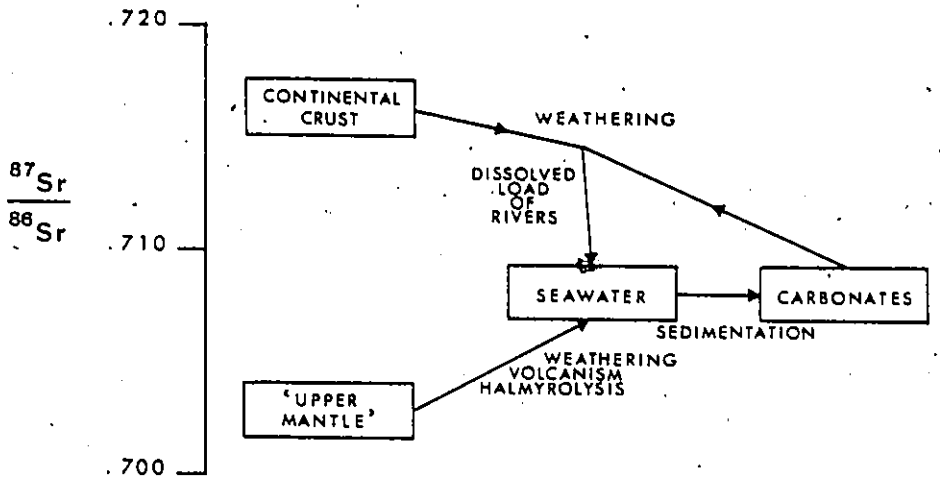



Fig. 1.1

Strontium exogenic cycle (modified from Veizer, 1976)

seawater, (x) represents the proportion of strontium with continental isotopic ratio, and (1-x) represents the contribution with basaltic isotopic ratio. The uncertainty in this equation is in the continental runoff term, which has been previously estimated from unweighed and unrepresentative data (Veizer and Compston, 1974; Brass, 1976). The purpose of this work is to obtain a more realistic estimate of the isotopic composition and the flux of continental strontium. This in turn shall be utilized to determine the relative contributions of strontium from continental and marine basaltic sources to ocean water.

1.2 Mechanisms of elemental supply to the oceans.

The products of continental weathering, carried by rivers, constitute quantitatively the most important flux to the oceans (Meybeck, 1976). The weathering process can be divided into two categories: 1. mechanical (wind, glaciation, frost heaving) and 2. chemical (dissolution, reprecipitation), both of which contribute to the river load. The river load itself is of two types, dissolved and suspended. A few elements, including Sr, Ca and Cl are carried by surface waters mainly in the dissolved form (Meybeck, 1979). In this treatise the emphasis will be placed on chemical weathering and the dissolved load.

1.2.1. Sources of Sr, Ca and Cl in river water.

Chemical weathering of silica (quartz), evaporites (anhydrite and gypsum) and carbonate minerals such as calcite ($Ca\ CO_3$) and dolomite $Ca\ Mg\ (CO_3)_2$ proceeds by congruent dissolution - the dissolved material has the same composition as the original solid phase -- (Holland, 1978; chapter 2). Carbonic acid -- carbonate equilibria result in the formation of soluble bicarbonates and the release of cations

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$$

$$Ca\ Mg\ (CO_3)_2 + 2CO_2 + 2H_2O = Ca^{2+} + 4HCO_3^-$$

In contrast, iron and silicate minerals weather by incongruent dissolution -- an original mineral dissolves to form a new mineral plus dissolved constituents - (Garrels and Mackenzie, 1971, p. 154). Reaction of aluminosilicate minerals with water will result in a mineral richer in Al than the original one and in a release of silica and cations into solution.

$$2\ Na,K\ Al\ Si_3\ O_8\ (\text{Albite, K-spar}) + 2\ CO_2 + 11\ H_2O =$$

$$Al_2\ Si_2\ O_5(OH)_4\ (\text{Kaolinite}) + 2K,Na^+ + 2HCO_3^- + 4H_4SiO_4$$

Most of the strontium in the earth's crust occurs in trace quantities dispersed in rock-forming and accessory minerals. Physical properties of elements most closely resembling Sr suggest that it should be

intermediate in behaviour to Ca and Ba and should also resemble K. The major host minerals of strontium are calcite, aragonite, sulfates (anhydrite and gypsum) and the feldspars (plagioclase and potassium feldspar). Strontium usually substitutes in lattice positions for Ca (Deer et al, 1975; pp 322, 478) because of their similar radii (1.08 vs. 1.21 Å; Whittaker and Muntus, 1970). Because of their divergent sizes, (.80 and .69Å; Whittaker and Muntus, 1970) Mg and Fe minerals usually contain less than a tenth of the Sr encountered in the coexisting feldspars. Sr can also form its own minerals: strontianite ($SrCO_3$) and celestite ($SrSO_4$). These are frequent in hydrothermal deposits and in evaporitic, carbonate and sulfate rocks (Mason and Berry 1968; pp 347, 362).

On the basis of Ca concentrations, it was suggested that carbonate rocks supply approximately 75% of the Sr in river water (Brass, 1976), with the remainder originating from silicate weathering (Garrels and Perry, 1974). Sr is carried in rivers in the 2+ ionic state and Martin and Meybeck (1979), utilizing the measurements of Durum et al. (1960), propose that its average concentration is 60 ppb.

Calcium forms 3.5% of the continental crust by weight (Hahn and Eysel, 1970) and is fifth in abundance among all elements. It is a major constituent of

many rock-forming minerals, in particular alumino-silicates, silicates, phosphates, carbonates, sulfates and fluorides. In igneous rocks the major Ca minerals are plagioclases and pyroxenes. In hydrothermal associations, calcite, dolomite and fluorite are dominant. Anhydrite, scheelite and zeolites can also be important. Because Ca is a major constituent of carbonate sediments, its behaviour in the weathering cycle is well known (Holland, 1978; p. 16). It is supplied primarily by plagioclase, pyroxene, amphibole and epidote in igneous and metamorphic environments and by calcite, dolomite, anhydrite and gypsum in sedimentary sequences. In natural waters, Ca concentrations are buffered by carbonates, phosphates and sulfates. Calculations (Holland, 1978, p. 115-123) show that roughly 85% of all Ca in sedimentary rocks is present in carbonate minerals. Equilibrium with atmospheric $CO_2$ (and with $CO_2$ derived from decomposition of organic matter), controls the bicarbonate concentration in rivers (Holland, 1978, p.16). River water contains on average 15 ppm Ca (Livingstone, 1963; Meybeck, 1979) in the $2+$ state.

Odum (1957) calculated that the average Sr/Ca ratio for world rivers is approximately $4.8 \times 10^{-3}$, while Turekian (1964) found this ratio to range between $4.5 \times 10^{-3}$ and $8.2 \times 10^{-3}$ in rivers of the United States.

Brass (1976) assumed a $Sr/Ca_i$ ratio of $5.0 \times 10^{-3}$ for limestone derived Sr and Ca and used this to calculate the average concentration of Sr in river water as 68 ppb. This value compares well with the previously quoted estimate of Durum et al. (1960).

Most of the chlorine released during weathering is carried as the $Cl^-$ ion in river water and its average concentration is estimated to be 7.8 ppm (Livingstone, 1963). Its major sources are atmospherically recycled sea salts and dissolution of sedimentary, particularly evaporitic, rocks (Hem, 1959; Holland, 1978; pp 93-95, 140). Volcanic gases and thermal springs may also contribute Cl into river water (Hem 1959). However, much of Cl in river waters may have been derived from industrial (e.g. chloride-containing fertilizers) rather than from natural sources (Hutchinson, 1968). In several areas (e.g. California and Japan), dry fallout has been found to contribute a greater percentage of Cl in river water than wet precipitation (Sugawara, 1967; Hem, 1959).

Chlorine is described as a cyclic element (Goldschmidt, 1954), derived directly or indirectly from the sea and returned there by river discharge. Recently, however, Stallard and Edmond (1981) studied the cyclicity of various elements at peak discharge in the Amazon River. Only 18% of Cl and 0.1% of Ca were

determined to be cyclic. These values are somewhat lower than expected, suggesting that Meybeck's (1979) figure of 20% for the cyclic portion of the river flux is too high.

### 1.2.2. Control of Sr Isotopic Composition in Weathering Products.

Rubidium is an alkali metal belonging to Group 1A along with Li, Na, K, Cs and Fr. Its ionic radius is 1.57 Å (Whittaker and Muntus, 1970) allowing it to substitute for potassium (1.46Å). Rb does not form any minerals of its own but is common in K- minerals such as muscovite, biotite, phlogopite and lepidolite. It is also found in certain clay minerals and in evaporite minerals. Rb has two isotopes: $^{85}_{37}$ Rb and $^{87}_{37}$ Rb. Their percentage abundances are 72.17 and 27.83 respectively (Faure, 1977, p. 75).

Strontium, an alkaline earth element from Group II A (Be, Ca, Mg, Ba, Ra), has an ionic radius (1.21 Å) (Whittaker and Muntus, 1970) enabling it to substitute for Ca and K in many minerals. Sr has 4 naturally occurring isotopes: $^{88}_{38}$Sr, $^{87}_{38}$Sr, $^{86}_{38}$Sr and $^{84}_{38}$Sr. The percentage abundances are 82.59, 6.98, 9.87 and 0.56 respectively (Faure, 1977; p. 78). $^{87}$Rb decays to $^{87}$Sr by the following process:

$$^{87}_{37}\text{Rb} = ^{87}_{38}\text{Sr} + \beta^- + \bar{\nu} + Q \qquad Q = .275 \text{ Mev.}$$

The growth of radiogenic $^{87}Sr$ can be described by the equation: $^{87}Sr = {}^{87}Sr_o + {}^{87}Rb\ (e^{\lambda t} - 1)$ where $^{87}Sr_o$ = $^{87}Sr$ initial concentration, $\lambda$ = decay constant for $^{87}Rb$. Dividing by the stable $^{86}Sr$ isotope, the equation is restated as:

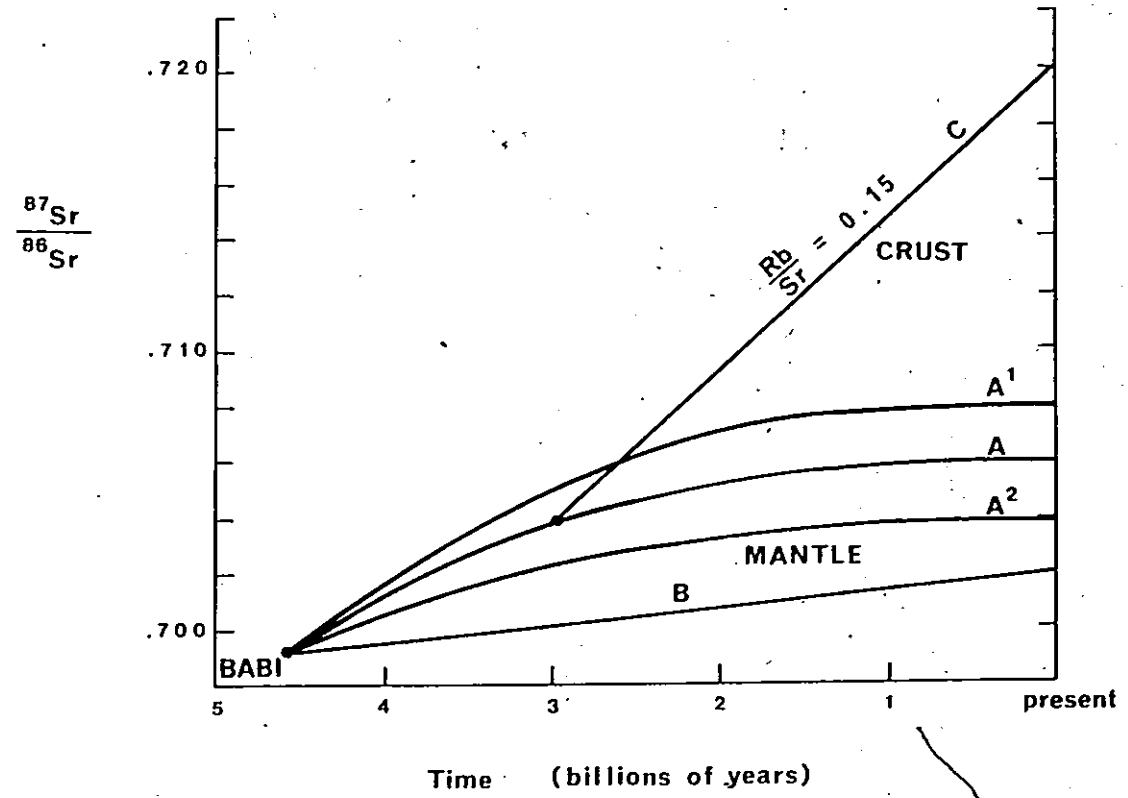
$$^{87}Sr/^{86}Sr = (^{87}Sr/^{86}Sr)_o + {}^{87}Rb/^{86}Sr\ (e^{\lambda t} - 1).$$

The isotopic composition of Sr in terrestrial systems has therefore been changing, the rate of change being dependent on the Rb/Sr ratio of the system. Continental crust, due to its fractionated nature, has an order of magnitude higher Rb/Sr ratio (.014 - .06 vs. .20 -.35; Gast, 1960) than is the case for the mantle. Consequently these two reservoirs have distinctly different Sr isotopic evolutionary pathways (Fig. 1.2).

The $^{87}Sr/^{86}Sr$ ratio of the oceans today is fairly uniform at .7091 (Wasserburg et al, 1969; Veizer and Compston, 1974). This value is controlled by the mixing of three isotopic varieties of Sr: young volcanics ($^{87}Sr/^{86}Sr \cong .703$); old crustal sialic rocks ($\cong .720$); and marine carbonates and other sediments ($\cong .708$) (Faure, 1977, chapter 8). Most of the Sr entering the oceans is derived from the chemical weathering of carbonates with smaller contributions from silicic and volcanic continental sources (Faure, 1977, p.128). The current estimate for the combined (carbonate and silicate derived) Sr isotopic ratio of river water is

Fig. 1.2

Isotopic evolution of terrestrial strontium (modified from Faure, 1977)




Explanations: $A^1$, A, $A^2$ represent possible evolutionary paths of Sr in the mantle. B represents Sr evolution in regions of the mantle depleted in Rb. C represents evolution of Sr separated from the mantle 2.9 b.y. ago and residing in an environment with Rb/Sr = 0.15, ie. continental crust. BABI stands for Basaltic Achondrite Best Initial; the 87Sr/86Sr ratio thought to be closest to the initial ratio of the earth ($\sim$ .699).

.716 - .720 (Veizer and Compston, 1974; Brass, 1976); a value considerably more radiogenic than that of ocean water.

Weathering of the continental crust supplies dissolved Sr to the ocean, with $^{87}Sr/^{86}Sr$ ratios reflecting the ages and compositions of the various crustal components as well as their relative contributions to the Sr load of rivers. During weathering of silicate rocks (eg. Mesozoic arkoses in New Zealand; Brass, 1975) the Sr in solid weathering products may become several percent more radiogenic than the parent material, but Sr in solution is only slightly less radiogenic than the source rock. This is due to the fact that radiogenic Sr is usually contained in the more stable mineral phases, which originally contained more Rb and thus more of the daughter $^{87}Sr$.

### 1.2.3 River Transport For Canada and the World.

For large river systems the composition of total dissolved solids is different for various tributaries due to variations in the nature of drainage basin geology. However, the integration of waters from many tributaries in the downstream parts of the rivers leads to similarities in river water chemistry. The larger the drainage basin of a river, the closer -- on average -- will its geology approach the mean chemical

composition of the upper continental crust. Consequently, the chemical composition of river water will also be more representative of the global mean. The concentrations of Ca, Cl, Sr and total dissolved solids in Canadian and world rivers are given in Table 1.1 and Fig. 1.3. Four estimates of the average world river composition are given in Table 1.2 and these can be compared with data in Table 1.3 showing the average composition of rivers of the U.S.S.R.

## 1.3 Mechanisms of Elemental Removal From The Oceans

Since the ocean is clearly a transitional reservoir for all chemical species carried by rivers, it is evident that removal processes must be of overwhelming significance for maintenance of seawater chemical composition (Sillén, 1961; Drever, 1971; Maynard, 1976; Holland, 1978, chapter 5; Li, 1981).

Authigenic mineral formation (carbonates) is the principal removal mechanism for Ca (Holland, 1978, pp 167-168) and Sr (Broecker, 1971; Li, 1981). The combined rate of deposition of calcite and aragonite (mainly as organic skeletons) is $8.5 \times 10^{14}$ g / year (Broecker, 1971). This corresponds to a removal of $12.3 \times 10^{12}$ g of Ca per year. Other sinks for Ca (sulfates, aluminosilicates) are insignificant in comparison to the carbonates (Holland, 1978, p. 167).

TABLE 1.1 CHEMICAL COMPOSITION OF CANADIAN AND WORLD RIVERS
(dissolved load only)

| RIVER | Ca (ppm) 1 | 2 | 3 | Av. | Cl (ppm) 1 | 3 | Av. | Sr (ppb) 1 | T.D.S. (ppm) 1 | 2 | 3 | Av. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Amazon | 12.5 | 16 | 7 | 11.8 | 2.3 | 4 | 3.2 | | 78.2 | 52.4 | 50 | 60 |
| Congo | 4.0 | 7.1 | 8 | 6.4 | 5.3 | 1.4 | 3.4 | | 84.7 | 38 | 80 | 68 |
| Yangtze | | | | | | | | | | 11.2 | | 11 |
| Orinoco | 3.2 | 3.0 | 2.5 | 2.9 | 1 | | 1 | | 53.5 | 52 | 68 | 58 |
| Plata-Parana | 7.3 | 5.9 | 2 | 5.1 | 15.9 | | 16 | | 114 | 100 | 110 | 108 |
| Yenisei | | | | | | | | | | 135 | | 135 |
| Brahmaputra | | | | | | | | | | 124 | | 124 |
| Lena | 18 | | | 18 | 15.2 | | 15 | | 143 | 165 | | 154 |
| Zambezi | | | | | | | | | | 70 | | 70 |
| Mekong | 32.1 | 5.9 | | 19 | 6.9 | | 6.9 | | 204 | 105 | | 155 |
| St. Lawrence | 36 | | 30 | 33 | 16 | 10 | 13 | | 206 | 161 | 160 | 176 |
| Mississippi | 34 | 16.7 | | 25 | 10.3 | 15 | 13 | 61 | 223 | 223 | 220 | 222 |
| Ganges | | 26.5 | | 27 | | | | | | 208 | | 208 |
| Ob | 24.3 | | | 24 | | | | | 129 | 130 | | 130 |
| Amur | | | | | | | | | | 57 | | 57 |
| Mackenzie | 37 | 71 | | 54 | 7.5 | 1 | 4.3 | 96 | 219 | 230 | 210 | 220 |
| Volga | 80.4 | | | 80 | 19.9 | | 20 | | 458 | 290 | | 374 |
| Yukon | 47 | | 35 | 41 | 0.7 | 1.8 | 1.3 | 123 | 268 | 174 | 200 | 214 |
| Indus | | | | | | | | | | 295 | | 295 |
| Danube | 58.3 | 45 | 30 | 44 | 2.6 | | 2.6 | | 332 | 300 | 230 | 287 |
| Niger | 6.5 | | 8 | 7.3 | 18 | 9 | 14 | | 98 | 53 | 95 | 82 |
| Columbia | 19 | | 15 | 17 | 1.1 | 3 | 2.1 | | 107 | 139 | 95 | 114 |
| Pechora | | | 4 | 4 | | 8 | 8 | | 45 | | | 45 |
| Fraser | 20 | | 12 | 16 | 1.5 | | 1.5 | 18 | 106 | | 80 | 93 |

TABLE 1.1 CHEMICAL COMPOSITION OF CANADIAN AND WORLD RIVERS (CONT'D.)
(dissolved load only)

| | Ca (ppm) | | | | Cl (ppm) | | | Sr (ppb) | T.D.S. (ppm) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RIVER | 1 | 2' | 3 | Av. | 1 | 3 | Av. | 1 | 1 | 2 | 3 | Av. |
| Dvina | | | 40 | 40 | | 15 | 15 | | 247 | | | 247 |
| Uruguay | 3.9 | | 1 | 2.5 | 0.2 | | 0.2 | | 49.6 | 50 | 48 | 49 |
| Nelson | 35 | | | 35 | 32 | | 32 | 86 | | | | |
| Nile | 15.8 | 40.3 | | 28 | 3.4 | | 3.4 | | 161 | 208 | 150 | 173 |
| Dnepr | 55.7 | | | 56 | 9.2 | | 9.2 | | 287 | 210 | 290 | 262 |
| Saguenay | 3.6 | | | 3.6 | 0.5 | | 0.5 | | 18.6 | | | 19 |
| Don | 82 | | 70 | 76 | 44 | | 44 | | 568 | 495 | 530 | 531 |
| St. John | 17 | | | 17 | 2.3 | | 2.3 | | 95 | | | 95 |
| St. Maurice | 4.8 | | | 4.8 | 0.8 | | 0.8 | | 32.1 | | | 32 |
| Churchill (Man.) | 14 | | | 14 | 1.6 | | 1.6 | 37 | 91.8 | | | 91 |

1. Livingstone (1963)
2. Meybeck (1976)
2' Martin and Meybeck (1978)
3. Holland (1978)

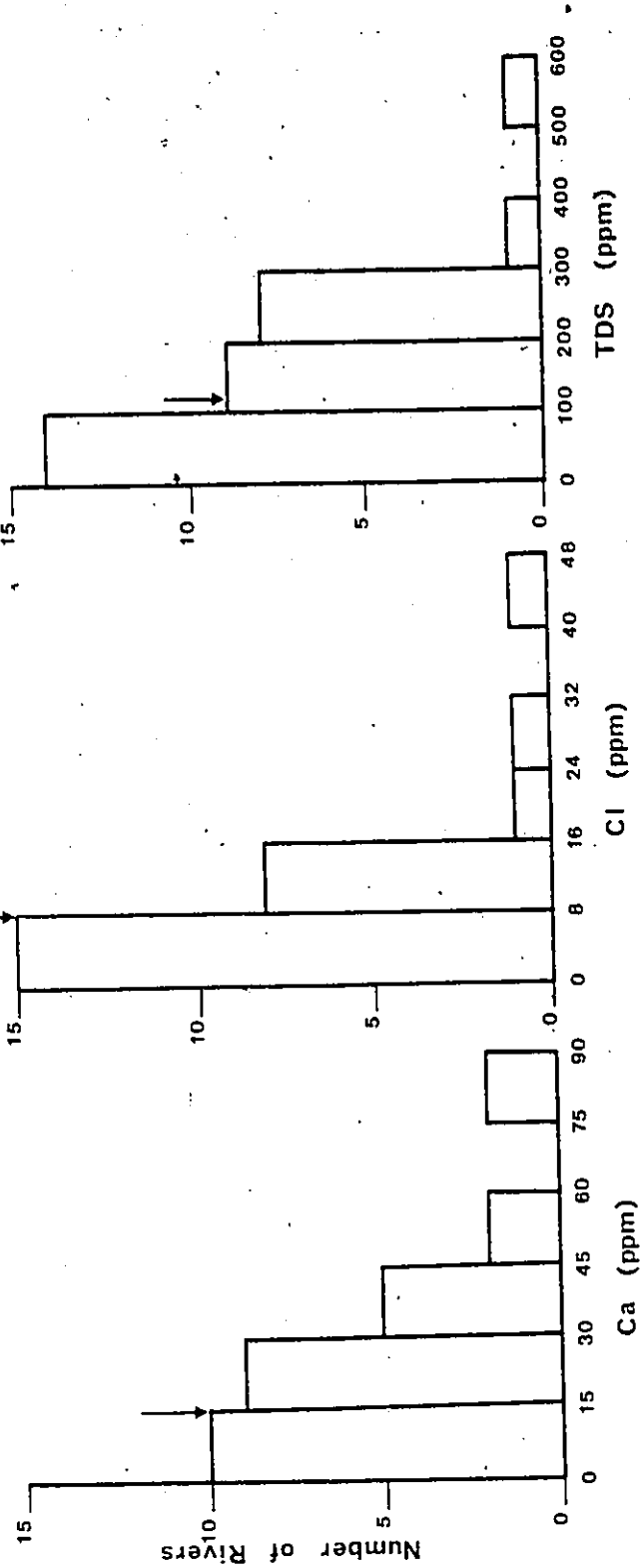



Fig. 1.3
Frequency histograms of selected chemical data for major world rivers (Averages from Table 1.1). Solid arrows show weighed world averages according to Livingstone (1963).

TABLE 1.2 AVERAGE CHEMICAL COMPOSITION OF RIVER DISSOLVED LOAD
(concentrations in ppm)

| Ca | Mg | Na+K | $HCO_3$ | $SO_4$ | Cl | $SiO_2$ | Total | Reference |
|---|---|---|---|---|---|---|---|---|
| 15 | 4.1 | 8.0 | 58.4 | 11.2 | 7.8 | 13.1 | 120 | Livingstone (1963) |
| 14.6 | 3.8 | 6.5 | 57.7 | 8.5 | 5.3 | 11.6 | 108 | Meybeck (1977) |
| 13.4 | 3.4 | 6.5 | 52 | 8.3 | 5.8 | 10.4 | 100 | Meybeck (1979) |
| 15.0 | 3.9 | 9.0 | 55.9 | 10.6 | 8.1 | 13.1 | 116 | Gibbs (1972) |

TABLE 1.3 AVERAGE DISSOLVED LOAD OF THE U.S.S.R. RIVERS
(Alekin and Braznikova, 1968)
(concentrations in ppm)

| Ca | Mg | Na+K | $HCO_3$ | $SO_4$ | Cl | TOTAL |
|---|---|---|---|---|---|---|
| 16.5 | 4.06 | 7.67 | 58.2 | 12.2 | 8.76 | 107.4 |

Brass and Turekian (1974) established significant variations in the Sr/salinity ratio of ocean water with depth. There is a gradual enrichment (1.5%) in Sr in the deep Pacific waters moving northwards. This is believed to result from precipitation of $SrSO_4$ tests by acantharians in the surface waters and their almost complete dissolution below 400 meters depth, combined with simultaneous dissolution of aragonite (Berner, 1977). Sr/Ca ratios of deep sea carbonates probably have not changed significantly with time over the past $6 \times 10^7$ years (Turekian, 1964) because Sr concentrations in marine shells, particularly brachiopods, did not vary appreciably since the Mississippian (Lowenstam, 1961).

Burial of pore water in sediments (Maynard, in press) is also considered important in the growth of authigenic minerals, in particular of authigenic silicate minerals such as montmorillonite and illite. However, the importance of this sink for Ca and Sr budgets has not been estimated.

Li (1981) advocates formation of surface complexes at hydrous oxide interfaces as the most important removal mechanism for elements (except those dominated by authigenic mineral formation) from the ocean. Overall Ca removal is therefore believed to be controlled by a combination of removal processes involving manganese oxide phases, aluminosilicates, carbonates and barite. Similarly, Sayles and Mangelsdorf (1977) concluded that clay minerals were

sufficiently abundant to absorb the major cations of seawater such as $Mg^{2+}$, $Ca^{2+}$, $Na^{+}$ and $K^{+}$ and that the exchange capacities of manganese oxide and iron hydroxide phases could absorb all other elements.

## 1.4 Seawater -- Basalt Interaction

The existence of submarine hydrothermal systems was first suggested by Elder (1965) on the basis of high conductive heat flow measurements and by analogy with subareal geothermal systems. Heat flow near the ridge axis is anomalously less, however, than predictions made from thermal models (Wolery and Sleep, 1976). Corliss et al. (1979a) contoured an oscillating heat flow pattern around ridge systems and concluded that this suggested a mechanism of a convectively cooling plate, with heat loss, by hydrothermal circulation, most intense at the ridge axis. The observed heat flow anomaly can be utilized to calculate the magnitude of flow of heated seawater from ridge hydrothermal systems and this, in turn, enables quantification of geochemical fluxes caused by seawater - basalt interaction. These fluxes were found to be comparable in their order of magnitude to fluxes into the oceans from rivers, (Mottl and Holland, 1978). The proposed overall chemical reactions of seawater with basalt are as follows (Garrels and Mackenzie, 1971; modified by Veizer, 1979).

1. basalt + $2CO_2$ + $H_2O$ = Na - feldspar + clay minerals
+ (Ca, Fe, Mn) carbonate + $2HCO_3^-$
+ Fe oxides + $SiO_2$

2. NaCl + Na, Ca - feldspar = Na- feldspar + $CaCl_2$

Veizer (in press) and Wolery and Sleep (in press), however, questioned the proposed magnitude of these hydrothermal fluxes for major elements (with the possible exceptions of Na and Ca) mostly because they are not sustainable on a geological time scale without causing enormous anomalies in the chemical composition of the global sedimentary mass.

Ca is enriched by 10.2 - 19.2 x $10^{22}$ g in the sedimentary mass (Ronov and Yaroshevski, 1969; Veizer, 1979). Lowengart (1975) has explained the Ca excess as a result of an initial magnesium excess followed by exchange of magnesium for mantle calcium through oceanic interaction. Pytkowicz (1979, 1980) also attributes the excess of Ca to oceanic weathering of basalts. Weathering of plagioclase generates soluble $Ca(HCO_3)_2$ which is then converted to $CaCO_3$ (actually $Ca_xMg_{1-x}CO_3$) in the oceans. Strontium, because of its affinity to Ca, may be expected to behave similarly. Li (1981) has calculated the river input and oceanic sediment output fluxes for various major and trace elements. The basis of his calculations are the total mass of sedimentary rocks today (M sed), the total mass of crustal igneous rocks (M ig) weathered to produce

the sedimentary mass (Mig = .88 Msed), the fractions of various sedimentary rock types, the total mass of seawater and the concentration of the given element in each reservoir. He has determined perfect mass balance for Sr indicating that all Sr in Msed originates solely from weathering of igneous rocks. Ca, in contrast, shows the largest excess in Msed, but seawater-basalt interaction is ruled out as a possible source of this Ca. Li would prefer to recalculate the sedimentary rock type fractions to eliminate the excess Ca.

Despite the above uncertainties, seawater-basalt interaction is becoming more and more attractive as the most likely mechanism (source or sink) for explanation of discrepancies in mass-balance calculations. It takes place under a wide range of temperatures and water/rock ratios. Uncertainties in prevailing conditions, however, are considerable. The available information for the fluxes of Sr, $^{87}Sr/^{86}Sr$ and Ca can be summarized as follows.

Andrews (1977), studying the effects of low temperature fluid alteration on oceanic layer II basalts, discovered that smectites were the most abundant alteration products, although alteration was not uniform. Cold seawater penetrated to at least 600 m, the maximum depth drilled and alteration was typified by the palagonite-phillipsite association and oxidation haloes. Ca, as calcite, was uniformly distributed throughout both oxidized

and adjacent unoxidized rocks. No consistent trend was observed for Sr. In some cases it was uniformly distributed, in others, the oxidized portion was enriched up to a factor of 2.

Lawrence et al. (1975) determined large and reasonably systematic decreases in the pore fluid $^{18}O/^{16}O$ with depth in the sediment column, possibly related to mineralogical changes which could be difficult to detect. Since the amount of oxygen is roughly the same in the pore fluids as in the solids, the observed change in the $^{18}O/^{16}O$ ratio of the pore fluids indicates substantial recrystallization of the solid phases and this is confirmed by the observed correlations between oxygen isotopes and major cation ($Ca^{2+}$, $Mg^{2+}$, $K^{+}$) abundances in pore waters. Reactions which could produce the observed gradients are alteration of: volcanic ash or basalt to montmorillonite or zeolites, detrital minerals to authigenic minerals, biogenic silica to chert, and carbonate fossils to chalk or limestone. However, these reactions do not explain the fact that the gradients are greatest at sites closest to fracture zones. Consequently, the low temperature weathering of basalt may be the real cause of oxygen isotope (Muehlenbachs and Clayton, 1972) and cation variations. In contrast to the major cations, $Sr^{2+}$ concentrations varied with sediment thickness and with sedimentation rate and thus the rate of carbonate recrystallization (Manheim and Sayles, 1971). In the

Galapagos area significant fracture control has been clearly demonstrated, also for high temperature alteration of basalts (Corliss et al. 1978, 1979a).

All studies, to date, have shown that the absence or presence of various mineral phases is paramount for mobility of specific elements. The relative distribution of these phases is dependent on temperature, pressure and water/rock ratio. However, the directions and magnitudes of chemical exchange and of alteration temperatures inferred from greenstone mineralogy are often equivocal.

Chlorite-rich and epidote-rich greenstones are the most common products of heated seawater/basalt interaction. Bulk-rock Ca contents of hydrothermally altered pillow basalts dredged from the Mid-Atlantic Ridge show a linear decrease with increasing water content; up to a factor of 3 from the centre to the edge (Humphris and Thompson, 1978). The epidote-rich assemblages have greater Ca contents than the chlorite-rich ones due to the retention - in epidote - of Ca released during the albitization of plagioclase. Staudigel et al. (1981) found that vein calcites deposited from circulated seawater had Sr/Ca ratios much lower than expected for marine calcite. The most probable mechanism for lowering the Sr/Ca ratio of a seawater solution is a preferential leaching of Ca from basalt. This has been consistently observed. Alteration to phases such as palagonite, smectite and chlorite appears to release Ca preferentially to Sr.

The landward extension of the Reykjanes Ridge into southern Iceland is considered to be analogous to mid-ocean ridge hydrothermal systems. Mottl and Holland (1978) determined experimentally that the formation of alteration mineral assemblages buffers the Reykjanes solutions. In all cases Ca was leached from basalt. Sr, in contrast, was leached in most cases but gained in others, depending on the nature of mineral phases formed. The formation of calcium silicate alteration phases and strontium enrichment in epidote-rich assemblages may represent the end product of seawater-basalt interaction at fairly low water/rock ratios and high temperatures (Menzies and Seyfried, 1979). Under these conditions, Sr is not solubilized but remains in one or more of the calcic alteration phases. At higher water/rock ratios, basalt is totally replaced by an alteration assemblage containing anhydrite, a sink for Sr. Considerable leaching of Ca from basalt precludes formation of calcic alteration phases. Sr is also leached and, in the absence of calcium silicate alteration phases, anhydrite provides a temporary reservoir for both elements.

The $^{87}Sr/^{86}Sr$ ratio of any product of reactions between seawater and basalt directly reflects the relative proportions of seawater and basalt Sr involved. O'Nions et al. (1978) compared the $^{87}Sr/^{86}Sr$ ratios in unaltered basalts to values obtained from basalts in the North Atlantic Ocean and the Southeast Indian Ridge. They

concluded that ocean floor basalt is an important sink for radiogenic marine Sr. DePaolo (1980), from the observations of Hart et al. (1974), suggested the possibility of selective return to the mantle of $^{87}Sr$. Based on a time dependent, two reservoir model, he estimated the mass of $^{87}Sr$ returned to the mantle to be $1.4 \times 10^{17}$ g/billion yrs. This corresponds to an increase in $^{87}Sr/^{86}Sr$ of about 0.00035 for 5 km of oceanic crust. The trend of increasing $^{87}Sr/^{86}Sr$ in altered basalts is consistent at various water/rock ratios.

Staudigel et al. (1981) compared alkali concentrations with $^{87}Sr/^{86}Sr$ for smectites and proto-celadonites (smectite structure but alkali concentrations of celadonite). They found no clear correlation, perhaps due to crystallographic considerations. The $^{87}Sr/^{86}Sr$ ratio of the smectite might reflect the $^{87}Sr/^{86}Sr$ ratio of the solution at the time and site of basalt-seawater reaction. It would be altered by additional, low temperature, circulating solutions because of its position in the octahedral layer. In contrast, Richardson et al. (1980) found a crude correlation between $^{87}Sr/^{86}Sr$ ratio of smectite in 108 my old oceanic crust and depth. The surface values are close to a seawater (calcite) value, but with depth an increasing basaltic component is evident. Where smectites coexist with calcites, Sr isotope disequilibrium suggests that these were precipitated from different solutions. Albarède

et al. (1981) used the $^{87}Sr/^{86}Sr$ ratios of East Pacific Rise hydrothermal waters to define a mixing line between ambient seawater and a hot (340 $\pm$ 30° C) hydrothermal solution deprived of significant magnesium. The $^{87}Sr/^{86}Sr$ ratio of their hydrothermal endmember was estimated as .7030. Since seawater originally had the Sr isotopic composition of 0.709, this must signify that, during its alteration into hydrothermal brine, most of its Sr was exchanged for Sr from basalts. This directly supports the proposition that basalts in the ridge systems act as a sink for radiogenic marine $^{87}Sr$ from circulating seawater.

A study of the Reykjanes geothermal system (Elderfield and Greaves, 1981) also confirmed that basalts had been subject to strontium isotopic contamination, as their $^{87}Sr/^{86}Sr$ ratios were higher than for fresh basalts. If the oceanic crust does remove $^{87}Sr$ from seawater and recycles it into the mantle, then the oceans must act as an important but intermediate reservoir for $^{87}Sr$. It is more difficult to detect this effect in the actual alteration, solid phases involved.

While the existence of Sr isotopic exchange between basalts and seawater appears to be firmly established, it is not yet clear how pervasive is this effect. Hart and Staudigel (1979) claim that circulation of seawater is significant as a geochemical flux only for the first 10 my after crust formation. Staudigel et al. (1981, in press) subsequently reduced this value to 3.5 my, because whole-

rock $H_2O$ values reach saturation at 3.5 my. However $CO_2$ concentrations are much higher in the 108 my old crust than in the 3.5 my old one, suggesting that carbonate precipitation is incomplete in the younger crust. Their model involves four stages: 1. Formation of palagonite, 2. Formation of smectite, 3. Precipitation of carbonate and 4. Dehydration and crustal settling. Stages one and two represent halmyrolysis (15 - 80°C) and last for approximately 3 my. During this time there is evidence of significant basaltic Sr in the reaction and alteration products, extending through at least the upper 500m of basaltic layer II. Stage three involves no basaltic Sr but apparently, basaltic Ca is utilized. No significant chemical changes take place during stage four. However, as previously discussed, $\delta^{18}O$ data from pore fluids (Lawrence et al., 1975; Lawrence and Gieskes, 1981) indicate that alteration continues well beyond these ages.

## 1.5 Summary

Both Sr and Ca in river water are derived primarily from the dissolution of carbonates and are carried in the dissolved load in the 2+ ionic state. Their concentrations in world average river water are 68 ppb and 15 ppm respectively. Cl is a cyclic element derived either directly or indirectly from the sea. It too is carried in the dissolved load with an average concentration of 7.8 ppm. The world

average for total dissolved solids of rivers is 120 ppm.

The $^{87}Sr/^{86}Sr$ ratios of the continental crust and mantle have been evolving along separate pathways and today these two reservoirs have distinctly different isotopic signatures. The $^{87}Sr/^{86}Sr$ ratio for continental crust is believed to be $\sim$ .716 and for the mantle (oceanic basalts) $\sim$ .703.

The oceans are capable of integrating the fluxes of Sr from sources with differing $^{87}Sr/^{86}Sr$ ratios and can therefore be used to monitor the respective Sr isotopic evolutions of the continental crust and the mantle.

The chemistry of the ocean is controlled by kinetic steady-states with material removed at essentially the same rate as it is supplied. The principal source of Sr and Ca in the oceans is the dissolved load of rivers. Authigenic mineral formation is the principal removal mechanism for both elements. However, the $^{87}Sr/^{86}Sr$ ratio of the continents is believed to be more radiogenic than that of the oceans, suggesting the existence of a complementary, non-radiogenic Sr source. In addition, from a mass balance point of view, the sediments contain an excess of Ca suggesting that this element may also be supplied by a source other than continental weathering.

One of the most important aspects of hydrothermal circulation of seawater through oceanic crust is its potential to act as a sink or source for elements on a

global scale. From the preceding discussion it is evident that there are many unanswered questions concerning the extent of this process for Ca and Sr.

Recent data confirm that Ca is released from basalt (due to weathering of feldspars) during seawater-basalt interaction, but not necessarily 1:1 for Mg. Results for Sr are equivocal. Most studies support the dependence of Sr and Ca hydrothermal fluxes on the modal mineral assemblages which buffer the composition of the solution. Water/rock ratios are also believed to be extremely significant for the fate of strontium. At low water/rock ratios Sr is not solubilized while at higher ratios it is mobilized.

Seawater-basalt interaction is known to increase the radiogenic $^{87}Sr$ component in basalt, but there is no significant relationship between $^{87}Sr/^{86}Sr$ ratios and Sr concentrations. This removal of radiogenic Sr may be of the same order of magnitude as the river Sr flux.

In general, hydrothermal fluxes could account for the excess of sedimentary calcium. They are likely unimportant for the mass balance of elemental Sr, but probably play an important role in maintaining the $^{87}Sr/^{86}Sr$ ratio of the oceans.

# 2. METHODOLOGY

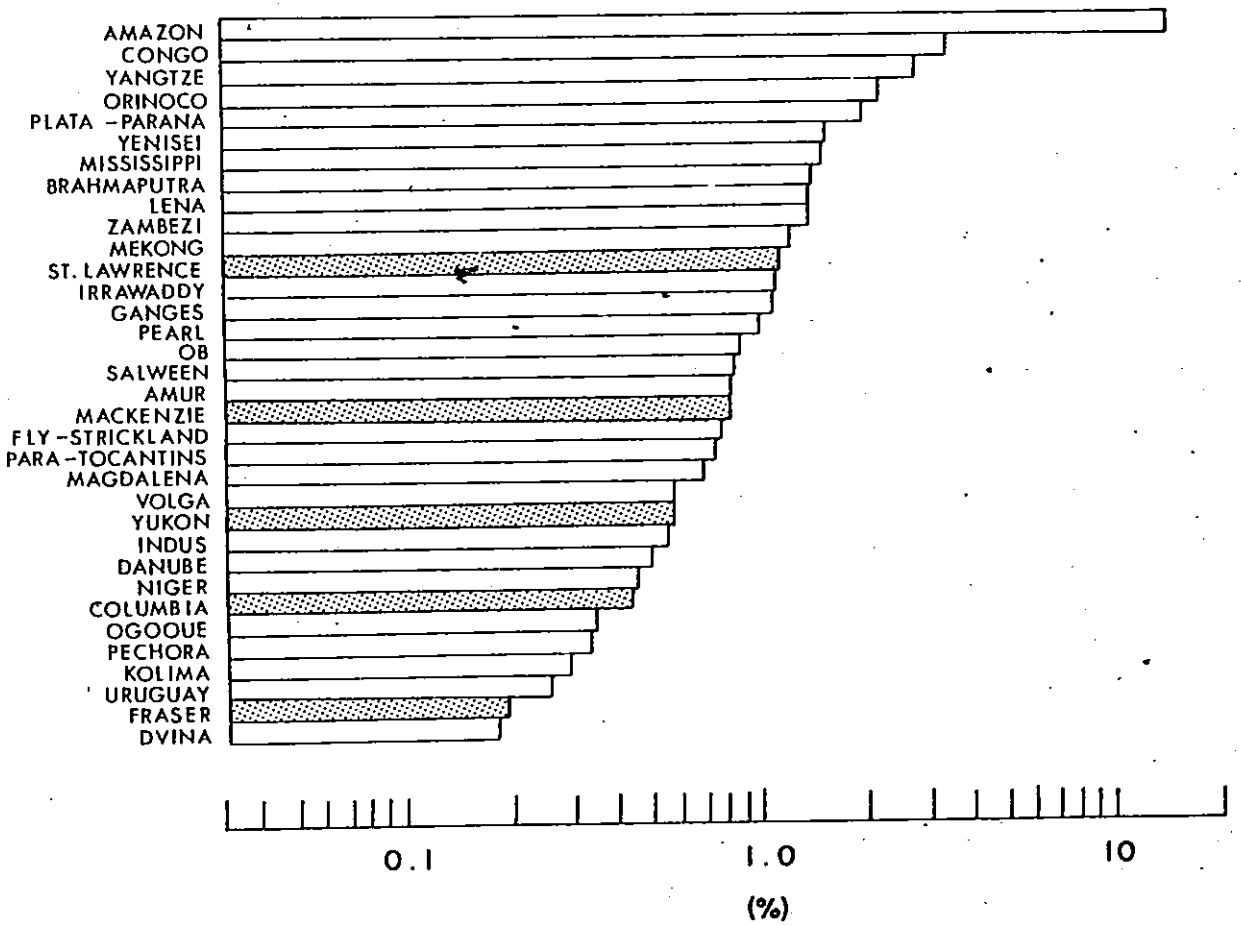
## 2.1 Data Base: Canadian vs. world rivers

The relative Sr flux between seawater and oceanic crust can be calculated indirectly if the following variables are known: 1. the isotopic composition of ocean water, 2. the isotopic composition of the oceanic crust ( = mantle), and 3. the isotopic composition of continental runoff. The first two parameters are well documented (Veizer and Compston, 1974; Hoffman and Hart, 1978). However, the $^{87}Sr/^{86}Sr$ ratio for continental runoff of .716 was based mostly on sparse data from the Canadian Shield (see Table 2 in Veizer and Compston, 1974) and is therefore somewhat uncertain; particularly in view of the suggestions (previous chapter) that continental crust may be less radiogenic ( $\sim$ .710 -- DePaolo, 1980; $\sim$ .711 -- Albarède et al, 1981) than previously believed.

Since the primary source of Sr in the oceans is the dissolved load of rivers, samples of major world rivers should be used for the estimate of global Sr flux and of the $^{87}Sr/^{86}Sr$ ratio. The distribution of major world rivers according to their discharge is given in Fig. 2.1. The world annual discharge is estimated to be $3.74 \times 10^{16}$ litres (Martin and Meybeck, 1979). The largest river, the Amazon accounts for 14% of this total. The significance of each river decreases rapidly with the top 10 world rivers accounting for 30.8% and the top 30 accounting for 46.5%

Fig. 2.1

Contribution to total world discharge by major rivers.
(data from Showers, 1979)
Stippled bars indicate rivers included in the present study.



of the world total. It is thus evident that the few largest rivers are paramount in terms of their contribution to total world discharge. However, sampling of world rivers was not financially feasible and the study had to be restricted to Canadian rivers. Fig. 2.2 shows that Canadian rivers have a similar distribution pattern to world rivers with the two largest Canadian rivers, the St. Lawrence and the Mackenzie accounting together for 16.5% of the total Canadian discharge.

Canada can be divided into 39 major river basins (Fig. 2.3), which feed 4 major water bodies, the Pacific Ocean, the Atlantic Ocean, the Arctic Ocean and Hudson Bay. The total Canadian discharge is $3.311 \times 10^{15}$ litres/year (National Atlas of Canada, 1978), which represents 8.85% of the world total and the 39 largest rivers account for 48% of the Canadian total. This ranks integrated Canadian rivers second to the Amazon in terms of their contribution to world Discharge.

The above 39 Canadian rivers were sampled at stations near their mouths (Fig. 2.4) but just upstream of significant tidal effects to ensure that the samples did not contain any seawater contributions. Even a minor contribution from the latter would swamp the sample with marine Sr because its concentration in seawater is 3 orders of magnitude higher than in river waters (Veizer and Compston; 1974). Most of the sampling was done by the Water Quality Branch of

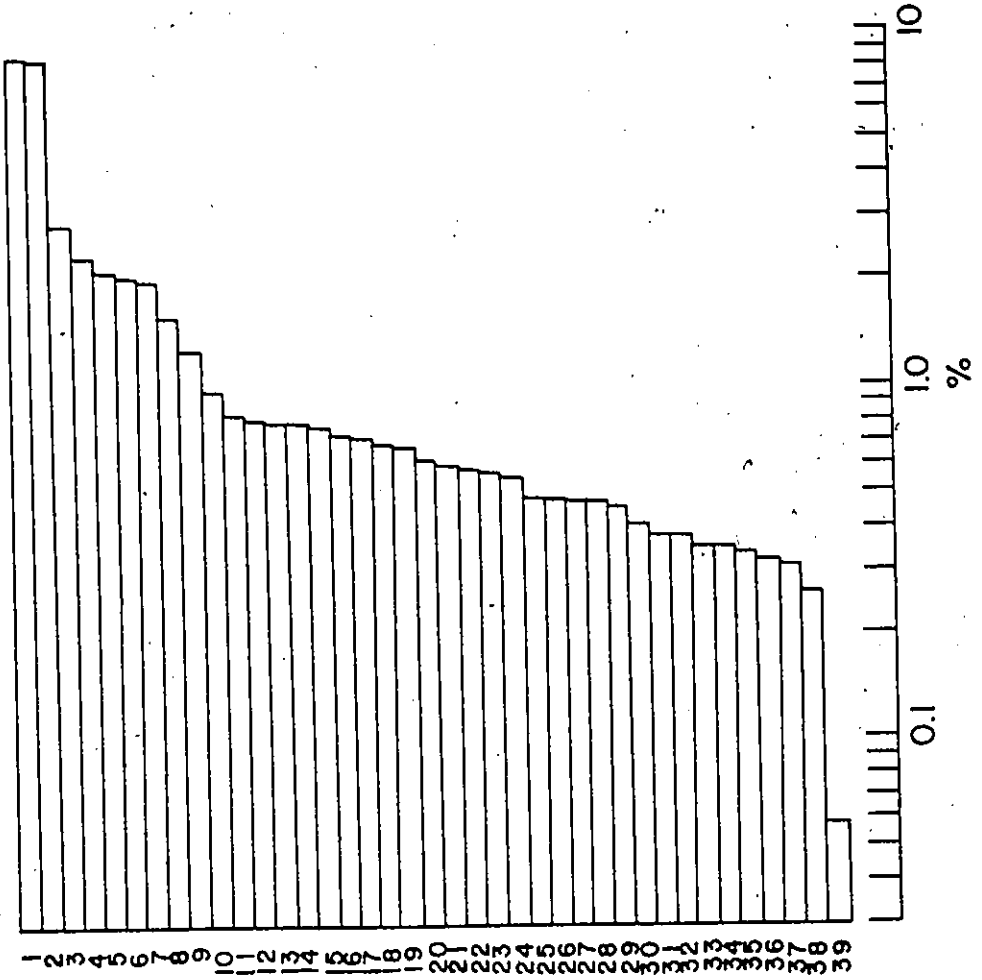



Fig. 2.2
Contribution to total Canadian discharge by 39 major rivers.

Fig. 2.2 (Cont'd.)
Explanation:
Only those rivers draining into surrounding oceans were considered. Rivers are numbered according to their decreasing contribution to Canadian discharge as follows: 1-St. Lawrence, 2-Mackenzie, 3-Fraser, 4-Columbia, 5-Churchill (Nfld.), 6-Nelson, 7-Yukon, 8-Koksoak, 9-Saguenay, 10-Nottaway, 11-Rupert, 12-Manicouagan, 13-St. John, 14-Skeena, 15-Nass, 16-LaGrande, 17-Stikine, 18-Albany, 19-Eastmain, 20-Severn, 21-Aux Feuilles, 22-St. Maurice, 23-Moose, 24-A la Baleine, 25-Grande Rivière de la Baleine, 26-Petit Mecatina, 27-Churchill (Man.), 28-Back, 29-Thelon, 30-Kazan, 31-Winisk, 32-Moisie, 33-Porcupine, 34-Aux Outardes, 35-Arnaud, 36-Hayes, 37-Natashquan, 38-Attawapiskat, 39-Harricana.

Sources: 1. Quebec rivers : Hydro Quebec (pers. com.)
2. Rest of Canada : Environment Canada, Surface Water Data Reference Index (1979, 1980)

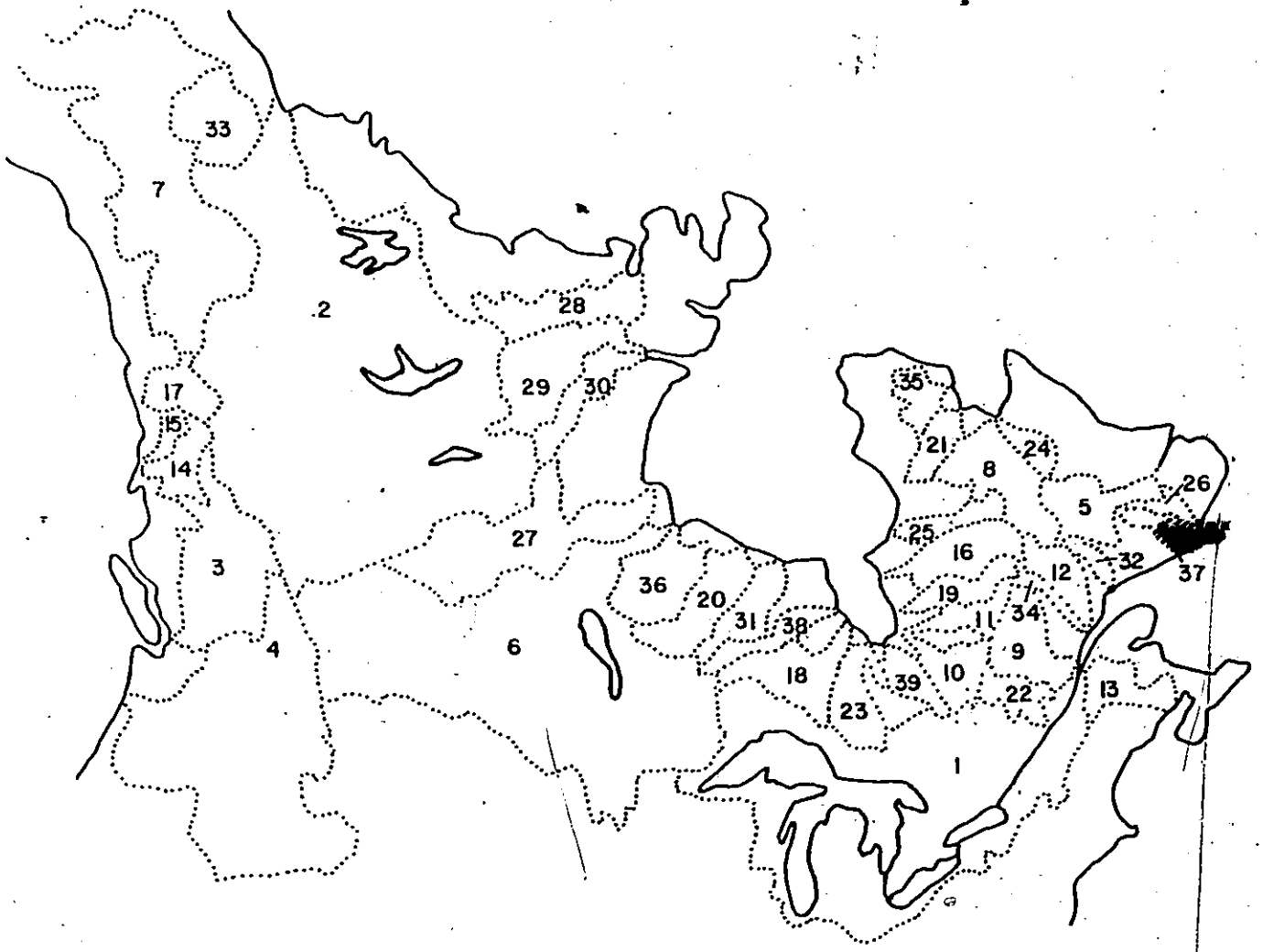



Fig. 2.3

Drainage basins of the 39 largest Canadian rivers.
Numbers correspond to those in Fig. 2.2

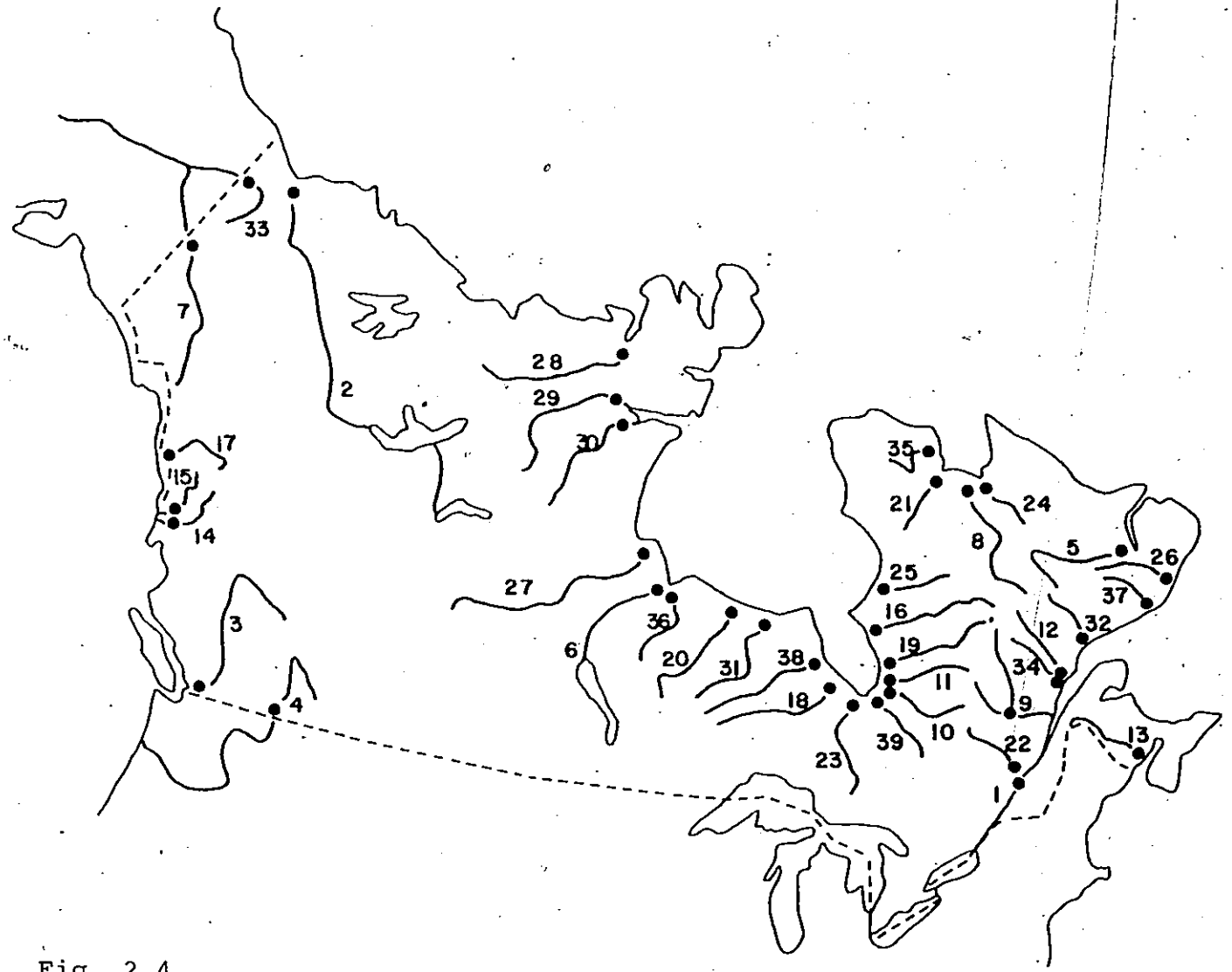



Fig. 2.4

Sample location map. See the text for further explanations. Numbers correspond to those in Fig. 2.2

Environment Canada (federal) and Hydro Quebec (provincial). 31 out of 39 rivers were sampled under more than one flow regime.

## 2.2 Sampling, Preservation and Storage

The basic aims of sampling (Wilson, 1974) are: 1. to obtain a sample whose concentrations of the desired elements are identical to those in the water at the time of sampling, 2. to repeat this sampling operation at times such that the required information or any change is obtained, and 3. to ensure that the concentrations do not change between sampling and analysis. Generally, it is more meaningful to analyze a number of separate samples taken at different times and at different locations than to try to compile and analyze a representative sample (Manahan, 1975).

The materials used for sampling should be chosen so that contamination is not expected. Plastics, such as polyethylene, are suitable especially when trace amounts of metals are to be determined. Some authors recommend that sample containers be rinsed 2 - 3 times with the sample before filling. This is preferable when dissolved materials are of interest. However, this is inconvenient when the sample is to be collected into some preserving agent. In general, it is probably better to ensure that sample containers are adequately clean and free of water and then collect the sample directly into the container. Most

analysts favour linear polyethylene bottles for analysis of metals whose concentrations are less than 1 ppm. Very thorough cleaning is recommended and the bottles should be tested with high purity water to ensure that contamination is not a problem. The preserving agent should be included in the testing. One type of contamination peculiar to polyethylene is diffusion of gaseous substances through the walls of the bottles in both directions. High density, linear polyethylene reduces this effect.

It is a common practice to acidify waters at the time of collection in order to reduce the possibility of loss of elements by adsorption onto the walls of the containers. Stability of most metals is ensured by acidification to pH 2 and samples can be stored for long periods of time if preserving agents are used. A maximum of 6 months is reported by Manahan (1975) but certain elements have been known to remain stable for many years.

The most general method of sample preservation is refrigeration to 4°C. Freezing should normally be avoided because of physical changes such as formation of precipitates and loss of gases, which may adversely affect sample composition. Biological activity, a common source of sample instability, is usually prevented or inhibited by storing the sample in the dark and at reduced temperature. Microbiological activity could, for example, convert residual chlorine into chloride.

The volume of sample collected is usually unimportant provided it is sufficient for the required analyses. A one litre sample, even considering the high dilution factors, is usually sufficient to ensure that the limits of analytical detection are met.

Two types of sample collection were carried out:

1. linear polyethylene bottles (one acidified with 2 ml ultrapure nitric acid), prepared according to standards established by the Inland Waters Directorate (1973), were sent to each sampling site, for each of high, medium and low flow periods. The samples were returned by mail to the University of Ottawa where each one was filtered through 0.45 μ Millipore apparatus. The samples were then stored at 4°C for subsequent analyses. 215 samples were obtained representing all 39 rivers. Sampling began in the summer (July) of 1979 and finished in the fall (October) of 1980 (Table 2.1).

2. The Ottawa River and the St. Lawrence River were selected as pilot rivers to monitor monthly fluctuations in water composition for the elements of interest. One location on the Ottawa River, the Champlain Bridge, and two locations on the St. Lawrence River, Prescott and Brockville, were sampled for one year (October, 1979 to October 1980). 18 (9 acidified, 9 untreated) samples of the Ottawa River and 36 (18 acidified, 18 untreated) samples of the St. Lawrence River were obtained. These were treated in the

TABLE 2.1 RIVER AND SAMPLE NUMBERS

| RIVERS | NO. | SAMPLE NUMBERS | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1979 | | | 1980 | | | |
| | | SUMMER | FALL | WINTER | SPRING | SUMMER | FALL | |
| Yukon | 7 | | | | 1 | 2 3 | | |
| Porcupine | 33 | | | | 1 | 2 3 | | |
| Stikine | 17 | | | | 1 | 2 | 3 | |
| Nass | 15 | | | | 1 | 2 | 3 | |
| Skeena | 14 | | | 1 | 2 | 3 | | |
| Fraser | 3 | | | | 1 | | | |
| Columbia | 4 | | 1 | 2 | | 3 | | |
| Mackenzie | 2 | 1 2 3 | | | | | | |
| Back | 21 | 1 | 2 | | | | | |
| Thelon | 29 | 1 | 2 | 3 | | | | |
| Kazan | 30 | 1 | | | | | | |
| Churchill (M) | 27 | | 1 | | | 2 | 3 | |
| Nelson | 6 | | 1 | | | 2 | 3 | |
| Hayes | 36 | 1 | | | | | 2 | |
| Severn | 20 | | | | 1 | 2 | | |
| Winisk | 31 | | | | 1 | 2 | | |
| Attawapiskat | 38 | | | | 1 | 2 | 3 | |
| Albany | 18 | | | | 1 | 2 | 3 | |
| Moose | 23 | | | | 1 | 2 | 3 | |
| Churchill (N) | 5 | 1 | 2 | | 3 | | | |
| St. John | 13 | 1 | | 2 | 3 | | | |

TABLE 2.1 RIVER AND SAMPLE NUMBERS
(Cont'd)

| RIVERS | NO. | SAMPLE NUMBERS | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1979 | | | 1980 | | |
| | | SUMMER | FALL | WINTER | SPRING | SUMMER | FALL |
| Harricana | 39 | | | | 1 | 2 | 3 |
| Nottaway | 10 | | | | 1 | 2 | 3 |
| Rupert | 11 | | | | 1 | 2 | 3 |
| Eastmain | 19 | | | | 1 | 2 | |
| La Grande | 16 | | | | | 1 | 2 |
| Grande Rivière de la Baliene | 25 | | | | 1 | 2 | |
| Arnaud | 35 | | | | 1 | 2 | 3 |
| Aux Feuilles | 21 | | | | 1 | 2 | |
| Koksoak | | | | | 1 | 2 | 3 |
| A la Baleine | 24 | | | | 1 | 2 | 3 |
| Petit Mecatina | 26 | | | | 1 | 2 | 3 |
| Natashquan | 37 | | | | 1 | 2 | |
| Moisie | 32 | | | | 1 | 2 | 3 |
| Manicouagan | 12 | | | | | 1 2 3 | |
| Aux Outardes | 34 | | | | | 1 2 3 | |
| Saguenay | 9 | | | | | | 1 |
| St. Maurice | 22 | | 1 | 2 | 3 | | |
| St. Lawrence | 1 | | | | 1 | 2 | 3 |

same manner as in 1.

Four of the bottles were washed with the same phosphate-free detergent as the sample bottles and were used for testing. Two mls of ultrapure $HNO_3$ were added to two of the bottles and all four were filled with deionized water. No contamination was observed for any of the desired elements throughout the entire period of analysis.

Initially, analyses were performed on both the acidified and unacidified samples with one acting as a control for the other. However, based on a comparison of total dissolved solids values for the two types of samples (Table 2.2), it was decided that acidified samples only should be used for subsequent analysis. It was apparent that the unacidified samples had lost a significant proportion (approximately half) of the analyte elements.

## 2.3 Analytical Techniques

The analytical methods used, together with corresponding precisions and accuracies, are summarized in Table 2.3 and their details are in the references cited and in the subsequent text.

### 2.3.1 Strontium Determinations By Carbon Rod Atomizer.

The carbon rod atomizer is an alternative means of atomization for atomic absorption, used to its greatest advantage where the flame method is weak. It is especially useful when greater analytical sensitivity is

TABLE 2.2 TOTAL DISSOLVED SOLIDS

ACIDIFIED VS. UNTREATED SAMPLES (ppm)

| RIVER | NO. | SAMPLE | |
|---|---|---|---|
| | | ACIDIFIED | UNTREATED |
| Yukon | 1 | 214 | 128 |
| Porcupine | 1 | 160 | 82 |
| Columbia | 2 | 174 | 98 |
| Nass | 1 | 116 | 63 |
| Skeena | 2 | 86 | 33 |
| Fraser | 1 | 159 | 59 |

Sample numbers correspond to those in Table 2.1

TABLE 2.3 ANALYTICAL TECHNIQUES, PRECISION AND ACCURACY

| PARAMETER | METHOD | CONCENTRATION RANGE | PRECISION[1] | ACCURACY[2] | REFERENCE |
|---|---|---|---|---|---|
| $Sr^{2+}$ | Flameless Atomic Absorption Spectroscopy | 5-195 ppb | $\pm$3.2 ppb | $\pm$2ppb | Varian Techtron Analytical Methods for Carbon Rod Atomizers (1975) |
| $^{87}Sr/^{86}Sr$ | Mass Spectrometry | .70459-.73844 | $\pm$.00016 | $\pm$.00005 | Brooks (1980) |
| $Ca^{2+}$ | Flame Atomic Absorption Spectroscopy | 0.6- 34 ppm | $\pm$ 2.6 ppm | $\pm$ 0.8 ppm | Varian Techtron Analytical Methods for Flame Spectroscopy (1972) |
| $Cl^-$ | Potentiometry Ion Specific Electrode | N.D. -28 ppm | $\pm$1.0 ppm | $\pm$0.9 ppm | Midgely and Torrence (1978). |
| T.D.S. | Gravimetric Analysis | 10 -339 ppm | $\pm$ 12 ppm | No standards for comparison | Analytical Methods Manual, Environment Canada 1974 |

1. Precision is expressed according to Hunter (1980) as $\pm 2\sigma$ where $\sigma$ corresponds to the standard deviation (S.D.). The equation for calculation of S.D. based on duplicate analyses is:

$$S.D. = \sum \text{differences between duplicate determinations} \div \text{No. of duplicate determinations} \div 1.128$$ (Clark, 1980).

2. See text for explanation.

required. The carbon rod is 20 - 500 x more sensitive than the flame for most elements. In addition, the required sample is much smaller ( $\leq$ 20 µl per determination). It is not advisable, however, to use the carbon rod when: 1) the sample can be easily analyzed by flame, 2) better than 2% analytical accuracy is required or 3) a very refractory element is to be analyzed (Varian Techtron, 1975).

The principle of analysis is the same for flame and flameless determinations; selective absorption of line radiation by atomic species in the vapour phase (Sturgeon, 1977). Analytical signals obtained with electrothermal atomizers are curves having peaks with the exact shape of the curves being determined by the physical and chemical properties of the matrix, by the geometry and construction material of the sample cell, by the heating rate of the atomizer and by the distortion of the signal caused by the finite response time of the amplifier - recorder system used.

Fortunately, aqueous matrices are among the easiest to analyse and they rarely require pretreatment. There should be no spatial or temporal thermal gradient in the sample cell (L'vov, 1970), ie. the temperature should be constant during the formation of atoms. It is best to use graphite tubes made from anisotropic pyrolytic graphite, a vapour deposited form

of graphite which produces a lamellar structure. As a result of this, the electrical and thermal conductivities are different in different directions. The thermal conductivity perpendicular to the lamellae (c-axis) is about 225 x greater than parallel to them (a-axis). Therefore in the a - direction pyrolytic graphite is a good conductor while in the c-direction it behaves more like an insulator. Consequently, heating of these tubes is relatively isothermal in time and along the length of the tube (Chakrabarti et al, 1980).

Heating rate is determined by several parameters, according to the nature of the analyte element. The rate at which a sample evaporates (and also the rate of molecular dissociation) depends on the rate of increase of temperature. " At temperatures at which the analyte has significant vapor pressure, it is important that the atomizer attain a sufficiently high temperature before a sizeable fraction of the element is lost from the analytical volume" (Sturgeon, 1977). On the other hand, the temperature should not be increased more than is necessary to completely vaporize (and dissociate) the analyte, since the rate of loss of atomic vapor becomes too great. After evaporation, Sr is in the form of a nitrate. It therefore atomizes upon heating, by dissociation its oxide according to the

following equation:

$$M_xO_y\ (s,l) = M_xO_y\ (g) = xM\ (g) + yO\ (g)$$

where M = metal and O = oxide (Sturgeon and Chakrabarti, 1978). This is vapour phase dissociation as opposed to condensed phase reduction by carbon. Since Sr is a relatively low volatility element, high rates of heating are expected to increase its sensitivity, Also, Sr can form a refractory carbide with the graphite tube. A slow rate of heating would give it time to react and would reduce sensitivity by creating a "memory effect". Temperatures $> 2800^{\circ}C$ are required to dissociate carbides (Varian Techtron Analytical Methods for C.R.A., 1975).

The residence time of the atom in the analysis volume is proportional to the square of the length of the absorbing medium (L'vov, 1970). The tube for the C.R.A.-90 has a small length and is not conducive to large ( $>$ 1 sec) residence times. This fact becomes important when choosing the method of signal measurement. The most widely used method of signal measurement is by measurement of the maximum or peak absorbance attained. If a sample is completely atomized in time t, which is less than the residence time of the atoms, the peak absorbance must correspond to the total number of atoms in the sample. In the case of the C.R.A.-90 the peak method was found to be the most suitable.

A sheath gas is used to provide an inert atmosphere for atomization. The peak absorbance decreases with decreasing molecular weight of the sheath gas because diffusion of atoms from the absorption cell becomes easier (Sturgeon and Chakrabarti, 1978). For this reason, an argon atomsphere was chosen.

One of the main differences between flame and flameless atomization is the mechanics of molecular dissociation. The nature (oxidizing, reducing) and chemistry (air-acetylene, nitrous oxide-acetylene) rather than the temperature of the flame are important for flame analyses, while it is the atomization temperature as well as the temperature of the reducing environment which control flameless atomization. Flameless atomization is achieved by a 3-stage heating program (DRY, ASH, ATOMIZE). An aliquot (5 - 10 µl) of the material to be analysed is placed inside the graphite tube with a micropipette. During the DRY stage the solvent is gently evaporated, leaving behind the analyte and the other dissolved solids. During the ASH stage portions of the matrix are thermally decomposed and removed from the tube. Finally, during the ATOMIZE stage the remaining compounds are dissociated and the analyte atoms enter the light beam so that absorption can be measured.

The following operating conditions were developed

for Sr on the Varian Techtron C.R.A. - 90:

WAVELENGTH: 4605.6 Å (460.56 nm)

DRY TEMPERATURE: 115°C

DRY TIME: 30 - 40 sec.

ASH TEMPERATURE: 1000°C

ASH TIME: 20 sec.

ATOMIZE TEMPERATURE: 2350°C

RAMP RATE: 800° C/sec

HOLD TIME: 2 sec

MODE: PEAK ABSORBANCE

The vast majority of elements have interference problems that are complex and not always predictable. These problems are the limiting factor in the use of electrothermal atomizers (Van Loon, 1980). In the case of Sr major interference was produced by the other cations present in the water (particularly Ca). A portion of the Ca is atomized under the same working conditions as Sr causing an enhancement of the Sr signal. Since the intensity of interference seemed to vary directly with Ca concentration, calibration curves were prepared to determine the exact effect of Ca on the Sr signal. Standards containing only Ca (and acid) in concentrations corresponding to the actual water samples were analyzed for Sr, using the carbon rod and reference curves were obtained. The apparent Sr absorbance readings were then compared with these curves

and the actual Sr concentrations determined.

Precision of the Sr determinations was calculated according to the formula for duplicate analysis given in Table 2.3. Table 2.4 shows the actual duplicate values obtained for 24 samples during Sr measurement.

Accuracy was estimated by measuring the Sr concentrations of three samples by isotope dilution. The details of the procedure are in Appendix C. The results are summarized in Table 2.5. They show that the agreement was better than 3 ppb or 12.5 relative percent.

### 2.3.2 Mass Spectrometric Determination of $^{87}Sr/^{86}Sr$

Mass spectrometry separates charged atoms and molecules by their masses on the basis of their behaviour in electrical and/or magnetic fields. For general principles of mass spectrometry see Faure (1977, pages 65 - 68). The strontium isotopic compositions for this study were determined on a single-stage, modified, National Bureau of Standards, 12 inch (30cm) radius, $60^{\circ}$ deflection, solid-source mass spectrometer (Brooks, 1980). Within-run precision is expressed as the 95% confidence interval around the mean according to the formula $\frac{2\sigma}{\sqrt{N}}$ where

$\sigma$ is the standard deviation of all measurements and

N is the number of ratio measurements made. By increasing the number of ratios the precision can be reduced to the desired value. In this way, the maximum error

TABLE 2.4 TABLE OF DUPLICATE ANALYSES FOR STRONTIUM PRECISION DETERMINATIONS

| RESULT #1 | RESULT #2 | DIFFERENCE |
|---|---|---|
| 108 (ppb) | 110 (ppb) | 2 (ppb) |
| 74 | 75 | 1 |
| 61 | 62 | 1 |
| 75 | 79 | 4 |
| 63 | 63 | 0 |
| 78 | 73 | 5 |
| 160 | 160 | 0 |
| 13 | 15 | 2 |
| 36 | 32 | 4 |
| 17 | 18 | 1 |
| 56 | 59 | 3 |
| 40 | 35 | 5 |
| 12 | 10 | 2 |
| 4 | 7 | 3 |
| 10 | 10 | 0 |
| 5 | 6 | 1 |
| 21 | 21 | 0 |
| 16 | 20 | 4 |
| 18 | 18 | 0 |
| 13 | 17 | 4 |
| 7 | 7 | 0 |
| 9 | 10 | 1 |
| 8 | 9 | 1 |

TABLE 2.5 COMPARISON OF A.A.S. AND ISOTOPE DILUTION RESULTS FOR Sr IN SELECTED SAMPLES

(sample numbers correspond to those in Table 2.1)

| RIVER | SAMPLE | CONCENTRATION BY A.A.S. | CONCENTRATION BY I.D. | ppb | RELATIVE % |
|---|---|---|---|---|---|
| Eastmain | 2 | 7 ppb | 8 ppb | 1 | 12.5 |
| Winisk | 1 | 17 | 17 | 0 | 0 |
| Nelson | 1 | 72 | 75 | 3 | 4 |

for $^{87}Sr/^{86}Sr$ ratios of the rivers was kept at $\sim$ .00010.

Overall precision was calculated as described in Table 2.3. Table 2.6 shows the results of duplicate $^{87}Sr/^{86}Sr$ analyses. Accuracy was determined by measuring the $^{87}Sr/^{86}Sr$ ratio of a standard sample of $SrCO_3$ prepared by Eimer and Amend. The ratio obtained in the laboratory is compared to the actual $^{87}Sr/^{86}Sr$ ratio of the standard (.7080) and the appropriate correction is made to each measurement. The Eimer and Amend standard was measured three times through the course of the analysis. The average obtained was .70815 ± .00005.

Sample Preparation: 50 and 100 ml teflon beakers were cleaned by soaking overnight in 50% reagent grade nitric acid with a few millilitres of hydrofluoric acid. As each beaker was removed from the acid solution it was rinsed 3 times with distilled water and 3 times with quartz distilled water.

30 - 50 mls of sample were placed in the 100 ml teflon beakers and evaporated (sub-boiling) on a hot plate. They were removed to cool. When cool and dry, 1-2 ml of 6.2N distilled HCl was added to dissolve the residue. This was dried on a hot plate. 1 ml of 2.5N distilled HCl was added with a micropipette to re-dissolve the sample. This 1 ml solution was poured into cleaned (as above) centrifuge tubes and centrifuged 10-15 minutes.

TABLE 2.6 TABLE OF DUPLICATE ANALYSES FOR $^{87}Sr/^{86}Sr$

PRECISION DETERMINATION

| RESULT #1 | RESULT #2 | DIFFERENCE |
|---|---|---|
| .71125 | .71131 | .00006 |
| .71257 | .71268 | .00011 |
| .72020 | .72020 | .00000 |
| .71971 | .71979 | .00008 |
| .71250 | .71242 | .00008 |
| .71987 | .72007 | .0002 |

The samples were then loaded onto ion exchange columns, which had been cleaned with 6.2 N HCl and back-washed twice or more if necessary, with 2.5N HCl. Three 2 ml washings were performed after loading to start the sample moving down the column. 60 ml of 2.5N HCl was then added to the columns to remove various cations ($Rb^+$ ,$Ca^{2+}$ , etc.) from the resin. Subsequently 18 ml was added and the eluate collected in the cleaned 50 ml teflon beakers; this portion containing the Sr.

The 18 ml portion was evaporated on a hot plate and then treated with 1 - 3 drops of perchloric acid to remove any organic material and then 1 - 3 drops of ultra pure $HNO_3$ and dried. The Sr is now in the form of $Sr(NO_3)_2$ suitable for loading into the mass spectrometer.

Loading: .02 mm-thick tantalum filaments were first loaded with $TaO_2$. This enhances the emission of Sr and generally gives longer sample life. Unfortunately it also enhances the emission of Rb but since Rb is ionized at a lower temperature than Sr, generally the advantages outweigh the disadvantages.

The sample was redissolved in 1 drop of $HNO_3$, loaded onto the filament, and dried before placing in the source.

Blanks: Blank samples were run and analytical error was determined to be negligible.

$^{90}Sr$: A scan was made of each sample for traces of $^{90}Sr$ but none were found.

### 2.3.3 Flame Atomic Absorption Spectroscopic Determination of Calcium

The technique is based on the absorption of radiation energy from a light source by valence electrons in the ground state atom population. The absorption of radiation is dependent on the population of the ground state, which is proportional to the solution concentration sprayed into the flame. General principles of flame atomic absorption analysis can be found in Walsh (1961), L'vov (1970), Willard et al. (1974) and many other texts. Operating parameters for Ca and details of the Varian Techtron Instrument are documented in "Varian Techtron Analytical Methods for Flame Spectroscopy" (1972).

Precision was determined as for Sr and $^{87}Sr/^{86}Sr$; according to the method described in Table 2.3. Table 2.7 shows the actual duplicate analyses for Ca.

Accuracy was estimated by comparison of analytical values with those of an Inland Waters Directorate Interlaboratory Study ($^{\#}32$) on a set of 10 reference waters. The results are summarized in Table 2.8. The standard deviation was estimated from the average difference in measured Ca concentrations. This value expressed in ppm is used as a measure of accuracy.

TABLE 2.7 TABLE OF DUPLICATE ANALYSES FOR CALCIUM PRECISION DETERMINATION

| RESULT #1 | RESULT #2 | DIFFERENCE |
|---|---|---|
| 35 ppm | 33 ppm | 2 ppm |
| 26 | 27 | 1 |
| 10 | 7 | 3 |
| 15 | 15 | 0 |
| 13 | 14 | 1 |
| 17 | 15 | 2 |
| 25 | 23 | 2 |
| 15 | 11 | 4 |
| 10 | 11 | 1 |
| 4 | 4 | 0 |
| 28 | 28 | 0 |

TABLE 2.8 COMPARISON OF ANALYTICAL RESULTS FOR CALCIUM ON SAMPLES FROM THE INTERNATIONAL JOINT COMMISSION INTERLABORATORY STUDY #32 FOR ESTIMATION OF ACCURACY

| PRESENT | RECOMMENDED | DIFFERENCE |
|---|---|---|
| 32.2 ppm | 31.4 ppm | 0.8 ppm |
| 25.4 | 25.3 | 0.1 |
| 34.0 | 34.0 | 0 |
| 12.4 | 13.3 | 0.9 |
| 1.0 | 0.52 | 0.48 |
| 0.9 | 0.70 | 0.2 |
| 2.2 | 1.75 | 0.45 |
| 25.2 | 23.0 | 2.2 |
| 61.4 | 58.3 | 3.1 |
| 0.2 | 0.1 | 0.1 |
| | | Ave.: 0.8 |

### 2.3.4 Potentiometric (Ion Specific Electrode) Determination of Cl

This method operates in the range of the Nernstein response of electrodes based on silver chloride for chloride concentrations of 10 - 350 ppm over a pH range of 1.5 to 12. Provision is also made for low level determinations (1 - 10 ppm) in the non-linear portion of the curve, in the same pH range (Orion, 1977).

Chlorides are present as simple ions in river water. Interferences come from processes which occur on the membrane electrode such as complex formation with $S^{2-}$, $CN^-$, $NH_3$, but the concentrations of these are very low in river water and consequently do not affect the determination. Neither trace elements nor major ions ($Na^+$, $K^+$, $HCO_3^-$, $SO_4^{2-}$) interfere with $Cl^-$ determinations by ion specific electrode (Zeinalova and Senyavin, 1975; Midgley and Torrence, 1978; Duff and Stuart, 1975).

Details concerning the analytical procedure can be found in the Instruction Manual - Halide Electrodes (Orion, 1977).

The precision of the $Cl^-$ analytical results was determined from 12 duplicate determinations (shown in Table 2.9) in the manner described for Ca. The accuracy was based on a comparison of results from the Inland Waters Directorate Interlaboratory Study (#32) (1981) as for Ca. These values are shown in Table 2.10.

TABLE 2.9 TABLE OF DUPLICATE ANALYSES FOR CHLORIDE PRECISION DETERMINATION

| RESULT #1 | RESULT #2 | DIFFERENCE |
|---|---|---|
| 0.5 ppm | 0.5 ppm | 0 ppm |
| 2.0 | 1.0 | 1.0 |
| 9.0 | 8.0 | 1.0 |
| 11.0 | 9.0 | 2.0 |
| 0.5 | 0.5 | 0 |
| 3.0 | 3.0 | 0 |
| 25.0 | 24.0 | 1.0 |
| 21.0 | 21.0 | 0 |

TABLE 2.10 COMPARISON OF ANALYTICAL RESULTS FOR CHLORIDE ON SAMPLES FROM THE INTERNATIONAL JOINT COMMISSION INTERLABORATORY STUDY #32 FOR ESTIMATION OF ACCURACY

| PRESENT | RECOMMENDED | DIFFERENCE |
|---|---|---|
| 17 ppm | 21 ppm | 3 ppm |
| 5.7 | 5.5 | 0.2 |
| 8.7 | 8.25 | 0.45 |
| 1.7 | 1.2 | 0.5 |
| 6.0 | 5.5 | 0.5 |
| 5.7 | 5.0 | 0.7 |
| | | Ave.: 0.9 ppm |

### 2.3.5 Gravimetric Determination of Total Dissolved Solids

Total dissolved solids is the term applied to the material left in a vessel after evaporation of a water sample that has been passed through a standard 0.45 μm filter and its subsequent drying to constant weight at 105°C.

The method of determination was taken from the Analytical Methods Manual, Environment Canada (1974).

Interference may result from large, floating particles (inhomogeneous materials) or floating oil and/or grease. However, residue determinations are generally not subject to the usual criteria of accuracy.

Precision was calculated based on the duplicate analyses shown in Table 2.11 according to the method described for Sr, $^{87}Sr/^{86}Sr$, Ca and Cl in Table 2.3.

TABLE 2.11 TABLE OF DUPLICATE ANALYSES

FOR TOTAL DISSOLVED SOLIDS PRECISION DETERMINATION

| RESULT #1 | RESULT #2 | DIFFERENCE |
|---|---|---|
| 95 (ppm) | 86 (ppm) | 9 (ppm) |
| 167 | 155 | 12 |
| 29 | 34 | 5 |
| 128 | 121 | 7 |
| 29 | 34 | 5 |
| 26 | 17 | 9 |
| 14 | 17 | 3 |
| 21 | 16 | 5 |
| 39 | 35 | 4 |
| 300 | 315 | 15 |

# 3. COMPOSITION AND CLASSIFICATION OF CANADIAN RIVERS

## 3.1 Composition of Canadian Rivers

The water samples were analyzed by the techniques listed in chapter 2. Complete data tables for each parameter are presented in Appendix A. Because of time considerations on the mass spectrometer, not all samples could be measured for their $^{87}Sr/^{86}Sr$ ratio. Instead, one sample from each river was analyzed and this was complemented by additional samples, chosen with consideration of all the chemical data to a total of 65 (Table 3.1). This abbreviated data set was used for the statistical evaluation of the controls on river water chemistry. The average composition of Canadian rivers is summarized in Table 3.2 and Fig. 3.1.

## 3.2 Classification of Canadian Rivers

Multivariate statistical analysis was used to determine the fundamental controls on river water composition by grouping the rivers on the basis of similar chemical characteristics. For a complete discussion of the mathematics involved see Jöreskog et al. (1976) or Krumbein and Graybill (1965).

Factor analysis is a technique of multivariate analyses which reduces the complexity of a data set to a small number of factors which account for the same information as the original data. R-mode factor analysis

TABLE 3.1 CHEMICAL COMPOSITION OF MAJOR CANADIAN RIVERS

| RIVER | NO. | SAMPLE | T.D.S. ppm | Ca ppm | Cl ppm | Sr ppb | $\frac{^{87}Sr}{^{86}Sr}$ | DISCHARGE $m^3/s$ | AREA $km^2$ | RUNOFF cm/yr |
|---|---|---|---|---|---|---|---|---|---|---|
| St. Lawrence | 1 | 1 | 339 | 28 | 21 | 145 | .70936 | 9070 | 1180000 | 24.2 |
| | | 2 | 267 | 27 | 22 | 135 | .70949 | 9130 | | 24.4 |
| | | 3 | 288 | 32 | 28 | 130 | .70952 | 9510 | | 25.4 |
| Mackenzie | 2 | 1 | 290 | 33 | 9 | 170 | .71102 | 22100 | 1660000 | 42.0 |
| Fraser | 3 | 1 | 159 | 15 | 0.5 | 80 | .71195 | 5700 | 228000 | 78.8 |
| Columbia | 4 | 2 | 167 | 20 | 0.5 | 78 | .71574 | 1853 | 155000 | 37.7 |
| | | 3 | 174 | 18 | 1.0 | 85 | .71553 | 2940 | | 59.8 |
| Churchill (N.) | 5 | 1 | 41 | 1.7 | 0.5 | 5 | .71756 | 2487 | 92500 | 84.8 |
| | | 2 | 31 | 1.7 | 0.5 | 9 | .71758 | 2050 | | 69.9 |
| Nelson | 6 | 1 | 249 | 24 | 11 | 72 | .71453 | 2190 | 1010000 | 6.84 |
| | | 2 | 228 | 23 | 11 | 68 | .71407 | 1090 | | 3.40 |
| | | 3 | 240 | 23 | 8.0 | 86 | .71528 | 2010 | | 6.27 |
| Yukon | 7 | 1 | 214 | 22 | 0.5 | 100 | .71614 | 2550 | 264000 | 30.5 |
| | | 2 | 279 | 35 | 0.5 | 115 | .71618 | 3240 | | 38.7 |
| Koksoak | 8 | 1 | 46 | 2.7 | 0.5 | 18 | .72865 | 360 | 133000 | 34.0 |
| | | 2 | 11 | 1.6 | 0.5 | 15 | .73161 | 2320 | | 219 |
| Saquenay | 9 | 1 | 24 | 4.0 | 0.5 | 23 | .71308 | 1200 | 90100 | 42.0 |
| Nottaway | 10 | 1 | 31 | 2.3 | 0.5 | 6 | .71857 | 368 | 65000 | 17.9 |
| | | 2 | 34 | 2.7 | 0.5 | 12 | .71722 | 1160 | | 57.3 |
| | | 3 | 51 | 3.3 | 0.5 | 15 | .71987 | 876 | | 42.5 |
| Rupert | 11 | 2 | 26 | 1.8 | 0.5 | 7 | .72832 | 1070 | 43300 | 77.9 |
| Manicouagan | 12 | 1 | 45 | 1.5 | 0.5 | 11 | .71686 | 735 | 45600 | 50.8 |
| St. John | 13 | 1 | 128 | 15 | 3.0 | 60 | .70977 | 336 | 39900 | 26.6 |

TABLE 3.1 (CONT'D.) CHEMICAL COMPOSITION OF MAJOR CANADIAN RIVERS

| RIVER | NO. | SAMPLE | T.D.S. ppm | Ca ppm | Cl ppm | Sr ppb | $\frac{^{87}Sr}{^{86}Sr}$ | DISCHAPGE $m^3/s$ | AREA $km^2$ | RUNOFF cm/yr |
|---|---|---|---|---|---|---|---|---|---|---|
| Skeena | 14 | 2 | 86 | 9.2 | 2.0 | 63 | .70459 | 1455 | 42200 | 109 |
| | | 3 | 86 | 10 | 0.5 | 78 | .70461 | 953 | | 71.2 |
| Nass | 15 | 1 | 116 | 12 | 0.5 | 110 | .70539 | 1232 | 19200 | 202 |
| | | 2 | 97 | 10 | 0.5 | 75 | .70541 | 1180 | | 194 |
| La Grande | 16 | 1 | 20 | 0.6 | 0.5 | 11 | .73456 | 1630 | 96900 | 53.1 |
| | | 2 | 10 | 0.5 | 0.5 | 12 | .73454 | 1000 | | 32.5 |
| Stikine | 17 | 1 | 183 | 16 | 0.5 | 60 | .70535 | 2020 | 36000 | 177 |
| | | 2 | 144 | 17 | 0.5 | 54 | .70548 | 1100 | | 96.4 |
| Albany | 18 | 1 | 130 | 13 | 0.5 | 19 | .71702 | 1604 | 118000 | 42.9 |
| | | 2 | 194 | 22 | 0.5 | 36 | .71448 | 352 | | 9.41 |
| Eastmain | 19 | 2 | 26 | 1.1 | 0.5 | 7 | .72845 | 1100 | 47400 | 73.9 |
| Severn | 20 | 2 | 201 | 18 | 0.5 | 40 | .71818 | 753 | 94300 | 25.2 |
| Aux Feuilles | 21 | 2 | 14 | 0.9 | 0.5 | 8 | .73471 | 873 | 43000 | 64.0 |
| St. Maurice | 22 | 1 | 45 | 2.7 | 1.6 | 13 | .71129 | 681 | 42700 | 50.3 |
| | | 3 | 32 | 2.0 | 0.5 | 7 | .71112 | 613 | | 45.3 |
| Moose. | 23 | 1 | 166 | 17 | 0.5 | 35 | .71363 | 1499 | 61100 | 77.4 |
| | | 2 | 214 | 25 | 0.5 | 60 | .71250 | 256 | | 13.2 |
| | | 3 | 203 | 25 | 0.5 | 30 | .71355 | 416 | | 21.5 |
| A la Baleine | 24 | 2 | 23 | 2.1 | 0.5 | 8 | .72647 | 482 | 31300 | 48.6 |
| Grande Riviere de al Baleine | 25 | 2 | 21 | 0.6 | 0.5 | 8 | .73844 | 954 | 42200 | 71.3 |
| Petit Mecatina | 26 | 2 | 40 | 0.8 | 0.5 | 7 | .71045 | 1540 | 19300 | 253.0 |
| Churchill (M.) | 27 | 2 | 147 | 18 | 0.5 | 23 | .72020 | 921 | 287000 | 9.02 |
| | | 3 | 202 | 20 | 1.0 | 28 | .71971 | 605 | | 6.65 |
| Back | 28 | 1 | 29 | 0.8 | 0.5 | 8 | .72910 | 2380 | 98200 | 76.4 |

TABLE 3.1 (CONT'D.) CHEMICAL COMPOSITION OF MAJOR CANADIAN RIVERS

| RIVER | NO. | SAMPLE | T.D.S. ppm | Ca ppm | Cl ppm | Sr ppb | $^{87}Sr/^{86}Sr$ | DISCHARGE $m^3/s$ | AREA $km^2$ | RUNOFF cm/yr |
|---|---|---|---|---|---|---|---|---|---|---|
| Thelon | 29 | 1 | 32 | 1.8 | 0.5 | 10 | .71880 | 1970 | 154000 | 40.3 |
| | | 3 | 38 | 1.8 | 0.5 | 20 | .71884 | 240 | | 4.92 |
| Kazan | 30 | 1 | 37 | 2.2 | 3.0 | 23 | .72579 | 1350 | 72300 | 58.9 |
| Winisk | 31 | 1 | 154 | 15 | 0.5 | 17 | .71769 | 478 | 50000 | 30.1 |
| Moisie | 32 | 1 | 39 | 3.5 | 0.5 | 13 | .71673 | 94.5 | 19200 | 15.5 |
| | | 2 | 16 | 1.5 | 0.5 | 7 | .71547 | 758 | | 125 |
| | | 3 | 32 | 2.6 | 0.5 | 17 | .71668 | 359 | | 59.1 |
| Porcupine | 33 | 1 | 160 | 13 | 0.5 | 30 | .71125 | 1340 | 55400 | 76.3 |
| | | 2 | 193 | 26 | 0.5 | 74 | .71257 | 585 | | 33.3 |
| Aux Outardes | 34 | 1 | 38 | 1.2 | 0.5 | 9 | .71864 | 314 | 18900 | 52.4 |
| Arnaud | 35 | 2 | 8 | 0.9 | 0.5 | 8 | .72638 | 815 | 49500 | 51.9 |
| Hayes | 36 | 1 | 250 | 27 | 0.5 | 38 | .71769 | 960 | 103000 | 29.4 |
| Natashquan | 37 | 2 | 26 | 0.8 | 0.5 | 6 | .71307 | 932 | 16800 | 175 |
| Attawapiskat | 38 | 2 | 172 | 20 | 0.5 | 38 | .71402 | 178 | 36000 | 15.6 |
| Harricana | 39 | 1 | 69 | 4.8 | 2.0 | 23 | .71786 | 143 | 29300 | 15.4 |
| | | 2 | 80 | 6.0 | 2.0 | 35 | .71576 | 40.5 | | 4.36 |
| | | 3 | 87 | 7.1 | 1.0 | 40 | .71578 | 44.5 | | 4.79 |

Explanation:
Rivers are numbered in order of decreasing mean annual discharge from 1 to 39. Sample number (1 to 3) denotes samples collected at different times of the year (see Table 2.1). Discharge and area data were taken from Environment Canada - Surface Water Data - Reference Index 1979, 1980.

TABLE 3.2 TABLE OF AVERAGE CONCENTRATIONS, DISCHARGES AND RUNOFF FOR THE MAJOR CANADIAN RIVERS

| RIVER | NO. | T.D.S. ppm | Ca ppm | Cl ppm | Sr ppb | $^{87}Sr/^{86}Sr$ | DISCHARGE $m^3/sec$ | AREA $km^2$ | RUNOFF cm/yr |
|---|---|---|---|---|---|---|---|---|---|
| St. Lawrence | 1 | 298 | 29 | 24 | 137 | .70946 | 9189 | 1180000 | 24.7 |
| Mackenzie | 2 | 291 | 33 | 9.0 | 175 | .71102 | 9170 | 1660000 | 42.0 |
| Fraser | 3 | 159 | 15 | 2.0 | 80 | .71195 | 3040 | 228000 | 78.8 |
| Columbia | 4 | 171 | 19 | 0.8 | 74 | .71563 | 2465 | 155000 | 48.8 |
| Churchill (N) | 5 | 34 | 1.8 | 0.5 | 7 | .71757 | 2230 | 92500 | 77.4 |
| Nelson | 6 | 239 | 23 | 10 | 75 | .71463 | 2145 | 1010000 | 5.5 |
| Yukon | 7 | 264 | 28 | 0.5 | 108 | .71616 | 2120 | 264000 | 34.6 |
| Koksoak | 8 | 28 | 2.4 | 0.5 | 15 | .73013 | 1657 | 133000 | 127 |
| Saguenay | 9 | 24 | 4.0 | 0.5 | 23 | .71308 | 1362 | 90100 | 42.0 |
| Nottaway | 10 | 39 | 2.8 | 0.5 | 11 | .71855 | 1032 | 65000 | 39.2 |
| Rupert | 11 | 23 | 1.8 | 0.5 | 7 | .72832 | 881 | 43300 | 77.9 |
| Manicouagan | 12 | 45 | 1.6 | 0.5 | 12 | .71686 | 866 | 45600 | 50.8 |
| St. John | 13 | 99 | 12 | 3.0 | 59 | .70977 | 839 | 39900 | 26.6 |
| Skeena | 14 | 89 | 10 | 2.8 | 71 | .70460 | 836 | 42200 | 90.0 |
| Nass | 15 | 106 | 12 | 0.5 | 97 | .70540 | 820 | 19200 | 198 |
| La Grande | 16 | 15 | 1.0 | 0.5 | 12 | .73455 | 775 | 96900 | 42.8 |
| Stikine | 17 | 166 | 17 | 0.5 | 58 | .70542 | 755 | 36000 | 137 |
| Albany | 18 | 171 | 18 | 0.5 | 28 | .71575 | 724 | 118000 | 26.2 |
| Eastmain | 19 | 20 | 1.0 | 0.5 | 6 | .72845 | 703 | 47400 | 73.9 |
| Severn | 20 | 173 | 17 | 0.5 | 34 | .71818 | 663 | 94300 | 25.2 |
| Aux Feuilles | 21 | 14 | 1.0 | 0.8 | 10 | .73471 | 630 | 43000 | 64.0 |
| St. Maurice | 22 | 39 | 2.1 | 1.0 | 11 | .71121 | 607 | 42700 | 47.8 |
| Moose | 23 | 194 | 22 | 0.5 | 42 | .71323 | 601 | 61100 | 37.4 |

TABLE 3.2 (Cont'd) TABLE OF AVERAGE CONCENTRATIONS, DISCHARGES AND RUNOFF FOR THE MAJOR CANADIAN RIVERS.

| RIVER | NO. | T.D.S. | Ca | Cl | Sr | $\frac{^{87}Sr}{^{86}Sr}$ | DISCHARGE | AREA | RUNOFF |
|---|---|---|---|---|---|---|---|---|---|
| | | ppm | ppm | ppm | ppb | | $m^3/sec$ | $km^2$ | cm/yr |
| A la Baleine | 24 | 38 | 3.7 | 0.5 | 14 | .72647 | 593 | 31300 | 48.6 |
| Grande Rivière de la Baleine | 25 | 14 | 0.8 | .0.5 | 9 | .73844 | 517 | 42200 | 71.3 |
| Petit Mecatina | 26 | 35 | 1.9 | 1.0 | 13 | .71045 | 517 | 19300 | 253 |
| Churchill (M) | 27 | 168 | 18 | 0.7 | 23 | .71996 | 507 | 287000 | 7.8 |
| Back | 28 | 26 | 0.7 | 0.5 | 8 | .72910 | 493 | 98200 | 76.4 |
| Thelon | 29 | 35 | 1.9 | 0.5 | 14 | .71882 | 478 | 154000 | 22.6 |
| Kazan | 30 | 37 | 2.2 | 3.0 | 23 | .72579 | 427 | 72300 | 58.9 |
| Winisk | 31 | 179 | 17 | 0.5 | 22 | .71769 | 400 | 50000 | 30.1 |
| Moisie | 32 | 29 | 2.5 | 0.5 | 12 | .71630 | 400 | 19200 | 66.5 |
| Porcupine | 33 | 209 | 20 | 0.5 | 63 | .71191 | 369 | 55400 | 54.8 |
| Aux Outardes | 34 | 38 | 1.2 | 0.5 | 9 | .71864 | 366 | 18900 | 52.4 |
| Arnaud | 35 | 10 | 1.1 | 1.7 | 8 | .72638 | 355 | 49500 | 51.9 |
| Hayes | 36 | 225 | 25 | 0.5 | 36 | .71769 | 335 | 103000 | 29.4 |
| Natashquan | 37 | 32 | 1.3 | 0.5 | 12 | .71307 | 328 | 16800 | 175 |
| Attawapiskat | 38 | 162 | 16 | 0.5 | 26 | .71402 | 271 | 36000 | 15.6 |
| Harricana | 39 | 79 | 6.0 | 1.7 | 33 | .71647 | 60 | 29300 | 4.8 |
| Arithmetic $\bar{x}$ | | 103 | 10 | 1.8 | 38 | .71703 | 1295 | 172000 | 62.5 |
| Weighed $\bar{x}$ | | 176 | 18 | 6.8 | 84 | .71113 | | | |

The quoted averages, with the exception of the discharge, were derived as arithmetic means of all seasonal values in Appendix A. Mean annual discharges were taken from the Environment Canada Surface Water Data Reference Index - 1979, 1980.

Churchill River (N.) - Newfoundland  Churchill River (M.) - Manitoba

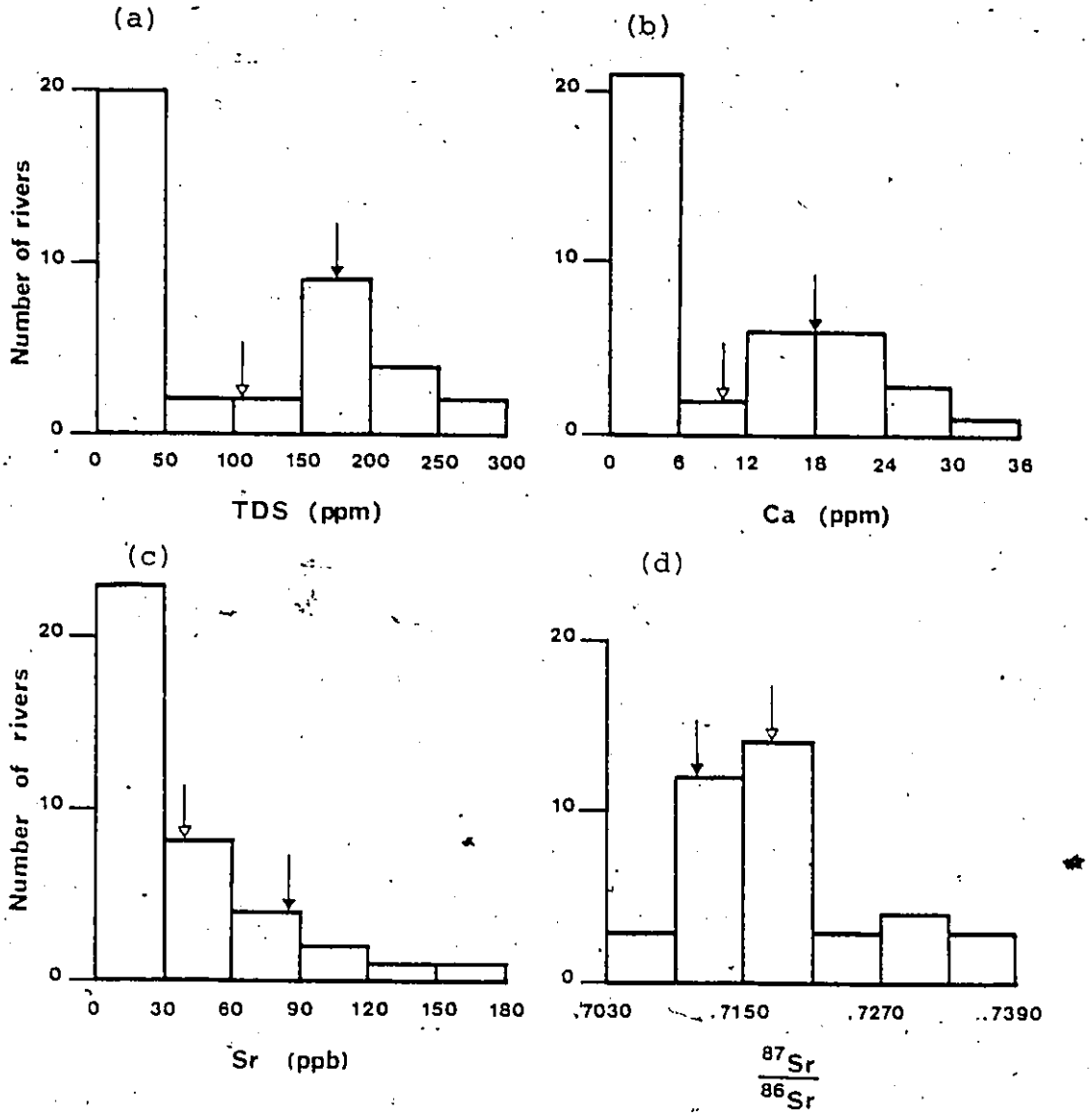



Fig. 3.1

Frequency histograms of the chemical data for the 39 largest Canadian rivers. Open arrows indicate the arithmetic and solid arrows the weighed Canadian means. Data from Table 3.2.

deals with the relationships among variables while Q-mode studies relationships between objects or samples. By examining inherent interdependencies in the data, a minimum number of "factors" are created such that they contain the most important information.

R-mode factor analysis (Table 3.3) shows that a single factor, which accounts for 82% of total variance, controls all of the observed chemical parameters. The high positive loadings of T.D.S., Ca and Sr show that the concentrations of these elements vary sympathetically. The $^{87}Sr/^{86}Sr$ ratio loads negatively onto the factor indicating an antithetic relationship. This suggests that concentrated rivers (high T.D.S., Ca, Sr) are relatively non-radiogenic and vice-versa. The rivers may therefore represent different degrees of a chemical and isotopic continuum between these two end members. This can be evaluated through Q-mode factor analysis. Q-mode factors 1 and 2 (Table 3.4; Fig.3.2), representing basically the two R-mode end members, account together for 97% of the information in the data. Rivers with high loadings ($>0.95$) on Q-mode factor 1 drain primarily sedimentary terranes. The chemical data for these rivers (Table 3.1) are characterized by the highest concentrations of Ca, Sr and T.D.S., but the lowest $^{87}Sr/^{86}Sr$ ratios. This is consistent with their Ca and Sr having been derived from carbonate minerals in sedimentary rocks, which are relatively soluble and contain low $^{87}Sr/^{86}Sr$ ratios.

TABLE 3.3 R-MODE FACTOR ANALYSIS OF COMPOSITION OF THE 39 LARGEST CANADIAN RIVERS

| VARIABLE | FACTOR 1 | COMMUNALITY |
|---|---|---|
| Sr | .88619 | .78532 |
| $^{87}Sr/^{86}Sr$ | -.65384 | .42751 |
| Ca | .98489 | .97002 |
| T.D.S. | .95901 | .91969 |

TABLE 3.4 Q-MODE FACTOR ANALYSIS OF COMPOSITION OF THE 39 LARGEST CANADIAN RIVERS

Sample No. as in Table 2.1

| RIVER NO. | SAMPLE NO. | FACTOR 1 | FACTOR 2 | COMMUNALITY |
|---|---|---|---|---|
| 1 | 1 | .967 | .237 | .992 |
| 1 | 2 | .966 | .239 | .991 |
| 1 | 3 | .968 | .239 | .994 |
| 2 | 1 | .960 | .258 | .987 |
| 3 | 1 | .948 | .304 | .991 |
| 4 | 2 | .925 | .370 | .994 |
| 4 | 3 | .926 | .366 | .992 |
| 5 | 1 | .572 | .735 | .868 |
| 5 | 2 | .660 | .745 | .991 |
| 6 | 1 | .938 | .346 | 1.000 |
| 6 | 2 | .940 | .340 | 1.000 |
| 6 | 3 | .934 | .354 | .997 |
| 7 | 1 | .927 | .365 | .992 |
| 7 | 2 | .934 | .351 | .995 |
| 8 | 1 | .584 | .809 | .996 |
| 8 | 2 | .277 | .906 | .897 |
| 9 | 1 | .860 | .444 | .936 |
| 10 | 1 | .597 | .754 | .926 |
| 10 | 2 | .753 | .655 | .995 |
| 10 | 3 | .752 | .659 | .999 |

TABLE 3.4 (Cont'd) Q --MODE FACTOR ANALYSIS OF COMPOSITION OF THE 39 LARGEST CANADIAN RIVERS

| RIVER NO. | SAMPLE NO. | FACTOR 1 | FACTOR 2 | COMMUNALITY |
|---|---|---|---|---|
| 11 | 2 | .369 | .922 | .987 |
| 12 | 1 | .712 | .680 | .969 |
| 13 | 1 | .962 | .267 | .996 |
| 14 | 2 | .981 | .145 | .983 |
| 14 | 3 | .976 | .142 | .973 |
| 15 | 1 | .971 | .159 | .968 |
| 15 | 2 | .976 | .164 | .979 |
| 16 | 1 | .150 | .971 | .966 |
| 16 | 2 | .022 | .956 | .915 |
| 17 | 1 | .984 | .176 | .999 |
| 17 | 2 | .984 | .176 | .999 |
| 18 | 1 | .872 | .464 | .977 |
| 18 | 2 | .926 | .368 | .993 |
| 19 | 2 | .293 | .954 | .997 |
| 20 | 2 | .897 | .440 | .998 |
| 21 | 2 | .108 | .987 | .985 |
| 22 | 1 | .891 | .445 | .992 |
| 22 | 3 | .807 | .522 | .923 |
| 23 | 1 | .930 | .361 | .996 |
| 23 | 2 | .949 | .313 | .999 |

TABLE 3.4 (Cont'd.) Q-MODE FACTOR ANALYSIS OF COMPOSITION OF THE 39 LARGEST CANADIAN RIVERS

| RIVER NO. | SAMPLE NO. | FACTOR 1 | FACTOR 2 | COMMUNALITY |
|---|---|---|---|---|
| 23 | 3 | .928 | .351 | .984 |
| 24 | 2 | .426 | .894 | .981 |
| 25 | 2 | .082 | .991 | .989 |
| 26 | 2 | .697 | .535 | .771 |
| 27 | 2 | .854 | .502 | .981 |
| 27 | 3 | .873 | .475 | .987 |
| 28 | 1 | .269 | .955 | .985 |
| 29 | 1 | .653 | .756 | .986 |
| 29 | 3 | .726 | .667 | .972 |
| 30 | 1 | .615 | .770 | .972 |
| 31 | 1 | .862 | .471 | .965 |
| 32 | 1 | .793 | .603 | .992 |
| 32 | 2 | .573 | .795 | .960 |
| 32 | 3 | .784 | .613 | .990 |
| 33 | 1 | .943 | .323 | .993 |
| 33 | 2 | .950 | .308 | .997 |
| 34 | 1 | .601 | .777 | .965 |
| 35 | 1 | .077 | .953 | .915 |
| 36 | 1 | .905 | .417 | .992 |
| 37 | 1 | .565 | .745 | .874 |

TABLE 3.4 Q-MODE FACTOR ANALYSIS OF COMPOSITION OF THE 39 LARGEST CANADIAN RIVERS (Cont'd.)

| RIVER NO. | SAMPLE NO. | FACTOR 1 | FACTOR 2 | COMMUNALITY |
|---|---|---|---|---|
| 38 | 1 | .930 | .361 | .996 |
| 39 | 1 | .839 | .544 | 1.000 |
| 39 | 2 | .888 | .454 | .994 |
| 39 | 3 | .895 | .438 | .994 |

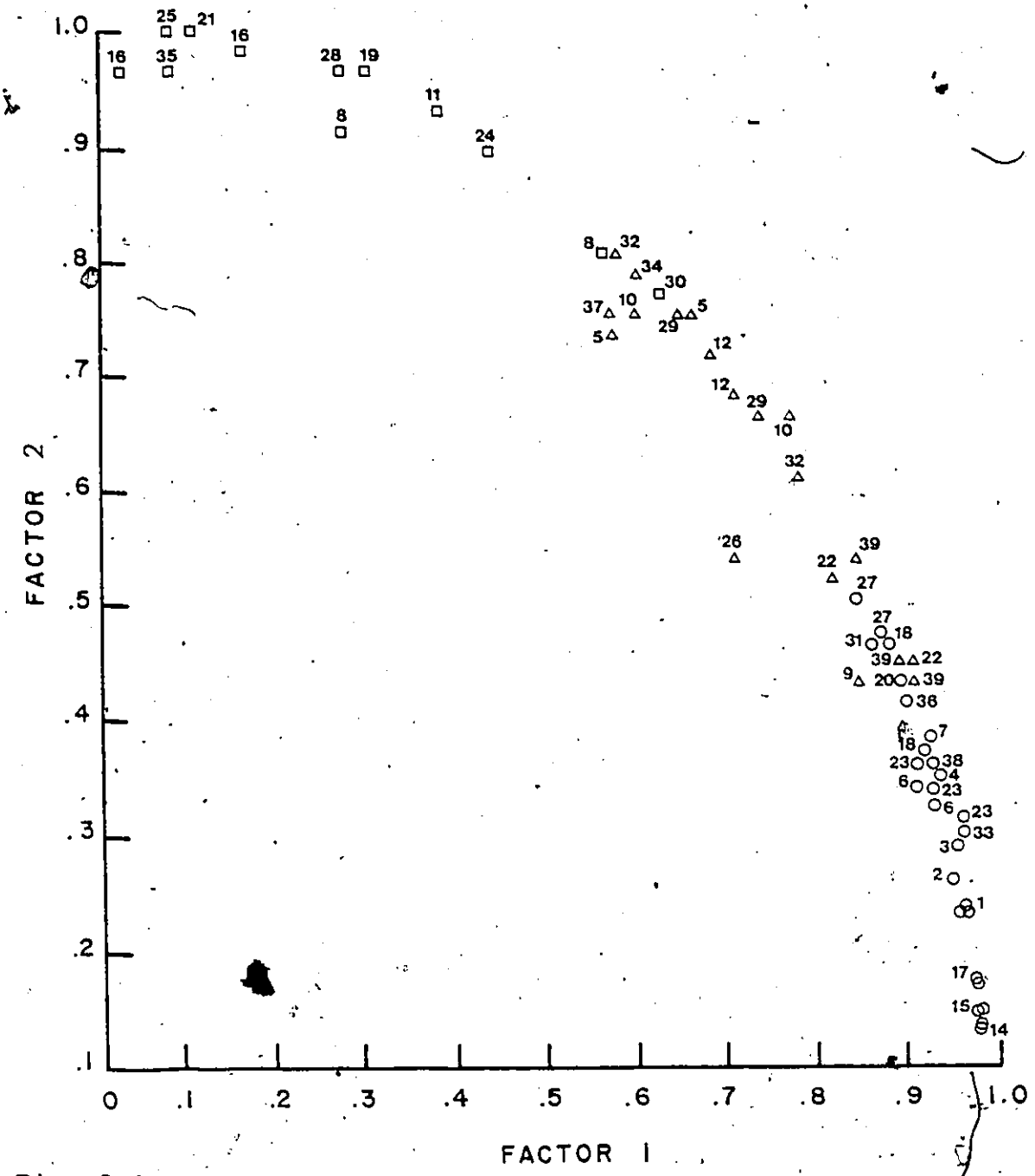



Fig. 3.2
Q-Mode factor analysis of composition of the 39 major Canadian rivers (Varimax "rotated" factor space).

In contrast, rivers with similarly high loadings on factor 2 are those which drain Archean igneous (or metamorphic) terranes. The chemical data (Table 3.1) indicate low concentrations of Ca and Sr, low T.D.S. and high $^{87}Sr/^{86}Sr$ ratios. Such chemistry may be a consequence of weathering of old, relatively insoluble material such as the Precambrian Shield. This is apparent from the geographic distribution of such rivers, which drain the Precambrian Shield in the vicinity of Hudson Bay (Fig. 3.3).

The above discussion shows that the major influence on river composition is its drainage basin geology. This accounts for their dilute vs. concentrated chemistry and for radiogenic vs. non-radiogenic Sr isotopic ratios.

The geology of the drainage basins was determined planimetrically from geological maps and histograms of the average geologic composition for drainage basins of the end-member rivers (Fig. 3.4) confirm the above interpretations. The intermediate rivers, with moderate loadings on both factors, seem to represent either those draining basins of Proterozoic geology or basins having a mixture of siliceous and carbonate terranes (cf. Fig. 3.4 and Table 3.5).

## 3.3 Additional Statistics

In addition to Factor Analysis, three other statistical techniques were applied to the data: 1. analysis of variance, 2. cluster analysis and 3. multiple linear regression for chemical as well as geological data.

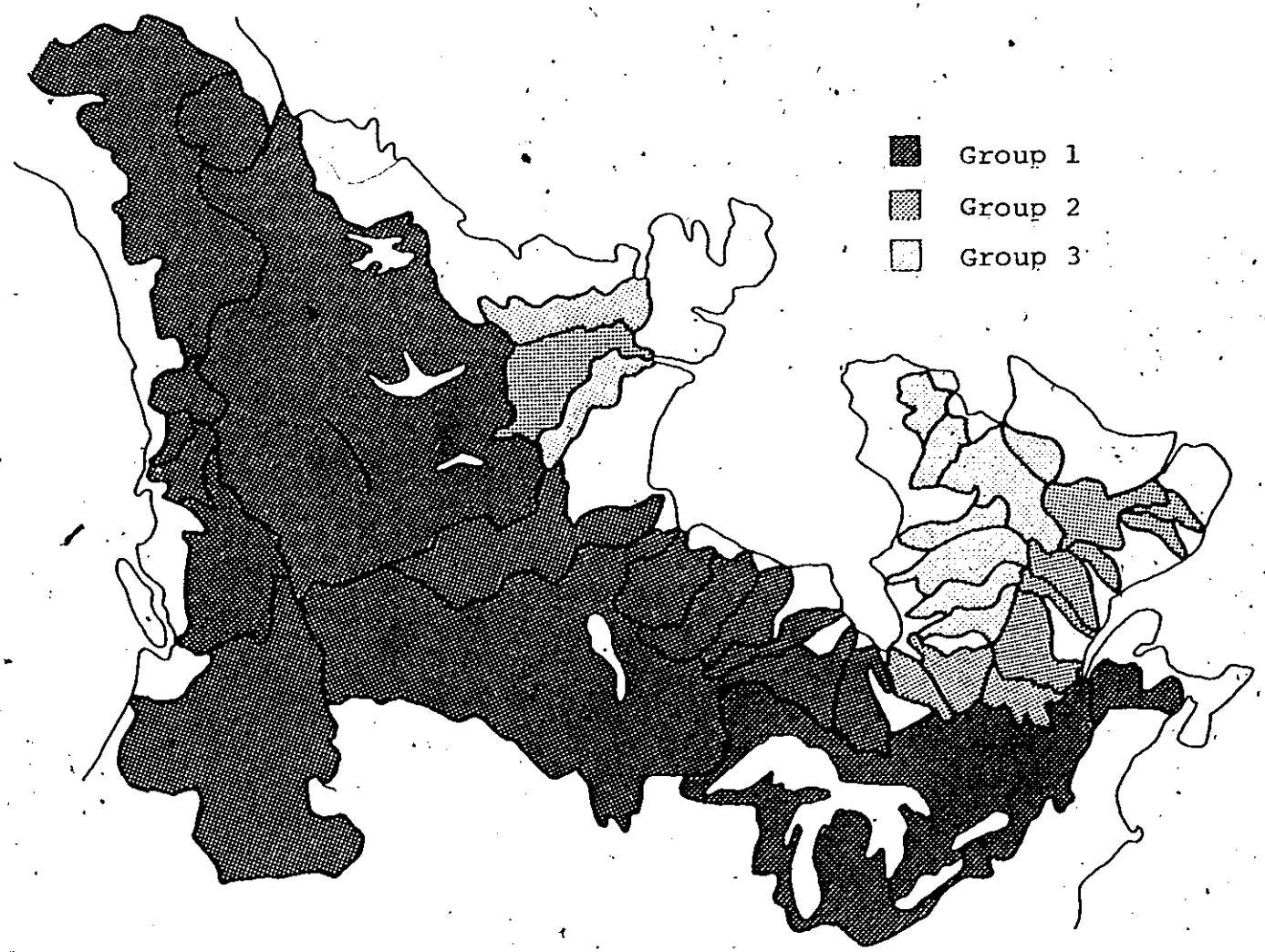



Fig. 3.3

Geographic distribution of group 1,2,3 rivers.

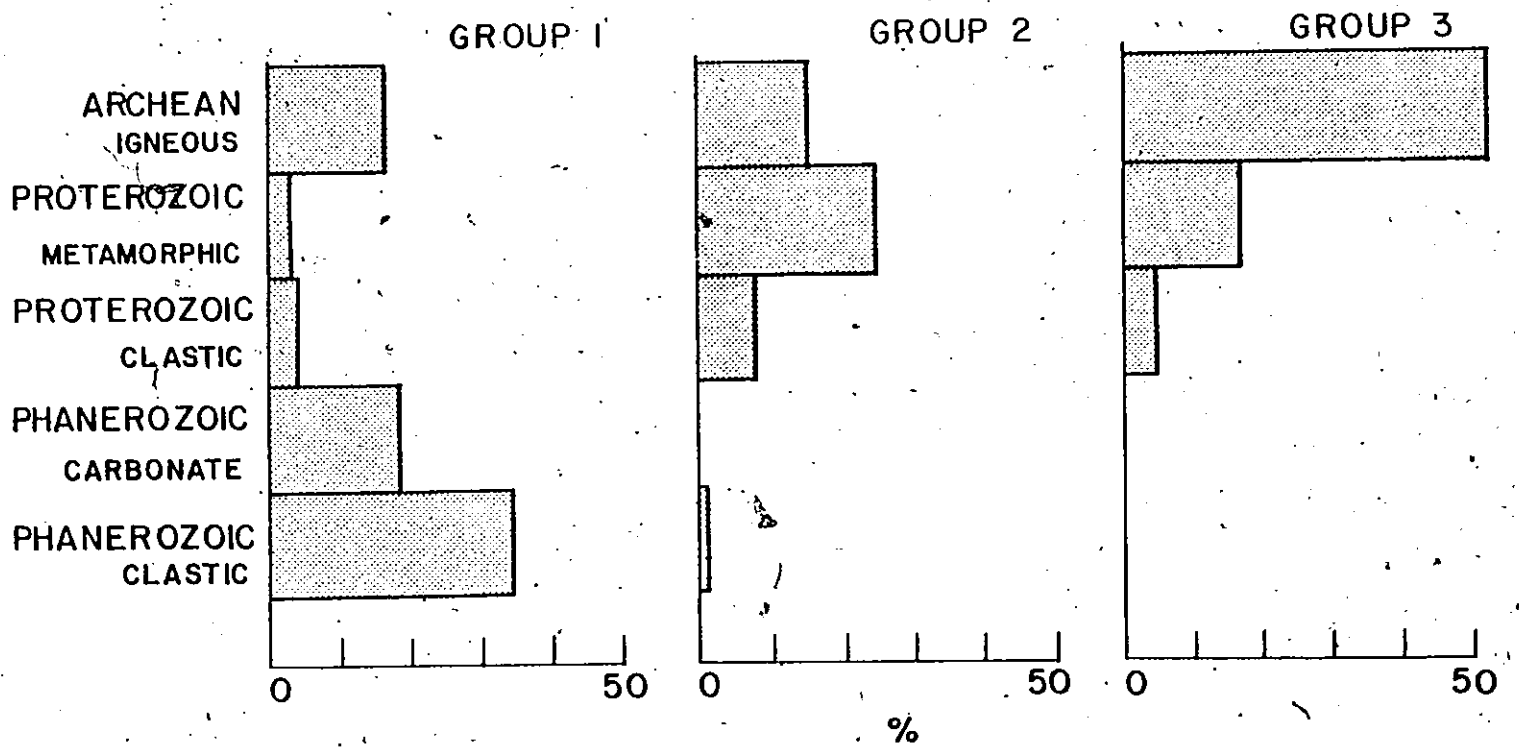



Fig. 3.4

Histograms showing the average geologic composition of the drainage basins for the endmember and intermediate rivers. Group 1 (concentrated and non-radiogenic) consists of 18 rivers, group 2 consists of 11 rivers and group 3 (dilute and radiogenic) consists of 10 rivers.

TABLE: 3.5

DRAINAGE BASIN GEOLOGY

| | | ARCHEAN | | | PROTEROZOIC | | | PALEOZOIC | | | MESOZOIC | | | CENOZOIC | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| RIVER | | S | N.S. | M | S | N.S. | M | S | N.S. | M | S | N.S. | M | S | N.S. | M | A.M. | E |
| Yukon | | | | | | | | 44 | 2 | | 16 | | | | 5 | | 33 | |
| Porcupine | | | | | | | 5 | 40 | | | 30 | | | 25 | | | | |
| Stikine | | | | | | | | 6 | | | 44 | 38 | | 5 | 7 | | | |
| Nass | | | | | | | | | | | 75 | 21 | | 2 | 2 | | | |
| Skeena | | | | | | | | 2 | 2 | | 49 | 41 | | 3 | 3 | | | |
| Fraser | | | | | | | | 4 | 4 | | 6 | 36 | | 24 | 20 | | 6 | |
| Columbia | | | | | 32 | | | 20 | | | 11 | 28 | | | 3 | | 6 | |
| Mackenzie | | | 25 | | | | | 26 | | | 37 | 2 | | | | | 7 | 3 |
| Churchill (M.) | FACTOR 1 | | 19 | 9 | 4 | 17 | 17 | 6 | | | 28 | | | | | | | |
| Nelson | | | 13 | 11 | 1 | 6 | 4 | 14 | | | 46 | | | 5 | | | | |
| Hayes | | | | 45 | 5 | | 10 | 30 | | | | | | | | | 10 | |
| Severn | | | 57 | 7 | | | | 36 | | | | | | | | | | |
| Winisk | | | 57 | 5 | | | | 38 | | | | | | | | | | |
| Attawapiskat | | | 27 | 3 | | | | 70 | | | | | | | | | | |
| Albany | | | 46 | 10 | | | | 43 | | | 1 | | | | | | | |
| Moose | | | 60 | 13 | | | | 4 | | | 14 | | | | | | | 4 |
| St. John | | | 3 | | | 9 | | 88 | | | | | | | | | | |
| St. Lawrence | | | 17 | 4 | 9 | 8 | 8 | 26 | | | | | | 28 | | | | |
| Thelon | | | | | 65 | | 35 | | | | | | | | | | | |
| Churchill (N.) | INTERMEDIATE | | 2 | 8 | 17 | 12 | 61 | | | | | | | | | | | |
| Harricana | | | 75 | 19 | | | | 1 | | | 5 | | | | | | | |
| Nottaway | | | 57 | 43 | | | | | | | | | | | | | | |
| Petit Mecatina | | | 36 | 48 | | 16 | | | | | | | | | | | | |

TABLE: 3.5 (CONT'D.)

DRAINAGE BASIN GEOLOGY

| RIVER | | ARCHEAN S | ARCHEAN N.S. | ARCHEAN M | PROTEROZOIC S | PROTEROZOIC N.S. | PROTEROZOIC M | PALEOZOIC S | PALEOZOIC N.S. | PALEOZOIC M | MESOZOIC S | MESOZOIC N.S. | MESOZOIC M | CENOZOIC S | CENOZOIC N.S. | CENOZOIC M | A.M. | E |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Natashquan | INTERMEDIATE | | 53 | 44 | | 3 | | | | | | | | | | | | |
| Moisie | INTERMEDIATE | | 5 | 33 | | 28 | 34 | | | | | | | | | | | |
| Manicouagan | INTERMEDIATE | | 1 | 70 | | 8 | 17 | | | | | | | | | | | |
| Aux Outardes | INTERMEDIATE | | 10 | 38 | 7 | 23 | 22 | | | | | | | | | | | |
| Saguenay | INTERMEDIATE | | 17 | 36 | 3 | 10 | 30 | | | | 4 | | | | | | | |
| St. Maurice | INTERMEDIATE | | 21 | | | | 76 | 3 | | | | | | | | | | |
| Back | FACTOR 2 | 8 | 12 | | 10 | 5 | 65 | | | | | | | | | | | |
| Kazan | FACTOR 2 | | | | 7 | 26 | 67 | | | | | | | | | | | |
| Rupert | FACTOR 2 | | 62 | 27 | 11 | | | | | | | | | | | | | |
| Eastmain | FACTOR 2 | | 36 | 62 | 2 | | | | | | | | | | | | | |
| La Grande | FACTOR 2 | | 76 | 24 | | | | | | | | | | | | | | |
| Grande | FACTOR 2 | | 99 | 1 | | | | | | | | | | | | | | |
| Arnaud | FACTOR 2 | | 89 | 11 | | | | | | | | | | | | | | |
| Aux Feuilles | FACTOR 2 | | 92 | 8 | | | | | | | | | | | | | | |
| Koksoak | FACTOR 2 | | 70 | 7 | 12 | 10 | 1 | | | | | | | | | | | |
| A la Baleine | FACTOR 2 | | 7 | 39 | 7 | 8 | 39 | | | | | | | | | | | |

Explanation:

S - sedimentary

N.S. - non-sedimentary

M - metamorphic

A.M. - assorted metamorphic (various ages)

E - evaporite

### 3.3.1 Analysis of Variance

This approach is based on the fact that the variance of a sum of random variables is equal to the sum of the variances of those variables if the variables concerned are uncorrelated. Therefore, uncorrelated factors which introduce variability can be evaluated in terms of their individual contributions to the total variability (Krumbein and Graybill, 1965). An important assumption is that the population variances are equal. If this assumption is not valid, the power of the F-test, for analysis of variance, is reduced. If, through testing, the data are found to have inhomogeneity of variance, certain transformations can be applied (ie. log, inverse, etc) to homogenize the variance within the individual populations. On the basis of this testing, log normal transformations were applied to Sr, Ca, Sr/Ca and T.D.S. while $^{87}Sr/^{86}Sr$ was left untransformed.

For the analysis of variance, an unbalanced, nested format was used as shown in Fig. 3.5. The samples were divided according to the rivers from which they were derived and the rivers were grouped geologically according to whether they drain predominantly Shield or non-Shield areas of Canada. Three levels of variability are represented (Table 3.6). (See Garrett and Goss (1980) for details of statistical approach).

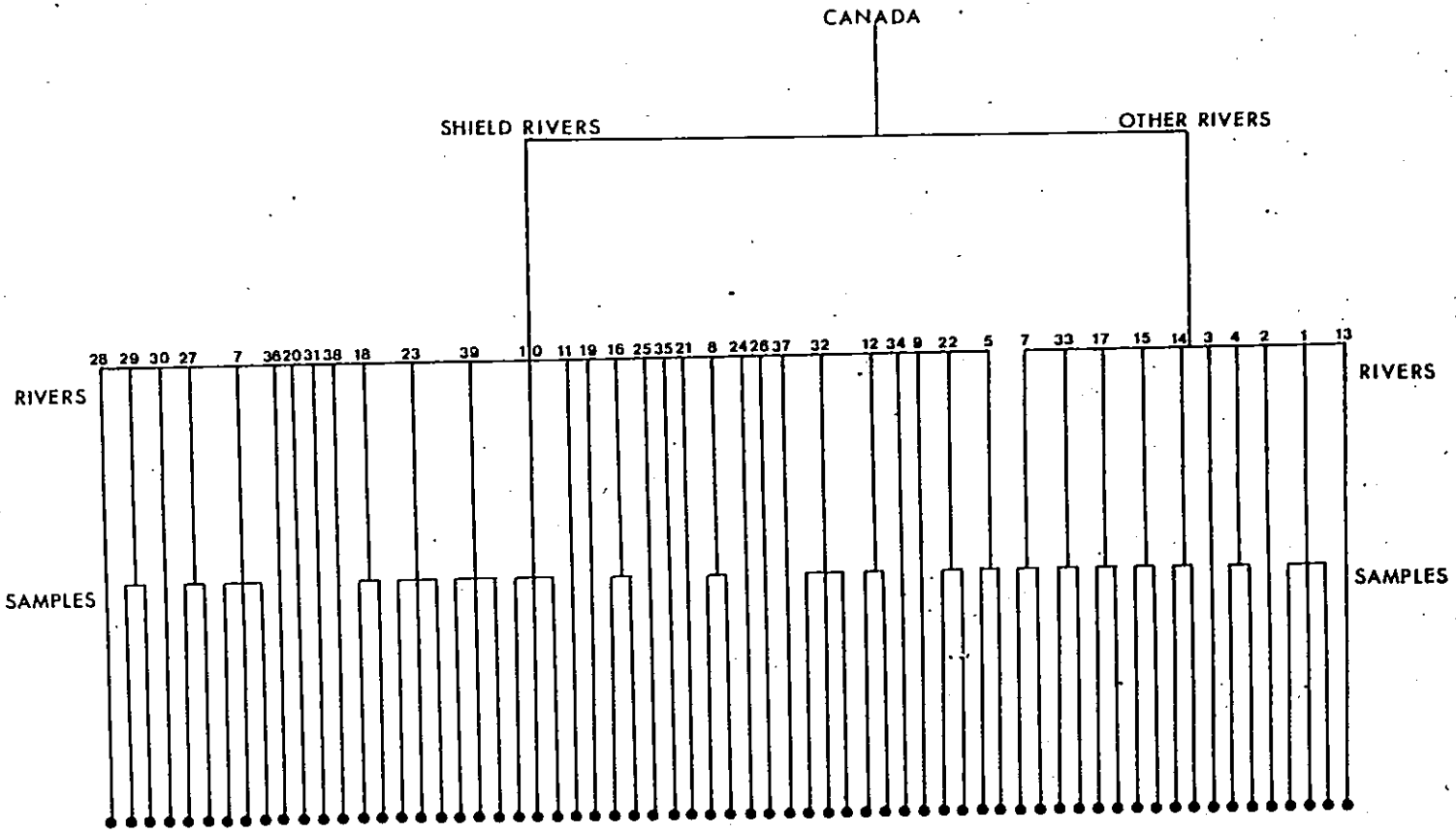



Fig. 3.5

Unbalanced nested hierarchy for analysis of variance (after Garrett and Goss, 1980) River numbers as in Table 2.1.

TABLE 3.6 ANALYSIS OF VARIANCE IN COMPOSITION FOR MAJOR CANADIAN RIVERS

| LEVEL | VARIATION BETWEEN | PERCENT OF TOTAL VARIANCE | | | |
|---|---|---|---|---|---|
| | | Sr | Ca | T.D.S. | $^{87}Sr/^{86}Sr$ |
| 3 | Geology | 73.80 | 49.09 | 46.07 | 51.19 |
| 2 | Rivers | 20.16 | 48.74 | 47.49 | 48.01 |
| 1 | Samples | 6.04 | 2.17 | 6.44 | 0.81 |

For Sr, 73.8% of the variance in concentration is accounted for by geological grouping of rivers. 20.2% is due to significant differences in Sr concentrations between rivers, and only 6.04% is explained by within-river concentration differences. This implies that multiple sampling is unnecessary when the whole Canadian picture is of interest.

The situations for Ca, T.D.S. and $^{87}Sr/^{86}Sr$ ratio are somewhat different in that the percentages of variance explained by geology and river differences are almost equal. This suggests somewhat different behavior for Sr than for Ca, T.D.S. and $^{87}Sr/^{86}Sr$.

The most significant result of this treatment is that, for every variable, the percentage of variance explained by seasonal fluctuations within rivers is very small. In other words, one sample per river or the average of all of the samples obtained is sufficient to describe the contribution of that river to the total Canadian picture.

### 3.3.2 Cluster Analysis

This is a form of correlation analysis. Unlike factor analysis it does not involve abstract or artificial factors but is a straightforward, pair by pair, comparison of variables. The results can be presented graphically in a two-dimensional hierarchical

diagram on which the natural breaks between groups are clearly observed. In this case, a sample of each river is depicted by a drawing of a tree whose characteristics are determined by the variables which were measured (for details of the actual construction of the trees refer to Kleiner and Hartigan, 1981).

Variables which behave similarly are identified by the computer and a template is created showing the associations. The trees are then constructed, sample by sample, with the same variable always on the same tree branch. An algorithm within the computer converts the concentrations of each variable to proportions between 0 and 1 according to the maximum and minimum values in the data. Therefore, the length of the branch for any variable indicates the relative concentration of that variable and can be compared from tree to tree. The result is that similar variables are close together so that direct comparisons can be made and trees that look alike represent rivers with similar chemical characteristics. Fig. 3.6 shows some examples. The data appear to represent a series with one endmember having high concentrations of Ca and T.D.S. (with strong correlation between them), high Sr concentrations (with similar but not identical behaviour), low $^{87}Sr/^{86}Sr$ and Sr/Ca ratios (Fig. 3.6a). The other endmember (Fig. 3.6d) shows a contrasting trend; low Ca, T.D.S. and Sr with

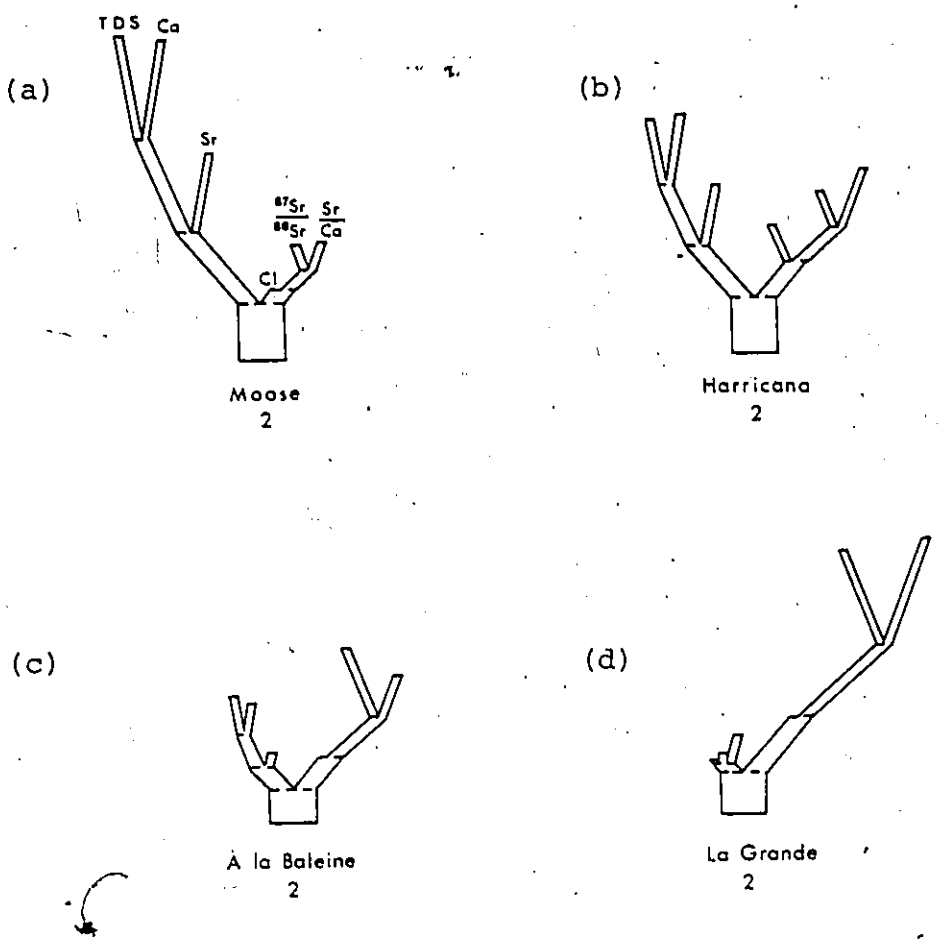



Fig. 3.6

Cluster Analysis - Tree diagrams showing inter-component relationships among the endmember and intermediate type rivers.

high $^{87}Sr/^{86}Sr$ and Sr/Ca ratios. Intermediate rivers are represented in Figs. 3.6b and 3.6c.

### 3.3.3 Multiple Linear Regression

Independent chemical variables usually tend to vary according to some pattern and often a single variable may depend on several independent ones. Multiple linear regression is designed to resolve this kind of situation (Krumbein and Graybill, 1965). A stepwise multiple linear regression of chemistry vs. geology was performed on the river data in an attempt to determine the extent of control of various rock types over particular chemical elements. The results (Table 3.7) confirm the conclusions concerning the significance of bedrock geology for river water chemistry discussed in section 3.2.

TABLE 3.7 STEPWISE MULTIPLE LINEAR REGRESSION ANALYSIS OF CHEMISTRY VS. GEOLOGY FOR THE MAJOR CANADIAN RIVERS

| ELEMENT | ROCK TYPE | % OF CHEMICAL VARIATION ACCOUNTED FOR |
|---|---|---|
| Sr | Mesozoic clastic sediments | 41.10 |
| | Paleozoic clastic sediments | 23.67 |
| | Cenozoic clastic sediments | 9.44 |
| | Evaporites | 3.76 |
| $^{87}Sr/^{86}Sr$ | Archean felsic igneous rocks | 33.06 |
| | Proterozoic clastic sediments | 11.96 |
| | Evaporites (negative relationship) | 6.51 |
| | Cenozoic clastic sediments (negative relationship) | 6.31 |
| Ca | Paleozoic carbonate sediments | 46.94 |
| | Mesozoic clastic sediments | 18.97 |
| | Paleozoic clastic sediments | 12.02 |
| | Evaporites | 3.52 |
| T.D.S. | Paleozoic carbonate sediments | 47.86 |
| | Mesozoic clastic sediments | 15.27 |
| | Paleozoic clastic sediments | 10.69 |
| | Evaporites | 3.27 |

# 4. SPECIFIC CONTROLS OF CHEMICAL AND ISOTOPIC COMPOSITION

More specific information on the control of river composition can be obtained by studying each chemical variable individually.

## 4.1 Chloride

The chloride determinations showed that concentrations, with the exception of the St. Lawrence River, were < 10ppm (Table A-2). This confirms that contributions from recycled marine salts to the chemical composition of each river at the chosen sampling locations was negligible.

## 4.2 Total Dissolved Solids

Fig. 4.1 shows total dissolved solids data for major world rivers (Livingstone, 1963; Table 1.1) plotted against runoff $\Delta f$. Runoff here is defined as discharge divided by drainage basin area (Holland, 1978, p. 86). The purpose of this normalization is to give large rivers in large drainage basins the same weight as small rivers in small drainage basins. This will accentuate differences in water chemistry rather than differences resulting from size.

An inverse relationship is almost always obtained between these two variables, because when $\Delta f$ is large, more water is flowing over a given area per unit time creating a more dilute solution (Leopold et al., 1964). Towards lower values of runoff, the concentrations of dissolved solids decrease less rapidly (Holland, 1978, p.89-90). Canadian

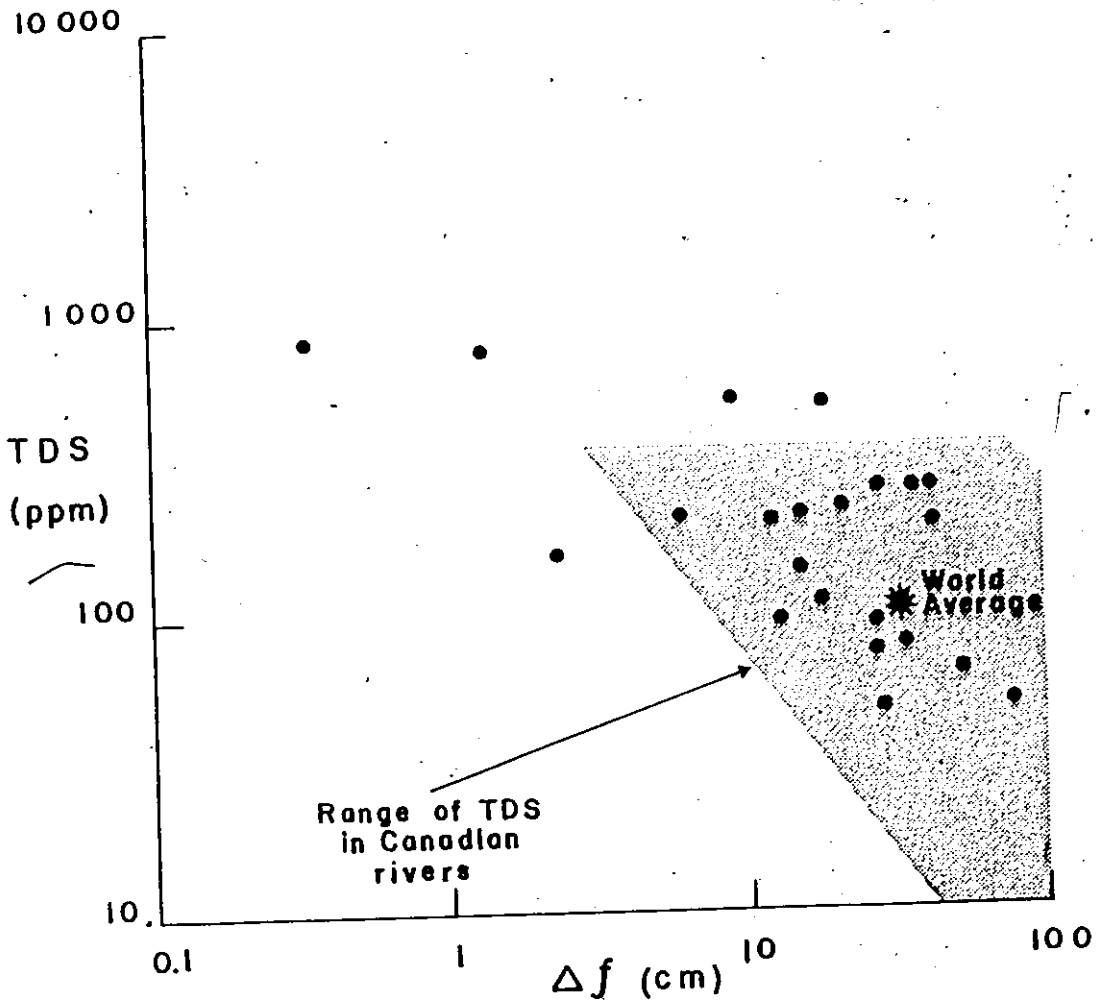



Fig. 4.1

Total dissolved solids vs. runoff for major world rivers. Modified from Holland (1978)

rivers fall into the region of distinct inverse relationship within the world values.

The world weighed average for T.D.S. is 120 ppm (Livingstone, 1963), while the weighed Canadian average is 176 ppm (Table 3.2). The difference could be due to the fact that the Canadian value is strongly influenced by the composition of the St. Lawrence River, which is exposed to much industrial and agricultural activity.

The plot of T.D.S. vs. $\Delta f$ for Canadian rivers only (Fig. 4.2) clearly separates the rivers into the sedimentary and non-sedimentary groups defined by Q-mode factor analysis. Each group behaves independently due to their different source terranes, but the inverse relationship is observed in both cases.

## 4.3 Calcium

Calcium consistently represents about 10% of the total dissolved load (Table A-4). It is not surprising, therefore, that its distribution (Fig. 4.3) mimics that of the T.D.S.

## 4.4 Elemental Strontium

Strontium, despite a degree of similarity to calcium (in that the sedimentary rivers have higher Sr concentrations than the non-sedimentary ones), shows a much greater variability in concentration over the whole range of runoff

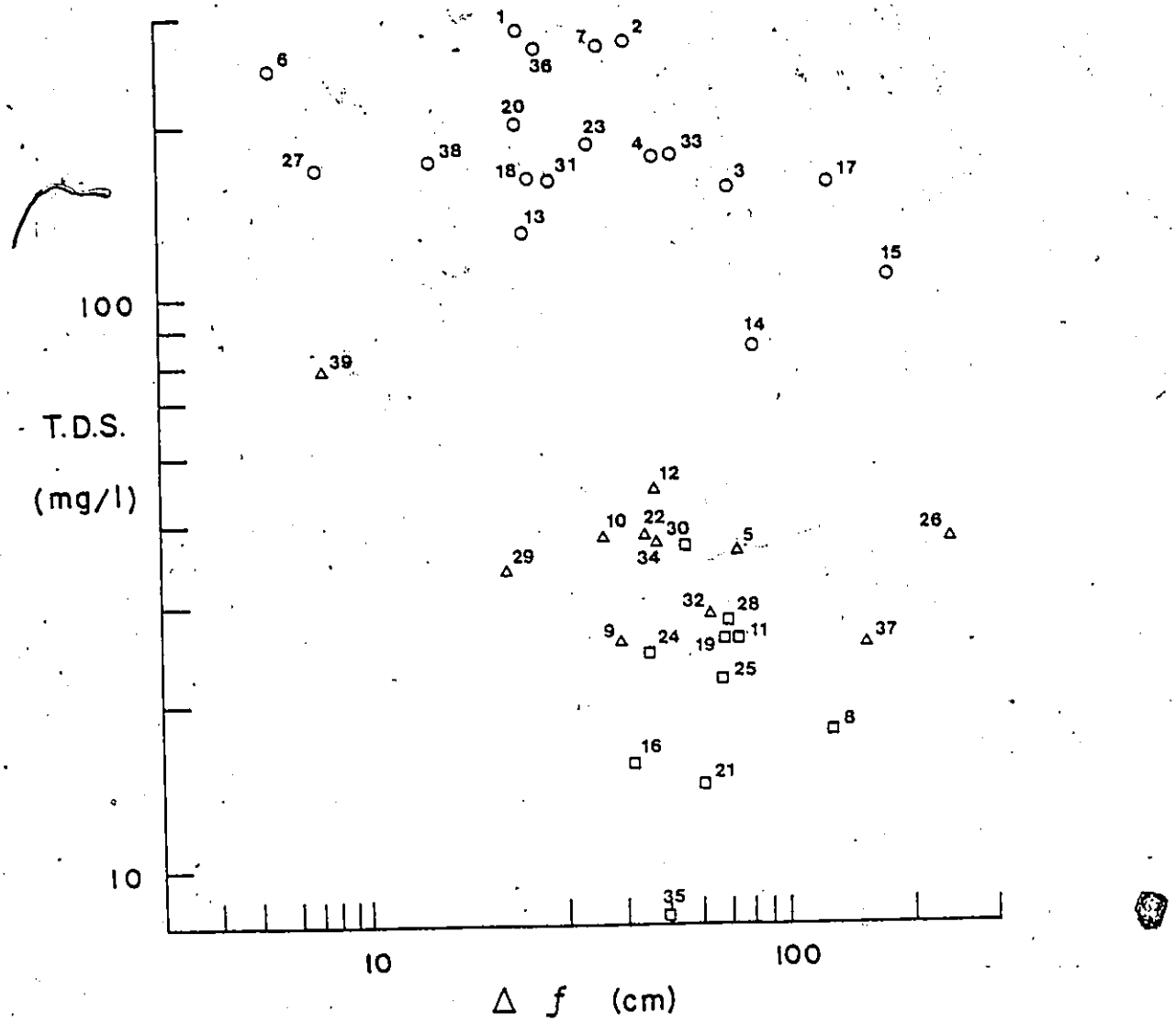



Fig. 4.2

Total dissolved solids plotted against runoff for the 39 major Canadian rivers. An average value is plotted for each river. Numbers correspond to those in Table 3.1. o represents Q-mode factor analysis group 1 or "sedimentary" rivers. Δ represents group 2 and □ represents group 3.

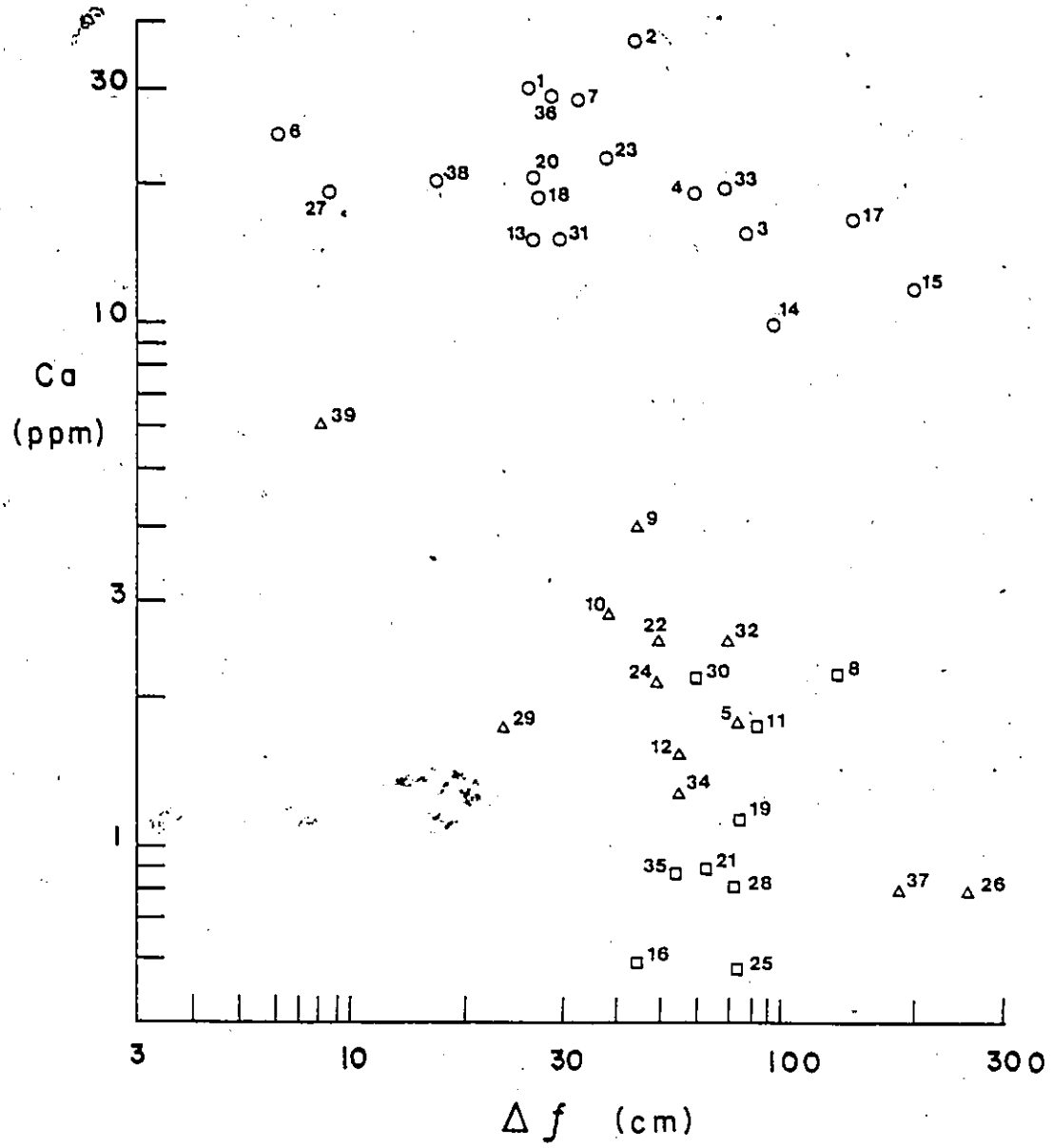



Fig. 4.3

Calcium is plotted against runoff for the 39 largest Canadian rivers. For explanation of numbers and symbols see Fig. 4.2.

values (Fig. 4.4). To analyze differences in the behaviour of these two elements, their ratio can be considered in relation to the element of interest, Sr (Fig. 4.5). Because of the established Ca in $\Delta f$ dilution relationship, it is expected that an increase in Sr concentration will result in increasing Sr/Ca ratios. This is evident only if the rivers are separated into two groups, each independently conforming to the expected relationship. The "sedimentary" rivers -- compared to the "non-sedimentary" ones -- although having higher Sr concentrations, must have correspondingly even higher Ca concentrations in order to reduce their observed Sr/Ca ratios below those of the second group. This implies two types of Sr release into surface waters. Rivers draining sedimentary areas obtain their Sr principally from carbonate minerals (in carbonates or clastics), which have typically lower Sr/Ca ratios than aluminosilicates. Rivers draining more resistant (and older, thus perhaps already leached?) regions tend to receive their Sr from weathering of feldspars (plagioclase).

## 4.5 Strontium Isotopes

In contrast to elemental Sr data, the plot of $^{87}Sr/^{86}Sr$ vs. $\Delta f$ (Fig. 4.6) does not separate the sedimentary from the non-sedimentary rivers. Instead, it distinguishes strongly radiogenic rivers draining Archean terranes (Q-mode factor 2) from those draining Proterozoic areas

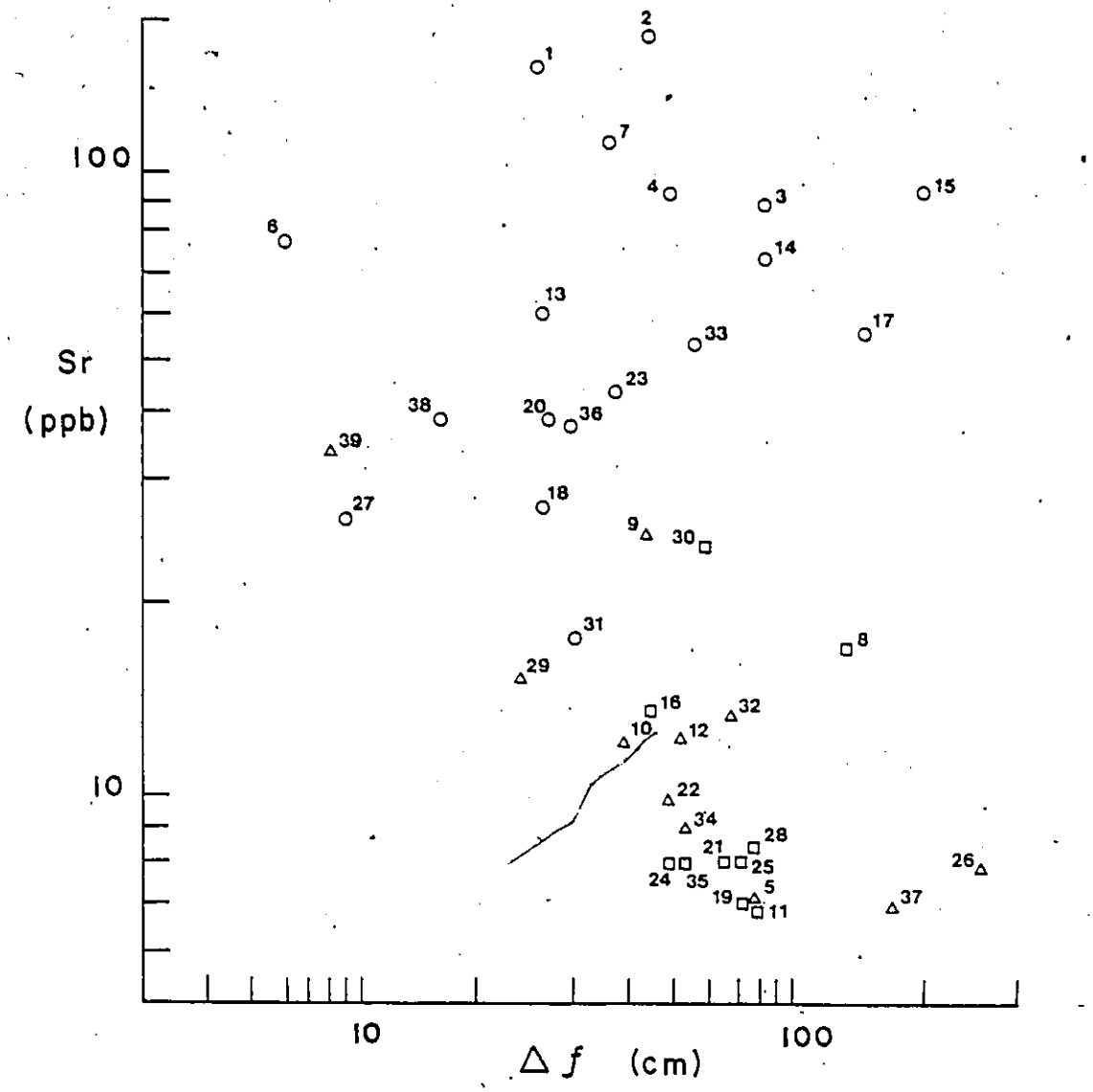



Fig. 4.4

Strontium plotted against runoff for the 39 major Canadian rivers. For explanation of numbers and symbols see Fig. 4.2.

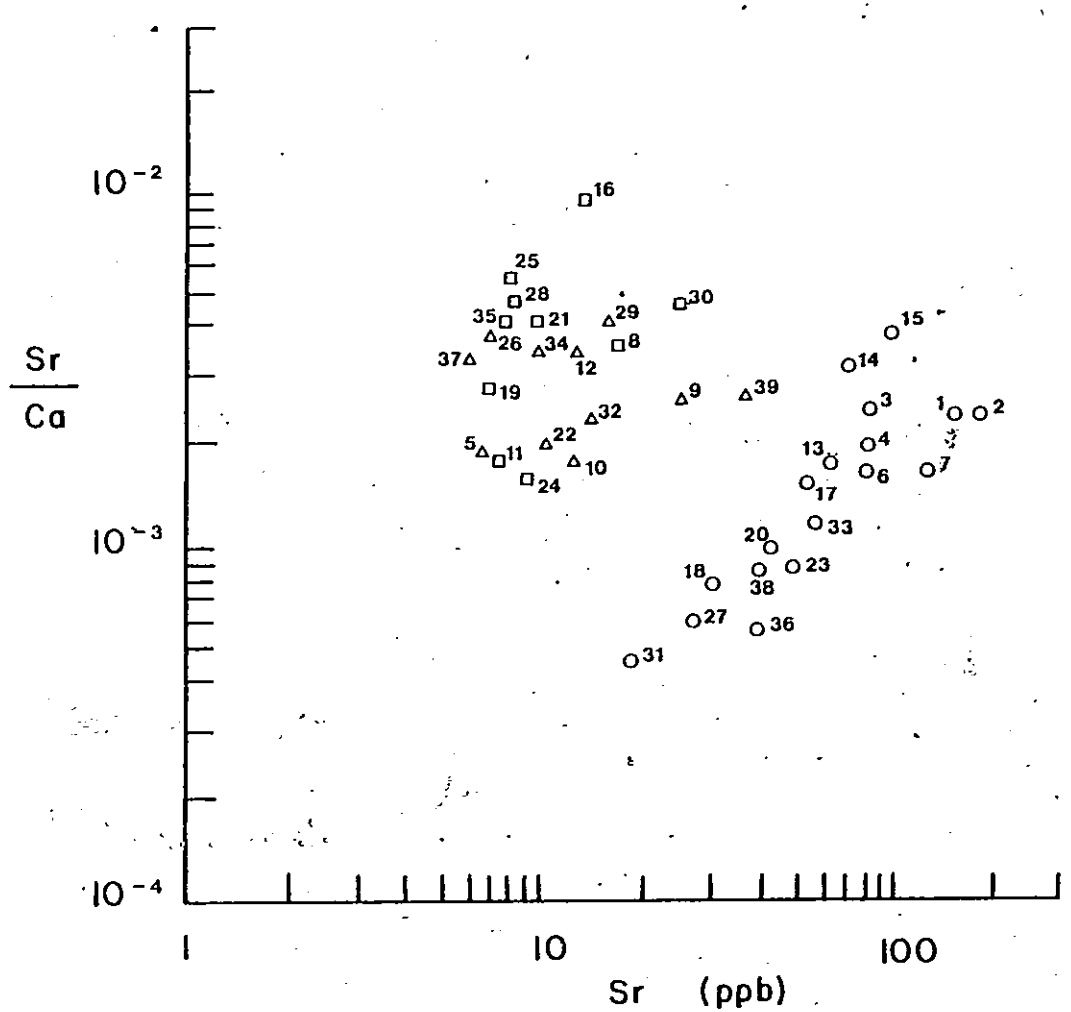



Fig. 4.5

Sr/Ca ratio plotted against strontium concentrations for the 39 major Canadian rivers. For explanation of numbers and symbols see Fig. 4.2.

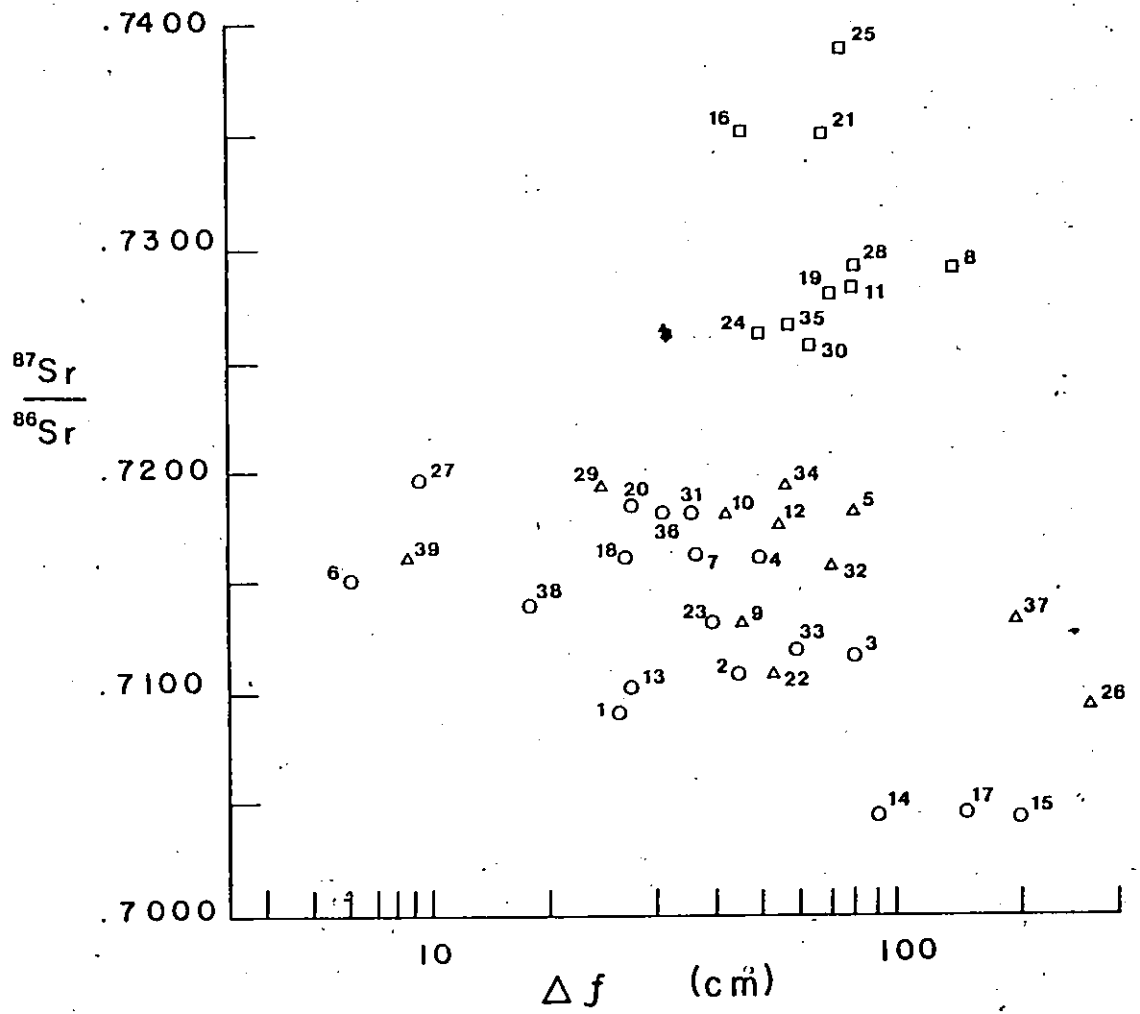



Fig. 4.6

$^{87}Sr/^{86}Sr$ ratio plotted against runoff for the 39 major Canadian rivers. For explanation of numbers and symbols see Fig. 4.2.

which have isotopic ratios similar to the sedimentary (carbonate controlled) rivers (factor 1). This is to some extent surprising because if Proterozoic feldspars were the source of strontium (as indicated by Fig. 4.5) the resulting $^{87}Sr/^{86}Sr$ ratio should be intermediate between the "Archean" and "sedimentary" rivers. Although there is some indication of this in the present data (Fig. 4.6) the trend is not distinct. The reason for this unusual grouping becomes clearer when the rivers are plotted on a structural map of Canada. The division between radiogenic and non-radiogenic (less radiogenic) rivers in Fig. 4.6 corresponds to the Superior - Grenville structural boundary. This could account for their similar Sr/Ca ratios but somewhat different Sr isotopic ratios. Although Sr may still have been derived from feldspars, the Grenville rocks are, in general, $\sim$ 1.5 Ga younger than their Superior Province counterparts and thus were not able to generate a comparable $^{87}Sr$ component. In contrast, the Grenville Province is only somewhat older ($\sim$ 0.6 Ga) than the mean age of Paleozoic rocks which control the chemistry of "sedimentary" rivers. Consequently, these two source lithologies may have somewhat similar strontium isotopic but different Sr/Ca ratios. Nevertheless, the absence of a significant $^{87}Sr$ component in the Grenville rivers is surprising and not fully explained by the above considerations.

## 4.6 Seasonal Variations

The pilot studies for the Ottawa and St. Lawrence Rivers did not (apart from T.D.S.) show any significant monthly fluctuations in their chemical composition (Table 4.1). This could be due to one or both of the following: 1. chemical buffering by the high proportion of sedimentary rocks in their drainage basins; 2. major industrial contamination, affecting chloride in particular.

Much greater fluctuations were found for the Porcupine, Nottaway and Koksoak Rivers (Tables A-3 to A-6), as demonstrated by the T.D.S. concentrations, $^{87}Sr/^{86}Sr$ isotopic ratios and to some extent by Sr and Ca data. Fluctuations observed in the pilot study of the St. Lawrence River did not affect the isotopic ratios.

TABLE 4.1 SEASONAL VARIATIONS IN CHEMICAL COMPOSITION OF ST. LAWRENCE AND OTTAWA RIVERS

1 Prescott
2 Brockville

Cl - (mg/l)

| RIVER | 1979 | | | 1980 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MONTH | 10 | 11 | 12 | 01 | 02 | 03 | 04 | 05 | 06 | 07 | 08 | 09 | 10 |
| St. Lawrence 1 | 26 | 29 | | | | 27 | 26 | 25 | 22 | 25 | | | |
| St. Lawrence 2 | 25 | 26 | | | | 22 | 24 | 26 | 22 | 26 | | | |
| Ottawa | 0.5 | 0.5 | | | | 0.5 | 0.5 | 0.5 | | 1.2 | | | |

T.D.S. (ppm)

| RIVER | 1979 | | | 1980 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MONTH | 10 | 11 | 12 | 01 | 02 | 03 | 04 | 05 | 06 | 07 | 08 | 09 | 10 |
| St. Lawrence 1 | 317 | 302 | | | | 201 | 356 | 319 | | | | | |
| St. Lawrence 2 | 310 | 315 | | | | 309 | 386 | 297 | | | | | |

Ca (ppm)

| RIVER | 1979 | | | 1980 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MONTH | 10 | 11 | 12 | 01 | 02 | 03 | 04 | 05 | 06 | 07 | 08 | 09 | 10 |
| St. Lawrence 1 | 32 | 33 | | | | 32 | 36 | | | | 34 | | |
| St. Lawrence 2 | 31 | 32 | | | | 29 | 37 | | | | 33 | 32 | |
| Ottawa | 7.1 | 7.1 | | | | 7.0 | 7.8 | 7.1 | | | 7.1 | 7.3 | |

TABLE 4.1 (Cont'd) SEASONAL VARIATIONS IN CHEMICAL COMPOSITION OF ST. LAWRENCE AND OTTAWA RIVERS

1 Prescott
2 Brockville

$^{87}Sr/^{86}Sr$

| RIVER | 1979 | | | 1980 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MONTH | 10 | 11 | 12 | 01 | 02 | 03 | 04 | 05 | 06 | 07 | 08 | 09 | 10 |
| St. Lawrence 2 | | | | | | .7093 | | | .7092 | | | | .7095 |

Sr (ppb)

| RIVER | 1979 | | | 1980 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MONTH | 10 | 11 | 12 | 01 | 02 | 03 | 04 | 05 | 06 | 07 | 08 | 09 | 10 |
| St. Lawrence 2 | | | | | | | | | 145 | | 185 | | 160 |

## 5. CALCULATION OF $^{87}Sr/^{86}Sr$ RATIO FOR CONTINENTAL RUNOFF

Using the mean annual discharges, average Sr concentrations, and the average measured $^{87}Sr/^{86}Sr$ ratios for each river (Table 3.2), the weighed mean $^{87}Sr/^{86}Sr$ ratio for Canadian river discharge was calculated to be .7111. This ratio is considerably less radiogenic than the current estimate for continental runoff (Veizer and Compston, 1974; Brass, 1976). The question arises whether the present results may be considered representative of the rivers of the world. It is evident from Fig. 5.1 that few major rivers contribute almost all of the Sr in the Canadian river total. The top 10 rivers in Canada, while accounting for 68% of the water discharge by major rivers, deliver almost 90% of the Sr. Since the largest rivers belong to the "sedimentary" group, and their $^{87}Sr/^{86}Sr$ ratio is buffered at approximately .710 by the source of their Sr, it is not surprising that they alone control the average isotopic ratio in the vicinity of seawater values (.709). A recalculation of the weighed mean $^{87}Sr/^{86}Sr$ ratio based on the top 10 rivers again gives .711. Therefore, it would appear that the smaller rivers, delivering variable, "non-buffered" $^{87}Sr/^{86}Sr$, are insignificant in terms of their contribution to the $^{87}Sr/^{86}Sr$ ratio.

The integrated Canadian major river flux (39 rivers) represents 4.4% of the total world discharge to the oceans. This places it second only to the Amazon (Fig. 2.1); the

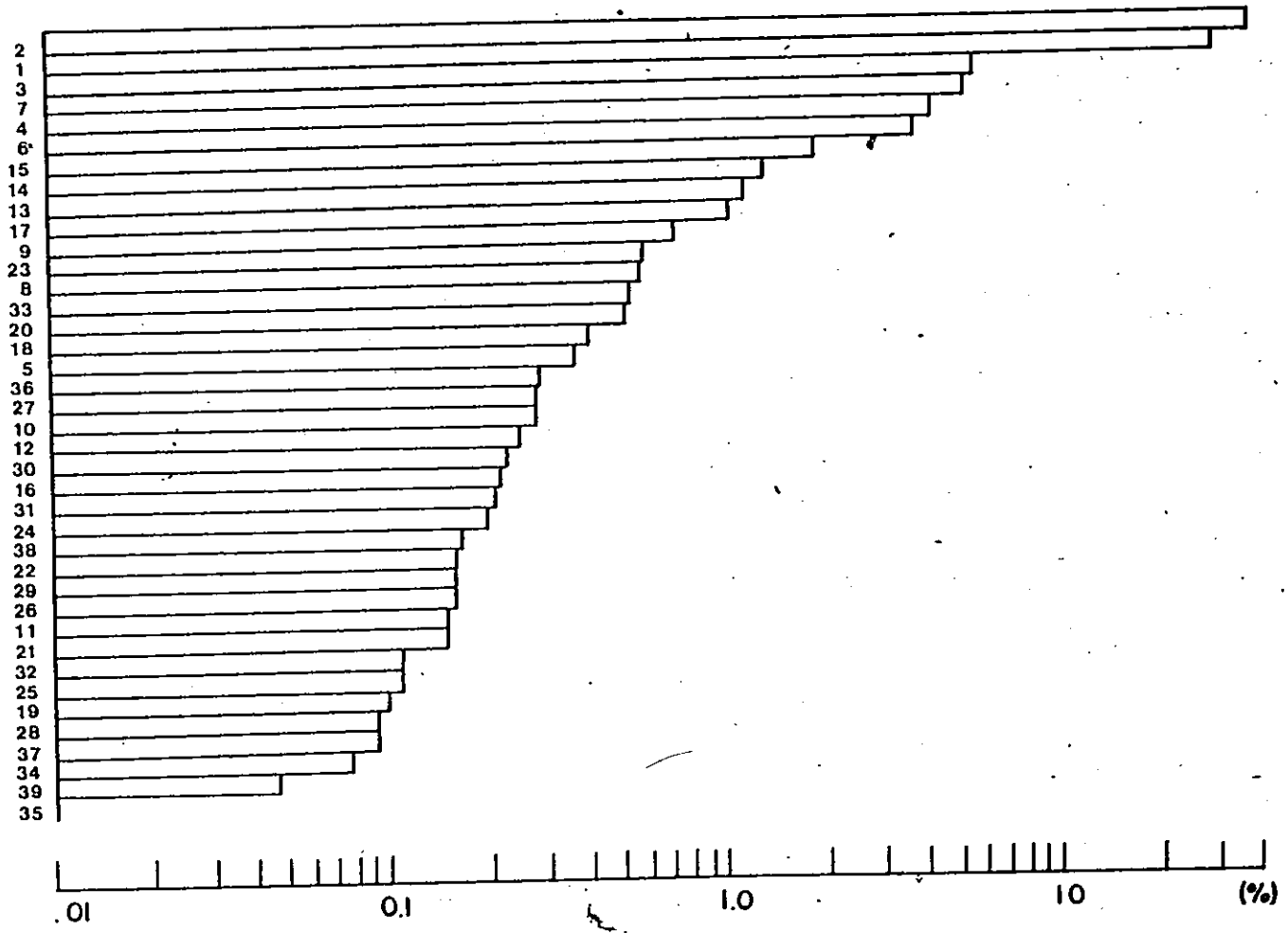



Fig. 5.1

Contributions by individual rivers to the total measured Sr flux from the 39 major Canadian rivers. Numbers correspond to those in Fig. 4.2.

latter also with $^{87}Sr/^{86}Sr$ ratio of .711 (Brass, 1976). Thus almost 20% of the total world discharge has a $^{87}Sr/^{86}Sr$ ratio of .711. Among the remaining major world rivers only the Mississippi has been measured for Sr isotopes. Again it is .710 (Brass, 1976). It would seem therefore, that the true world value for the $^{87}Sr/^{86}Sr$ ratio of continental runoff is closer to .71 than to .72 and this supports the validity of the present estimate. This agrees well with the estimate of Albarède et al. (1981), who bracketed this ratio between .7097 to .7113 from balance calculations based on studies of sea-water-basalt exchange flux on the East Pacific Rise. More recently, Elderfield and Greaves (1981) estimated - from similar considerations - the $^{87}Sr/^{86}Sr$ ratio of river input to be .7112.

## 6. GLOBAL IMPLICATIONS

Using the calculated $^{87}Sr/^{86}Sr$ ratio for continental runoff of .7111 (Chapter 5), the $^{87}Sr/^{86}Sr$ ratio for ocean water of .7091 (Compston and Pidgeon, 1962; Turekian, 1964; Faure et al., 1967 ; Veizer and Compston, 1974) and the $^{87}Sr/^{86}Sr$ ratio for oceanic basalt of .7028 (Hoffman and Hart, 1978), the relative contributions of continental rivers vs. seawater-basalt interaction to the Sr budget of the oceans can be calculated according to the following equation:

$$\left(\frac{^{87}Sr}{^{86}Sr}\right)_{\text{Seawater}} = \left(\frac{^{87}Sr}{^{86}Sr}\right)_{\text{Continental runoff}} \cdot (x) + \left(\frac{^{87}Sr}{^{86}Sr}\right)_{\text{oceanic basalt}} \cdot (1-x)$$

where x represents the fraction of Sr of continental isotopic composition delivered to the oceans by rivers and 1-x the proportion contributed through interaction with basalts at the ridges. Calculations show that the continental flux outweighs the "mantle" flux by a factor of almost 4 to 1 (or precisely 77% : 23%). This is shown in Fig. 6.1.

There is some question whether the ridges are a source of Sr or whether they are merely a sink for radiogenic $^{87}Sr$ through isotopic exchange reactions. Consideration of these two limiting cases numerically gives different estimates for the amount of "mantle" Sr involved in the marine cycle. The global river discharge of Sr is $2.24 \times 10^{12}$ grams per year ($60 \times 10^{-6}$ g/l $\times$ $3.74 \times 10^{16}$ l/yr; Durum and Hafty, 1963 ; Martin and Meybeck, 1979). For the situation where the ridges act as a source of Sr this value of $2.24 \times 10^{12}$ g represents only 77% of

the total Sr budget and the additional 23% ($6.7 \times 10^{11}$ g) must be contributed by the "mantle". Thus, a total of $2.91 \times 10^{12}$ grams per year of Sr are being deposited in sediments (particularly carbonates) on the ocean floor. Alternatively, if the ridges are only sites of Sr isotopic exchange (no net mantle flux) the $2.24 \times 10^{12}$ g represents the total yearly budget of marine Sr; 23% of this, or $5.6 \times 10^{11}$ g, being the product of exchange with basalts. These results compare favourably in order of magnitude to those of Albarède et al. (1981) and Elderfield and Greaves (1981). They estimate that $8.76 \times 10^{11}$ and $9.1 \times 10^{11}$ grams of Sr respectively are cycled annually in the hydrothermal systems. In contrast, the present estimate is an order of magnitude less than that of Spooner (1976) ($3.6 \times 10^{12}$ g / yr); the latter based on continental $^{87}Sr/^{86}Sr$ ratio of .716.

In conclusion, interaction between seawater and basalts at oceanic ridges is an important parameter in the geochemical cycle of Sr. It has the potential to influence significantly the global Sr budget and its exogenic cycle. This may have important implications for the interpretation of secular variations in Sr isotopic composition during geologic history (Peterman et al., 1970; Veizer and Compston 1974,1976; Veizer et al., 1982); a topic beyond the scope of this project.

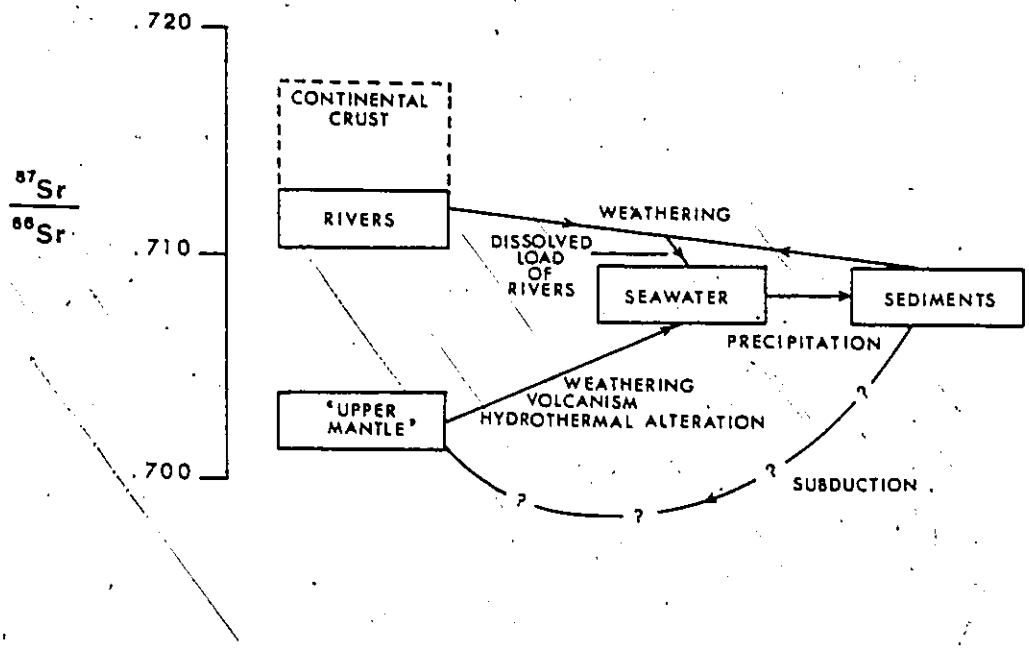



Fig. 6.1

Revised strontium exogenic cycle.

## 7. SUGGESTIONS FOR FURTHER RESEARCH

1. $^{89}Sr$ and $^{90}Sr$ are two Sr isotopes produced by nuclear fission. They are among the most dangerous substances present in fission products and can pose a serious hazard to human and animal life when present in water or foods (Skougstad and Horr, 1963). Therefore, determination of Sr concentration levels in natural waters will be useful for evaluating this potential hazard.

2. The data from this project show two fundamental types of bedrock control of river water chemistry. These two mechanisms will undoubtedly control the distribution of background concentrations of other elements and isotopes. Background values for Canadian rivers should be reestablished with this in mind particularly for programmes in toxicology and pollution.

3. There is good evidence that the results of this study are globally applicable. However, an augmentation of Canadian rivers by Sr data on major world rivers would improve the reliability of the river flux determination. It may be that the actual Sr isotopic composition of river flux is still somewhat less radiogenic than the present estimate. If so, the calculated "mantle" fluxes of Sr into oceans must be considered only as an upper limit.

## 8. SUMMARY

Strontium is one of the major dissolved species in seawater. Its concentration and isotopic composition are homogeneous throughout the oceans; 8 ppm and .709 respectively. Since continental runoff is more radiogenic ($^{87}Sr/^{86}Sr$ = .716-.72) than seawater, Sr in seawater must be a mixture of this radiogenic and a complementary non-radiogenic source such as oceanic crust ($^{87}Sr/^{86}Sr$ = .703). Although information concerning seawater - basalt interaction is equivocal, this mechanism is commonly advocated to explain discrepancies in mass-balance calculations.

In order to evaluate the relative contributions by the continents and oceanic basalt to the Sr isotopic composition of seawater a more confident estimate of the $^{87}Sr/^{86}Sr$ ratio of continental runoff was required.

Sr is carried primarily in the dissolved load of rivers in the 2 + ionic state. It is produced by chemical weathering of carbonate and silicate minerals. In order to estimate their flux of Sr and its isotopic composition, the 39 largest Canadian rivers (by discharge) were sampled just upstream from confluence with the oceans and during different flow regimes. When returned to the laboratory, the samples were analyzed for elemental Sr by carbon rod atomic absorption spectroscopy (A.A.S.), Ca by flame A.A.S., Cl by ion specific electrode, T.D.S. by gravimetry and $^{87}Sr/^{86}Sr$ by mass spectrometry. The geology of

the drainage basins was compiled from geologic maps.

Q - mode factor analysis classified the rivers chemically as a two endmember series. The two endmembers were identified by R - mode factor analysis as 1. concentrated chemistry but non-radiogenic and 2. dilute chemistry and more radiogenic. When these results were compared with the drainage basin geology, an interesting pattern was observed. Endmember 1 rivers drain areas of Phanerozoic sediments and endmember 2 rivers drain the "insoluble" Canadian Shield. These two groups of rivers can also be distinguished on the basis of individual chemical variables. Thus bedrock geology exerts a major control over the chemical composition of the dissolved load of Canadian rivers.

A weighed mean $^{87}Sr/^{86}Sr$ ratio for continental runoff was calculated to be .7111 based on analyses of the 39 major Canadian rivers. This value is less radiogenic than the previous estimate but is supported by measurements of two major world rivers, the Amazon and Mississippi.

The calculated $^{87}Sr/^{86}Sr$ ratio was used to estimate the relative contributions of continental and mantle Sr to the Sr isotopic composition of seawater. The continental flux was found to outweigh the "mantle" flux by almost 4:1, or more accurately 77%:23%. In the Sr exogenic cycle, this 23% mantle component is an upper limit and -- depending whether mid-oceanic ridges act as a source of Sr or only as a site of isotopic exchange reactions -- the amount of Sr released from, or exchanged with, basalts is $\leq 6.7 \times 10^{11}$ g/year or $\leq 5.6 \times 10^{11}$ g/year

respectively.

Augmentation of these data by Sr data from major world rivers would improve the reliability of the river flux estimate.

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# APPENDIX A

## Tables of Analytical Values

TABLE A-1 MEAN SEASONAL DISCHARGE AT OR NEAR SAMPLING SITES OF 39 MAJOR CANADIAN RIVERS

($m^3$/sec)

| RIVER | NO. | 1979 SUMMER | 1979 FALL | 1979 WINTER | 1980 SPRING | 1980 SUMMER | 1980 FALL |
|---|---|---|---|---|---|---|---|
| Yukon | 7 | | | | 2550 M | 3240 H | |
| Porcupine | 33 | | | | 1340 H | 580 M | |
| Stinine | 17 | | | | 2020 H | 1100 M | 1090 M |
| Nass | 15 | | | | 1232 H | 1180 M | 811 M |
| Skeena | 14 | | | 190 L | 1455 H | 953 M | |
| Fraser | 3 | | | | 5700 H | | |
| Columbia | 4 | | 2400 M | 1853 L | | 2940 H | |
| Mackenzie | 2 | 22100 H | | | | | |
| Back | 28 | 2380 H | | | | | |
| Thelon | 29 | 1970 H | 1070 M | 240 L | | | |
| Kazan | 30 | 1350 H | | | | | |
| Churchill (M.) | 27 | | 239 L | | | 821 H | 605 M |
| Nelson | 6 | | 2190 M | | | 1090 L | 2010 H |
| Hayes | 36 | 960 H | | | | | 555 M |
| Severn | 20 | 1980 data not available. 1979 data has been substituted | | | 982 H | 753 M | |
| Winisk | 31 | | | | 478 H | 436 M | |
| Attawapiskat | 38 | | | | 332 H | 178 L | 345 M |
| Albany | 18 | | | | 1604 H | 352 L | 685 M |
| Moose | 23 | | | | 1499 H | 256 L | 416 M |
| Churchill (N.) | 5 | 2487 H | 2050 M | | 2767 H | | |
| St. John | 13 | 336 L | | | 1190 H | | |
| Harricana | 39 | | | | 143 H | 40.5 M | 44.5 M |
| Nottaway | 10 | | | | 368 L | 1180 H | 876 M |
| Rupert | 11 | | | | 1210 H | 1070 H | 899 M |

TABLE A-1 (CONT'D.) MEAN SEASONAL DISCHARGE AT OR NEAR SAMPLING SITES OF 39 MAJOR CANADIAN RIVERS

($m^3$/ sec.)

| RIVER | NO. | 1979 SUMMER | 1979 FALL | 1979 WINTER | 1979 SPRING | 1980 SUMMER | 1980 FALL |
|---|---|---|---|---|---|---|---|
| Eastmain | 19 | | | | 272 L | 1110 H | |
| La Grande | 16 | | | | | 1630 H | 1000 M |
| Grande Riviere de la Baleine | 25 | | | | 379 L | 954 H | |
| Arnaud | 35 | | | | 167 L | 815 M | |
| Aux Feuilles | 21 | | | | 79.2 L | 873 H | |
| Koksoak | 8 | | | | 360 L | 2320 H | 1510 M |
| A la Baleine | 24 | | | | 82.3 L | 482 H | 400 M |
| Petit Mecatina | 26 | | | | 105 L | 1540 H | 474 M |
| Natashquan | 37 | | | | 61.5 L | 932 H | |
| Moisie | 32 | | | | 94.5 L | 758 H | 359 M |
| Manicouagan | 12 | | | | | 735 L | |
| Aux Outardes | 34 | | | | | 314 L | |
| Saguenay | 9 | | | | | | 1200 M |
| St. Maurice | 22 | | 681 L | 692 H | 613 M | | |
| St. Lawrence | 1 | | | | 9070 M | 9130 M | 9510 H |

Explanations:
- L - Low Flow Regime
- M - Medium
- H - High
- Churchill (M.) - Churchill River, Manitoba
- Churchill (N.) - Churchill River, Newfoundland

River numbers correspond to those in Table 2.1

Sources: 1. Quebec rivers : Hydro Quebec (pers. com.)
2. Rest of Canada : Environment Canada, Surface Water Data Reference Index (1979, 1980)

TABLE A-2

CHLORIDE DETERMINATIONS (ppm)

| RIVER | NO. | 1979 SUMMER | 1979 FALL | 1979 WINTER | 1979 SPRING | 1980 SUMMER | 1980 FALL |
|---|---|---|---|---|---|---|---|
| Yukon | 7 | | | | 0.5 | 0.5 | |
| Porcupine | 33 | | | | 0.5 | 0.5 | |
| Stikine | 17 | | | | 0.5 | 0.5 | 0.5 |
| Nass | 15 | | | | 0.5 | 0.5 | |
| Skeena | 14 | | | 6 | 2 | 0.5 | |
| Fraser | 3 | | | | 2 | | |
| Columbia | 4 | | 1 | 0.5 | | 1 | |
| Mackenzie | 2 | 9 | | | | | |
| Back | 28 | 0.5 | 0.5 | | | | |
| Thelon | 29 | 0.5 | 0.5 | 0.5 | | | |
| Kazan | 30 | 3 | | | | | |
| Churchill (M.) | 27 | | 0.5 | | | 0.5 | 1 |
| Nelson | 6 | | 11 | | | 11 | 8 |
| Hayes | 36 | 0.5 | | | | | 0.5 |
| Severn | 20 | | | | 0.5 | | |
| Winisk | 31 | | | | 0.5 | 0.5 | 0.5 |
| Attawapiskat | 38 | | | | 0.5 | 0.5 | 0.5 |
| Albany | 18 | | | | 0.5 | 0.5 | 0.5 |
| Moose | 23 | | | | 0.5 | 0.5 | 0.5 |
| Churchill (N.) | 5 | 0.5 | 0.5 | | 0.5 | | |
| St. John | 13 | 3 | | | 3 | | |
| Harricana | 39 | | | | 2 | 2 | 1 |
| Nottaway | 10 | | | | 0.5 | 0.5 | |
| Rupert | 11 | | | | 0.5 | 0.5 | |

TABLE A - 2 (CONT'D.)

CHLORIDE DETERMINATIONS
(ppm)

| RIVER | NO. | (1979) SUMMER | FALL | WINTER | SPRING | (1980) SUMMER | FALL |
|---|---|---|---|---|---|---|---|
| Eastmain | 19 | | | | 0.5 | 0.5 | |
| La Grande | 16 | | | | | 0.5 | |
| Grande Riviere de la Baleine | 25 | | | | 0.5 | 0.5 | |
| Arnaud | 35 | | | | 4 | 0.5 | 0.5 |
| Aux Feuilles | 21 | | | | 3 | 0.5 | 0.5 |
| Koksoak | 8 | | | | 0.5 | 0.5 | 0.5 |
| A la Baleine | 24 | | | | 0.5 | 0.5 | 0.5 |
| Petit Mecatina | 26 | | | | 2 | 0.5 | 0.5 |
| Natashquan | 37 | | | | 0.5 | 0.5 | |
| Moisie | 32 | | | | 0.5 | 0.5 | 0.5 |
| Manicouagan | 12 | | | | | 0.5 | |
| Aux Outardes | 34 | | | | | 0.5 | |
| Saguenay | 9 | | | | | | 0.5 |
| St. Maurice | 22 | | 2 | 0.5 | 0.5 | | |
| St. Lawrence | 1 | | | | 21 | 22 | 28 |

Explanations: as for Table A-1

TABLE A-3

TOTAL DISSOLVED SOLIDS
(ppm)

| RIVER | NO. | 1979 SUMMER | 1979 FALL | 1979 WINTER | 1980 SPRING | 1980 SUMMER | 1980 FALL |
|---|---|---|---|---|---|---|---|
| Yukon | 7 | | | | 214 | 279 300 | |
| Porcupine | 33 | | | | 160 | 193, 273 | |
| Stikine | 17 | | | | 183 | 144 | 172. |
| Nass | 15 | | | | 116 | 97 | 105 |
| Skeena | 14 | | | 87 | 86 | 95 | |
| Fraser | 3 | | | | 159 | | |
| Columbia | 4 | | 171 | 167 | | 174 | |
| Mackenzie | 2 | 279,290,304 | | | | | |
| Back | 28 | 29 | 23 | | | | |
| Thelon | 29 | 32 | 36 | 38 | | | |
| Kazan | 30 | 37 | | | | | |
| Churchill (M.) | 27 | | 155 | | | 147 | 202 |
| Nelson | 6 | | 249 | | | 228 | 240 |
| Hayes | 36 | 250 | | | | | 199 |
| Severn | 20 | | | | 145 | 201 | |
| Winisk | 31 | | | | 154 | 203 | |
| Attawapiskat | 38 | | | | 158 | 172 | 157 |
| Albany | 18 | | | | 130 | 194 | 190 |
| Moose | 23 | | | | 166 | 214 | 203 |
| Churchill (N.) | 5 | 41 | 31 | | 29 | | |
| St. John | 13 | 128 | | 81 | 87 | | |
| Harricana | 39 | | | | 69 | 80 | 87 |
| Nottaway | 10 | | | | 31 | 34 | 51 |
| Rupert | 11 | | | | 16 | 26 | 26 |

TABLE A-3 (CONT'D.)

TOTAL DISSOLVED SOLIDS
(ppm)

| RIVER | NO. | 1979 SUMMER | 1979 FALL | 1979 WINTER | 1980 SPRING | 1980 SUMMER | 1980 FALL |
|---|---|---|---|---|---|---|---|
| Eastmain | 19 | | | | 14 | 26 | |
| La Grande | 16 | | | | | 20 | 10 |
| Grande Riviere de la Baleine | 25 | | | | 7 | 21 | |
| Arnaud | 35 | | | | 12 | 8 | 10 |
| Aux Feuilles | 21 | | | | 14 | 14 | |
| Koksoak | 8 | | | | 46 | 11 | 26 |
| A la Baleine | 24 | | | | 25 | 23 | 67 |
| Petit Mecatina | 26 | | | | 40 | 40 | 25 |
| Natashquan | 37 | | | | 38 | 26 | |
| Moisie | 32 | | | | 39 | 16 | 32 |
| Manicouagan | 12 | | | | | 45 | |
| Aux Outardes | 34 | | | | | 38 | |
| Saguenay | 9 | | | | | | |
| St. Maurice | 22 | | 45 | 39 | 32 | | |
| St. Lawrence | 1 | | | | 339 | 267 | 288 |

Explanations: as for Table A-1

TABLE A-4

CALCIUM DETERMINATIONS
(ppm)

| RIVER | NO. | 1979 SUMMER | 1979 FALL | 1979 WINTER | 1980 SPRING | 1980 SUMMER | 1980 FALL |
|---|---|---|---|---|---|---|---|
| Yukon | 7 | | | | 22 | 34 | |
| Porcupine | 33 | | | | 13. | 27 | |
| Stikine | 17 | | | | 16 | 17 | 19 |
| Nass | 15 | | | | 12 | 10 | 13 |
| Skeena | 14 | | | 10 | 9.2 | 10 | |
| Fraser | 3 | | | | 15 | | |
| Columbia | 4 | | 20 | 20 | | 18 | |
| Mackenzie | 2 | 31,34,34 | | | | | |
| Back | 28 | 0.8 | 0.6 | | | | |
| Thelon | 29 | 1.8 | 2.1 | 1.8 | | | |
| Kazan | 30 | 2.2 | | | | | |
| Churchill (M.) | 27 | | 17 | | | 18 | 20 |
| Nelson | 6 | | 24 | | | 23 | 23 |
| Hayes | 36 | 27 | | | | | 23 |
| Severn | 20 | | | | 15 | 18 | |
| Winisk | 31 | | | | 15 | 18 | |
| Attawapiskat | 38 | | | | 14 | 20 | 15 |
| Albany | 18 | | | | 13 | 22 | 19 |
| Moose | 23 | | | | 17 | 25 | 25 |
| Churchill (N.) | 5 | 1.7 | 1.7 | | 2.1 | | |
| St. John | 13 | 15 | | 10 | 12 | | |
| Harricana | 39 | | | | 4.8 | 6.0 | 7.1 |
| Nottaway | 10 | | | | 2.3 | 2.7 | 3.3 |
| Rupert | 11 | | | | 1.3 | 1.8 | 2.3 |

TABLE A-4

CALCIUM DETERMINATIONS

(ppm)

| RIVER | NO. | 1979 SUMMER | 1979 FALL | 1979 WINTER | 1980 SPRING | 1980 SUMMER | 1980 FALL |
|---|---|---|---|---|---|---|---|
| Eastmain | 19 | | | | 0.8 | 1.1 | |
| La Grande | 16 | | | | 1.2 | 0.8 | |
| Grande Riviere de la Baleine | 25 | | | | 0.9 | 0.6 | |
| Arnaud | 35 | | | | 0.9 | 0.9 | 1.4 |
| Aux Feuilles | 21 | | | | 1.2 | 0.9 | |
| Koksoak | 8 | | | | 2.7 | 1.6 | 3.0 |
| A la Baleine | 24 | | | | 2.9 | 2.1 | 6.0 |
| Petit Mecatina | 26 | | | | 2.5 | 0.8 | 2.4 |
| Natashquan | 37 | | | | 1.8 | 0.8 | |
| Moisie | 32 | | | | 3.5 | 1.5 | 2.6 |
| Manicouagan | 12 | | | | | 1.6 | |
| Aux Outardes | 34 | | | | | 1.2 | |
| Saguenay | 9 | | | | | | 4.0 |
| St. Maurice | 22 | | 2.7 | 1.6 | 2.0 | | |
| St. Lawrence | 1 | | | | 28 | 27 | 32 |

Explanations: As for Table A-1

TABLE A-5

STRONTIUM DETERMINATIONS
(ppb)

| RIVER | NO. | 1979 SUMMER | 1979 FALL | 1979 WINTER | 1980 SPRING | 1980 SUMMER | 1980 FALL |
|---|---|---|---|---|---|---|---|
| Yukon | 7 | | | | 100 | 115,108 | |
| Porcupine | 33 | | | | 30 | 75, 85 | |
| Stikine | 17 | | | | 60 | 54 | 61 |
| Nass | 15 | | | | 110 | 75 | 105 |
| Skeena | 14 | | | 75 | 63 | 78 | |
| Fraser | 3 | | | | 80 | | |
| Columbia | 4 | | 58 | 78 | | 85 | |
| Mackenzie | 2 | 170<br>195,160 | | | | | |
| Back | 28 | 8 | 8 | | | | |
| Thelon | 29 | 10 | 13 | 20 | | | |
| Kazan | 30 | 23 | | | | | |
| Churchill (M.) | 27 | | 18 | | | 23 | 28 |
| Nelson | 6 | | 72 | | | 68 | 86 |
| Hayes | 36 | 38 | | | | | 34 |
| Severn | 20 | | | | 27 | 40 | |
| Winisk | 31 | | | | 17 | 27 | |
| Attawapiskat | 38 | | | | 20 | 38 | 20 |
| Albany | 18 | | | | 19 | 36 | 30 |
| Moose | 23 | | | | 35 | 60 | 30 |
| Churchill (N.) | 5 | 5 | 9 | | 8 | | |
| St. John | 13 | 60 | | | 56, 60 | | |
| Harricana | 39 | | | | 23 | 35 | 40 |
| Nottaway | 10 | | | | 6 | 12 | 15 |
| Rupert | 11 | | | | 7 | 7 | 8 |

TABLE A-5 (CONT'D.)

STRONTIUM DETERMINATIONS
(ppb)

| RIVER | NO. | 1979 SUMMER | 1979 FALL | 1979 WINTER | 1980 SPRING | 1980 SUMMER | 1980 FALL |
|---|---|---|---|---|---|---|---|
| Eastmain | 19 | | | | 4 | 7 | |
| La Grande | 16 | | | | | 11 | 12 |
| Grande Riviere de la Baleine | 25 | | | | 9 | 8 | |
| Arnaud | | | | | 10 | 8 | 5 |
| Aux Feuilles | 21 | | | | 11 | 8 | |
| Koksoak | 8 | | | | 18 | 15 | 13 |
| A la Baleine | 24 | | | | 16 | 8 | 19 |
| Petit Mecatina | 26 | | | | 18 | 7 | 13 |
| Natashquan | 37 | | | | 17 | 6 | |
| Moisie | 32 | | | | | 12 | |
| Manicouagan | 12 | | | | 11 | 13 | |
| Aux Outardes | 34 | | | | 9 | 8 | |
| Saguenay | 9 | | | | | | 23 |
| St. Maurice | 22 | | 13 | 12 | 7 | | |
| St. Lawrence | 1 | | | | 145 | 135 | 130 |

Explanations: as for Table A-1

TABLE A-6

STRONTIUM ISOTOPIC COMPOSITIONS

| RIVER | NO. | 1979 SUMMER | 1979 FALL | 1980 WINTER | 1980 SPRING | 1980 SUMMER | 1980 FALL |
|---|---|---|---|---|---|---|---|
| Yukon | 7 | | | | .71614± 9 | .71618±10 | |
| Porcupine | 33 | | | | .71125± 9 | .71257± 9 | |
| Stikine | 17 | | | | .70535± 8 | .70548± 8 | |
| Nass | 15 | | | | .70539± 8 | .70541± 8 | |
| Skeena | 14 | | | | .70459± 7 | .70461± 8 | |
| Fraser | 3 | | | | .71195± 9 | | |
| Columbia | 4 | | | .71574± 7 | | .71553± 8 | |
| Mackenzie | 2 | .71102± 8 | | | | | |
| Back | 28 | .72910± 9 | | | | | |
| Thelon | 29 | .71880± 8 | | .71884± 8 | | | |
| Kazan | 30 | .72579± 8 | | | | | |
| Churchill (M.) | 27 | | | | | .72020± 8 | .71979± 8 |
| Nelson | 6 | | .71453±10 | | | .71407± 8 | .71528± 8 |
| Hayes | 36 | .71769± 7 | | | | | |
| Severn | 20 | | | | | .71818± 9 | |
| Winisk | 31 | | | | .71769± 9 | | |
| Attawapiskat | 38 | | | | | .71402± 8 | |
| Albany | 18 | | | | .71702± 8 | .71448± 8 | |
| Moose | 23 | | | | .71363± 9 | .71250±10 | .71355± 8 |
| Churchill(N.) | 5 | .71756± 8 | .71758± 12 | | | | |
| St. John | 13 | .70977± 8 | | | | | |
| Harricana | 39 | | | | .71786±10 | .71576±10 | .71578± 8 |
| Nottaway | 10 | | | | .71857± 9 | .71722± 9 | .71987±11 |
| Rupert | 11 | | | | | .72832± 8 | |

TABLE A-6 (CONT'D.) STRONTIUM ISOTOPIC COMPOSITIONS

| RIVER | NO. | 1979 SUMMER | 1979 FALL | 1979 WINTER | 1980 SPRING | 1980 SUMMER | 1980 FALL |
|---|---|---|---|---|---|---|---|
| Eastmain | 19 | | | | | .72845± 7 | |
| La Grande | 16 | | | | | .73456± 9 | .73454± 7 |
| Grande Riviere de la Baleine | 25 | | | | | .73844± 8 | |
| Arnaud | 35 | | | | | .72638± 9 | |
| Aux Feuilles | 21 | | | | | .73471± 9 | |
| Koksoak | 8 | | | | .72865± 8 | .73161± 9 | |
| A la Baleine | 24 | | | | | .72647±10 | |
| Petit Mecatina | 26 | | | | | .71045± 9 | |
| Natashquan | 37 | | | | | .71307± 9 | |
| Moisie | 32 | | | | .71673± 8 | .71547± 8 | .71669±10 |
| Manicouagan | 12 | | | | | | .71686± 8 |
| Aux Outardes | 34 | | | | | .71864±10 | |
| Saguenay | 9 | | | | | | .71308± 9 |
| St. Maurice | 22 | | .71129± 8 | | .71112± 9 | | |
| St. Lawrence | 1 | | | | .70936±12 | .70949± 8 | .70952± 8 |

Explanations:

All ratios have been corrected for fractionation within the mass spectrometer to a $^{86}Sr/^{88}Sr$ ratio of .1194, and all ratios were normalized to the Eimer and Amend $SrCO_3$ value of .7080.

Remainder - as in Table A-1.

# APPENDIX B

## Tables of Drainage Basin Geology

GEOLOGY OF THE YUKON RIVER DRAINAGE BASIN

(Includes drainage basins of Porcupine, White, Stewart, Pelly Teslin)

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Triassic sandstone, siltstone, shale, limestone | 5 | MF 01 |
| Lower Jurassic conglomerate, greywacke, argillite, coal | 11 | ME 01 |
| Tertiary basalt, andesite, dacite, trachyte, rhyolite, tuff | 5 | CE 05 |
| Metamorphic rocks of various ages: quartzite, quartz-mica schist, slate, limestone, greenstone, gneiss | 33 | AM |
| Ordovician and Silurian chert and shale | 14 | PA 01 |
| Cambrian quartzite, grit, conglomerate, slate | 16 | PA 01 |
| Devonian and Carboniferous conglomerate, quartzite, greywacke, chert, slate | 5 | PA 01 |
| Carboniferous, mainly Pennsylvanian limestone, shale, chert | 9 | PA 02 |
| Carboniferous, mainly Pennsylvanian andesite, basalt, breccia, diorite, phyllite, limestone, chert | 2 | PA 05 |
| | 100 | |

Source: Geological Survey of Canada

Department of Mines and Technical Surveys

Map 30 - 1963

Geology Yukon Territory and Northwest Territories

Scale: 1 : 3,000,000

GEOLOGY OF THE PORCUPINE RIVER DRAINAGE BASIN.

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Carboniferous, mainly Pennsylvanian limestone, shale, chert | 10 | PA 02 |
| Carboniferous, mainly Mississippian limestone and shale | 20 | PA 02 |
| Mixed Ordovician, Silurian and Devonian limestone and dolomite | 10 | PA 02 |
| Lower and Upper Cretaceous intermixed shale, sandstone and conglomerate | 30 | ME 01 |
| Quaternary and Recent surficial deposits obscuring bedrock relationships | 25 | CE 01 |
| Proterozoic phyllite | 5 | PR 06 |
| | 100 | |

Source: See Yukon River

GEOLOGY OF THE STIKINE RIVER DRAINAGE BASIN.

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Late Paleozoic clastic sedimentary rocks | 6 | PA 01 |
| Upper Cretaceous clastic sedimentary rocks | 5 | ME 01 |
| Triassic clastic sedimentary rocks | 14 | ME 01 |
| Upper Jurassic carbonate sedimentary rocks | 25 | ME 02 |
| Upper Jurassic to Middle Cretaceous intrusives - mainly granodiorite, quartz diorite, granite, quartz monzonite, monzonite, syenite, ... | 10 | ME 03 |
| Jurassic or Cretaceous acidic and intermediate rocks - granodiorite, quartz diorite, granite, quartz monzonite, syenite, diorite, gabbro | 8 | ME 03 |
| Mesozoic mafic and intermediate volcanics | 6 | ME 05 |
| Triassic mafic and intermediate volcanics | 14 | ME 05 |
| Early Tertiary clastic sedimentary rocks | 5 | CE 01 |
| Late Tertiary and Quaternary felsic and mixed volcanic rocks | 7 | CE 05 |
| | 100 | |

Source: Geological Survey of Canada

Map 932A (2nd Edition)

Geological Map of British Columbia

1962

Scale: 1 : 1,267,000

GEOLOGY OF THE NASS RIVER BASIN.

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Upper and Lower cretaceous clastic sedimentary rocks | 71 | ME 01 |
| Triassic clastic sedimentary rocks | 4 | ME 01 |
| Jurassic or Cretaceous acidic and intermediate rocks -- granodiorite, granite, syenite,... | 14 | ME 03 |
| Upper Jurassic to Middle Cretaceous intrusives - mainly granodiorite, granite, syenite,... | 3 | ME 03 |
| Triassic Volcanic rocks. | 4 | ME 05 |
| Late Tertiary and Quaternary clastic sedimentary rocks. | 2 | CE 01 |
| Late Tertiary volcanic rocks | 2 | CE 05 |
| | 100 | |

Source: See Stikine River.

GEOLOGY OF THE SKEENA RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Late Paleozoic clastic sedimentary rocks | 2 | PA 01 |
| Upper Jurassic and Lower Cretaceous shale and sandstone. | 39 | ME 01 |
| Jurassic shale and sandstone | 10 | ME 01 |
| Upper Jurassic to Middle Cretaceous intrusives - mainly granodiorite, granite syenite, gabbro | 11 | ME 03 |
| Lower and Middle Jurassic acidic and intermediate rocks - granite, granodiorite, manzonite, syenite. | 6 | ME 03 |
| Jurassic or Cretaceous acidic and intermediate rocks | 13 | ME 03 |
| Jurassic volcanic rocks | 13 | ME 05 |
| Late Tertiary and Quaternary clastic sedimentary rocks | 3 | CE 01 |
| Late Tertiary Volcanic rocks | 3 | CE 05 |
| | 100 | |

Source: See Stikine River

GEOLOGY OF THE FRASER RIVER DRAINAGE BASIN

Includes Nechako, Chilcotin, Thompson and Fraser Rivers

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Pennsylvanian and Permian clastic sedimentary rocks | 4 | PA 01 |
| Pennsylvanian and Permian volcanic rocks | 4 | PA 05 |
| Upper Triassic and cretaceous clastic sedimentary rocks | 7 | ME 01 |
| Jurassic and/or Cretaceous felsic and intermediate rocks - granodiorite, granite, quartzdiorite, manzonite, gabbro | 31 | ME 03 |
| Upper Triassic volcanic rocks | 3 | ME 05 |
| Upper Cretaceous volcanic rocks | 1 | ME 05 |
| Late Tertiary and Quaternary clastic sedimentary rocks. | 12 | CE 01 |
| Early and Late Tertiary volcanic rocks | 20 | CE 05 |
| Drift covered areas; bedrock relationships obscured | 5 | CE 01 |
| Lower Cenozoic clastic sedimentary rocks | 7 | CE 01 |
| Precambrian or later granitoid gneiss, schist, quartzite, marble, slate, phyllite. | 6 | AM |
| | 100 | |

Source: See Stikine River.

GEOLOGY OF THE COLUMBIA RIVER DRAINAGE BASIN

Includes Okanagan and Kootenay drainage basins. Only 14% of the Columbia drainage basin is located in Canada.

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Proterozoic clastic sedimentary, argillaceous, calcareous | 32 | PR 01 |
| Lower Cambrian clastic sedimentary rocks | 2 | PA 01 |
| Devonian, Mississippian, Pennsylvanian and Permian clastic and calcareous sedimentary rocks | 6 | PA 01 |
| Cambrian, Ordovician and Silurian calcareous sedimentary rocks | 12 | PA 02 |
| Lower Cretaceous and Early Tertiary clastic sedimentary rocks | 6 | ME 01 |
| Upper Jurassic and/or cretaceous acidic and intermediate rocks; mainly granodiorite, quartz diorite, granite, quartz manzonite | 23 | ME 03 |
| Early Tertiary felsic rocks mainly granite, syenite, manzonite | 3 | CE 03 |
| Precambrian granitoid gneiss; schist, quartzite, marble, slate, phyllite | 6 | AM |
| Triassic clastic sedimentary rocks | 5 | ME 01 |
| Triassic volcanic rocks | 5 | ME 05 |
| | 100 | |

Source: See Stikine River

GEOLOGY OF THE MACKENZIE RIVER DRAINAGE BASIN.

Includes drainage basins of the Peel, Great Bear, Laird, Taltson, Hay, Peace, Athabasca rivers and the Great Slave System.

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean granites, syenites, gneisses | 25 | AR 03 |
| Ordovician and Silurian limestone, dolomite and shale | 26 | PA 02 |
| Cretaceous marine shale, non-marine shale and sandstone. | 37 | ME 01 |
| Mesozoic acid plutonic intrusions (granites) | 2 | ME 03 |
| Mixed Precambrian metamorphic rocks | 7 | AM |
| Devonian evaporites: halite, gypsum | 3 | E |
| | 100 | |

Source: Hydrogeochemistry of the Surface Waters of the Mackenzie River Drainage Basin, Canada - I. Factors controlling inorganic composition. S.W. Reeder, B. Hitchon and A.A. Levinson, 1972 Geochim. Cosmochim. Acta, 36, 825 - 865.

GEOLOGY OF THE BACK RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean greywacke with quartzite, slate, phyllite | 8 | AR 01 |
| Archean granite, granodiorite, allied gneissic rocks, muscovite-biotite granites | 3 | AR 03 |
| Archean basalt, andesite | 9 | AR 05 |
| Middle Proterozoic sandstone, grit arkose | 10 | PR 01 |
| Lower Proterozoic (Paleohelikian) intermediate to mafic volcanics | 5 | PR 05 |
| Lower Proterozoic metamorphics: granitic gneiss, migmatite and mylonite | 65 | PR 06 |
| | 100 | |

Source: See Yukon River

GEOLOGY OF THE THELON RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Middle Proterozoic sandstone, grit, arkose | 55 | PR 01 |
| Middle Proterozoic conglomerate and sandstone | 10 | PR 01 |
| Lower Proterozoic quartzite metasedimentary | 10 | PR 06 |
| Lower Proterozoic metamorphics; granitic gneiss, migmatite and mylonite; includes some massive granites | 25 | PR 06 |
| | 100 | |

Source: See Yukon River

GEOLOGY OF THE KAZAN RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Lower Proterozoic greywacke, quartzite, slate | 7 | PR 01 |
| Proterozoic anorthosite, diabase, gabbro | 11 | PR 04 |
| Lower Proterozoic intermediate to basic volcanic rocks; greenstone, amphibolite | 9 | PR 05 |
| Middle Proterozoic quartz-feldspar and pyroxene-biotite extrusive porphyry | 6 | PR 05 |
| Lower Proterozoic granitic gneiss and schist derived from sediments and volcanics | 7 | PR 06 |
| Lower Proterozoic metamorphics; granitic gneiss, migmatite and mylonite; includes some massive granites | 60 | PR 06 |
| | 100 | |

Source: See Yukon River

GEOLOGY OF THE CHURCHILL RIVER DRAINAGE BASIN (MANITOBA)

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean remobilized granite and granitoid orthogneiss | 2 | AR 03 |
| Precambrian granite, granodiorite, quartz manzonite -- massive or gneissic | 17 | AR 03 |
| Archean migmatite and mylonite zones -- mixed sediment and granite | 4 | AR 06 |
| Precambrian amphibolite and hornblende - bearing gneisses -- maybe volcanic, intrusive or sedimentary in origin | 5 | AR 06 |
| Lower Proterozoic (Churchill structural province) arkose, arenite, feldspathic wacke -- arkosic gneiss and migmatite | 4 | PR 01 |
| Ordovician, thin basal sandstone, limestone and dolomite | 6 | PA 02 |
| Lower Proterozoic felsic metamorphic and metasedimentary rocks of the Churchill structural province; greywacke and mudstone derived psammitic and semi-pelitic gneiss, schist and migmatite | 5 | PR 06 |
| Proterozoic intrusives of the Churchill structural province; granite, granodiorite, tonalite | 17 | PR 03 |
| Precambrian pelitic schists and gneisses -- aluminous metasediments | 12 | PR 06 |
| Cretaceous grey, non-calcareous clayey silt and silty clay | 7 | ME 01 |
| Cretaceous interbedded fine to coarse sand, silt and clay | 16 | ME 01 |
| Cretaceous grey, silty clay-shale; some parts calcareous, some non-calcareous | 5 | ME 01 |
| | 100 | |

GEOLOGY OF THE CHURCHILL RIVER DRAINAGE BASIN

Source: Map 79-2 Geological Map of Manitoba

Manitoba Mineral Resources Division,

1979; Scale: 1 : 1,000,000

Geological Map of Saskatchewan

Dept. Mineral Resources,

Geological Sciences Branch and
Saskatchewan Research Council

Geological Division, 1972.

GEOLOGY OF THE NELSON RIVER DRAINAGE BASIN

Because of the large percentage of the Churchill River being diverted into the Nelson River for hydroelectric purposes, the geology of the two drainage basins has been combined to reflect more accurately the areal extent of rock types contributing to the chemistry of the sample of the Nelson River. When the 2 rivers are combined, the Churchill represents 22% of the whole. The nature of the diversion is such that the geology of the Churchill River drainage basin is represented in the chemistry of the sample of that river but it also contributes 22% of the chemistry of the Nelson River sample.

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Paleozoic carbonate sedimentary | 2 | PA 02 |
| Upper Mesozoic carbonate sedimentary | 2 | ME 02 |
| Lower Cenozoic clastic sedimentary | 5 | CE 01 |
| Upper Mesozoic clastic sedimentary | 42 | ME 01 |
| Middle Paleozoic carbonate sedimentary | 5 | PA 02 |
| Archean felsic igneous | 11 | AR 03 |
| Lower Paleozoic carbonate sedimentary | 7 | PA 02 |
| Lower Proterozoic felsic metamorphic | 1 | PR 06 |
| Lower Proterozoic felsic igneous | 6 | PR 03 |
| Archean felsic metamorphic | 1 | AR 06 |
| Middle Mesozoic clastic sedimentary and evappritic | 2 | ME 01 |
| Archean felsic metamorphic | 8 | AR 06 |

GEOLOGY OF THE NELSON RIVER DRAINAGE BASIN (CONT'D.)

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean volcanic | 2 | AR 05 |
| Archean metasedimentary | 2 | AR 06 |
| Lower Proterozoic felsic metamorphic or metasedimentary | 1 | PR 06 |
| Lower Proterozoic clastic metasedimentary | 3 | PR 01 |
| | 100 | |

Sources:
1. Map 79 - 2
   Geological Map of Manitoba
   Manitoba Mineral Resources Division, 1979
   Scale: 1:1,000,000
2. Geological Map of Saskatchewan
   Department of Mineral Resources,
   Geological Sciences Branch
   and Saskatchewan Research Council,
   Geological Division, 1972
3. Geological Map of Alberta
   Research Council of Alberta
   Map 35, 1972
   Scale: 1:1,267,000

GEOLOGY OF THE HAYES RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean metamorphosed early intrusive rocks--tonalite, minor granodiorite, granite and related gneiss; undifferentiated granitic rocks | 40 | AR 06 |
| Ordovician sandstone - shale | 7 | PA 01 |
| Ordovician limestone and dolomite | 5 | PA 02 |
| Silurian limestone, dolomitic limestone and dolomite | 13 | PA 02 |
| Silurian limestone, skeletal calcarenites; in part argillaceous and dolomitic | 5 | PA 02 |
| Archean metamorphosed early intrusive rocks -- gneisses and migmatites, felsic granulites with minor gabbro and anorthosite | 5 | AR 06 |
| Proterozoic layered migmatitic gneiss derived from Archean early intrusives, aplite, pegmatite | 5 | PR 06 |
| Proterozoic mafic/ultramafic meta-volcanics -- basalt, komatiite | 5 | PR 06 |
| Proterozoic greywacke, argillite, slate with pelitic and semi-pelitic schists | 5 | PR 01 |
| Mixed basalt - andesite, granodiorite-tonalite-migmatite, greywacke-arkose | 10 | AM |
| | 100 | |

Source: Map 79 - 2

Geological Map of Manitoba

Manitoba Mineral Resources Division, 1979

Scale 1:1,000,000

GEOLOGY OF THE SEVERN RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Upper Silurian limestone, dolomite, siltstone, shale, mudstone, sandstone, gypsum, salt | 2 | PA 02 |
| Middle Silurian dolomite and limestone | 25 | PA 02 |
| Upper Ordovician shale and sandstone | 4 | PA 01 |
| Upper Ordovician limestone and dolomite | 5 | PA 02 |
| Early Precambrian felsic igneous and metamorphic rocks -- granodiorite, trondhjemite, quartz diorite, quartz monzonite, granite, syenite, quartz and feldspar porphyries, pegmatite, aplite | 57 | AR 03 |
| Early Precambrian mafic metavolcanics -- basalt, andesite (flows, tuff, breccia) | 6 | AR 06 |
| Early Precambrian metasediments -- conglomerate, greywacke, arkose, orthoquartzite, argillite, slate, marble,... | 1 | AR 06 |
| | 100 | |

Source: Ontario Department of Mines and Northern Affairs

Ontario Geological Maps Nos. 2196 - 2201

1970

Scale 1:1,013,760 (1 in : 16 mi.)

GEOLOGY OF THE WINISK RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Middle Silurian dolomite and limestone | 27 | PA 02 |
| Upper Ordovician shale and sandstone | 5 | PA 01 |
| Upper Ordovician limestone and dolomite | 6 | PA 02 |
| Early Precambrian mafic metavolcanics -- basalt, andesite (flows, tuff, breccia). | 5 | AR 06 |
| Early Precambrian felsic igneous and metamorphic rocks -- granodiorite, trondhjemite, quartz diorite, quartz monzonite; granite, syenite, pegmatite, aplite,... | 57 | AR 03 |
| | 100 | |

Source: See Severn River

GEOLOGY OF THE ATTAWAPISKAT RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Middle Silurian dolomite and limestone | 63 | PA 02 |
| Upper Ordovician limestone and dolomite | 3 | PA 02 |
| Upper Ordovician shale and sandstone | 4 | PA 01 |
| Early Precambrian felsic igneous and metamorphic rocks -- granodiorite, trondhjemite, quartz diorite, quartz monzonite, granite, syenite, quartz and feldspar porphyries, pegmatite, aplite, ... | 27 | AR 03 |
| Early Precambrian mafic metavolcanics -- basalt, andesite (flows, tuff, breccia) | 3 | AR 06 |
| | 100 | |

Source: See Severn River

GEOLOGY OF THE ALBANY RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Lower Cretaceous clay, sand, lignite, kaolinitic quartz sand | 1 | ME 01 |
| Middle Devonian limestone, dolomite, shale, gypsum | 11 | PA 02 |
| Lower Devonian sandstone, arkose, conglomerate, siltstone, shale, limestone | 5 | PA 01 |
| Upper Silurian limestone, dolomite, siltstone, shale, mudstone, sandstone, gypsum, salt | 12 | PA 02 |
| Middle Silurian dolomite and limestone | 13 | PA 02 |
| Upper Ordovician shale and sandstone | 1 | PA 01 |
| Upper Ordovician limestone and dolomite | 1 | PA 02 |
| Early Precambrian felsic igneous and metamorphic rocks -- granodiorite, trondhjemite, quartz diorite, quartz monzonite, granite... | 46 | AR 03 |
| Early Precambrian metasediments -- conglomerate, greywacke, arkose, orthoquartzite, argillite, slate, marble | 3 | AR 06 |
| Early Precambrian mafic metavolcanics-- basalt, andesite | 7 | AR 06 |
| | 100 | |

Source: See Severn River

GEOLOGY OF THE MOOSE RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Early Precambrian felsic igneous and metamorphic rocks -- granodiorite, trondhjemite, quartz diorite | 60 | AR 03 |
| Early Precambrian mafic metavolcanics -- basalt, andesite (flows, tuff, breccia) | 12 | AR 06 |
| Early Precambrian mafic metasediments -- conglomerate, greywacke, arkose, orthoquartzite, argillite, slate, marble | 5 | AR 01 |
| Early Precambrian felsic to intermediate metavolcanics -- rhyolite, dacite, rhyodacite | 1 | AR 06 |
| Middle Devonian limestone, dolomite, shale | 4 | PA 02 |
| Middle Paleozoic gypsum | 4 | E |
| Lower Cretaceous clay, sand, lignite | 14 | ME 01 |
| | 100 | |

Source: See Severn River

GEOLOGY OF THE CHURCHILL RIVER DRAINAGE BASIN (NEWFOUNDLAND)

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Paleohelikian adamellite suite; monzonite, syenite, granodiorite, granite and their pyroxene bearing equivalents | 3 | PR 03 |
| Paleohelikian gabbro, norite, anorthositic gabbro, troctolite, diorite; derived basic gneiss and amphibolite | 5 | PR 04 |
| Helikian granitic gneiss, mainly pink quartzo-feldspathic gneisses, commonly banded and migmatitic | 4 | PR 06 |
| Helikian paragneisses, granitoid gneisses of probable sedimentary origin; minor quartzite and marble | 14 | PR 06 |
| Helikian sillimanite gneiss, commonly migmatitic -- minor amphibolite | 8 | PR 06 |
| Aphebian granitic gneiss, granodioritic gneiss, migmatite, amphibolite | 9 | PR 06 |
| Aphebian granulite, pyroxene gneiss, charnockite, minor granitic gneiss, mylonitic gneiss | 2 | PR 06 |
| Aphebian sillimanite gneiss with abundant intrusive pegmatitic material | 6 | PR 06 |
| Aphebian metasedimentary granitoid gneisses | 16 | PR 06 |
| Aphebian granulitic - dioritic to granodioritic gneiss | 1 | PR 06 |
| Paleohelikian anorthosite suite: anorthosite, anorthositic gabbro, leucotroctolite | 4 | PR 04 |
| Aphebian iron formation | 1 | PR 06 |
| Aphebian grit, arkose, conglomerate, quartzite, greywacke, slate | 16 | PR 01 |

GEOLOGY OF THE CHURCHILL RIVER BASIN (NEWFOUNDLAND) (CONT'D.)

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean foliated pyroxene-bearing granodiorite and syenodiorite | 1 | AR 03 |
| Archean massive granite and quartz monzonite | 1 | AR 03 |
| Aphebian dolomite, marble, quartzite | 1 | PR 02 |
| Archean pyroxene granulite, unseparated felsic intrusives | 8 | AR 06 |
| | 100 | |

Source: Geological Map of Labrador

Scale 1:1,000,000

Mineral Resources Division

Dept. of Mines, Agriculture and Resources

Province of Newfoundland and Labrador

GEOLOGY OF THE ST. JOHN RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Devonian shale, limestone, sandstone, minor greywacke, tuff and volcanics | 13 | PA 01 |
| Silurian greywacke, slate, siltstone, sandstone, conglomerate, limestone | 7 | PA 01 |
| Ordovician and/or Silurian calcareous and argillaceous sedimentary rocks | 10 | PA 01 |
| Silurian and Devonian mixed greywacke and slate, sandstone and conglomerate, minor volcanics -- rhyolite, trachyte, tuff | 9 | PA 01 |
| Devonian granite, quartz monzonite, granodiorite and related rocks | 8 | PA 03 |
| Mississippian red to grey sandstone, conglomerate, shale, minor limestone | 7 | PA 01 |
| Ordovician argillaceous sedimentary rocks, greywacke, quartzite, conglomerate | 6 | PA 01 |
| Pennsylvanian red to grey sandstone, conglomerate, siltstone | 35 | PA 01 |
| Precambrian sedimentary and volcanic rocks | 3 | AR 01 |
| Mississippian silicic volcanic flows, tuffs and related intrusive rocks | 1 | PA 05 |
| Mississippian and/or Pennsylvanian red to grey conglomerate, siltstone, including silicic to mafic volcanic flows | 1 | PA 01 |
| | 100 | |

Source: Department of Natural Resources,

Geological Map of New Brunswick,

R.R. Potter, E.V. Jackson, J.L. Davies,

No. NR - 1, 1968

Scale: 1:500,000

GEOLOGY OF THE ARNAUD RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean quartzitic diorite, granodiorite, tonalite, trondhjemite, foliated granite, granitic gneiss - Superior Prov. | 51 | AR 03 |
| Archean charnockitic rocks; pyroxene (hypersthene) granites | 23 | AR 03 |
| Archean Na,K-feldspar massive granites, granite, monzonite, granodiorite, syenite, granitic gneiss | 15 | AR 03 |
| Archean metasedimentary and pyroclastic rocks; metagreywacke, tuff, quartzite | 3 | AR 06 |
| Archean foliated granite, granitic gneiss, paragneiss and migmatites of the Churchill Structural Province | 8 | AR 06 |
| | 100 | |

Source: Carte Géologique du Québec

Edition Provisoire, Dossier Publique No. 735

Gouvernement de Québec

Ministère de l'Energie et des Ressources

Direction générale de la recherche geologique et minérale, 1980

Scale: 1:1,500,000

GEOLOGY OF THE HARRICANA RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Non-differentiated gneiss -- paragneiss, orthogneiss, amphibolites, migmatites | 6 | AR 06 |
| Archean basic and intermediate flows; amphibolite, some sedimentary rocks | 40 | AR 05 |
| Archean metasedimentary and pyroclastic rocks; metagreywackes, tuff, quartzite | 12 | AR 06 |
| Archean felsic igneous and metamorphic rocks; quartzitic diorite, granodiorite, tonalite, trondhjemite, foliated granite granitic gneiss | 15 | AR 03 |
| Archean Na,K-feldspar granites, granite, monzonite, granodiorite, syenite, granitic gneiss | 20 | AR 03 |
| Mesozoic red sandstone and siltstone; Silurian limestone, dolomite, siltstone; Ordovician limestone and sandstone | 5 | ME 01 |
| Lower Devonian sandstone, arkose; conglomerate, siltstone, shale, limestone | 1 | PA 01 |
| Early Precambrian mafic metavolcanics -- basalt, andesite | 1 | AR 06 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF THE NOTTAWAY RIVER DRAINAGE BASIN

(The Superior-Grenville Structural Province boundary passes through the Southeastern portion of the drainage basin)

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean mafic and intermediate metavolcanics; amphibolite | 17 | AR 06 |
| Archean rhyolite and felsic pyroclastics | 1 | AR 05 |
| Archean metasedimentary and pyroclastic rocks; metagreywackes, tuff, quartzite | 12 | AR 06 |
| Archean anorthosite, anorthositic gabbro, gabbro | 1 | AR 04 |
| Archean diorite, gabbro and ultramafics such as peridotite, pyroxenite, serpentinite | 2 | AR 04 |
| Archean quartzitic diorite, granodiorite, tonalite, trondhjemite, foliated granite, granitic gneiss | 27 | AR 03 |
| Archean Na,K-feldspar granites, monzonite, granodiorite, syenite, granitic gneiss | 24 | AR 03 |
| Archean non-differentiated gneisses | 9 | AR 06 |
| Archean para- and orthogneiss with some amphibolites | 5 | AR 06 |
| Archean granitoid rocks; biotite or hornblende granite, syenite, monzonite, granitic gneiss | 2 | AR 03 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF THE RUPERT RIVER DRAINAGE BASIN

(84% of the drainage basin is in the Superior Structural Province with the remaining 16% in the Grenville Structural Province).

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean quartzitic diorite, granodiorite, tonalite, trondhjemite, foliated granite, granitic gneiss | 37 | AR 03 |
| Lower Proterozoic sandstone, conglomerate, greywacke, argillite, quartzite, dolomite | 11 | PR 01 |
| Archean Na,K-feldspar granites, monzonite, granodiorite, syenite, granitic gneiss | 16 | AR 03 |
| Archean metasedimentary and pyroclastic rocks; metagreywackes, tuff, quartzite | 16 | AR 06 |
| Archean mafic and intermediate flows mixed with diorite, gabbro and ultramafics such as peridotite, pyroxenite and serpentinite | 4 | AR 04 |
| Archean para- and orthogneiss with some amphibolites | 9 | AR 06 |
| Archean alkaline intrusives | 1 | AR 03 |
| Archean granitoid rocks; biotite or hornblende granite, syenite, monzonite, granitic gneiss | 4 | AR 03 |
| Archean mafic and ultramafic metamorphic rocks | 2 | AR 06 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF THE EASTMAIN RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean metasedimentary and pyroclastic rocks; metagreywackes, tuff, quartzite | 58 | AR 06 |
| Archean quartzitic diorite, granodiorite, tonalite, trondhjemite, foliated granite, granitic gneiss | 30 | AR 03 |
| Proterozoic sandstone, conglomerate, greywacke, argillite, quartzite, dolomite | 2 | PR 01 |
| Archean Na,K-feldspar granites (massive), monzonite, granodiorite, syenite, granitic gneiss | 6 | AR 03 |
| Archean mafic and intermediate flows; amphibolite, rhyolite and felsic pyroclastic rocks | 4 | AR 06 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF LA GRANDE RIVIERE DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean Na,K-feldspar massive granites; granite, monzonite, granodiorite, syenite, granitic gneiss | 26 | AR 03 |
| Archean quartzitic diorite, granodiorite, tonalite, trondhjemite, foliated granite, granitic gneiss | 48 | AR 03 |
| Archean metasedimentary and pyroclastic rocks; metagreywackes, tuff, quartzite | 22 | AR 06 |
| Archean mafic and intermediate flows; amphibolite | 2 | AR 06 |
| Archean charnockitic rocks - pyroxene (hypersthene) granites | 2 | AR 03 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF THE GRANDE RIVIERE DE LA BALEINE DRAINAGE BASIN

(Basin located in the Superior Structural Province)

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean Na,K-feldspar massive granites; granite, monzonite, granodiorite, syenite, granitic gneiss | 42 | AR 03 |
| Archean quartzitic diorite, granodiorite, tonalite, trondhjemite, foliated granite, granitic gneiss | 57 | AR 03 |
| Archean basic and intermediate flows; metavolcanic amphibolite | 1 | AR 06 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF THE AUX FEUILLES RIVER DRAINAGE BASIN

(Drainage basin is totally within the Superior Structural Province)

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean quartzitic diorite, granodiorite, tonalite, trondhjemite, foliated granite granitic gneiss | 62 | AR 03 |
| Archean charnockitic rocks -- pyroxene (hypersthene) granites | 26 | AR 03 |
| Archean metasedimentary and pyroclastic rocks; metagreywacke, tuff, quartzite | 8 | AR 06 |
| Archean Na,K-feldspar massive granites, granite, monzonite, granodiorite, syenite, granitic gneiss | 4 | AR 03 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF THE KOKSOAK RIVER DRAINAGE BASIN

(Includes Aux Mélèzes and Caniapiscau which join to form the Koksoak River.
The northeastern 25% of the drainage basin is in the Churchill Structural Province. The remaining 75% is in the Superior Structural Province.)

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Lower Proterozoic sedimentary rocks--sandstone, greywacke, siltstone, shale | 12 | PR 01 |
| Lower Proterozoic gabbro and other ultramafic rocks | 5 | PR 04 |
| Lower Proterozoic mafic and felsic flows and pyroclastics with their metamorphic equivalents | 5 | PR 05 |
| Archean felsic igneous rocks | 1 | AR 03 |
| Proterozoic foliated granite and granitic gneiss, paragneiss and migmatites | 1 | PR 03 |
| Archean quartzitic diorite, granodiorite, tonalite, trondhjemite, foliated granite, granitic gneiss | 22 | AR 03 |
| Archean charnockitic rocks | 23 | AR 03 |
| Archean Na,K-feldspar massive granites, granite, monzonite, granodiorite, syenite, granitic gneiss | 24 | AR 03 |
| Archean metasedimentary and pyroclastic rocks; metagreywacke, tuff, quartzite | 7 | AR 06 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF RIVIÈRE À LA BALEINE DRAINAGE BASIN

(Drainage basin is located entirely within the Churchill Structural Province).

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean foliated granite and granitic gneiss, paragneiss and migmatite | 39 | AR 06 |
| Archean granodiorite, granite and other intrusives | 7 | AR 03 |
| Lower Proterozoic sedimentary rocks -- sandstone, greywacke, siltstone, shale | 7 | PR 01 |
| Proterozoic foliated granite and granitic gneiss, paragneiss and migmatite | 39 | PR 06 |
| Lower Proterozoic gabbro and other ultramafic rocks | 2 | PR 04 |
| Proterozoic felsic igneous rocks -- granites and other intrusives | 6 | PR 03 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF RIVIERE DU PETIT MECATINA DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean non-differentiated gneiss, paragneiss, orthogneiss, amphibolites, migmatites | 48 | AR 06 |
| Archean mafic and ultramafic rocks, orthoamphibolites | 1 | AR 04 |
| Middle Proterozoic anorthosite, anorthositic gabbro, gabbro | 16 | PR 04 |
| Archean charnockitic rocks | 16 | AR 03 |
| Archean granitoid rocks -- biotite or hornblende granite, syenite, monzonite, granitic gneiss | 19 | AR 03 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF THE NATASHQUAN RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean non-differentiated gneiss -- paragneiss, orthogneiss, amphibolites, migmatites | 24 | AR 06 |
| Archean paragneiss and amphibolite -- differentiated | 4 | AR 06 |
| Archean mixed non-differentiated and differentiated gneiss | 16 | AR 06 |
| Proterozoic mafic and ultramafic rocks - orthoamphibolites | 3 | PR 04 |
| Archean granitoid rocks -- biotite or hornblende granite, syenite, monzonite, granitic gneiss | 53 | AR 03 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF THE MOISIE RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean non-differentiated gneiss; paragneiss, orthogneiss, amphibolites, migmatites | 15 | AR 06 |
| Proterozoic non-differentiated gneiss; paragneiss, orthogneiss, amphibolites, migmatites | 14 | PR 06 |
| Lower Proterozoic paragneiss and amphibolite | 2 | PR 06 |
| Archean mixed differentiated and non-differentiated gneiss | 18 | AR 06 |
| Proterozoic mixed differentiated and non-differentiated gneiss | 18 | PR 06 |
| Proterozoic mafic and ultramafic rocks -- orthoamphibolites | 12 | PR 04 |
| Middle Proterozoic anorthosite, anorthositic gabbro, gabbro | 8 | PR 04 |
| Archean granitoid rocks | 5 | AR 03 |
| Proterozoic biotite or hornblende granite, syenite, monzonite, granitic gneiss | 5 | PR 03 |
| Middle Proterozoic charnockitic rocks | 3 | PR 03 |
| | 100 | |

Source: See Arnaud R.

GEOLOGY OF THE MANICOUAGAN RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Proterozoic metamorphic | 2 | PR 06 |
| Archean granulite and charnockite | 3 | AR 06 |
| Archean granitic gneiss, migmatite; undifferentiated plutonic, sedimentary and volcanic rocks | 56 | AR 06 |
| Proterozoic gneiss and schist derived from sedimentary rock | 15 | PR 06 |
| Archean gneiss and schist derived from sedimentary rock | 11 | AR 06 |
| Archean granite and allied plutonic rocks | 1 | AR 03 |
| Proterozoic anorthosite | 5 | PR 04 |
| Proterozoic gabbro, diorite | 3 | PR 04 |
| Mesozoic volcanic and pyroclastic | 4 | ME 05 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF THE AUX OUTARDES RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Proterozoic sandstone, conglomerate, greywacke, argillite, quartzite, dolomite | 7 | PR 01 |
| Archean Na,K-feldspar massive granites, granite, monzonite, granodiorite, syenite, granitic gneiss | 6 | AR 03 |
| Archean metasedimentary and pyroclastic rocks; metagreywackes, tuff, quartzite | 4 | AR 06 |
| Proterozoic anorthosite, anorthositic gabbro, gabbro | 23 | PR 04 |
| Archean non-differentiated gneiss; paragneiss, orthogneiss, amphibolites, migmatites | 23 | AR 06 |
| Proterozoic non-differentiated gneiss, paragneiss, orthogneiss, amphibolites, migmatites | 22 | PR 06 |
| Archean charnockitic gneiss | 11 | AR 06 |
| Archean charnockitic rocks | 4 | AR 03 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF THE SAGUENAY RIVER DRAINAGE BASIN

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean quartzitic diorite, granodiorite, tonalite, trondhjemite, foliated granite, granitic gneiss | 10 | AR 03 |
| Archean Na,K-feldspar massive granites, granite, monzonite, granodiorite, syenite, granitic gneiss | 1 | AR 03 |
| Archean charnockitic rocks -- pyroxene (hypersthene) granites. | 4 | AR 03 |
| Proterozoic sandstone, conglomerate, greywacke, argillite, quartzite, dolomite | 3 | PR 01 |
| Archean metasedimentary and pyroclastic rocks; metagreywacke, tuff, quartzite | 2 | AR 06 |
| Archean non-differentiated gneiss; paragneiss, orthogneiss, amphibolite, migmatite | 30 | AR 06 |
| Proterozoic non-differentiated gneiss; paragneiss, orthogneiss, amphibolite, migmatite | 30 | PR 06 |
| Archean orthoamphibolites | 2 | AR 04 |
| Proterozoic mafic and ultramafic rocks | 2 | PR 04 |
| Proterozoic anorthosite, anorthositic gabbro, gabbro | 8 | PR 04 |
| Mesozoic red sandstone and siltstone--- Silurian limestone; dolomite; Ordovician limestone and sandstone | 4 | ME 01 |
| Archean charnockitic gneiss | 4 | AR 06 |
| | 100 | |

Source: See Arnaud River

GEOLOGY OF THE ST. MAURICE RIVER DRAINAGE BASIN

(Drainage basin is located entirely within the Grenville Structural Province, except the southernmost tip which is in the St. Lawrence Lowlands Structural Province)

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Lower Proterozoic undifferentiated gneiss; paragneiss, orthogneiss, amphibolites, migmatites | 50 | PR 06 |
| Lower Paleozoic shale and sandstone (flysch) | 3 | PA 01 |
| Archean charnockitic rocks | 7 | AR 03 |
| Archean granitoid rocks; biotite or hornblende granite, syenite, monzonite, granitic gneiss | 14 | AR 03 |
| Lower Proterozoic charnockitic gneiss | 26 | PR 06 |
| | 100 | |

Source: See Arnaud River

| DESCRIPTION OF ROCK UNITS | PERCENT | CLASSIFICATION |
|---|---|---|
| Archean mafic and ultramafic rocks | 1 | AR 04 |
| Archean felsic igneous rocks | 9 | AR 03 |
| Lower Paleozoic clastic sedimentary rocks | 5 | PA 01 |
| Lower Paleozoic carbonate sedimentary rocks | 8 | PA 02 |
| Archean orthogneiss | 3 | AR 06 |
| Proterozoic paragneiss and amphibolites | 4 | PR 06 |
| Proterozoic anorthosite, anorthositic gabbro and gabbro | 2 | PR 04 |
| Archean charnokitic rocks | 7 | AR 03 |
| Proterozoic granitoid rocks -- biotite or hornblende granite, syenite, monzonite | 3 | PR 04 |
| Middle Paleozoic carbonate sedimentary rocks | 6 | PA 02 |
| Middle to upper Proterozoic clastic sedimentary rocks | 7 | PR 01 |
| Middle to upper Proterozoic felsic igneous | 1 | PR 03 |
| Middle to upper Proterozoic carbonate metasedimentary | 1 | PR 06 |
| Upper Proterozoic clastic sedimentary and volcanic | 2 | PR 01 |
| Archean mafic metavolcanics | 1 | AR 06 |
| Middle Proterozoic metasedimentary rocks | 3 | PR 06 |
| Upper Paleozoic clastic sedimentary rocks | 5 | PA 01 |
| Upper Paleozoic carbonate sedimentary rocks | 2 | PA 02 |
| Cenozoic clastic sedimentary rocks | 28 | CE 01 |
| Middle Proterozoic volcanic rocks | 2 | PR 05 |
| | 100 | |

GEOLOGY OF THE ST. LAWRENCE RIVER DRAINAGE BASIN (CONT'D.)

Source: Ontario portion: See Severn River

Québec portion: See Arnaud River

# APPENDIX C

## Determination of Strontium Concentrations by Isotope Dilution

## DETERMINATION OF STRONTIUM BY ISOTOPE DILUTION

Three samples were analyzed for their Sr concentrations by isotope dilution: Eastmain #2, Winisk #1, Nelson #1, (see Faure, 1972 pp. 68 - 70 for principles).

The measurement of the isotopic ratio is affected by fractionation in the mass spectrometer. Because Sr has 4 naturally occurring isotopes this effect can be corrected using the slope of fractionation of $^{84}Sr/^{88}Sr$ vs. $^{86}Sr/^{88}Sr$.

Sample Eastmain #2:

A. The slope of fractionation for $^{84}Sr/^{88}Sr$ vs. $^{86}Sr/^{88}Sr$ of the spike alone has been determined to be $y_1 = 37.856x_1 + (-4.513)$.

For the mixture of spike and sample the $^{84}Sr/^{88}Sr$ vs. $^{86}Sr/^{88}Sr$ was calculated from the mass spectrometric readings

$$y_2 = 14.180\ x_2 + (-1.063)$$

Let $y_1 = y_2$

$$14.180\ x_2 + (-1.063) = 37.856\ x_1 + (-4.513)$$

$$23.675\ x = 3.450$$

$$x = 0.1457$$

where x now represents the corrected $^{86}/88$ ratio.

Substituting:

$$y_1 = 37.856\ (.1457) + (-4.513)$$

$$y_1 = 1.0037$$

where y now represents the corrected $^{84}/88$ ratio.

DETERMINATION OF STRONTIUM BY ISOTOPE DILUTION (CONT'D.)

B. Calculation of Abundances (Ab) and Weight (W) of Normal Sr (N) and Spike strontium (S) is as follows:

$^{84}/86_N = 0.05658$

$^{86}/86_N = 1.00000$

$^{88}/86_N = 8.37521$

$^{87}/86_N = .72830 = .72845$ corrected for Eimer and Amend $SrCO_3$.

$^{84}/86 + {}^{86}/86 + {}^{88}/86 + {}^{87}/86 = 10.16024.$

Divide each ratio by the sum and multiply by the mass of the isotope in the numerator:

$^{84}Ab_N = .005568766 \times 83.9134 = .46729408$

$^{86}Ab_N = .098422871 \times 85.9092 = 8.4554301$

$^{87}Ab_N = .071696141 \times 86.9088 = 6.2310255$

$^{88}Ab_N = .82431222 \times 87.9056 = 72.46166$

$^{84}Ab_n + {}^{86}Ab_N + {}^{87}Ab_N + {}^{88}Ab_N = 87.615639 = W\ Sr_N$

Spiked:

$^{84}/86_S = 22.660$

$^{86}/86_S = 1.0000$

$^{87}/86_S = 0.4208$

$^{88}/86_S = 3.367$

27.4478

DETERMINATION OF STRONTIUM BY ISOTOPE DILUTION (CONT D.)

$^{84}Ab_S = 0.825562139 \times 83.9134 = 69.27572599$

$^{86}Ab_S = 0.036433224 \times 85.9092 = 3.129949127$

$^{87}Ab_S = 0.015333849 \times 86.9088 = 1.332646416$

$^{88}Ab_S = 0.122670788 \times 87.9056 = 10.78344922$

$^{84}Ab_S + {}^{86}Ab_S + {}^{87}Ab_S + {}^{88}Ab_S = 84.52177076 = W\ Sr_S$

C. Isotope dilution calculation using Faure's equation

$$N_W = \frac{S_W \times W_N}{W_S} \left[ \frac{Ab_S^A - R_m Ab_S^B}{R_m Ab_N^B - Ab_N^A} \right]$$

Calculation of $S_W$ (weight in µg of Sr added by the spike)

concentration of spike = 3.2733 µg/g Sr

weight of spike added = 0.08785 g

3.2733 x 0.08785 = 0.287559405 µg

$W_N = W\ Sr_N = 87.615639$ g

$W_S = W\ Sr_S$ = constant = 84.52177076 g

$Ab_S^A = {}^{84}Ab_S = .825562139$ = constant

$R_m$ = ratio of mix $^{84}/88$ corrected for fractionation = 1.03731099

$Ab_S^B = {}^{88}Ab_S = .122670788$ = constant

$Ab_N^B = {}^{88}Ab_N = .82431222$

$Ab_N^A = {}^{84}Ab_N = .005568766$

$N_W$ = 0.24503522 µg of total normal Sr

$$\frac{N_W}{\text{wt. sample}} = \frac{0.24503522 \ \mu g}{29.88764 \ g} = 8.1985462 \times 10^{-3} \ \mu g/g$$

Concentration of sample Eastmain #2 is 8.199 µg/g or 8.2 ppb.

Following the same procedure the concentrations of samples Winisk #1 and Nelson #1 were determined to be 17 and 75 ppb respectively.