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THE COLDWELL COMPLEX: MAGMATIC AFFINITY

THE COLDWELL ALKALINE COMPLEX, ONTARIO: MAGMATIC AFFINITY AS DETERMINED BY AN ISOTOPIC AND GEOCHEMICAL STUDY

By

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ABSTRACT

The Proterozoic Coldwell Alkaline Complex is the southernmost intrusion of a number of N-S trending igneous bodies occurring in the Midcontinental Rift system exposed in the Lake Superior area. The Coldwell complex is host to several Ni-Cu-PGE-bearing intrusions two of which; the Two-Duck Lake intrusion (Marathon deposit) and the Geordie Lake gabbro (MacRae occurrence) have been investigated in some detail with respect to PGE mineralisation. Both of these have been suggested to have experienced crustal contamination in conjunction with mineralisation. As a test of this possibility, a detailed Sm-Nd, oxygen isotope, and whole-rock geochemical study of these mineralised occurrences as well as of the Dunlop occurrence and the Middleton occurrence, together with unmineralised rocks of the complex was undertaken. The primary objectives are to determine whether crustal contamination is indicated in mineralised rocks and to try and ascertain the nature of the magma which formed the complex.

The Coldwell complex is thought to have been formed by emplacement of magma at three intrusive centres. Sm-Nd data for rocks from these three centres reveal similar isotopic values, with slight variations; samples taken from the western gabbros exhibit ϵNd values averaging -0.9 ranging from -2.9 to 0.9, whereas rocks from the eastern margin and centre of the complex have ϵNd values of about an average of 0.5 ranging from -0.5 to 1.2 suggesting that the magma that formed these rocks has undergone a lesser degree of crustal contamination. This data, supported by oxygen isotope and whole-rock geochemical information indicates that crustal contamination seems to play a small, and varied role in the genesis of the Coldwell magmas. The Nd isotope data all clusters at values for CHUR, which indicates that it has been enriched relative to the depleted mantle. It has been postulated that an enriched mantle plume resided under the rift and promoted rift-related magmatism. The data from this study would seem to support this supposition.

Geochemical parameters utilised to define fields to geochemically delineate possible end member contributors to this primarily plume-derived magma indicate, that in addition to small, variable amounts of assimilation of upper and lower crust, the plume magmas also interacted with the lithospheric upper mantle to a small degree.

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1.0 INTRODUCTION

The Coldwell Complex situated on the North shore of Lake Superior is host to a number of mineralised occurrences, some of which contain platinum group metals. The focus of this thesis is to determine whether rocks which host PGM's have a crustal or a mantle geochemical signature, thus constraining the source of the sulphides and PGM's.

Osmium is one of the few metallic elements in PGE ore with a variable isotopic composition which can be readily measured. Studies of the Os isotopic composition of some Ni-Cu-PGE deposits reveal that many mantle-derived magmas with PGE mineralisation contain both mantle and crustal osmium (Hulbert and Grégoire, 1993). The sulphide occurrences in the complex, only one of which is large enough to attain deposit status are relatively disseminated and of uneconomic grade. As a result of this, only samples from the Two Duck Lake intrusion of the Marathon deposit yielded enough sulphide minerals to make analyses possible. It was decided that because data could only be retrieved from one location in the complex it was not worthwhile pursuing this avenue. The resultant data would have been statistically weak since data from one sample location in a deposit is not enough on which to base comprehensive scientific conclusions relevant to the variety of deposits hosted by the Coldwell complex.

The objective of the research was to characterise the isotopic and chemical properties of Coldwell complex rock in order to determine the origin of the parental magma, and define possible constituents of said magma. Specifically, the question of crustal contamination was a major concern, since the amount or nature of crustal contamination could play a major role in the genesis of the Cu-Ni-PGE deposits found in the Coldwell complex both by inducing sulphur immiscibility and/or by contributing PGE's.

Several geochemical techniques have been employed to help delineate the genesis of mineralised occurrences in the Coldwell complex. Primarily, Sm-Nd isotopic analyses is utilised to determine if a crustal or mantle signature exists. In addition to Sm-Nd mass spectrometric analyses, oxygen isotope analyses were also undertaken because $\delta^{18}O$ can be a sensitive indicator of contamination and alteration. Whole rock geochemical analyses were also performed to provide additional information and to corroborate the evidence given by oxygen and Sm-Nd analyses.

Nickel-Cu-PGE mineralisation occurs in several areas of the

Coldwell complex, predominately in the Eastern gabbro unit of Centre 1 (see figure 2.3.1). The Eastern gabbro is an arcuate body of relatively homogeneous gabbro that occurs at the northeast periphery of the complex, defining the boundaries of Centre 1. The mineralisation takes on different characteristics in different deposits and occurrences. The largest known sulphide deposit in the Coldwell complex is the Marathon deposit currently held by Fleck Resources. The Marathon deposit is hosted in the lower Two-Duck Lake intrusion, a small volume, pegmatitic gabbro intruding the Eastern gabbro near its contact with the Archaean sediments and greenstones. The mineralisation in this deposit consists of large(1 cm), blocky and vein-like sulphides occurring in the interstices of the pegmatitic lower gabbro of the Two-Duck Lake intrusion which is termed a biotite-apatite bearing olivine gabbronorite by Good (1993). Platinum group minerals have been shown to be spatially related to sulphides, predominantly chalcopyrite (Mulja and Mitchell, 1990). Pyrrhotite and pentlandite also exist in smaller quantities. The other main site of mineralisation in the complex, also in the Eastern gabbro is the MacRae occurrence at Geordie Lake which is a heterogeneous magnetite-bearing gabbro with albite pods which are associated with sulphide mineralisation. The sulphide mineralisation in the Geordie Lake gabbro consists of rare chalcopyrite stringers and disseminated fine-grained chalcopyrite and occasional bornite which is associated with secondary actinolite. Other mineralised zones include the Middleton occurrence in the Western gabbro, which contains disseminated chalcopyrite in a hydrothermally altered gabbro; the Wullie Lake occurrence, a magnetiferous gabbro with disseminated chalcopyrite; and the Dunlop occurrence, a heterogeneous fine-grained gabbro with stringers of chalcopyrite. The latter two occurrences are in the Eastern gabbro with all the aforementioned sulphide occurrences being found in Centre 1.

Important to delineating the nature of the magmas which formed the complex is an understanding of the various end member constituents which may have mixed together to form the unique isotopic and chemical signature displayed by the complex. Trace element analyses as well as Nd isotopic data were utilised in conjunction with one-another to try and define broad geochemical fields for the possible end members which are; upper and lower crust, lithospheric upper mantle, and asthenospheric mantle. The chemical composition of the Coldwell complex rocks are then plotted with respect to these fields to not only characterise the individual rock types in the complex, but to also try and determine which end members had the most amount of influence on the genesis of the precursor magmas which formed the various rocks. Sm-Nd isotopic data generally clusters around CHUR, indicating that depleted mantle was not a primary constituent of the Coldwell source magma. Solely on the basis of Sm-Nd isotopes primitive mantle could be construed to be a contributor; this possibility is ruled out on the basis of the trace element composition of the complex.

The isotopic data and the whole-rock geochemical data point towards an enriched mantle plume as a possible source candidate for the Coldwell magma. This theory was first postulated by Paces and Bell, (1989), as well as Hutchinson *et al.,* (1990) and Nicholson and Shirey, (1990). Modern plumes display ϵNd values 4-5 epsilon units below those reported for depleted mantle of the same age (White, 1985), therefore; because the depleted mantle is estimated to have had an ϵNd value of approximately +5 at 1108 Ma, a mantle plume should have a value of about 0. Other sources of material which may have contributed to the genesis of the Coldwell complex include lower crust, upper crust, and lithospheric upper mantle. Had crustal constituents contributed to the Coldwell magma, the result would have been a low negative ϵNd signature in the Coldwell rocks due to the fact that the Archaean crust in this area would have had an ϵNd value of between -12 to -17 (Nicholson and

Shirey, 1990). Lithospheric upper mantle may have been incorporated into the plume, this is a possibility which is alluded to by the isotopic and trace element data but is difficult to prove conclusively because the exact geochemical parameters of the lithospheric upper mantle below the MCR and specifically the Coldwell complex are not known. It is difficult to quantitatively evaluate the extent to which the aforementioned potential contributors may have interacted with the Keweenawan mantle plume because of the fact that pertinent local data on the trace-element composition of these possible contributing sources is unavailable. This has the effect of significantly limiting the usefulness of trace elements in determining the constituents of the Coldwell magma.

Oxygen isotope analyses are useful, not so much for characterising the source of a magma, but for determining local effects which may act to mask or change certain characteristics of a rock. These local effects are things such as metamorphism, diagenesis, and especially alteration. Oxygen isotopes will be used in this study to determine whether or not certain assemblages have been exposed to hydrothermal alteration, thus changing the chemistry of the rock, a factor which must be taken into account when interpreting the whole-rock geochemical data.

2.0 GEOLOGY OF THE COLDWELL COMPLEX

2.1 PREVIOUS STUDIES

The Coldwell Complex, or Port Coldwell Alkaline Complex as it is also called has been studied by a number of researchers. Important reviews include: Mulja (1989), Good (1993), Heaman and Machado (1987), Mitchell and Platt (1982) and Walker *et al.,* (1993).

The complex was mapped by Puskas (1967) and by Currie (1980). It was subsequently remapped at 1:20000 scale by Walker, Sutcliffe, Shaw, Shore, and Penczak in 1993. This mapping was done in great detail, with attendant geochemical and geophysical data and as such does not suffer many of the inadequacies that plague small scale early maps of much of the Canadian Shield. Hence, the present author did not endeavour to map any of the units of interest and confined the study to a geochemical survey, using the geological units as defined by Walker *et al.,* (1993).

2.2 LOCATION

The Coldwell Complex is situated on the North shore of Lake Superior, with nearly a third of it's area underwater (see figure 2.2.1). The port town of Marathon is situated at the eastern edge of the complex. Highway 17 bisects the southern portion of the complex (figure 2.3.1), with numerous logging and drill roads extending north from the highway. Access can also be had by boat from either the Pic River which is easily navigable or from Lake Superior itself. Some lakes in the northern portion may support float plane access. Alternate access can also be had from the Canadian Pacific Railway Line or from the E-W trending Bamoos Lake Power Line which can be reached from the Pic River and provides a reasonable walking path to the road at the northern extent of the Marathon deposit.

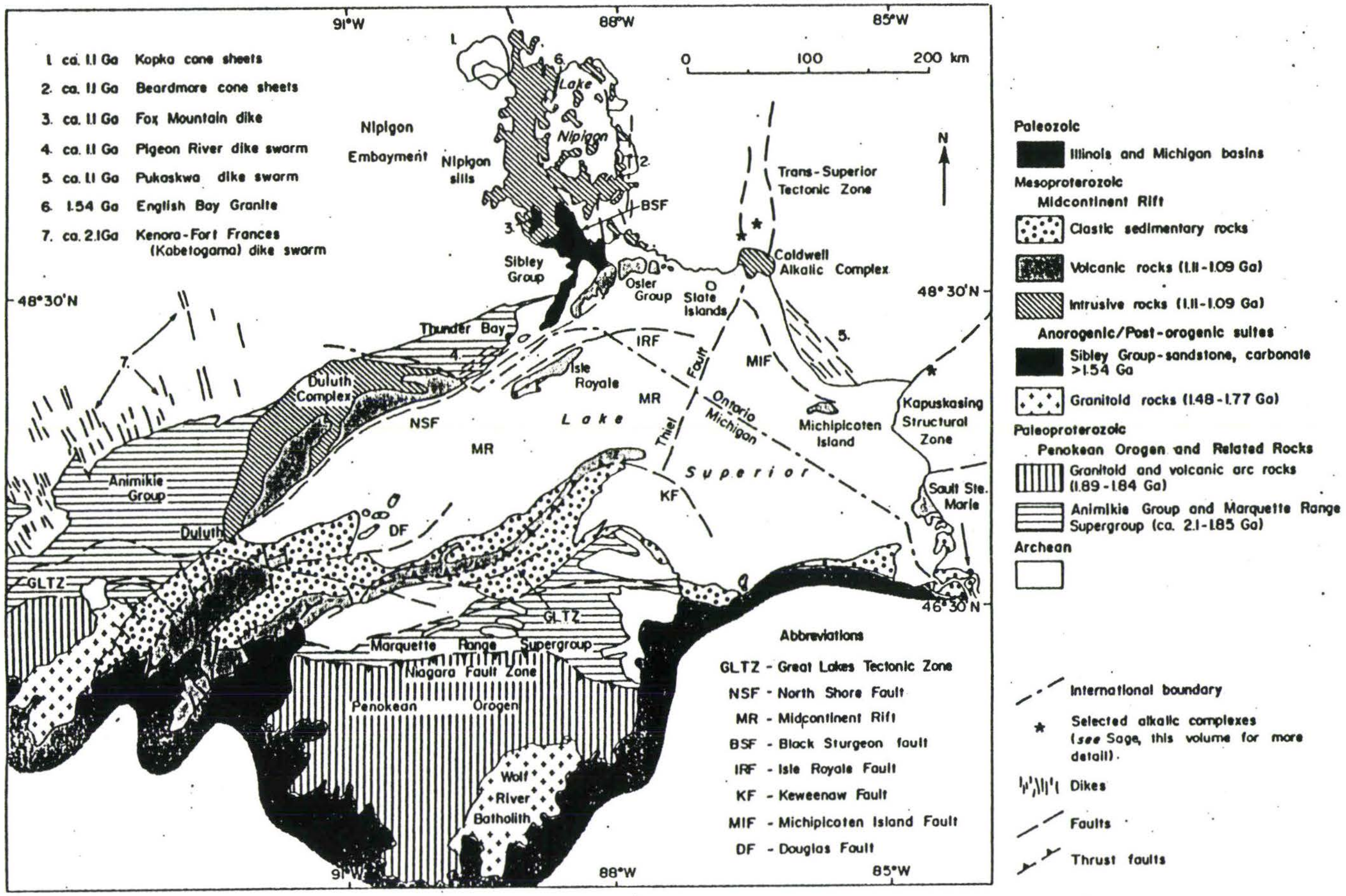


Figure 2.2.1: Regional geology map of the Lake Superior area (Sutcliffe, 1991).

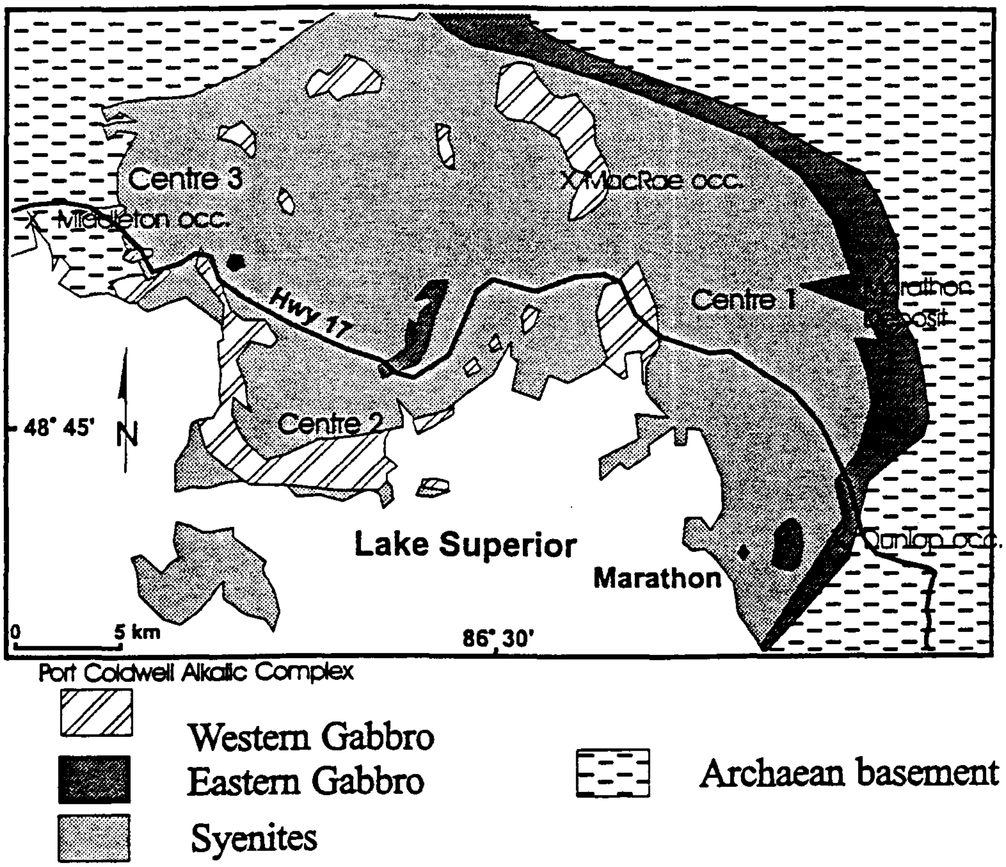
2.3 GENERAL GEOLOGY

The 580 km^2 Coldwell Complex is one of the largest alkaline bodies in the Proterozoic Midcontinent Rift of North America, and is the largest alkaline body in Canada. The Midcontinent Rift is one of the largest continental rifts and can be traced for 2000 km from Kansas to Lake Superior. Seismic evidence reveals that in the Lake Superior region, rift related volcanics and sediments comprise about 32 km of the 40 km thick rift (Behrendt *et al.*, 1988). Researchers utilising U-Pb zircon geochronology have determined that Keweenawan (Mesoproterozoic) volcanism took place between 1108 (Davis and Sutcliffe, 1985) and 1087 Ma (Palmer and Davis, 1987).

The Coldwell Complex is the southernmost igneous body in a N-S trend of contemporaneous intrusions proximal to the Thiel fault which include the Killala Lake alkalic complex, as well as the Chipman Lake and Prairie Lake carbonatite complexes and various diatremes including the Dead Horse Creek diatreme (Sage, 1991) (see figure 2.2.1). These bodies are related to a failed rift of a Keweenawan triple junction according to Weiblen (1982), and Mitchell and Platt (1982). The Thiel fault represents the northern part of the Trans-Superior Tectonic Zone (Sage, 1991).

The Coldwell Complex intrudes Archaean metasediments, metavolcanic and meta-intrusive rocks of the Schreiber-White River granite-greenstone belt. Contact metamorphism of the ~ 2.7 Ga Archaean basement to the pyroxene hornfels grade is evident within 50 m of the contact (Puskas, 1967).

Three distinct intrusive centres are recognised by geophysical data as well as by field relationships and geochemical attributes (Currie, 1980; Mitchell and Platt, 1982; Mitchell *et al.,* 1983; Sage, 1991) and consist of Centre 1 gabbros, Centre 2 nepheline syenites with alkaline gabbro and Centre 3 quartz syenites (figure 2.3.1). The intrusive centres are roughly contemporaneous but do young to the west. Based upon U/Pb zircon/baddeleyite dating, Heaman and Machado (1992) believe that the majority of the complex was emplaced into Archaean crust at 1108 ± 1 Ma and underwent rapid cooling at the onset of rifting and Keweenawan tholeiitic magmatism. Evidence for the low pressure formation of the magmas of each centre is the presence of miarolitic cavities and porphyritic-aphanitic rock types, suggesting that structural controls on magma emplacement such as, caldera subsidence, ring dykes and stoping may have been important (Walker *et al.,* 1993).



(after Sage, 1991)

Figure 2.3.1: General geology of the Coldwell complex showing the location of the intrusive centres.

3.0 ISOTOPE SYSTEMATICS

Both radiogenic and stable isotope analyses were undertaken during this study to help gain an understanding of the mineralised rocks of the Coldwell Complex. In order to place the resultant isotopic data in the proper context a review of both Sm-Nd and oxygen isotope systematics is in order. Sm-Nd is one of the better understood radiogenic isotope pairs utilised in geochemistry and geochronology. In comparison with the Rb-Sr isotopic system Sm-Nd is often a better indicator of original isotopic composition, particularly useful because the parent and daughter products are less mobile than Rb and Sr in response to metamorphic or metasomatic conditions. Sedimentary and metamorphic processes do not significantly fractionate Sm and Nd within the continental crust, thereby retaining initial values of the parent/daughter ratio. Because of this characteristic however, small amounts of assimilated continental crust in a large amount of mantle material may be isotopically invisible (Rollinson, 1993). For a complete review of the Sm-Nd system one should consult the classic papers of DePaolo and Wasserburg, (1976a, and b), the textbook of Dickin,

(1995) which also has a thorough review of the subject.

Oxygen, one of the stable isotope systems routinely used in geochemistry can provide useful information about the history of hydrothermal alteration. Oxygen isotope analyses were performed to determine whether or not the mineralised rocks of the Coldwell Complex were hydrothermally altered, and to help corroborate the data gleaned from Sm-Nd analyses. For a complete review of oxygen isotope systematics in igneous rocks the reader is referred to the textbooks of Hoefs (1987), and Faure (1986), as well as to the classic paper by H.P. Taylor, Jr. (1974).

3.1 Sm-Nd

^{147}Sm, one of seven naturally occurring isotopes of the lanthanide element Sm, decays to ^{143}Nd with a half-life of 1.06×10^{11} years. Both Sm and Nd, atomic numbers 62 and 60 respectively, exhibit very similar chemical and physical properties and are thereby rarely seen to display strong fractionation from one another. Sm^{+3} has an ionic radius of 1.04 Å, while Nd^{+3} has an ionic radius of 1.08Å. Their radii, like those of the other REE, decrease with increasing atomic number, as does their cosmogenic abundance, thus there is less samarium than neodymium in the solar system. Faure (1986) points out that the Sm/Nd ratio in terrestrial rocks does not differ appreciably from the ratio of Sm/Nd in the solar system (0.31) due to the fact that the physical and chemical similarity between the two generally precludes fractionation of these two elements.

Radioactive decay of ^{147}Sm to ^{143} Nd through time increases the ^{143}Nd/^{144}Nd ratio of the Earth. DePaolo and Wasserburg (1976a) developed a model called CHUR which stands for chondritic uniform reservoir. This model assumes that terrestrial Nd evolved in a uniform reservoir with a Sm/Nd ratio equal to that of chondritic meteorites. The model utilises the age of the Earth, it's current Sm/Nd ratio, and primordial ^{143}Nd/^{144}Nd ratio, with the age of the Earth and the primordial ^{143}Nd/^{144}Nd ratio being derived from the analyses of stoney meteorites. The presently accepted values for ^{143}Nd/^{144}Nd and^{147} Sm/^{144} Nd are 0.512638 and 0.1966 respectively (Hamilton *et al.,* 1983). Given this information we can calculate CHUR for any time in the past. DePaolo and Wasserburg (1976a) proposed an epsilon notation which describes initial ^{143}Nd/^{144}Nd ratios in parts per 10^{4}deviation from the CHUR evolution line (equation 3.1.1).

Equation 3.1.1:

$$\varepsilon \mathrm{Nd(t)} = \left[\frac{(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})_{\mathrm{sample}}(\mathrm{t})}{(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})_{\mathrm{CHUR}}(\mathrm{t})} - 1 \right] \times 10^{4}$$

Initial ratios of ^{143}Nd/^{144}Nd for the rock are calculated from the whole-rock isochron and ϵ^{0}CHUR is calculated from the measured ^{143}Nd/^{144}Nd ratio. ϵ^{t} CHUR denotes the difference between the ^{143}Nd/^{144}Nd initial ratio of a rock and the corresponding value in CHUR at this time (t) which is the time of crystallisation of the rock. Generally this time (t) is determined by an independant method such as U-Pb geochronology, and then the Sm-Nd parameters are assessed relative to this age. A positive epsilon value implies that the rocks in question were derived from residual solids in a reservoir from which magma had been tapped, and thereby depleted in LIL elements which are preferentially partitioned into the liquid phase during partial melting (Faure, 1986). A negative epsilon value will be shown by rocks derived from sources with a lower Sm/Nd ratio than CHUR. Such a source reservoir might arise in crust whose Sm/Nd ratio had been lowered upon separation from a chondritic reservoir. An epsilon value of 0 means that the rock is indistinguishable from CHUR and may have formed from the chondritic reservoir (see figure 3.1.1) (Faure, 1986).

With respect to the problem of crustal contamination, a simple two-component mixing model can be invoked to explain the addition of a crustal component to mantle-derived magma. Dickin (1995) points out that to adequately delineate mixing environments in which more than one degree of freedom is present, two or more measured variables are necessary; for example, isotopic ratios, elemental ratios or elemental abundances. For instance, a combination of trace element data and isotopic data can prove useful as can elemental ratios such as K/Zr which represents a ratio between a highly incompatible element and a moderately incompatible element. Correlation between this ratio and the Sm-Nd isotopic ratio is indicative of contamination, while a lack of correlation may indicate that the mantle source is heterogeneous.

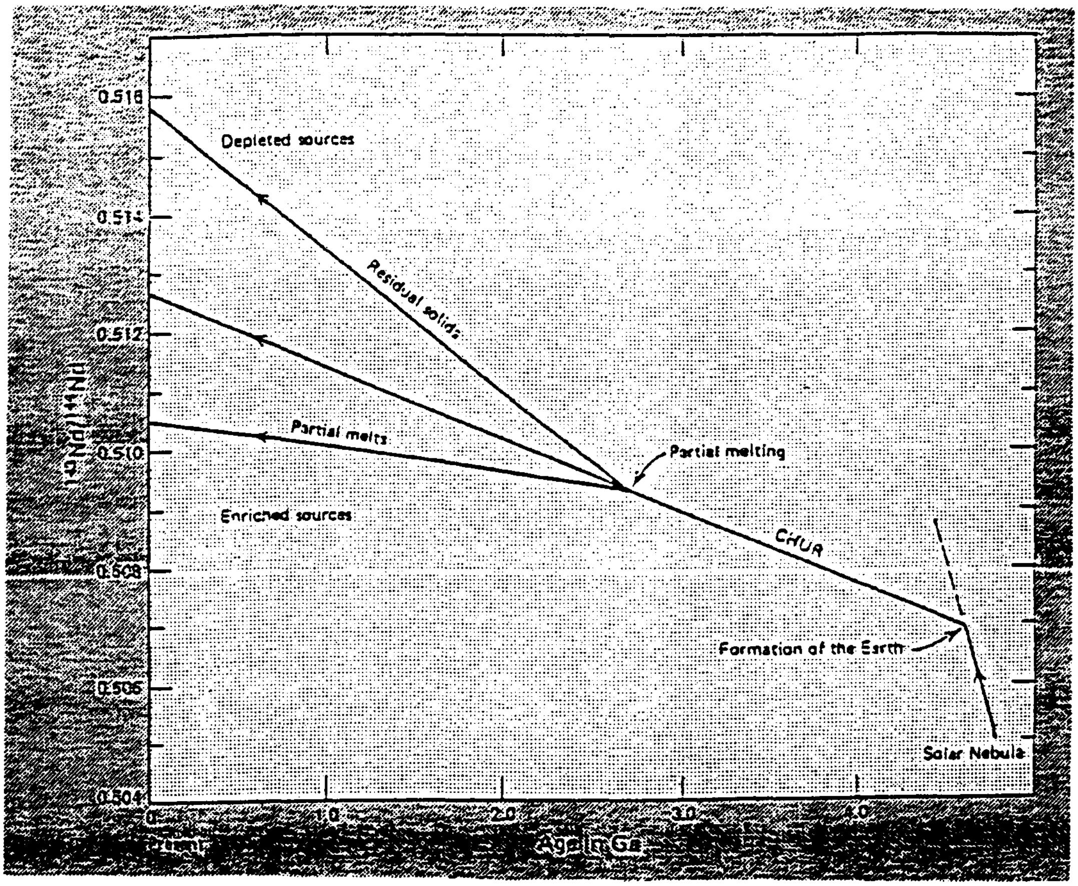


Figure 3.1.1: isotopic evolution of Nd in a chondritic uniform reservoir, (Faure, 1986).

3.2 $\delta^{18}O$

Another important geochemical tool for determining the origin of fluids including those of magmatic derivation is the oxygen isotope system.

In elements lighter than Ca it is possible for physical processes to cause natural variations (fractionation) in stable isotopes of certain elements due mainly to the difference in mass between the isotopes, with the amount of mass fractionation being proportional to the mass differences between isotopes. Thus the study of stable isotopes provides a useful insight into the geochemistry of the light elements, particularly H, C, N, O and S (Rollinson, 1993).

Three stable isotopes, ^{16}O, ^{17}O and ^{18}O with relative abundances of 99.63, 0.0375 and 0.1995 respectively comprise the most abundant element in the Earth's crust, oxygen. Stable isotope ratios are measured relative to a standard, SMOW (standard mean ocean water) which is used for the analysis of fluids and non carbonate rocks with the isotopic composition of samples expressed as parts per thousand differences (per mil-‰) (see equation 3.2.1).

Equation 3.2.1:

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{\text{sample}} - (^{18}O/^{16}O)_{\text{SMOW}}}{(^{18}O/^{16}O)_{\text{SMOW}}}\right] \times 10^3$$

Positive $\delta^{18}O$ values mean that a sample is enriched in ^{18}O relative to SMOW, whereas negative values indicate that the sample is depleted relative to SMOW.

Isotopic fractionation occurs in nature in at least three ways: isotopic exchange reactions, wherein heavy isotopes are exchanged for light isotopes in a chemical reaction; physical and chemical processes such as evaporation and condensation, diffusion, melting and crystallisation; and lastly by kinetic isotope effects, often in conjunction with biochemically mediated processes.

Most of the variations of $\delta^{18}O$ in nature occur in meteoric water (-50‰ to +30 ‰). Igneous rocks and minerals show much smaller $\delta^{18}O$ ranges which are generally positive with respect to SMOW and usually fall in the range of +5‰ and +11‰, although it should be noted that pegmatites which are volumetrically insignificant in the crust can be as high as +15‰ (figure 3.2.1). Deviations from this range may provide clues to the rock's history with regard to alteration and interaction with meteoric or magmatic water. Epstein and Taylor (1967) ranked some common rock-forming minerals according to their tendency to concentrate

^{18}O at a given temperature. The ranking is as follows: quartz, dolomite, alkali feldspar, calcite, plagioclase (An 50), muscovite, anorthite, pyroxene, hornblende, olivine, garnet, biotite, chlorite, ilmenite, and magnetite with magnetite having the lowest proclivity for incorporating ^{18}O. Mafic assemblages such as those present in gabbroic rocks would be depleted in ^{18}O relative to felsic assemblages because the mafic rock would be made up of minerals with a lesser tendency to concentrate heavy oxygen.

Important in recognising crustal contamination in igneous rock, or defining mantle and crustal reservoirs are correlation diagrams between radiogenic isotopes and oxygen because these two systems vary independently of each other. Crustal rocks are enriched in ^{18}O relative to mantle rocks, not just because of the aforementioned tendency of different minerals to concentrate heavy oxygen, but because crustal rocks are further enriched by long exposure to the atmosphere and hydrosphere which results in δ^{18}O enrichment due to low temperature processes (Rollinson, 1993), such as water-rock interactions, weathering and other surficial processes. As crustal reservoirs are depleted in ^{143}Nd/^{144}Nd relative to the mantle, bivariate plots of the Nd isotopic ratio versus the O isotopic ratio can prove useful in determining if mantle-derived rocks have become contaminated with continental crust (Rollinson, 1993).

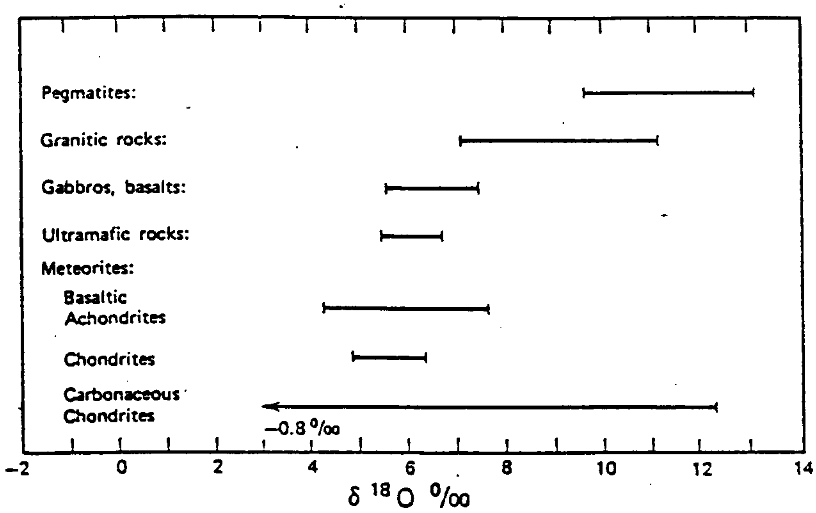


Figure 3.2.1: The range of values for $\delta^{18}O$ in various reservoirs (Faure, 1986).

4.0 WHOLE ROCK GEOCHEMISTRY

4.1 TRACE ELEMENT SYSTEMATICS

Due to the fact that they are often resistant to changes during alteration unlike most major elements, some trace elements have become a vital part of geochemical analyses. Trace element concentrations can provide important insights into the genesis of a rock, and coupled with other geochemical observations such as isotopic ratios can prove especially useful. Geochemical data can be divided into four main categories: radiogenic isotopes, stable isotopes, major elements and trace elements. Each of the aforementioned categories can again be subdivided into smaller sub-categories based upon different isotopic systematics or different classes of trace elements. A study which utilizes data from each of the four main groups as it were stands the best chance of gleaning the most pertinent information from a rock or suite of rocks. Trace elements are usually defined as those whose concentrations in rocks are less than 0.1%.

It is important to note that while the source composition will determine the nature of magmatic rocks, the whole rock element composition of such rocks will depend in part on the degree of partial melting which the source has undergone as well as processes affecting the magma en route to the surface such as contamination or fractional crystallisation (see figure 4.1). Trace element and major element studies are important in delineating these processes.

When the mantle undergoes melting trace elements can either exhibit a preference for the melt or for the solid phase. Those trace elements which are incompatible in the crystal lattices of the minerals making up the source mantle rocks will preferentially leave the solid phases and transfer to the melt. These trace elements are termed incompatible elements although this term can lead to some ambiguity, and the descriptive term; hygromagmatophile is probably a better term to use. Trace elements that are similar, usually in terms of ionic size, charge and bonding properties to a major element in one of the mineral phases under consideration may proxy for it in that rock-forming mineral. These elements are termed compatible trace elements. Elements with small ionic radii and a low charge are often compatible, Cr^{3+} is an exception in that it has a high charge yet is a compatible element. It should be noted however that in melts of different composition, the same trace element may behave as either a compatible or incompatible element. Hygromagmatophile elements can be subdivided into high field strength (HFS) and low field strength (LFS) elements. This division is based on ionic potential (IP) which is the valence/ionic radius ratio. HFS cations have an IP >2, LFS cations have an IP <2. LFS cations are also referred to as the large ion lithophile elements (LILE), and again those cations with similar properties can behave in a similar manner geochemically.

Partition coefficients indicate the allocation of trace elements between different phases. The Nernst distribution coefficient is used extensively in geochemistry and takes the following form:

$$\mathrm{Kd} = \mathrm{C}^{\mathrm{mineral}}_{\mathrm{element}\,i} \,/\, \mathrm{C}^{\mathrm{melt}}_{\mathrm{element}\,i}$$

where C is the concentration of element *I* in ppm or wt% and Kd (the Nernst distribution coefficient) is a function of P and T as well as melt composition, but is independent of the trace element concentration. A Kd >1.0 means that *I* is compatible in that system, whereas a Kd < 1.0 indicates that the trace element *I* is hygromagmatophile in that system (Rollinson, 1993). Derived from the Nernst distribution coefficient is the bulk partition coefficient expressed as:

$$D_i = {}_{x1}Kd_1 + {}_{x2}Kd_2 \ldots$$

where x_1 is the weight percent of mineral 1 in a rock and Kd_1 is the Nernst partition coefficient for trace element *I* in mineral 1. Researchers have determined the bulk partition coefficients for trace elements for a variety of different rocks, and these values are available to geochemists in a variety of compilations; however, temperature, pressure, oxygen fugacity and rock composition are variables which can act to change the Kd of an element, and thus care must be taken when using published values for D.

4.1.1 Rare Earth Elements

La-Lu, the elements with atomic numbers 57-71 make up the rare earth elements (REE) or lanthanides. Yttrium, with an ionic radii of 1.019Å, similar to holmium (1.015Å) and with the same charge is sometimes included in this category. REE are often divided into the light REE and the heavy REE, all of which can exist as stable ions in the 3^+ oxidation state. La-Sm comprise the LREE, while Eu-Lu make up the HREE, sometimes geochemists further subdivide the series by designating Sm-Ho as middle rare earth elements (MREE).

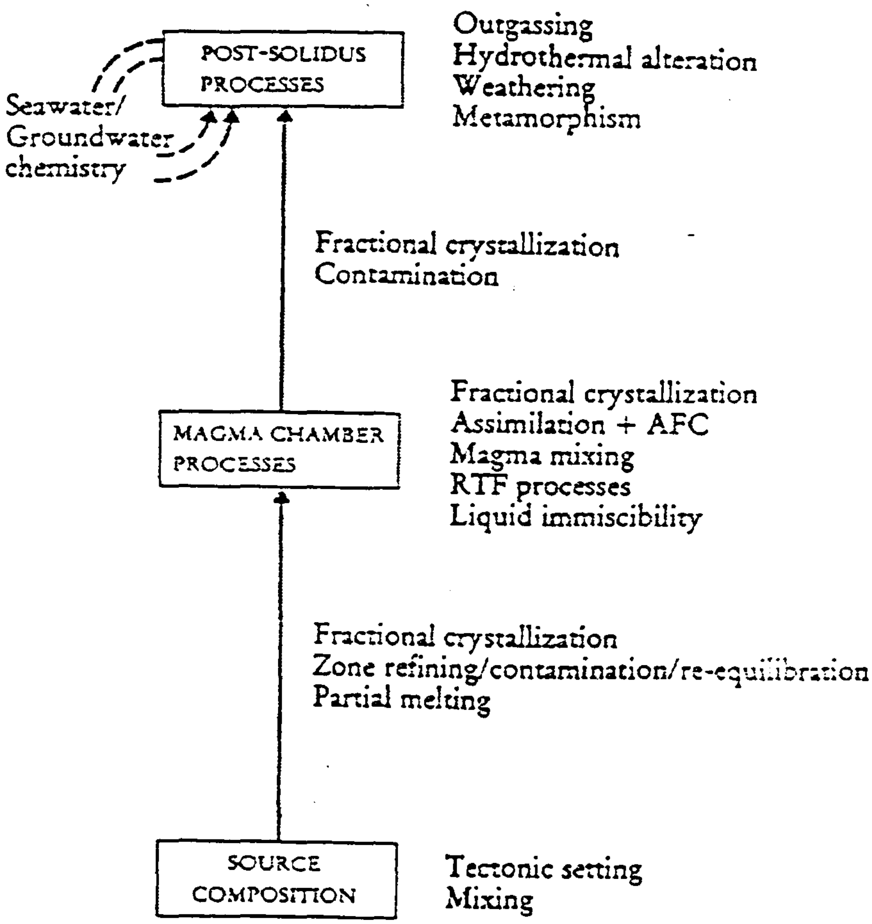


Figure 4.1: flow chart of the principal processes which contribute to the chemical composition of an igneous rock (Rollinson, 1993).

Weak to moderate fractionation can occur in the REE as a result of changes in chemical behaviour due to the increase in ionic radii with increasing atomic number. The REE are among the least soluble of all the trace elements in silicate magmas, and are consequently considered especially useful because they are very robust to hydrothermal activity and alteration processes making them relatively immobile even in low to medium grade metamorphic regimes. A caveat to this statement is the element europium, which in various environments ranging from magmatic to weathering can be converted to the 2^+ state from the normal$^+$3 oxidation state and subsequently substitute for Ca or Sr creating a Eu anomaly (ie: a depletion or addition of Eu relative to its nearest neighbours Sm and Gd). Europium anomalies can form as a result of partial melting where feldspars, particularly plagioclase are a residual phase if the melt occurs within the plagioclase stability field (Taylor and McLennan, 1985).

Those REE with even atomic numbers are more stable than those with odd atomic numbers in terms of nuclear structure, and therefore the even atomic numbered REE are more abundant in the solar system relative to odd atomic numbered REE. It is therefore convenient to normalise these element patterns to a certain standard such as chondrite REE values, resulting in a smooth pattern rather than the saw tooth pattern that would result from plotting REE concentration versus atomic number. It is the shape of this REE pattern that is of major interest to the geochemist. This normalisation can be a source of some complication. Variability in analytical methods used and in the types of chondrites analysed has given rise to several different chondrite normalisation schemes. Some rely on an average of chondrites, while others use only C1 chondrites. Care must be taken by the geochemist to identify which normalisation convention is being utilised.

4.2 MAJOR ELEMENT SYSTEMATICS

Major elements are those which predominate in a rock, and include Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P. Their concentrations are expressed in terms of oxide weight percents. It is assumed that these cations are bonded to an appropriate amount of oxygen, and therefore the sum of the oxide weight percents should total very near to 100% (Rollinson, 1993). H_2O, CO_2 and S are volatiles and together are expressed as a total LOI or 'loss on ignition' at 1000°C. Major element analyses are used primarily for rock classification, often in variation diagrams and are also used in conjunction with trace elements to aid in determining the tectonic setting of a suite of rocks. For example, oxide-oxide plots utilising Na and K versus Si (total alkalis versus silica or TAS plot of Wilson, 1989), can be useful in classifying plutonic rocks.

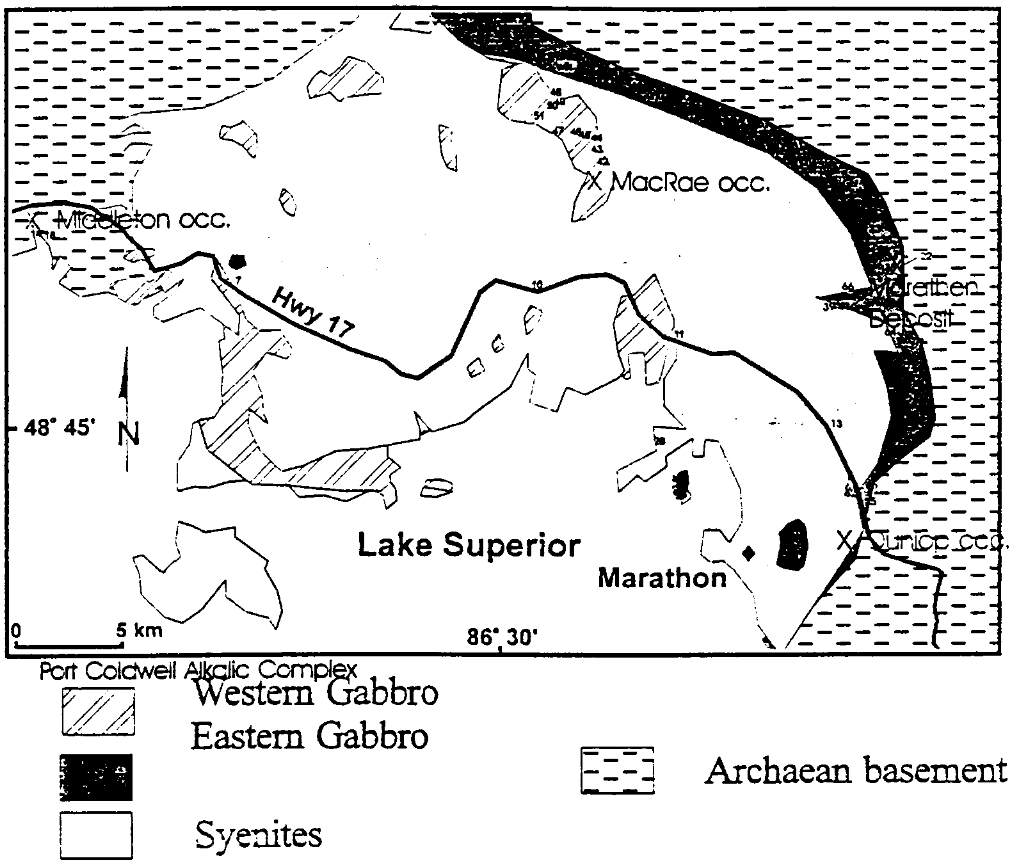
5.0 RESULTS

5.1 Sm-Nd EXPERIMENTS

Contamination of magmas by continental crust can occur as a result of bulk assimilation of crustal material, by assimilation of a partial melt of crustal material, or by the transfer of elements from the crust to the melt via crustal fluids (Rollinson, 1993). It was decided to utilise the Sm-Nd method to characterise the isotopic signature of the Coldwell complex rocks because of the low tendency of Sm and Nd; two of the REE, to be segregated by alteration or metamorphism.

A suite of 29 samples were analysed by the Sm-Nd method. Samples were taken from the major known mineralised occurrences in the Coldwell complex, samples from adjacent non-mineralised rocks and from other rock types in the complex were also collected, but the majority of samples are from areas associated with sulphide mineralisation in the

Centre 1 gabbro units (see sample location map, figure 5.1.1). All ϵNd data at 1108 Ma, as can be seen from table 5.1.1 and figure 5.1.2 fall between -2.93 and +2.51, with most samples clustering around CHUR (ϵNd=0). The more evolved rocks to the west in Centre 3 exhibit average ϵNd values of -0.9, whereas the Eastern Gabbros have an average of +0.5 (see figures 5.1.2, 5.1.3 and 5.1.4) with 2σ errors on Sm-Nd analyses of 4.4×10^{-5} (Table 5.1.2). Published Sm-Nd data (see figure 5.1.4) from the complex mirrors this general trend with more evolved granites and syenites from the western end of the complex displaying ϵNd values from -6.4 to -4.6 and earlier gabbroic phases exhibiting values from +0.5 to +1.6 (Heaman and Machado, 1992). The majority of the basalt in the Midcontinent rift has a chondritic isotopic signature, with epsilon Nd values having a low of -2.5 and an observed high of +3.5, and olivine tholeiites being restricted to between -0.3 and +0.8 (Dosso, 1984; and Brannon, 1984 as cited in Heaman and Machado, 1992; Paces and Bell, 1989; Nicholson and Shirey, 1990).



(after Sage, 1991)

Figure 5.1.1: Sample location map for the Coldwell complex.

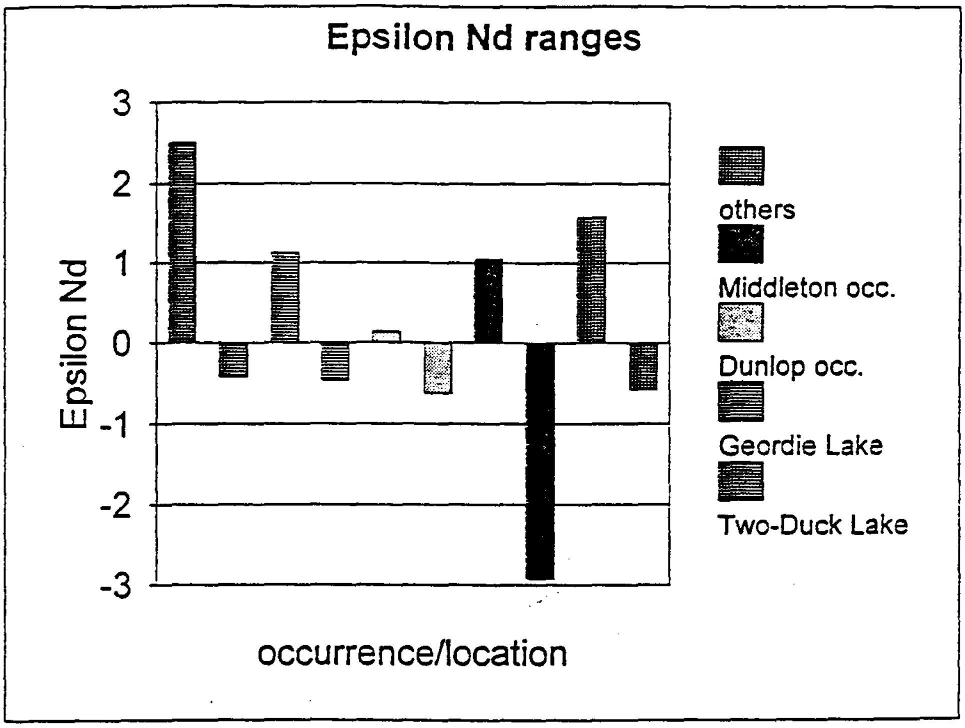


Figure 5.1.2: Histogram of εNd data from Table 5.1.1.

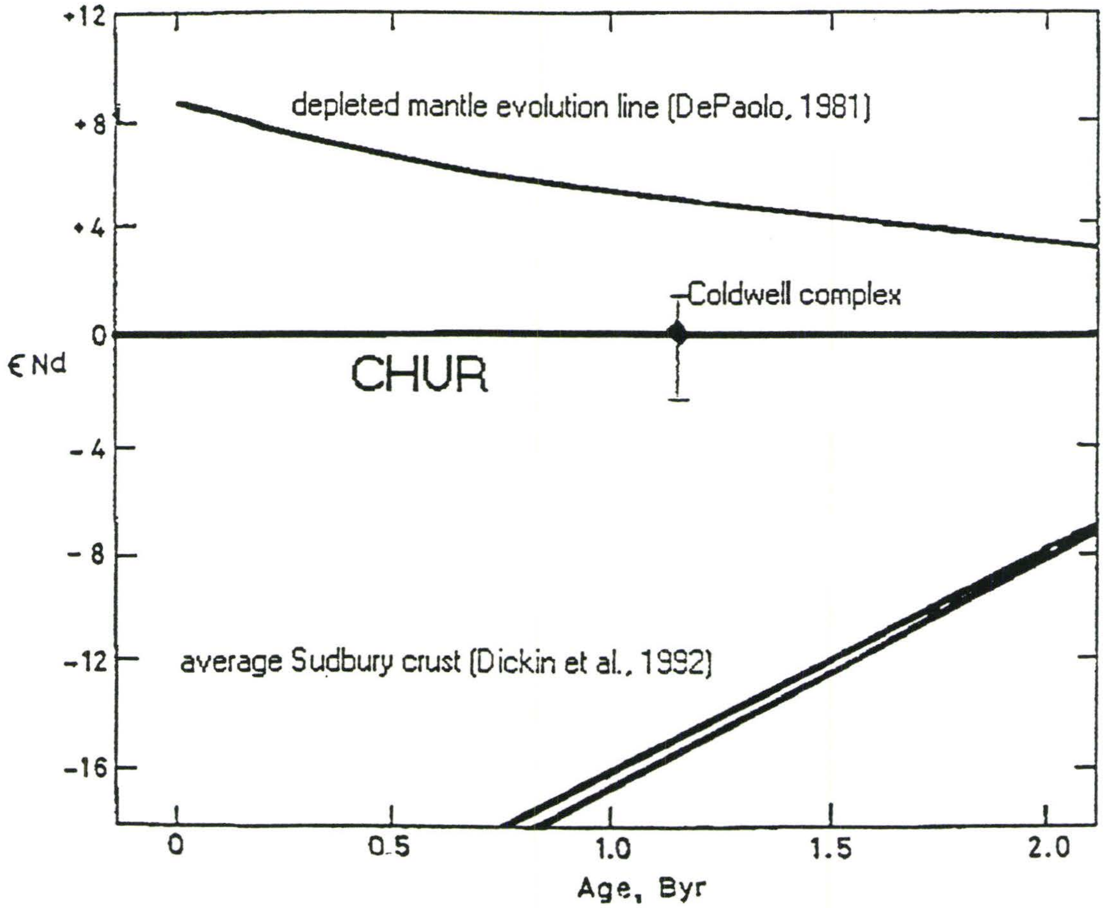


Figure 5.1.3: Graph of epsilon Nd vs. Time for the Coldwell complex data, depleted mantle curve is that of DePaolo, (1981), value for Sudbury crust from Dickin *et al.*, (1992).

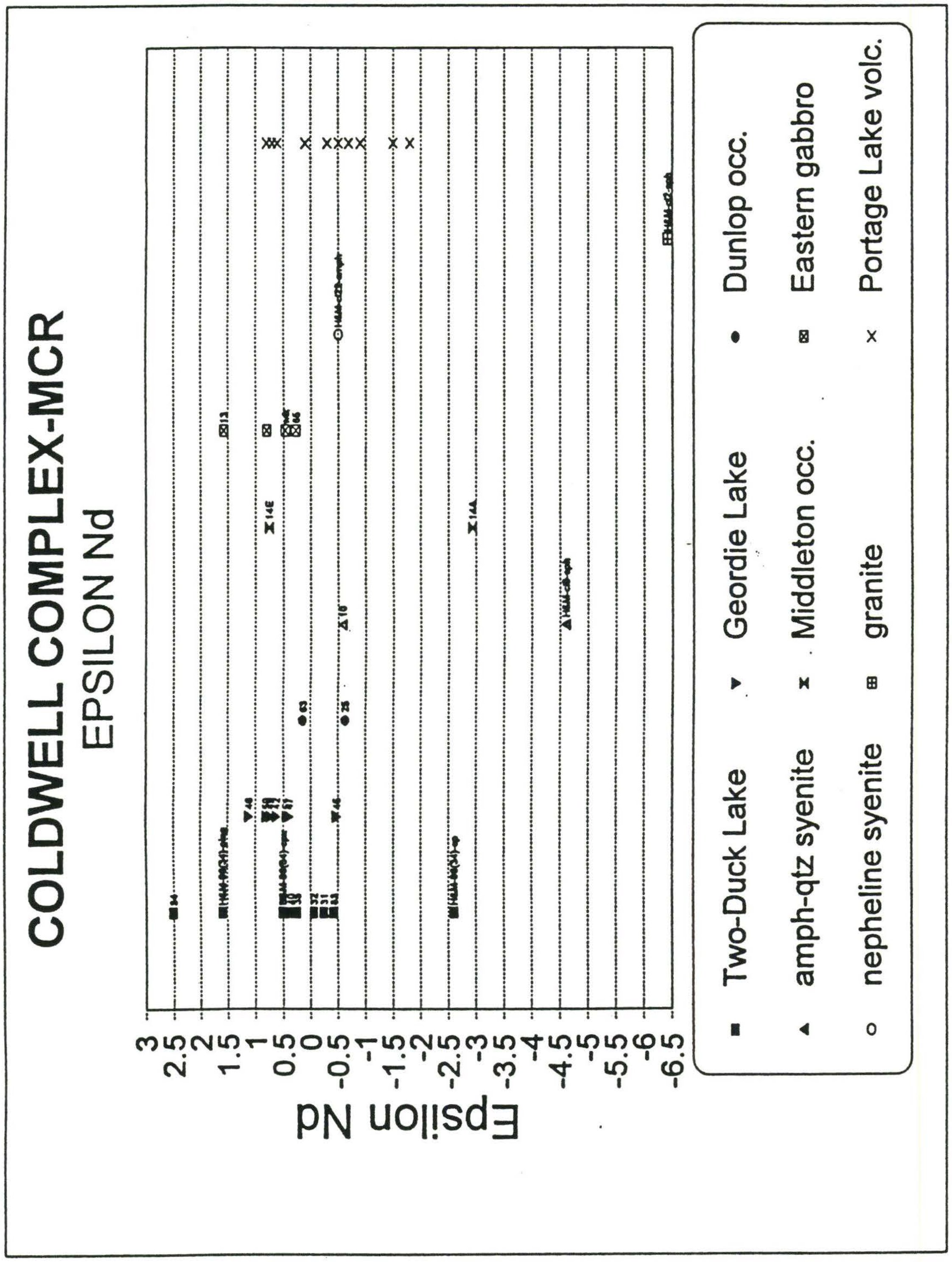


Figure 5.1.4: ranges of epsilon Nd data for rocks of the Coldwell complex and the Portage Lake volcanic group, (H&M=Heaman and Machado, 1992); data for Portage Lake volcanic group from Paces and Bell, (1989).

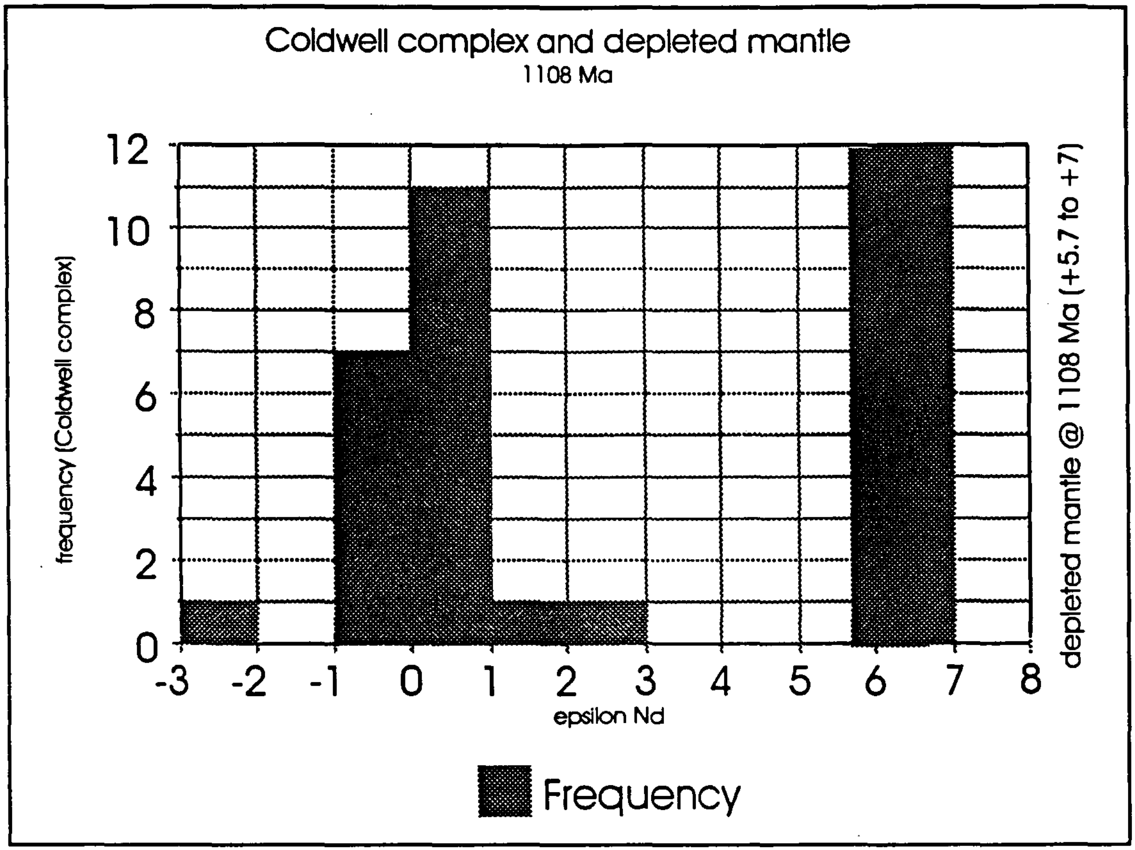


Figure 5.1.5: histogram showing distribution of ϵNd data for the Coldwell complex in comparison to expected values of depleted mantle at 1108 Ma illustrates that Coldwell complex alkaline rocks have lower ϵNd values than depleted mantle.

Many authors have theorised on the provenance of the Midcontinent Rift System (MRS) rocks, with two main hypotheses being prevalent. One theory is that the relevant magmas originate from the depleted asthenospheric mantle and mixed with some component of the sub-continental mantle lithosphere to produce the observed Nd isotopic compositions which cluster around zero. This model has been proposed for the Karoo (Hawkesworth *et al.,* 1984 as cited in Nicholson and Shirey, 1990) and the Columbia River flood basalts, (Carlson, 1984). Another plausible theory that has been popularised by Heaman and Machado, (1992); Nicholson and Shirey, (1990); Hutchinson *et al.,* (1990); and Green, (1983) is the mantle plume or Keweenawan hot spot theory which suggests that a hot spot ~ 150°C hotter than the ambient mantle temperature (1280 °C) could cause melting and extension, and would generate the requisite 15 km of melt beneath the rift. (White *et al.,* 1987). A third theory which although supported by isotopic evidence, is quickly ruled out on the basis of trace element signatures is that the MRS rocks have their origin in the primitive mantle.

If the Coldwell complex data are plotted on the depleted mantle evolution diagram of DePaolo (1981) (figure 5.1.3), it is seen that the data cluster around CHUR. Since the age is well constrained by U-Pb dating, we can calculate that the expected epsilon Nd values for the Coldwell complex rocks would be about +5.0 had they evolved from a depleted mantle source at 1108 Ma (see fig 5.1.3). On the other hand, had the magma which formed the Coldwell complex interacted with the considerably older Archaean continental crust, expected epsilon Nd values would be quite negative. Even small amounts of crustal contamination should be easily detected, because of the large age difference between the complex and the surrounding country rock, and the attendant difference in isotopic composition between the depleted mantle (ϵNd +5) and the country rock (ϵNd -12 to -17) at the time of Coldwell complex magma emplacement. Some evidence for small scale crustal contamination in other rocks of the MRS has been reported. Paces and Bell (1989) indicate slight crustal contamination in early Portage Lake tholeiitic basalt flows (ϵNd -1.5, figure 5.1.4), and in Portage Lake rhyolites (ϵNd -2, figure 5.1.4), while Nicholson and Shirey (1990) report an epsilon Nd value of -16 for a Portage Lake type II rhyolite. It has been suggested by Heaman and Machado (1992) that the identical ϵNd values of chemically distinct Centre 1 gabbros and Centre 2 nepheline syenites is evidence against large scale crustal contamination with Archaean country rock because mixing between the crust and depleted mantle from two separate magma sources would not likely occur such that both rocks exhibit nearly identical isotopic signatures. Heaman and Machado (1992) point out that the Centre 1 and Centre 2 magmas could not have been tapped from a single differentiating magma reservoir at different times and experienced increasing crustal contamination because they have similar initial Nd isotopic compositions. Centre 1 syenites and Centre 3 granites have quite distinct isotopic signatures compared with Centre 1 gabbros and silica undersaturated Centre 2 rocks (Heaman and Machado, 1992 and this study). Heaman and Machado (1992) suggest that they would have found Archaean zircons in their U-Pb study if crustal contamination of a differentiating gabbroic magma had been responsible for emplacing Centre 1 syenites and Centre 3 granites. They found no Archaean age zircons despite the large volume of assimilation which would have had to occur to generate the granites, making this possibility unlikely in their opinion. However, it must be noted that although they did not find any Archaean age zircons in their survey this does not mean that such zircons do not exist. Heaman and Machado (1992) instead prefer to invoke a distinct magma source for Centre 1 syenites and Centre 3 granites, and propose that this source is a partial melt of Archaean granulite-facies lower crust. Corroboration of this theory comes from the analyses of siliceous rhyolites from the MRS volcanic rocks by Nicholson and Shirey (1990) which have ϵNd values between -13 and -16, and have been interpreted by them to represent partial melting of Archaean crust. It should be pointed out that the Centre 1 syenites and Centre 3 granites (average ϵNd values of -4.6 to -6.4 for sphene; Heaman and Machado, 1992) have vastly different values than the type II rhyolite analysed by Nicholson and Shirey (1990). The values observed for the siliceous rhyolites in the Portage Lake Volcanic group more closely resemble the epsilon Nd values of the average Archaean crust in the area, whereas the values for the Centre 1 ferro-augite syenites and the Centre 3 granites are considerably higher.

Useful in detecting crustal contamination is a plot of initial Nd isotope ratio vs the reciprocal of the Nd concentration (see figure 5.1.6), This plot should show that the samples with the lowest Nd (the most primitive samples) exhibit the greatest amount of contamination, (Dickin, 1995). The data, however, is equivocal in the case of the Coldwell complex. There is no observed correlation between more or less evolved rocks and Nd isotopic composition on this diagram suggesting an absence of crustal contamination.

Isotopic data gleaned from MRS volcanics by previous researchers can provide insight into the magmatic affinity of the rift-related rocks, as well as the extent to which crustal contamination has taken place. Nicholson and Shirey (1990) suggest that, based on the isotopic signatures of the rift-related tholeiites and associated plutonic rocks, several possible reservoirs might exist. These reservoirs are: 1)primitive bulk earth mantle, 2) depleted mantle plus enriched crust or lithosphere, 3)subcontinental lithospheric mantle created and enriched during the early Proterozoic or earlier, 4) an enriched mantle plume.

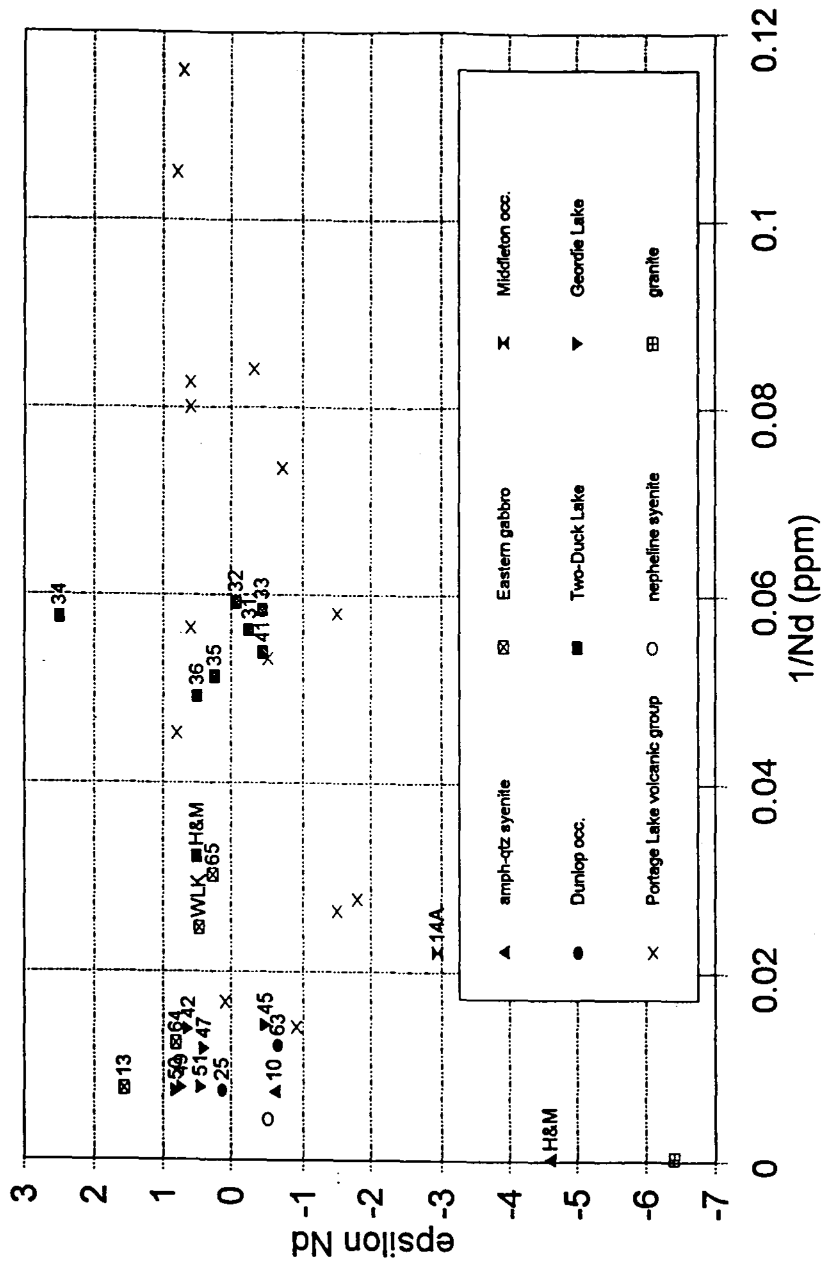


Figure 5.1.6: Initial Nd isotopic ratio in the form of epsilon Nd against the reciprocal of Nd concentration (H&M= Heaman and Machado, 1992; Portage Lake Volcanic group data from Paces and Bell, 1989).

Sample	Rock type	Sm (ppm)	Nd (ppm)	^{147}Sm/ ^{144}Nd	^{143}Nd/ ^{144}Nd	^{143}Nd/ ^{144}Nd^{init}	εNd 1108 Ma
10	qtz-sy	20.35	131.86	0.0933	0.51186	0.51118	-0.58
13	gabbro	20.58	127.76	0.0973	0.51200	0.51129	1.58
14A	gabbro	7.34	43.95	0.1009	0.51179	0.51106	-2.93
14E	gabbro	11.81	70.18	0.1017	0.51199	0.51125	0.76
21	gabbro	3.26	20.23	0.975	0.51196	0.51125	0.76
25	gabbro	24.00	140.95	0.1029	0.51196	0.51122	0.14
28	gabbro	13.68	78.74	0.1050	0.51192	0.51116	-1.03
31	gabbro	3.89	19.93	0.1180	0.51205	0.51195	-0.24
32	gabbro	3.23	17.93	0.1089	0.51200	0.51121	-0.06
33	gabbro	3.37	16.88	0.1208	0.51207	0.51119	-0.42
34	gabbro	3.48	19.47	0.1060	0.51211	0.51134	2.51
35	gabbro	3.80	20.56	0.1118	0.51203	0.51122	0.25
36	gabbro	3.91	21.94	0.1098	0.51203	0.51123	0.50
40	gabbro	5.32	27.55	0.1168	0.51208	0.51123	0.36
41	gabbro	3.62	18.98	0.1154	0.51203	0.51119	-0.43
42	gabbro	12.24	75.19	0.0984	0.51196	0.51124	0.63
45	gabbro	13.12	72.95	0.1087	0.51198	0.51184	-0.47
46	gabbro	14.39	88.71	0.0981	0.51198	0.51127	1.13
47	gabbro	14.99	93.52	0.0969	0.51193	0.51123	0.40
49	gabbro	20.64	133.85	0.0932	0.51192	0.51125	0.74
50	gabbro	21.22	137.85	0.0930	0.51193	0.51125	0.82
51	gabbro	20.51	132:12	0.0939	0.51191	0.51123	0.45
63	gabbro	14.70	87.56	0.1015	0.51194	0.51120	-0.63
64	gabbro	12.69	82.22	0.0933	0.51193	0.51125	0.81
65	gabbro	5.34	30.04	0.1075	0.51200	0.51122	0.28
WLK	gabbro	9.75	56.65	0.1040	0.51199	0.51124	0.47

Table 5.1.1: εNd data for rocks from the Coldwell complex

$^{143}Nd/^{144}Nd$ (measured)	Date
0.511858	23Oct. 95
0.511887	28Nov. 95
0.511867	09Jan. 96
0.511904	26Feb. 96
0.511879	27Feb. 96
0.511854	25Mar. 96
0.511837	27Mar. 96
0.511839	17Apr. 96
0.511866	average
0.000044	2σ error (population)

Table 5.1.2: 2σ error (population) on 8 analyses of the international standard La Jolla.

The average initial εNd values of about 0 or CHUR reported for most of the rocks of the Coldwell complex, as well as for other mafic rocks in the MRS, can, in a most simplified sense, be interpreted to represent partial melting of the primitive mantle. Reported values for $^{87}Sr/^{86}Sr$ and Pb isotopic values for MRS basalts are also similar to the estimated isotopic compositions of primitive mantle. However Nicholson and Shirey (1990) rule out primitive mantle as a possible source for MRS rocks on the grounds of incompatible trace element ratios. As will be discussed in more depth in the following discussions on trace element data, ratios like Zr/Y, La/Yb, Th/Ta and Hf/Th are thought to be relatively insensitive to partial melting and crystal fractionation, and should exhibit ratios equivalent to their source. The MRS rocks including the Coldwell complex data do not have incompatible trace element ratios indicative of primitive mantle as defined by Taylor and McClennan (1985).

Another possible source for the MRS magmas is a mixture of depleted mantle and crust. This has been advocated for the Rio Grande rift (Perry *et al.,* 1987 as cited in Nicholson and Shirey, 1990) and the Columbia River Plateau (Carlson, 1984 as cited in Nicholson and Shirey, 1990). In areas where mixing between a consistent depleted mantle source and variable amounts of a crustal component has occurred and formed volumetrically large amounts of basalt, observed Nd isotopic ratios fluctuate between depleted and enriched values. The MRS rocks and the Coldwell complex rocks exhibit relatively tightly constrained values for ϵNd, which means that mixing of depleted mantle and crust would have to have been extremely regular, which is unlikely in the episodic, multi-pulse system represented in the MRS.

Nicholson and Shirey (1990) also investigated the possibility of subcontinental lithospheric mantle as a possible contributor to MRS magma. They consider that if initially depleted subcontinental lithospheric mantle was subsequently enriched prior to Keweenawan rifting by subduction during or prior to the Penokean orogeny, or by metasomatic processes, then it could attain the requisite isotopic and chemical characteristics to become an MRS source candidate. Again, the isotopic homogeneity of the MRS volcanics makes this scenario unlikely since decompression melting of the large volume of material necessary to form the MRS volcanics, and to account for accompanying basaltic underplating, would result in a large volume of partial melt of asthenospheric mantle filling the resultant void. This would result in a spatial and temporal shift from lithospheric to asthenospheric melts as is seen in the Rio Grande rift (Perry *et al.,* 1987 as cited in Nicholson and Shirey, 1990) which is not evident in the MRS. Also the wide range in ages of subcontinental lithosphere adjacent to the rift would be unable to generate the isotopic homogeneity observed in the rocks of the Coldwell complex and the MCR basalts.

The most widely cited theory first invoked by Paces and Bell, (1989) and by Hutchinson *et al.,* (1990) is that a mantle plume associated with the so-called Keweenaw hot spot is responsible for the formation of the melts which formed the MRS rocks. Modern plumes like Hawaii and

Iceland-Reykjanes exhibit ϵNd values 4-5 epsilon units more negative than those reported for depleted mantle (White, 1985). While the Pb isotopic evidence gathered by other workers is equivocal as to whether it indicates a depleted or enriched mantle source, the Nd isotopic evidence indicates enrichment in LREE over expected values for depleted mantle at 1108 Ma (see figure 5.1.5).

As previously mentioned, the isotopic evidence alone does not necessarily distinguish between an enriched plume or a subcontinental lithospheric source enriched at about 1900 Ma. The age of 1900 Ma is derived from model Nd isotopic growth curves (Nicholson and Shirey, 1990). The large volume of basalt extruded and the isotopic homogeneity of the MRS rocks are evidence for the input of a plume rather than simple lithospheric melting since the lithosphere in the vicinity of the rift consists of heterogeneous rocks with contrasting ages ranging between 3.6 and 1.8 Ga. If a plume did indeed contribute to the formation of the MRS one might expect a hot spot track to exist in the area. While no such track has been identified, Nicholson and Shirey (1990) imply that hot spot tracks are difficult to identify when they occur across continental lithosphere, especially across thick areas. They also suggest that the absence of absolute ages for Proterozoic volcanism spatially related to Keweenawan volcanism makes tracking of a hot spot difficult. Also indicative of the contribution of a plume is the dominantly tholeiitic composition of the rift-related igneous rock, and the subaerial nature of the eruption (Campbell and Griffiths, 1990), as well as the short span of time (~2 Ma) over which the extrusion of the bulk of the magma occurred (Davis and Paces, 1990).

5.2 WHOLE ROCK ANALYSES

Equivocal information gleaned from Sm-Nd experiments makes the integration of whole rock chemical analyses of Coldwell complex rocks a necessary part of this study. Because the Sm-Nd data is open to several different interpretations, independent criteria are needed to further evaluate the data and validate the theory that a mantle plume contributed to the MRS magmas. That independent line of evidence can come from major element and trace element analyses used either in conjunction with or independently of the isotopic data.

Twenty five samples were analysed by ACT-Labs (Ancaster, Ontario) for whole rock analyses. Major elements were analysed by inductively coupled plasma emission spectrometry (ICP), trace elements abundances were determined by inductively coupled plasma mass spectrometry (ICP-MS). Six of the same samples were also submitted to the McMaster University, Department of Geology's X-ray fluorescence (XRF) facility for major element analyses and Rb, Sr, Y, Nb, Zr analyses. Results of these whole rock analyses are compiled in appendix 1.

5.2.1 Major element analyses

Sample Name	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI
7*	57.92	1.48	16.38	11.84	0.23	1.32	4.48	4.71	4.81	0.54	1.69
10	58.84	0.95	15.10	9.07	0.16	1.05	2.25	5.57	4.62	0.31	0.52
10*	61.28	1.04	15.53	8.79	0.17	0.87	2.32	5.73	4.73	0.30	0.51
10*duplicate	62.74	1.06	15.93	8.49	0.17	0.90	2.36	5.95	4.76	0.31	0.51
13	40.67	2.20	13.80	17.77	0.30	5.98	12.75	2.39	0.31	2.08	-0.06
14A	35.52	2.57	12.39	27.29	0.28	6.84	9.61	1.77	0.25	1.38	0.88
14D	49.05	0.68	24.29	4.21	0.05	1.20	10.65	4.28	0.93	0.43	2.75
14D*	48.18	0.72	24.87	4.09	0.07	1.09	10.85	4.18	0.95	0.43	2.56
14D*duplicate	51.12	0.73	26.02	3.92	0.07	1.18	11.05	4.59	0.98	0.45	2.56
25	60.55	0.53	14.67	7.88	0.18	0.37	1.82	6.16	5.04	0.13	1.32
28	50.15	1.59	13.68	14.27	0.26	3.69	6.57	4.20	2.56	0.90	1.34
31	45.90	0.76	14.99	12.17	0.17	7.58	12.45	2.17	0.38	0.18	0.92
32	46.76	0.71	17.13	13.02	0.19	6.92	10.34	2.70	0.42	0.38	-0.45
33	48.81	0.91	17.44	7.86	0.12	5.14	12.37	2.92	0.47	0.17	2.38
34	45.52	0.76	14.35	13.36	0.16	8.00	12.71	1.93	0.34	0.14	1.02
34*	48.43	0.81	14.65	15.99	0.17	7.87	13.22	1.17	0.33	0.15	1.46
35	48.09	0.76	15.34	11.77	0.18	7.51	12.26	2.36	0.46	0.17	0.11
36	48.83	0.58	17.57	9.43	0.14	6.63	12.06	2.70	0.45	0.22	0.58
41	46.83	0.76	16.26	11.73	0.12	4.57	11.90	2.87	0.51	0.20	2.85
42	41.83	1.80	12.20	20.33	0.31	4.63	8.99	3.13	0.95	1.14	0.27
42*	48.09	2.05	12.28	21.92	0.30	4.59	9.56	2.99	1.02	1.35	0.24
43	59.58	0.81	14.55	8.96	0.32	1.13	2.80	4.29	4.93	0.27	0.97
43*	62.05	0.90	15.21	10.69	0.31	0.98	2.93	4.17	4.98	0.27	0.91
45	43.14	2.46	11.53	21.96	0.34	5.27	7.63	2.62	1.82	0.99	0.36
47	45.24	2.22	12.58	19.39	0.29	4.12	7.77	3.44	1.97	1.09	0.39
49	59.00	0.75	13.86	10.72	0.26	0.13	3.22	5.36	5.04	0.12	0.21
50	58.01	0.77	13.53	11.52	0.28	0.12	3.41	5.34	4.85	0.13	0.14
51	58.42	0.79	13.67	11.62	0.29	0.15	3.51	5.33	4.92	0.14	-0.12
61	51.27	0.58	14.47	9.68	0.18	7.65	8.25	2.97	0.45	0.52	2.01
63	37.48	1.95	13.04	19.25	0.24	6.46	10.98	2.09	0.78	3.08	3.12
64	52.97	1.09	17.85	8.93	0.17	1.72	6.94	5.25	2.07	0.80	0.90
65	43.78	1.63	13.88	16.60	0.22	6.65	11.00	2.48	0.37	0.49	1.22
WLK	40.50	2.65	12.65	20.01	0.24	6.24	11.42	2.15	0.50	1.40	1.10

Table 5.2.1.1: Major element analyses, those samples denoted with an asterisk were analysed by XRF at McMaster University, Department of Geology all others analysed by ICP at Activation Laboratories Ltd., Ancaster, Canada.

The ten elements commonly listed as oxides in major element chemical analyses

can be used together in rock classification or in variation diagrams to determine if there is any genetic link between individual rocks of a particular assemblage or locality. Although these rocks have been previously classified mainly by petrographical studies by previous researchers (Mitchell and Platt, 1978; Dahl *et al.*, 1987; Mulja, 1989; McLaughlin, 1990; Good, 1993; Shaw, 1995; Shore, 1995), it is still useful to plot the geochemical data on standard classification schemes in order to characterise the rock type by its chemical composition. The total alkalis versus silica diagram or TAS plot adapted for plutonic rocks by Wilson (1989) is particularly useful in classifying plutonic assemblages. Figure 5.2.1.1 illustrates the classification of the Coldwell complex rocks sampled for whole-rock geochemistry. Also useful for classification is the cationic method of de la Roche *et al.*, (1980). This method has the advantage that the entire major element chemistry of a rock is utilised in determining its classification. It also avoids the criticism that wt% oxides from norm calculations do no accurately reflect the cation distribution of a rock (Rollinson, 1993) and as such is the preferred method (see figure 5.2.1.2) although both schemes generally classify the rocks similarly.

In order to explore the possibility of a genetic link between rocks from a similar locality, such as the suite of igneous rocks from the Coldwell complex, a variation diagram between two major elements is often used. Strong correlation between the two elements implies that some particular geochemical process is common to both rocks. Frequently SiO_2 is plotted against other major elements to try and identify chemical trends which are usually due to mixing or fractional crystallisation.

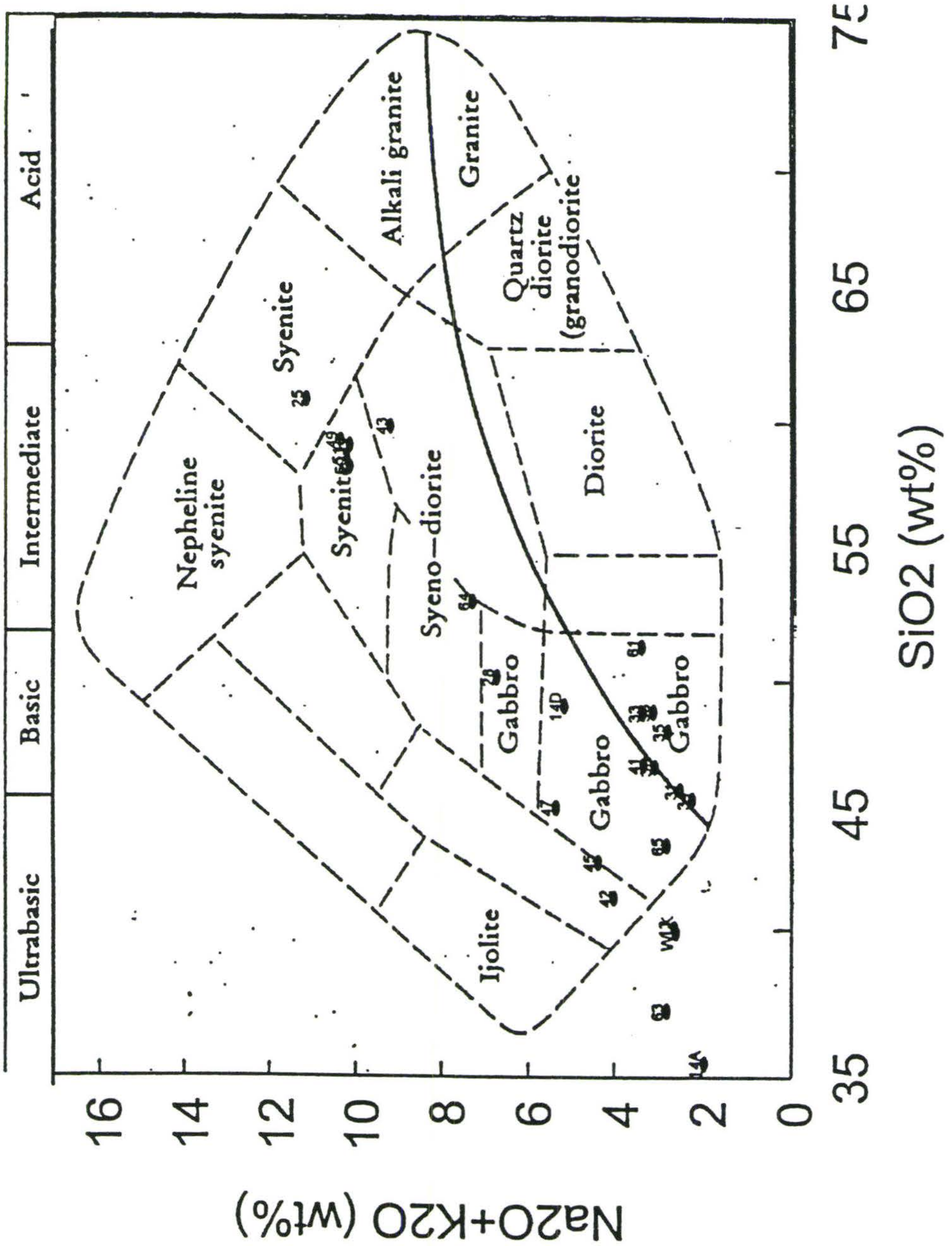


Figure 5.2.1.1: Total alkalis versus silica plot of selected rocks from the Coldwell complex (after Wilson, 1989). The curved solid line separates the subalkalic and alkalic rocks.

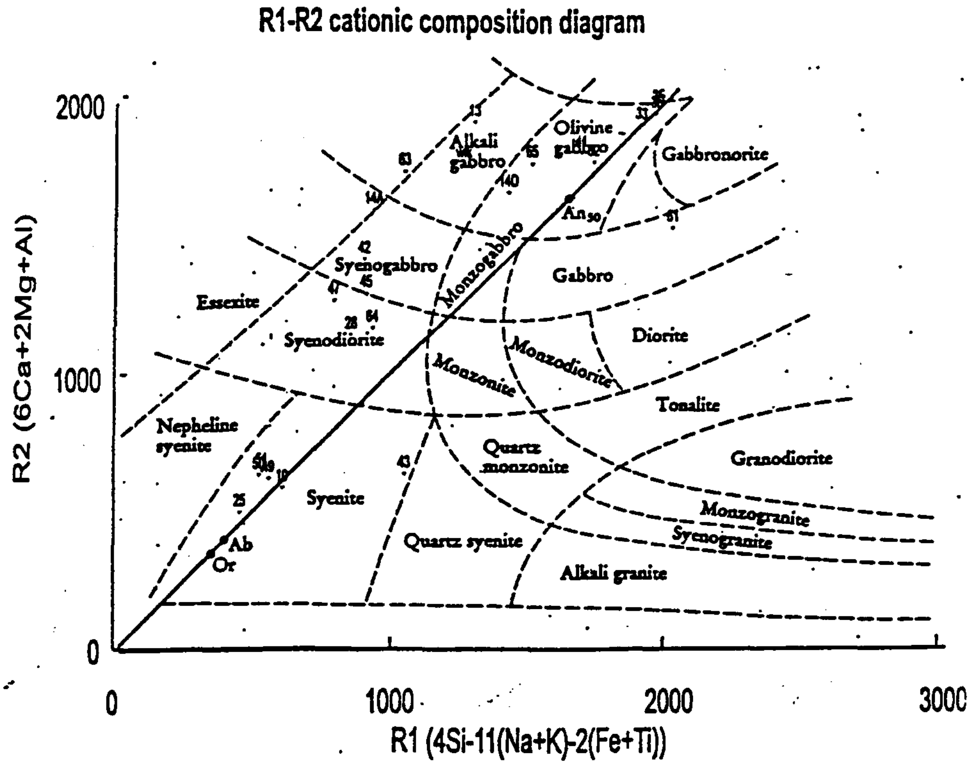


Figure 5.2.1.2: R1-R2 classification diagram calculated from millication proportions. R1=4Si-11(Na+K)-2(Fe+Ti); R2=6Ca+2Mg+Al (after de la Roche *et al.*, 1980).

This mixing may be simple mixing between magmas, or may be a result of contamination or changes in fractional crystallisation paths due to assimilation. In the case of the Coldwell complex, MgO rather than SiO_2 is the better element for comparison with other major elements, since these rocks are Si-poor. Figure 5.2.1.3 is a graph illustrating Ti, Al, Fe, Ca, Na, and K as oxides, plotted against MgO. A reasonably good negative correlation is observed between MgO and Na_2O. The correlation with Na, is not easily explained, but is likely due to the fractional crystallisation of sodic plagioclase which is a major Na sink and pyroxene which is low in Na. A plot of the same data on a conventional Harker diagram with SiO_2 on the x-axis show correlations between SiO_2 and Fe_2O_3, and Na_2O (Figure 5.2.1.4).

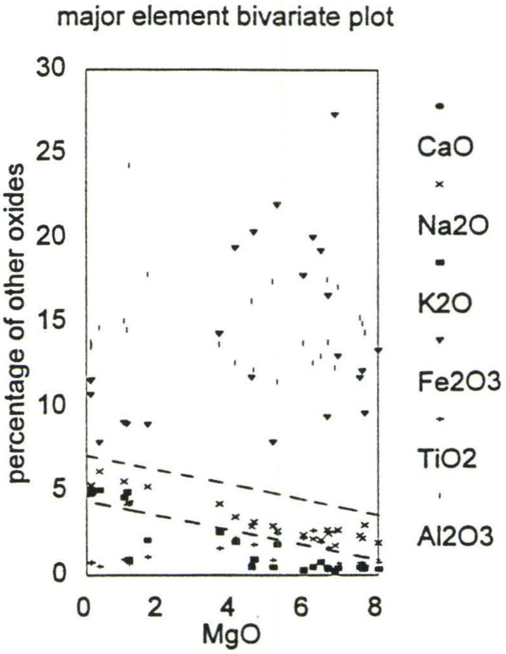


Figure 5.2.1.3: major element bivariate plot of MgO versus other oxides for the Coldwell complex.

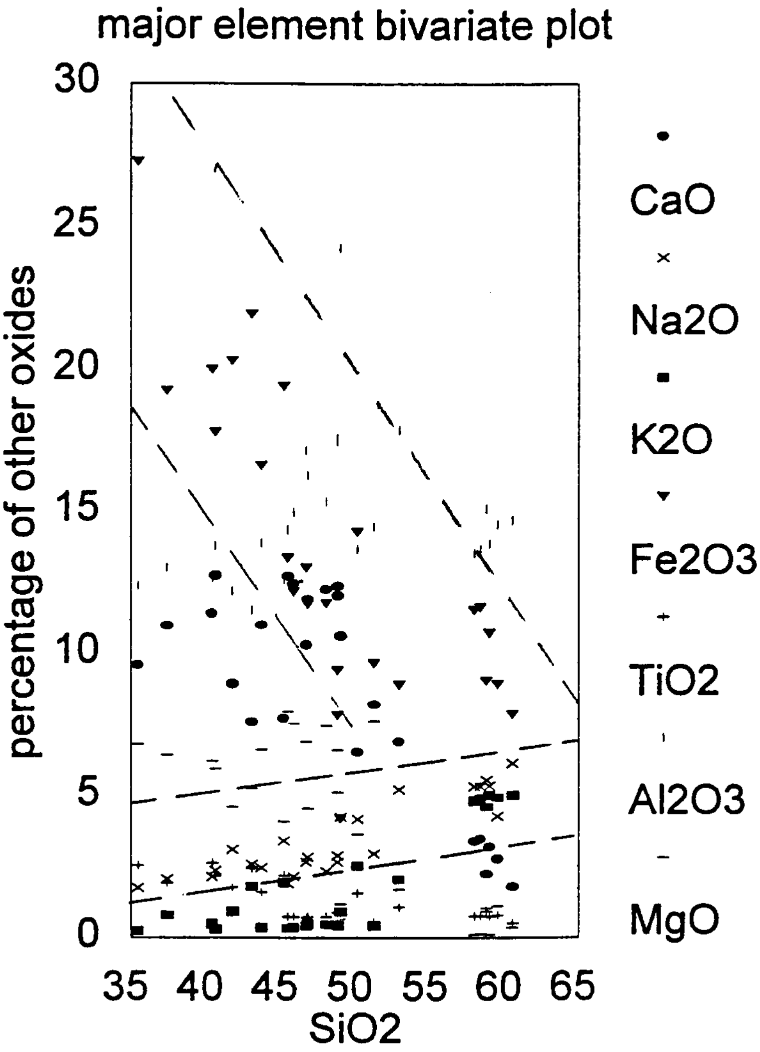


Figure 5.2.1.4: major element bivariate plot of SiO_2 versus other oxides (Harker diagram) for the Coldwell complex.

5.2.2 Trace element analyses

Commonly trace elements are defined as those elements which are present in a rock in concentrations of less than 1000 ppm. Trace elements can provide useful information on the evolution of a rock, although the factors which control trace element distribution in a rock must be taken into careful consideration. One of the main geologic controls on trace element distribution is stability of the host mineral phase under given temperature and pressure regimes. Alteration and metamorphism of a rock may result in the transfer of some of its elemental constituents. A consequence of this mobility is that any inferences made about a rock's petrogenesis on the basis of trace element information is only valid if it can be shown that the elements in question are immobile under the P-T conditions in question. Generally immobile elements include Co, Ni, V, and Cr as well as Sc, Y, Th, Zr, Hf, Ti, Nb, Ta, P, and the REE (Pearce, 1983).

5.2.2.1 REE

Particularly useful in geologic situations are the lanthanides (atomic numbers 57-71) which comprise the rare earth elements (REE) (see section 4.1.1). Although the REE are generally thought to be robust to weathering, alteration and low-grade metamorphism, they are not entirely immobile. As a measure of the degree of fractionation of the REE with changing REE content, the La/Yb ratio is often plotted against Ce or Yb (generally all chondrite-normalised) on a bivariate diagram. La and Ce are LREE, whereas Yb is a heavy rare-earth element. Figure 5.2.2.1.1 and figure 5.2.2.1.2 illustrate the degree of REE fractionation present in the Coldwell rocks based on La/Yb vs. Ce and Yb. Data is compiled in Appendix 2.

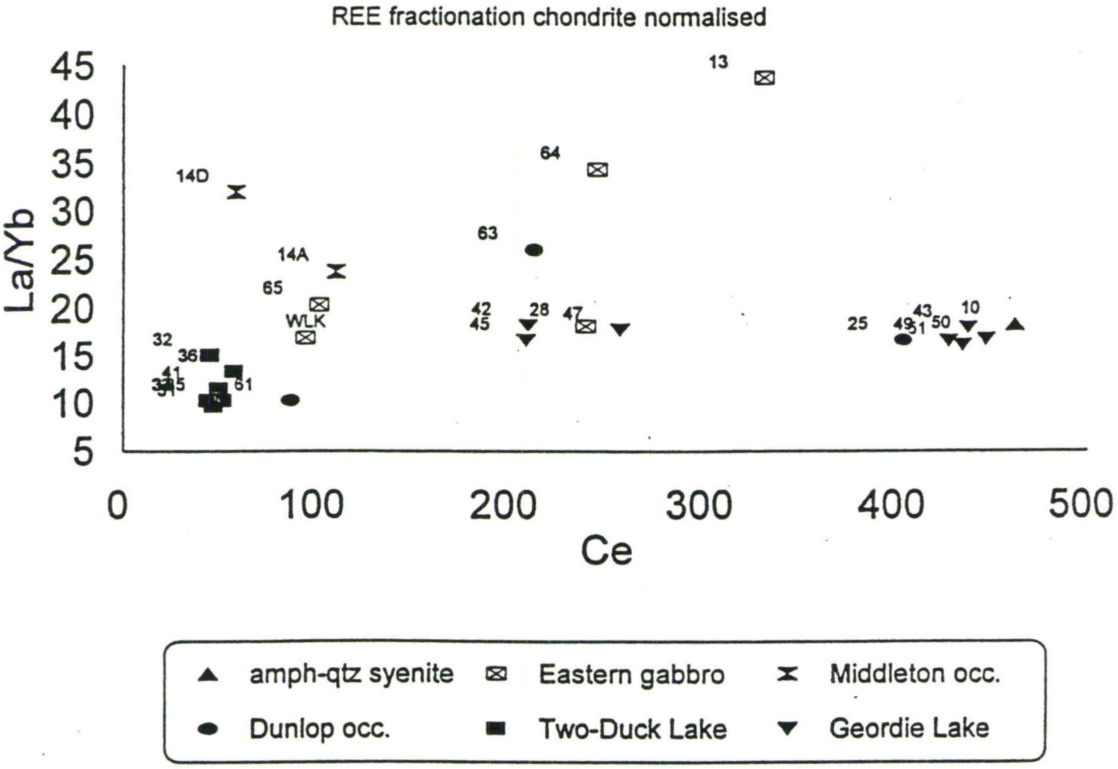


Figure 5.2.2.1.1: La/Yb versus Ce REE fractionation diagram for the Coldwell complex.

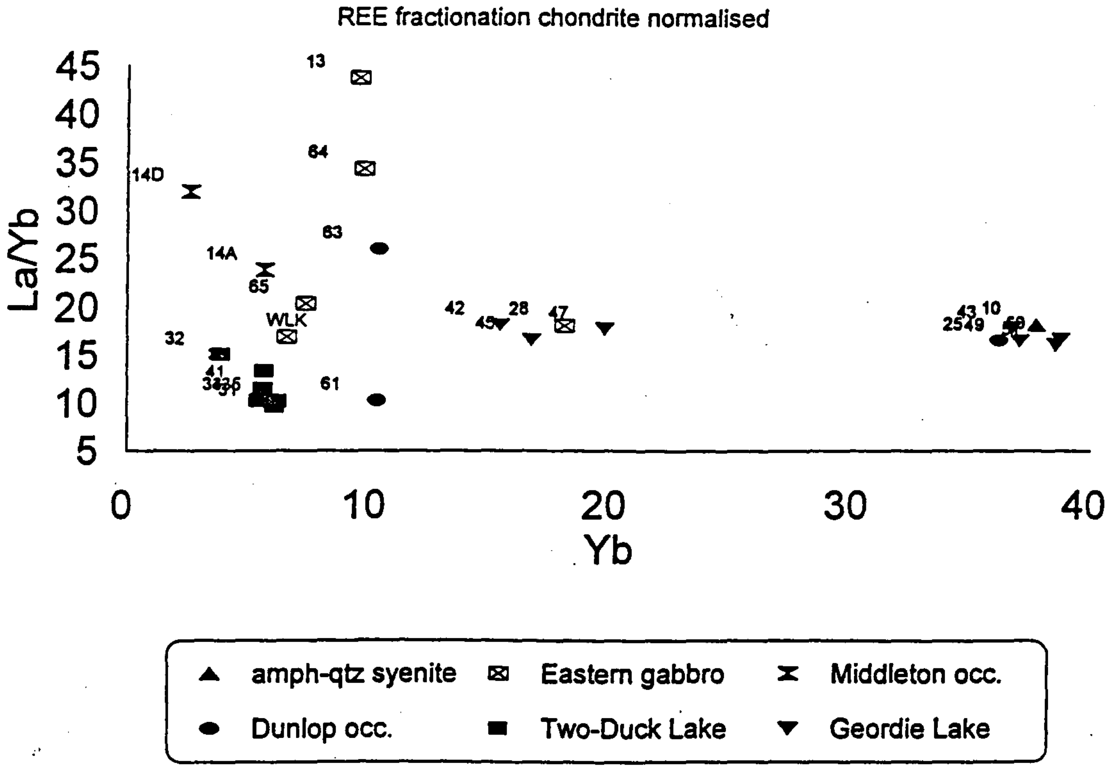


Figure 5.2.2.1.2: La/Yb versus Yb REE fractionation diagram for the Coldwell complex.

Indicative in figures 5.2.2.1.1 and 5.2.2.1.2 is a fractionation trend which clearly indicates that the Two-Duck Lake, Middleton, and Dunlop samples are fractionated with respect to the REE whereas the Geordie Lake rocks are not appreciably fractionated with respect to one another, i.e.; they exhibit large variations in La/Yb ratio relative to Geordie Lake. This may just reflect the relatively close sampling density of the Geordie Lake samples, or it may illustrate that some petrological process is operating in the other three mineralised areas which is not operating at Geordie Lake. Fractionation is often controlled by mineralogy, for example fractionation of the LREE relative to the HREE is generally caused by the presence of orthorhombic or monoclinic pyroxene or olivine. The observed fractionation in the Coldwell samples is in agreement with both the hydrothermal nature of alteration at the sample locations (from petrologic descriptions of petrographic thin-sections) and the observed mineralogy. Apatite, which exhibits a very high partition coefficient, will preferentially fractionate the MREE as will sphene.

It should be noted that Mulja and Mitchell (1990) and Good and Crocket (1994) suggest that hydrothermal alteration occurred at Geordie Lake, which resulted in the formation of albite pods and microdykes in the magnetite-gabbro. This study did not sample areas which displayed obvious petrological evidence of hydrothermal alteration in the case of the MacRae occurrence at Geordie Lake, and as such, the REE analyses of these samples would not reflect any fractionation caused by the late stage hydrothermal alteration which resulted in the development of the albite pods. Observed REE fractionation in the Two-Duck Lake intrusion can be attributed to the high amounts of F and Cl (table 5.4.1) present in these rocks, since REE in a melt are soluble in the presence of these halogens.

REE diagrams can be used to show the degree of fractionation between different rocks which have undergone varying degrees of magmatic evolution. Figure 5.2.2.1.3 illustrates the REE patterns of deposits situated in different intrusive centres in the Coldwell complex. Normalisation is to average chondrites following the schemes of Nakamura (1971) with additions from Haskin *et al.*, (1968). The diagrams show that slightly different REE patterns exist for rocks from the various intrusive centres of the Coldwell complex, reflecting their different crystallisation histories and chemical compositions. For example; all areas display moderately steep patterns, with the exception of Geordie Lake which appears to flatten out in the MREE because of an increase in the LREE and MREE, yielding a relatively pronounced concave upwards trend. This can likely be attributed to the presence of apatite which segregates the MREE, and olivine and clinopyroxene which fractionate the LREE. The observed fractionation is not extreme because in liquids of basaltic composition, the REE are relatively incompatible in the aforementioned minerals (Rollinson, 1993). Also of interest is the observation that the Two-Duck Lake samples display a much lower REE concentration than the other mineralised rocks. The reason for this is not clear, although one might speculate that the REE are concentrated in some later crystallising phase such as the granophyre which is present in the Two-Duck Lake gabbro. This may be a result of the high halogen content of the gabbro which may have enabled the REE to mobilise and become incorporated into the granophyre.

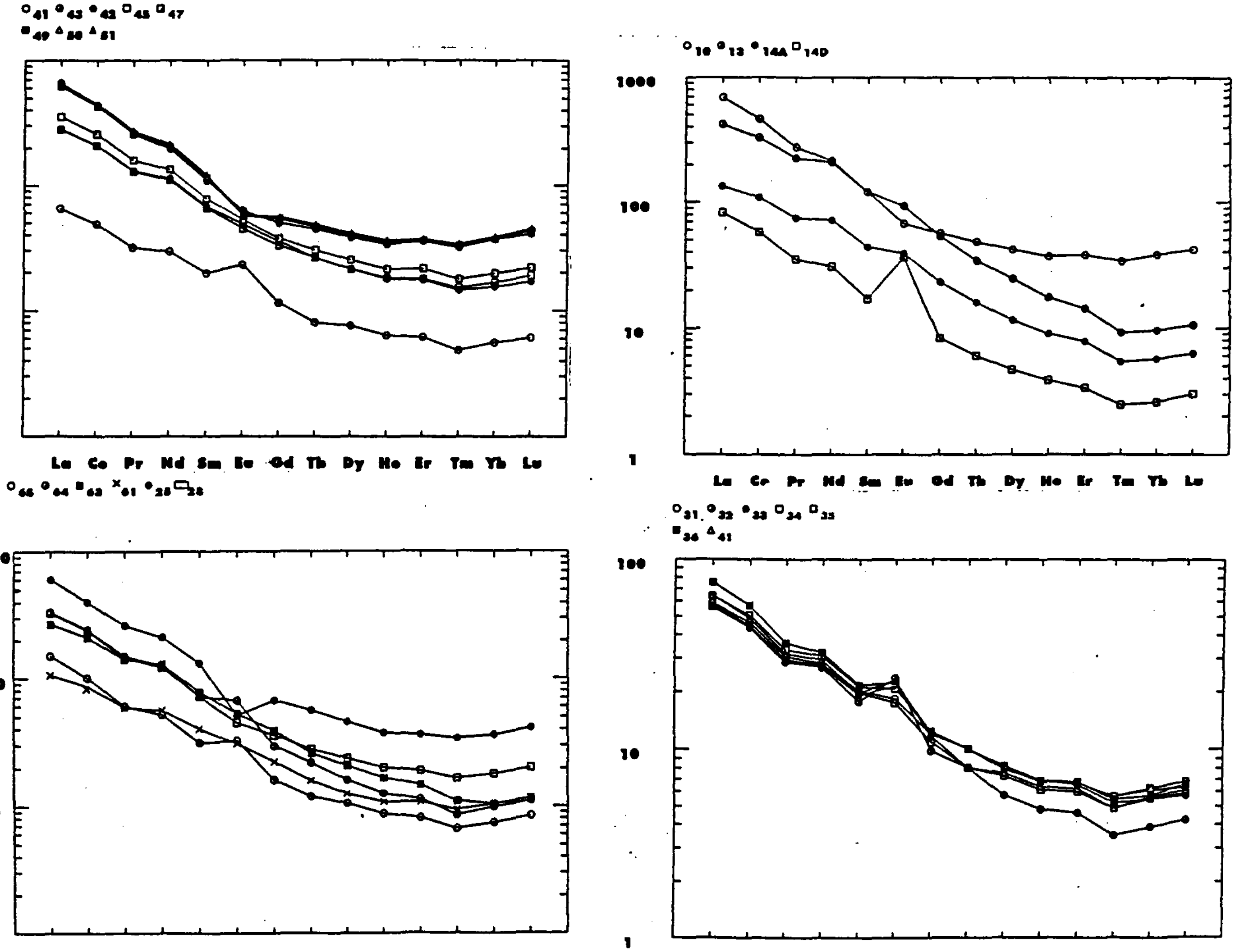


Figure 5.2.2.1.3: REE patterns for rocks from various intrusive centres, Coldwell complex (concentrations in ppm).

As alluded to in chapter 5, section 1; primitive mantle can be ruled out as a source of material for the Coldwell complex on the basis of the Zr/Y, La/Yb, Th/Ta, and Hf/Th ratios of the complex which do not emulate those of the primitive mantle. Table 5.2.1 illustrates that in fact, that the La/Yb and Hf/Th ratios of the Coldwell complex rocks vary greatly from those of the primitive mantle whereas the Th/Ta and Zr/Y ratios vary slightly from those of the primitive mantle as defined by Taylor and McLennan (1985).

Sample	Ta	Hf	Zr	Y	Th	La	Yb	Zr/Y	La/Yb	Th/Ta	Hf/Th
10	13.00	16.80	710.87	73.90	34.12	226.99	8.29	9.62	27.38	2.62	0.49
13	2.70	1.60	64.71	33.60	3.48	138.25	2.11	1.93	65.52	1.29	0.46
14A	0.97	0.76	26.34	18.40	1.38	44.46	1.25	1.43	35.57	1.42	0.55
14D	1.30	0.86	37.59	7.70	2.21	27.29	0.57	4.88	47.88	1.70	0.39
25	8.10	10.80	473.14	74.60	22.56	198.46	7.95	6.34	24.96	2.79	0.48
28	4.70	6.40	259.54	41.10	12.36	108.47	3.99	6.31	27.19	2.63	0.52
31	0.91	1.40	48.41	13.30	1.97	19.47	1.34	3.64	14.53	2.16	0.71
32	1.30	0.75	24.87	9.50	0.90	19.20	0.85	2.62	22.59	0.69	0.83
33	1.20	1.30	46.20	12.90	1.34	18.50	1.20	3.58	15.42	1.12	0.97
34	0.88	1.30	45.78	11.90	1.67	18.53	1.20	3.85	15.44	1.90	0.78
35	1.40	1.40	50.28	12.90	1.98	21.12	1.37	3.90	15.42	1.41	0.71
36	1.10	1.60	56.44	13.50	2.02	25.00	1.25	4.18	20.00	1.84	0.79
41	0.83	1.10	37.09	12.20	1.06	21.33	1.23	3.04	17.34	1.28	1.04
43	13.00	16.30	651.29	65.90	33.87	216.70	8.07	9.88	26.85	2.61	0.48
42	3.70	3.00	144.86	35.90	9.18	92.58	3.40	4.04	27.23	2.48	0.33
45	4.50	4.00	180.40	36.10	9.70	91.85	3.68	5.00	24.96	2.16	0.41
47	4.90	5.00	231.06	42.40	11.31	115.88	4.35	5.45	26.64	2.31	0.44
49	10.80	11.60	476.89	66.70	26.66	201.88	8.14	7.15	24.80	2.47	0.44
50	11.50	12.60	521.38	70.20	29.18	213.61	8.52	7.43	25.07	2.54	0.43
51	11.30	12.40	510.55	66.90	28.51	204.76	8.48	7.63	24.15	2.52	0.43
61	0.64	1.80	61.78	21.50	2.74	35.03	2.27	2.87	15.43	4.28	0.66
63	1.50	1.00	47.21	33.50	3.28	88.60	2.28	1.41	38.86	2.19	0.30
64	4.70	3.30	143.52	24.50	4.13	110.59	2.15	5.86	51.44	0.88	0.80
65	1.40	1.30	44.04	16.00	1.02	49.48	1.62	2.75	30.54	0.73	1.27
WLK	0.74	0.94	30.08	19.00	0.91	36.83	1.45	1.58	25.40	1.23	1.03
prim. mantle; T&M, (1985)	0.04	0.27	8.30	3.40	0.06	0.55	0.37	2.44	1.48	1.60	4.20

Table 5.2.2.1: Trace element data for the Coldwell complex (analysed by ICP, reported in ppm) and trace element concentrations of the primitive mantle from values published by Taylor and McLennan, (1985).

5.2.2.2 Spider diagrams

Incompatible element diagrams or spider diagrams (spidergrams) can indicate departure of a magma composition from a primitive composition. In the scope of this study, chondrite normalised diagrams are preferred to primitive mantle or MORB-normalised diagrams. These diagrams have an advantage over REE diagrams in that mobile elements can be characterised. The large ion lithophile elements (LIL); Cs, Rb, K, Ba, Sr, and Eu may be enriched due to a fluid phase or contamination with continental crust whereas the less mobile high field strength elements (HFS); Y, Hf, Zr, Ti, Nb, and Ta are controlled by the composition of the source, and evolution which that source has undergone (Rollinson, 1993).

A useful indicator of crustal contamination is niobium concentration. Negative Nb anomalies are characteristic of the continental crust (Rollinson, 1993). Nb is concentrated in titanite, ilmenite and rutile, and crustal rocks tend to display negative Nb anomalies. A negative Nb anomaly may belie the involvement of continental crust. Figure 5.2.2.2.1 is a compilation of extended element spider diagrams for the various rocks of the Coldwell complex. As can be seen from the spider diagrams of the various locales in the complex, no significant Nb anomaly exists. This can be interpreted as further evidence for a lack of significant crustal involvement in the genesis of the complex. In fact, the more evolved Centre 3 rocks which one might expect to show some slight evidence of contamination due to longer residence times in the crust exhibit no Nb anomaly. The Two-Duck Lake intrusion displays a slight positive Nb anomaly which can be interpreted to be a result of the accessory ilmenite present in the Two-Duck Lake gabbro, indicative of a lack of crustal contamination in this assemblage. The troughs observed at Sr for some spider diagrams is a function of fractional crystallisation of plagioclase in these rocks.

Gabbros from the complex display similar extended element trends, while the syenites are markedly different as one would expect. Those samples which show hydrothermal alteration in outcrop also prove to have different extended element plots as is seen in the case of 14D, an intensely altered gabbro in a shear zone only 15 metres north of 14A, a relatively fresh mineralised gabbro. Sample 14D is depleted in incompatible elements with respect to sample 14A (figure 5.2.2.2.1). Other petrographical outcrop-scale assumptions are borne out by observations from spidergrams, such as the fact that the Two-Duck Lake intrusion is more evolved than the Eastern Gabbro which it intrudes. While this may seem to be stating the obvious, it is important to make sure that these simple relationships are proven by geochemical techniques as proof that the techniques themselves are valid and not subject to gross analytical error which could result in the geochemist drawing a tenuous conclusion from the data.

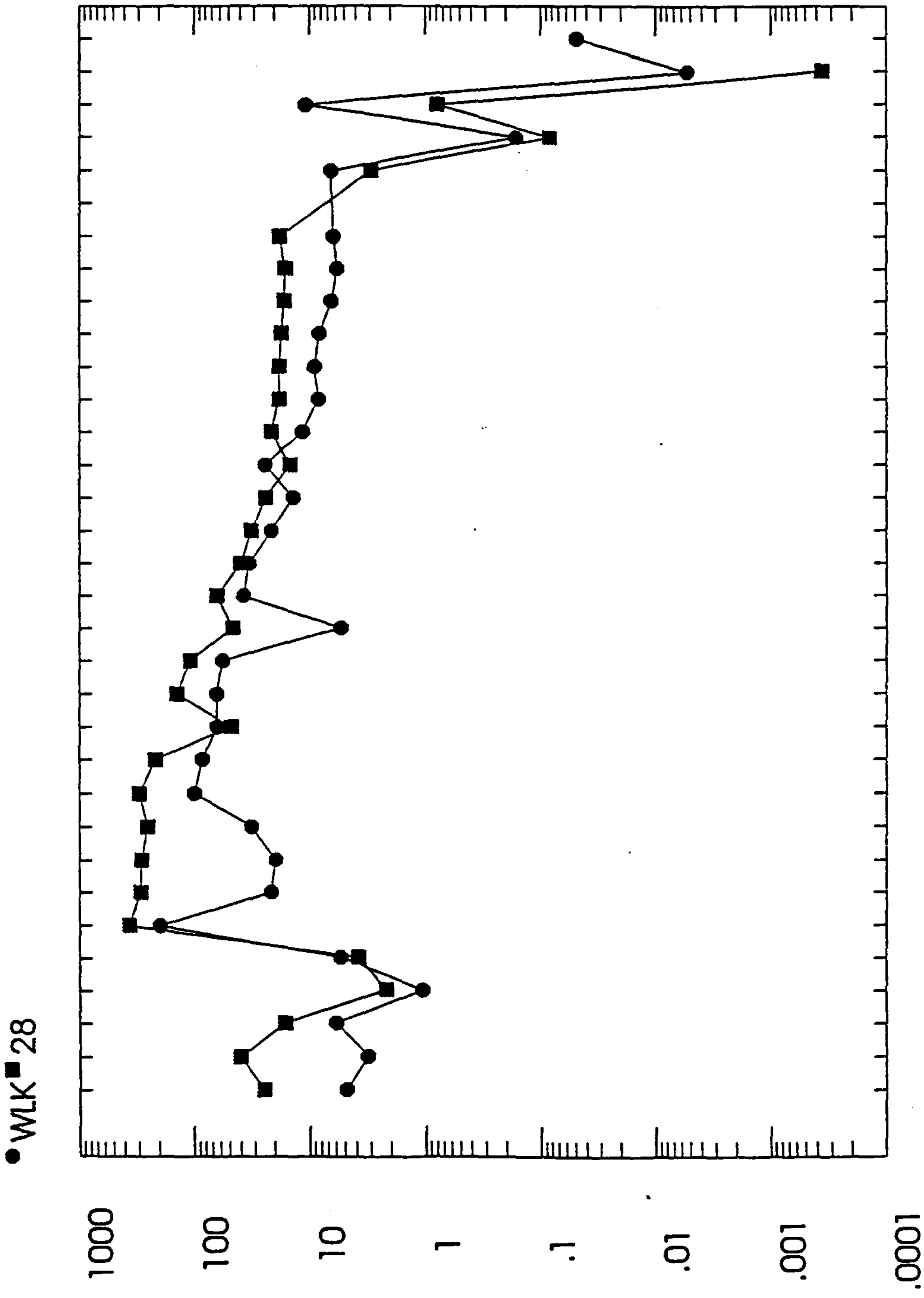


Figure 5.2.2.2.1a: Spider diagrams for Coldwell complex rocks. -Eastern Gabbro

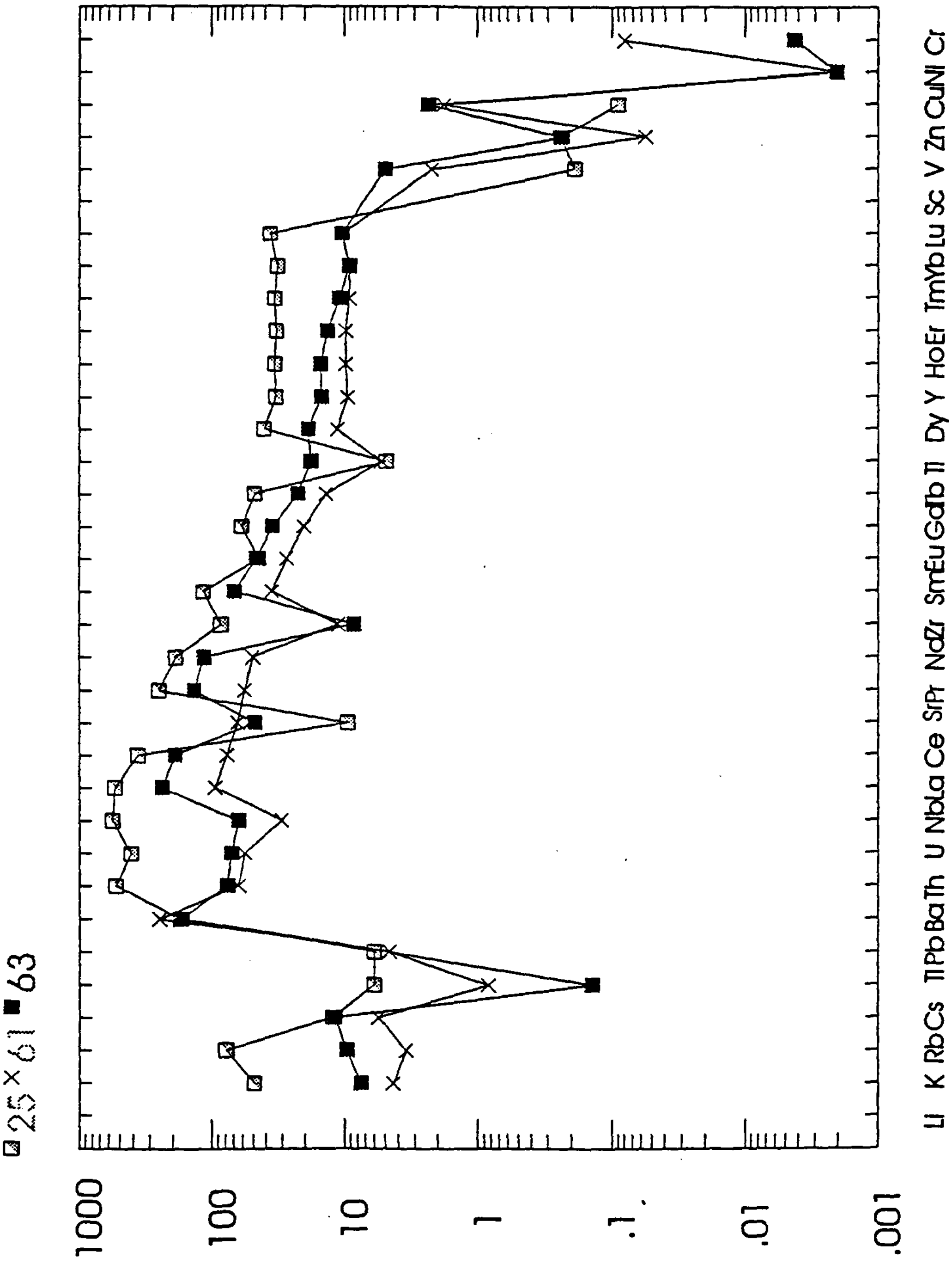


Figure 5.2.2.2.1b: Spider diagrams for Coldwell complex rocks. -Dunlop occ.

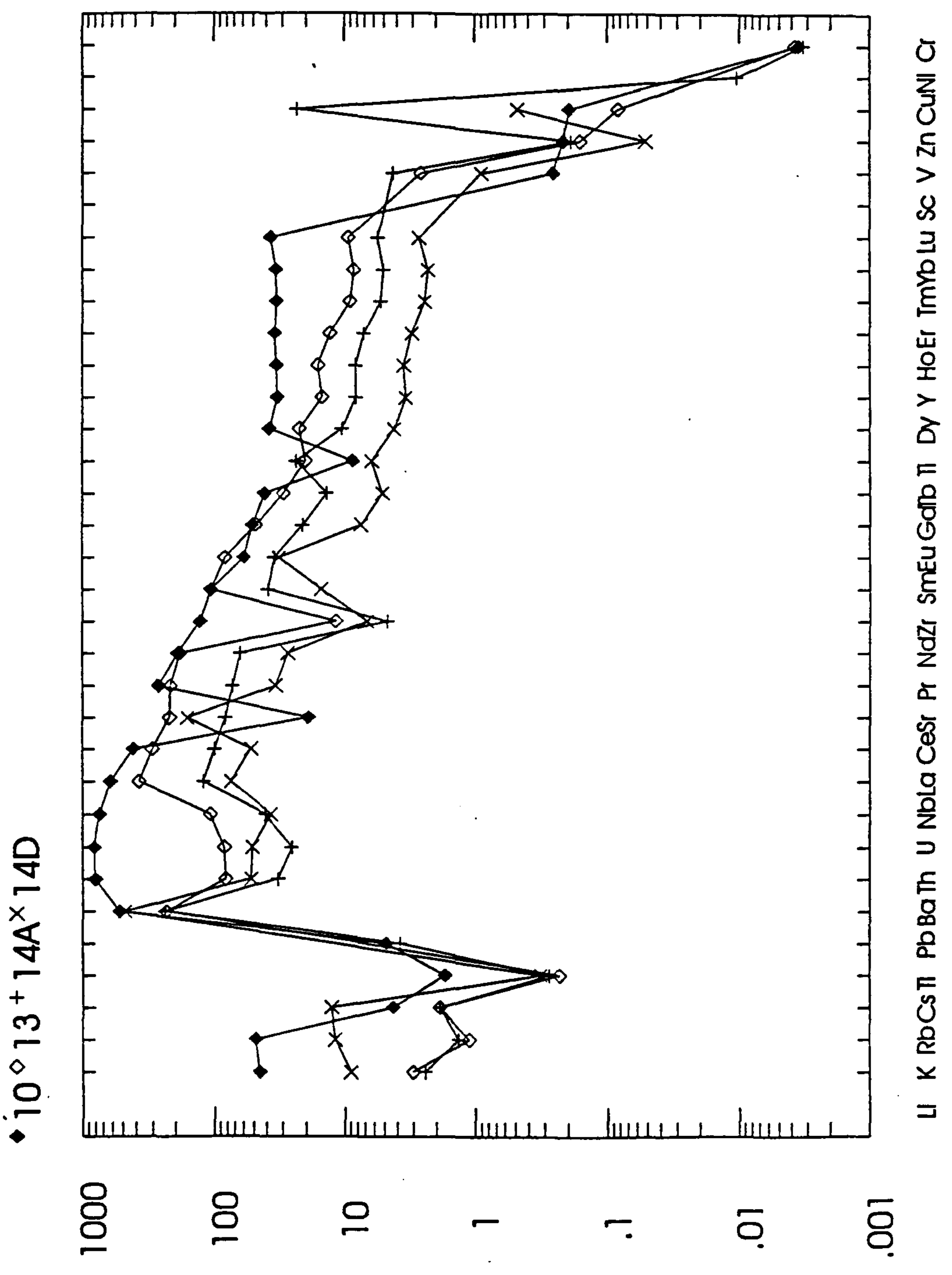


Figure 5.2.2.2.1c: Spider diagrams for Coldwell complex rocks. -Middleton occ.

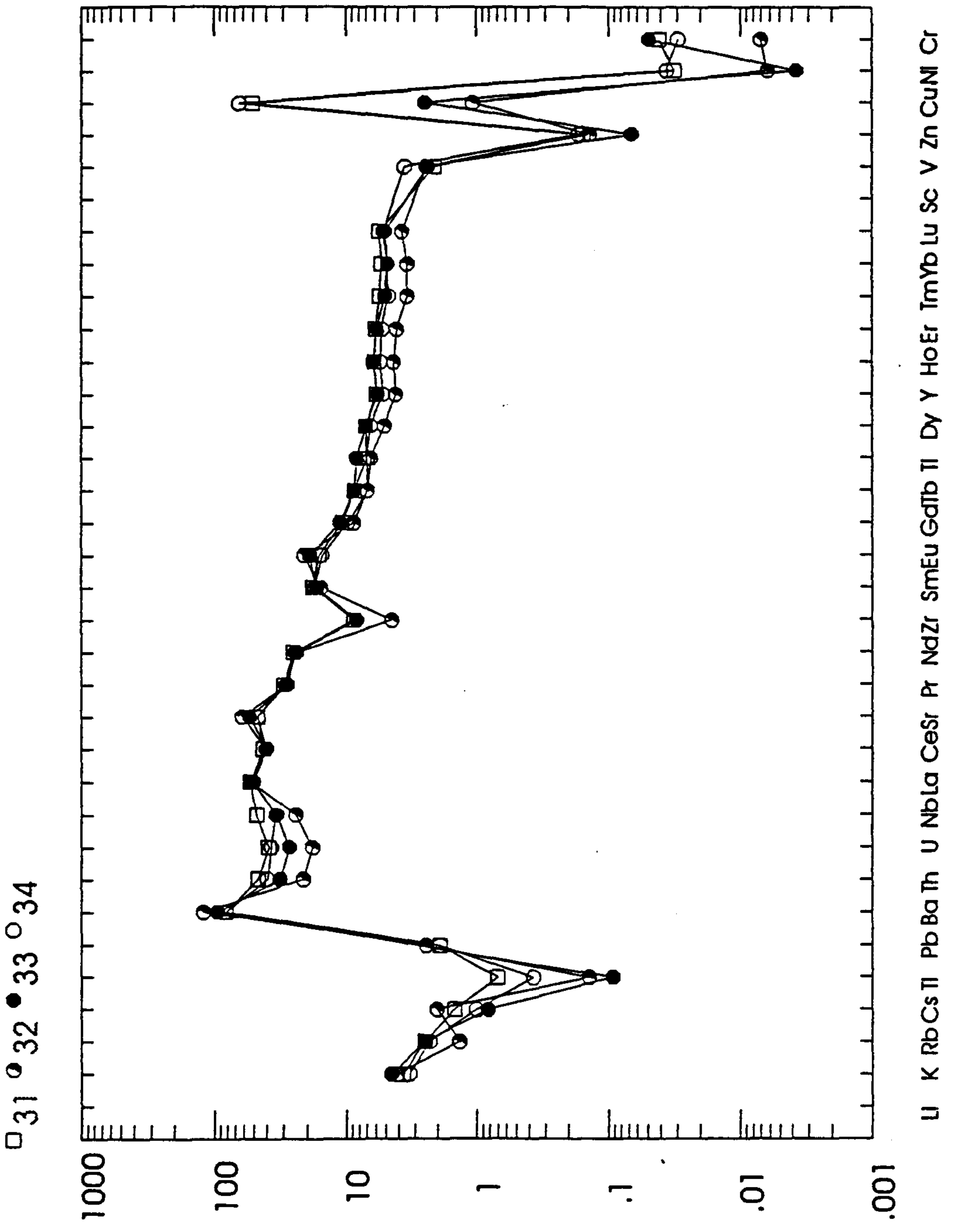


Figure 5.2.2.2.1d: Spider diagrams for Coldwell complex rocks. -Various Two Duck Lake

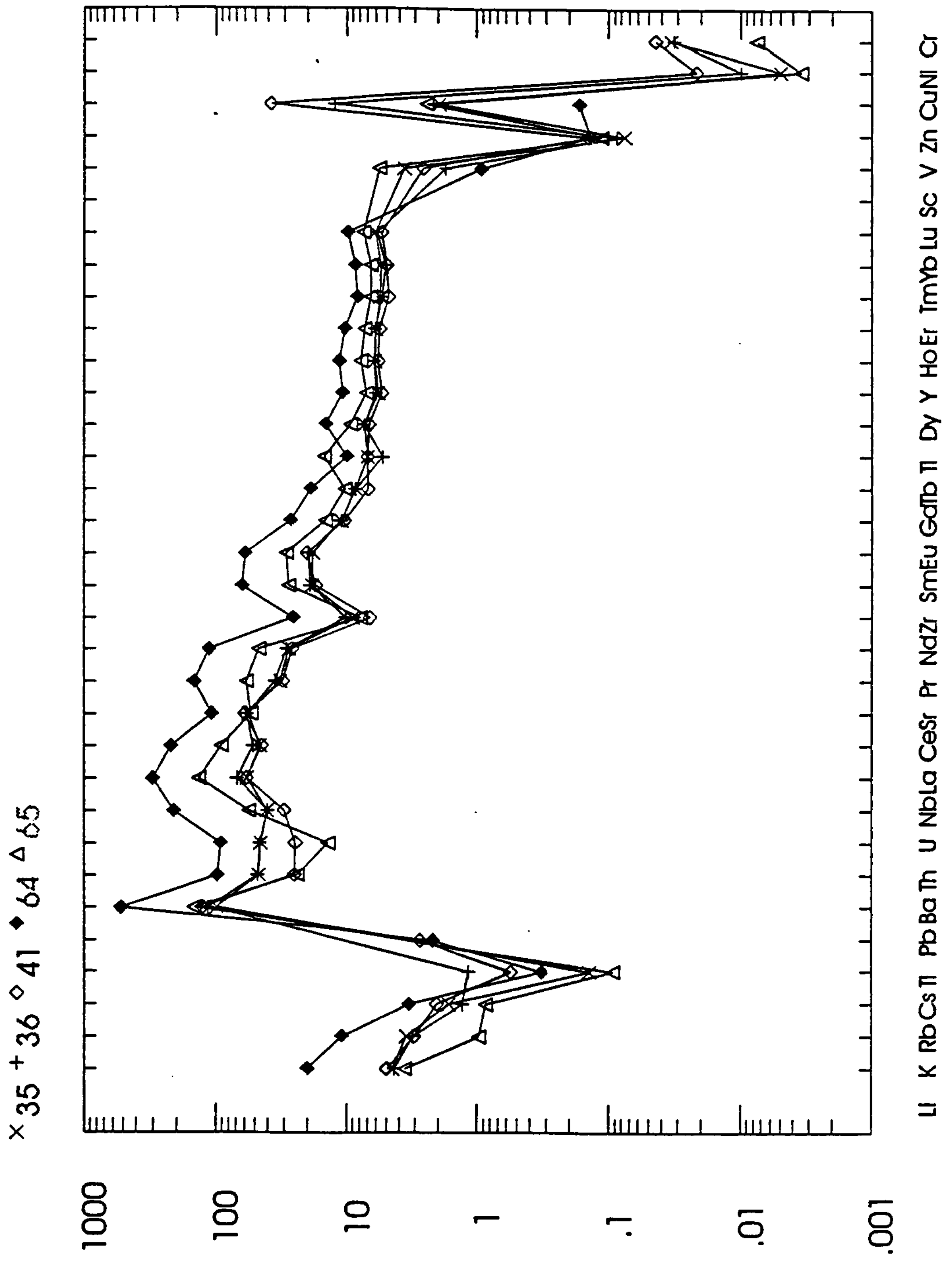


Figure 5.2.2.2.1e: Spider diagrams for Coldwell complex rocks. -Various Two-Duck Lake

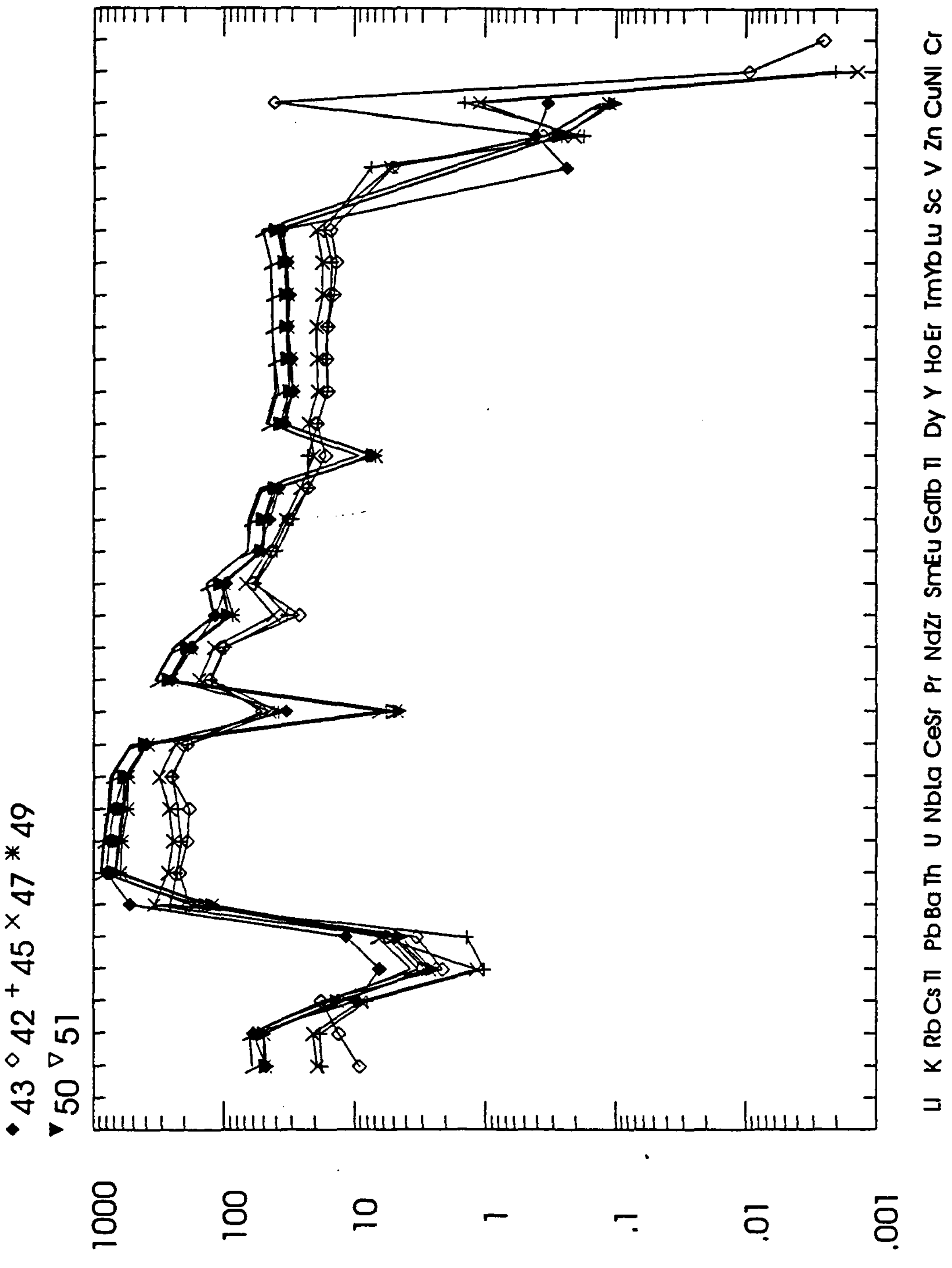


Figure 5.2.2.2.1f: Spider diagrams for Coldwell complex rocks. -Geordie Lake

Trace elements which display extreme behaviour with respect to compatibility are useful in geochemical studies. Bivariate trace element plots can be very useful; especially in determining source heterogeneity such as might arise from contamination. Trace elements which exhibit nearly identical bulk partition coefficients during mantle melting are used in bivariate plots to illustrate the ratio of the elements in the source. The ratio is defined by the slope of a correlation line between the two incompatible trace elements. Variation in the observed ratio is a result of contamination or mixing in the source. One such pair is Cs-Ba (figure 5.2.2.2.2).

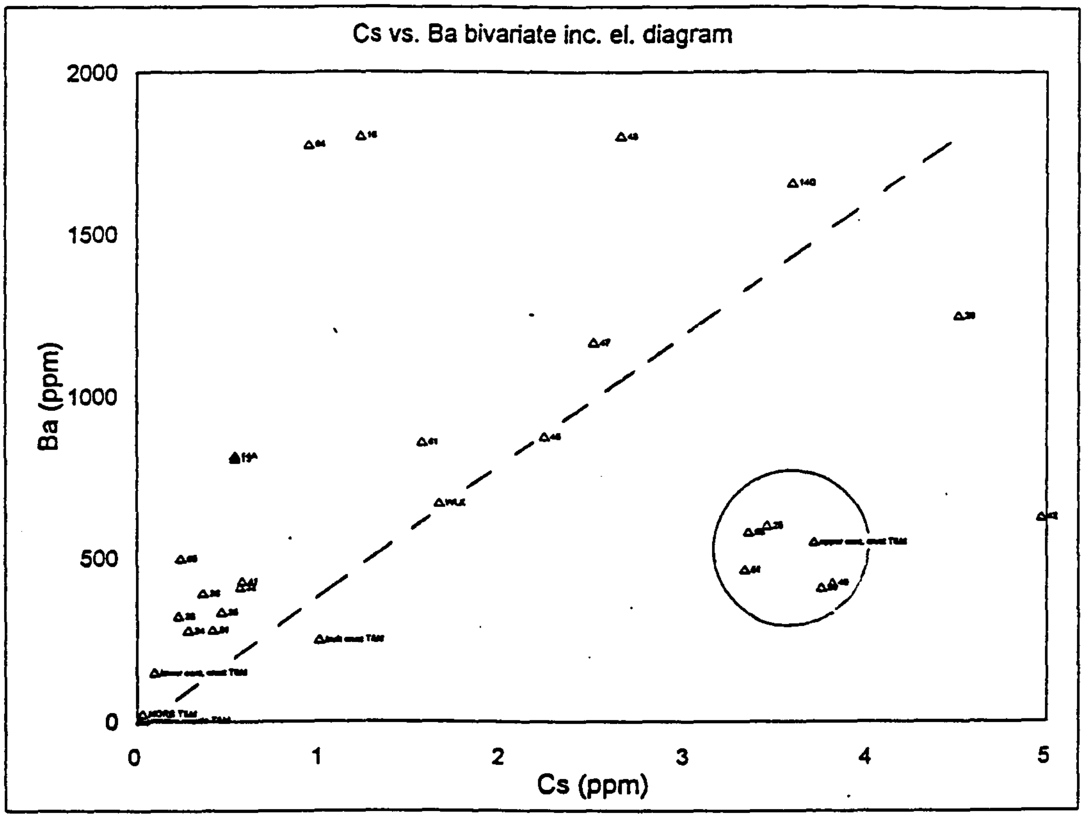


Figure 5.2.2.2.2: Cs-Ba bivariate incompatible element plot.

The previous diagram (figure 5.2.2.2.2) indicates that while some samples fall on the array defined by homogeneous source rock, other samples, specifically visibly altered Geordie Lake gabbro and some Dunlop occurrence samples, lie off of the trend and appear to cluster around the values observed for the general values suggested for the upper continental crust by Taylor and McLennan, (1985). While not conclusive evidence, this may indicate that some small-scale local crustal contamination took place. It is important to note that while crustal contamination is not a major contributor to the evolution of the Coldwell complex, some small-scale assimilation of country rock must have occurred, especially in the more evolved rocks which have spent the longest duration of time in the crust, and those gabbros which have intruded at the periphery of the ring structure.

5.2.2.3 Potential contributors to MCR and Coldwell complex magma

Geochemists often try and delineate compositional fields of potential contributors to a magma to demonstrate the source of the contributing melts as for example in the case of the plume-dominated lavas of the Yampa area of the Rio Grande Rift (Leat *et al.,* 1991). In order to apply this approach to the Coldwell complex, some typical end member compositions were be chosen for the possible contributing melts. These include an OIB source to define the composition of the enriched plume component, for which global estimate for OIB from Sun, (1980) will be used. Also important is the composition of the potential assimilant (continental crust) in the local area. Unfortunately the composition of relevant local crust is problematic for several reasons: 1) the intrusion is funnel shaped and therefore the composition of the crust at the contact with the complex at the present erosional level may not accurately reflect the composition of the assimilant, 2) the crust which the rift magmas intrude is not uniform, but consists of Archaean granite-greenstones, and sediments as well as early Proterozoic crust, causing further complications. In addition to difficulty in determining the nature of upper crust which may have been assimilated, it should also be noted that lower crust may have also contributed to the generation of the complex. Often, lower crustal composition can be deduced from xenoliths. No xenoliths have been identified in the Coldwell complex and as a result, approximate trace element values for lower crust from Taylor and McLennan (1985) are utilised. Another possible contributor to the plume-derived magmas which formed the rocks of the MCR is lithospheric mantle. Leat *et al.,* (1991) used a contemporaneous minette from the Yampa area to define the composition of lithospheric mantle in the area. For the MCR, Mesoproterozoic Nipigon dykes of the Keweenawan dyke swarm which were emplaced coevally with the rift volcanism may best approximate the lithospheric mantle in the area. These dykes have been investigated by Sutcliffe (1986) who found them to have enriched trace element signatures, suggesting that they too have been influenced by plume-derived magmas. Since these dykes appear to be influenced by the plume they would not prove to be very useful in the context of a 'window' into the lithosphere. The next best assumption is to assume that the Mesoproterozoic Abitibi dyke swarm dated at 1140.6±2Ma, Krogh *et al.*, (1987) is representative of the lithospheric upper mantle in the area. This dyke swarm trends east-northeast and is related to Keweenawan rifting. The dykes appear to fan out from the rift centre, and as such are thought to be related to the very earliest Keweenawan stratigraphy (Osmani, 1991). These dykes also exhibit signs of enriched elemental abundances (Osmani, 1991) indicating involvement with the plume as well. Finally we turn to the carbonatite complexes in the rift. Bell and Blenkinsop (1986) investigated the isotopic compositions of several of the carbonatites and show that their observed ϵNd values range from depleted mantle to CHUR. The carbonatite development lines intersect the bulk Earth and CHUR development lines at 2900 Ma, suggesting that a LIL-depleted reservoir formed as the residual material after genesis of the Superior Province granitoids. This reservoir is thought to represent subcontinental lithospheric mantle (Bell and Blenkinsop, 1986). Subsequent enrichment of LREE prior to carbonatite eruption is indicated by the lower Sm/Nd ratios observed for the carbonatites compared with their initial ratios which define the source. The Nd ratios for the carbonatites lie very near to the end member of OIB, interpreted by Bell and Blenkinsop (1986) to mean that lithospheric delamination may generate some oceanic islands. Therefore a reasonably accurate analogue of lithospheric mantle in the area does not seem to exist in outcrop since LREE enrichment of the carbonatites, which are thought to represent lithospheric mantle, results in a geochemical signature which is no longer representative of the source. As a result of these difficulties in obtaining chemical data on representatives of upper crust (likely primary assimilant), lower crust, and lithospheric mantle for the MCR, petrogenetic modelling for the MCR such as performed for the Rio Grande Rift (Leat *et al.*, 1991) will be less definitive. This is primarily because of the numerous assumptions that must be made. Nevertheless the fields defined by the broad, averaged data available may provide some clues as to the genesis of the rocks of the MCR. This may be especially true with regard to the contribution of the lower crust.

Nicholson and Shirey (1990) compiled parameters for the εNd values of the above mentioned reservoirs at 1095 Ma which they used to support their argument for the involvement of a plume to initiate and sustain rifting and resultant tholeiitic and alkaline magmatism. These parameters are listed in table 5.2.2.3.1.

Reservoir	**εNd**
depleted mantle-DM	+5.7 to +7
enriched mantle-EM	-3 to +3
Archaean lower crust-ALC	-12 to -17
Archaean upper crust-AUC	-12 to -17
Proterozoic upper crust-PUC	-7 to -14

Table 5.2.2.3.1: Estimated ranges of εNd for various model reservoirs at 1095 Ma. From Nicholson and Shirey (1990), DM-estimated from constant mantle evolution from 0 at 4.5 Ga to +10 at present. EM-estimated from the systematic difference between OIB and MORB. ALC and AUC-calculated from data from the Rainy Lake area and the Vermillion District of the Wawa subprovince (Shirey and Hanson, 1986). PUC-estimated from mid-Proterozoic mafic volcanic rocks (Horan *et al.*, 1986).

Chondrite-normalised REE plots are characterised by moderately steep and flat LREE slopes with concave upwards trends in the MREE (figure 5.2.2.1.3), with La_N/Yb_N ratios in the range 10-44, all features peculiar to alkaline mafic magmas generated by small-scale partial melting of a garnet-bearing peridotite source (Alibert *et al.,* 1983 as cited in Leat *et al.,* 1991). However, just as in the Yampa lavas, the Coldwell magmas exhibit highly variable incompatible element signatures. Ratios of two incompatible elements show a wide range of dispersion which cannot even be explained in the context of differentiation as evidenced when they are plotted against the K_2O/Na_2O ratio (refer to figure 5.2.2.3.1). Leat *et al.* (1991) plot La/Ta versus the ratio of K_2O/Na_2O to define geochemical fields for their proposed source rocks including, an OIB source, crustal components and lithospheric mantle. Complete La and Ta data does not exist for the lavas of the MCR and therefore other incompatible element ratios for which complete data does exist are used in the place of La/Ta. Specifically, Zr/Hf is plotted against K_2O/Na_2O to define fields for the MCR. Again, an adequate proxy for lithospheric mantle does not exist in this area, since all likely candidates display enriched OIB-like signatures, so the values for the lithospheric mantle field cannot be estimated. Likewise, only average values for upper and lower crust as defined by

Taylor and McLennan (1985) can be plotted. The plot of Zr/Hf versus K_2O/Na_2O illustrates that some of the Fe-augite syenites of centre 1 cluster around the field defined by upper continental crust.

As a result of spotty trace element data gleaned from the literature with respect to the geochemistry of the end members in question, new discriminators had to be sought out. Trace element data which exists for all fields is scarce, however sufficient data does exist for Ba, Rb, Zr, and Nb concentrations. It was decide to plot ratios of these incompatible elements against one another to try and delineate some geochemical fields on the basis of the composition of potential end members. Figure 5.2.2.3.2 is such a plot and it indicates that some broad geochemical fields can be drawn for the rocks of the Coldwell complex, and the Partridge River intrusion (Grant and Chalokwu, 1992). These chemical fields can then be related to the composition of relevant end members. It can be seen that the Partridge River intrusion gabbros cluster in the vicinity of values for the average lower continental crust and for the average carbonatite intrusion in the area, as well as the average primitive mantle values. If the average carbonatite values are taken to represent lithospheric mantle as is suggested by Bell and Blenkinsop (1986), then it may be postulated that the Partridge River gabbroic-troctolitic intrusion may have its origin in the

the upper mantle, which may have assimilated lower crust to yield an enriched signature similar to primitive mantle. The Coldwell complex rock values all cluster around the values for OIB and a sample of the Prairie Lake carbonatite, and it is possible that some mixture between enriched mantle plume-magmas and lithospheric upper mantle may have acted to form the rocks of the Coldwell complex.

The next logical step is to incorporate the isotopic analyses into these diagrams to further define the fields observed in the trace element data. Leat *et al.* (1991) plotted neodymium ratios versus strontium ratios to delineate end member fields. Strontium analyses were not performed during this study, and the oxygen isotope ratios are subject to too much change as a result of metamorphism and diagenesis to be useful in this context so it was decided to turn to a plot of Zr/Nb versus ϵNd to try and define fields for the end members in question (figure 5.2.2.3.3). This figure shows that the majority of the Coldwell complex rocks cluster at CHUR and a Zr/Nb ratio of between 2 and 3. It is conceivable that an enriched mantle source formed the Coldwell complex rocks which were then variably contaminated with lithospheric upper mantle (represented in this case by carbonatite compositions) and upper crust. Epsilon Nd values for lower crust in the region are not available. It must be pointed out that the carbonatite magmas seem to exhibit enriched trace element signatures making it possible that these magmas also interacted with plume material and as such do not accurately reflect the geochemistry of the sub-continental lithospheric mantle in the area.

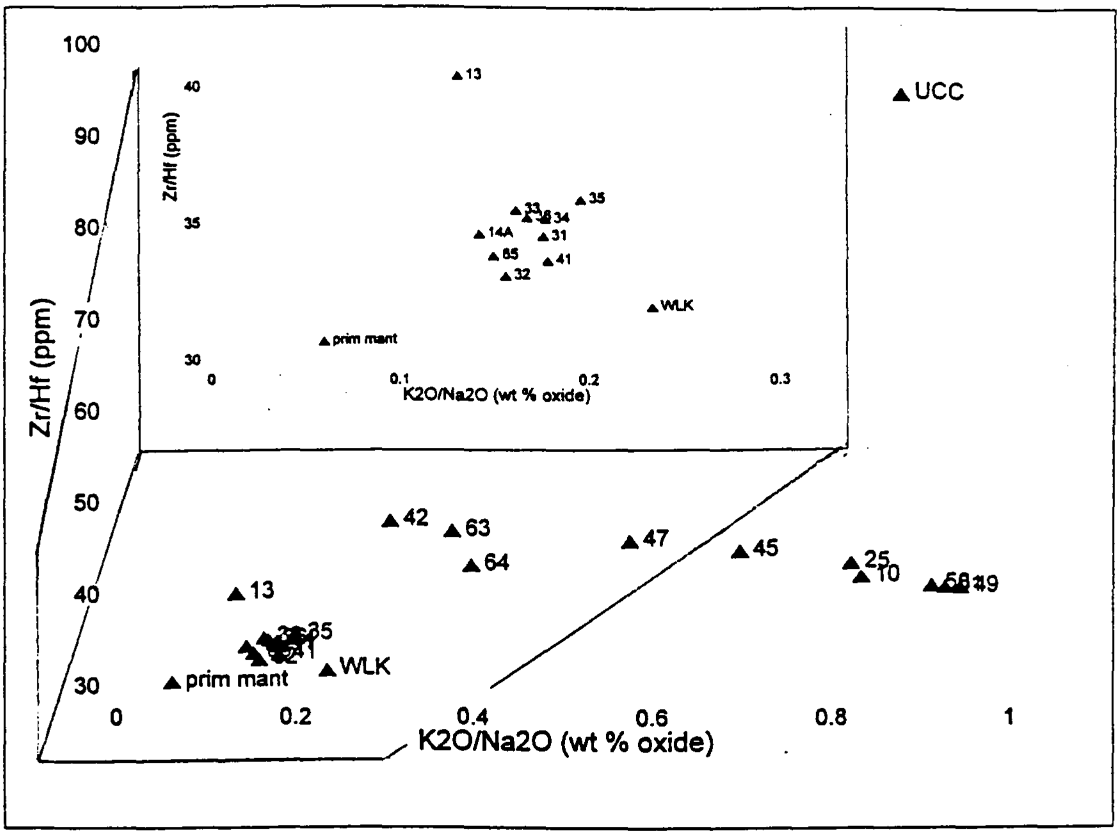


Figure 5.2.2.3.1: K_2O/Na_2O versus incompatible element ratios for Coldwell complex magmas and MCR volcanic rocks as well as for Loihi basanites and alkali basalts (Frey and Clague, 1983 as cited in Leat *et al.*, 1990).

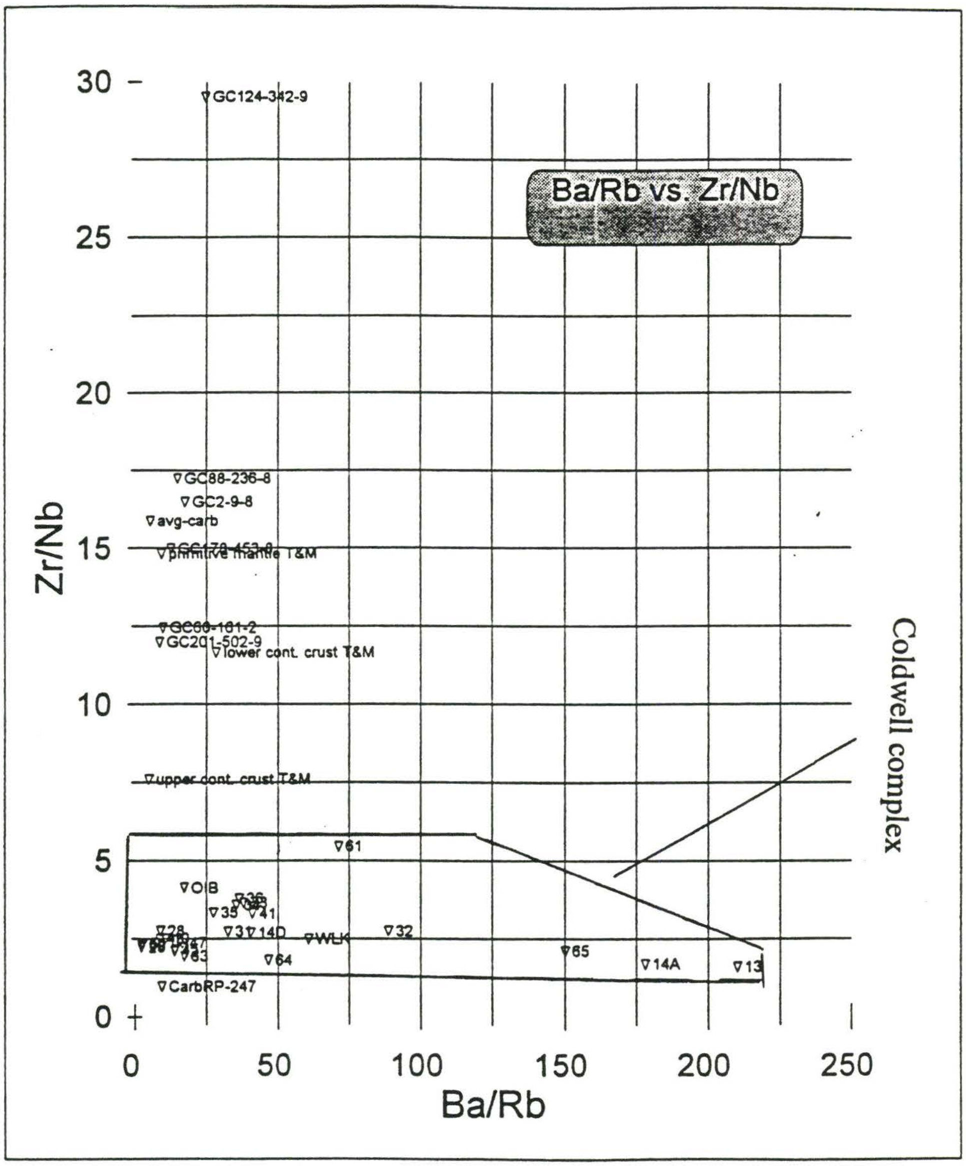


Figure 5.2.2.3.2: Ba/Rb vs. Zr/Nb for rocks of the Coldwell complex, the Partridge River intrusion (Grant and Chalokwu, 1992), average and specific Prairie Lake carbonatite (Sage, 1987), and average crustal values from Taylor and McLennan (1985), as well as average OIB data from Sun, (1980).

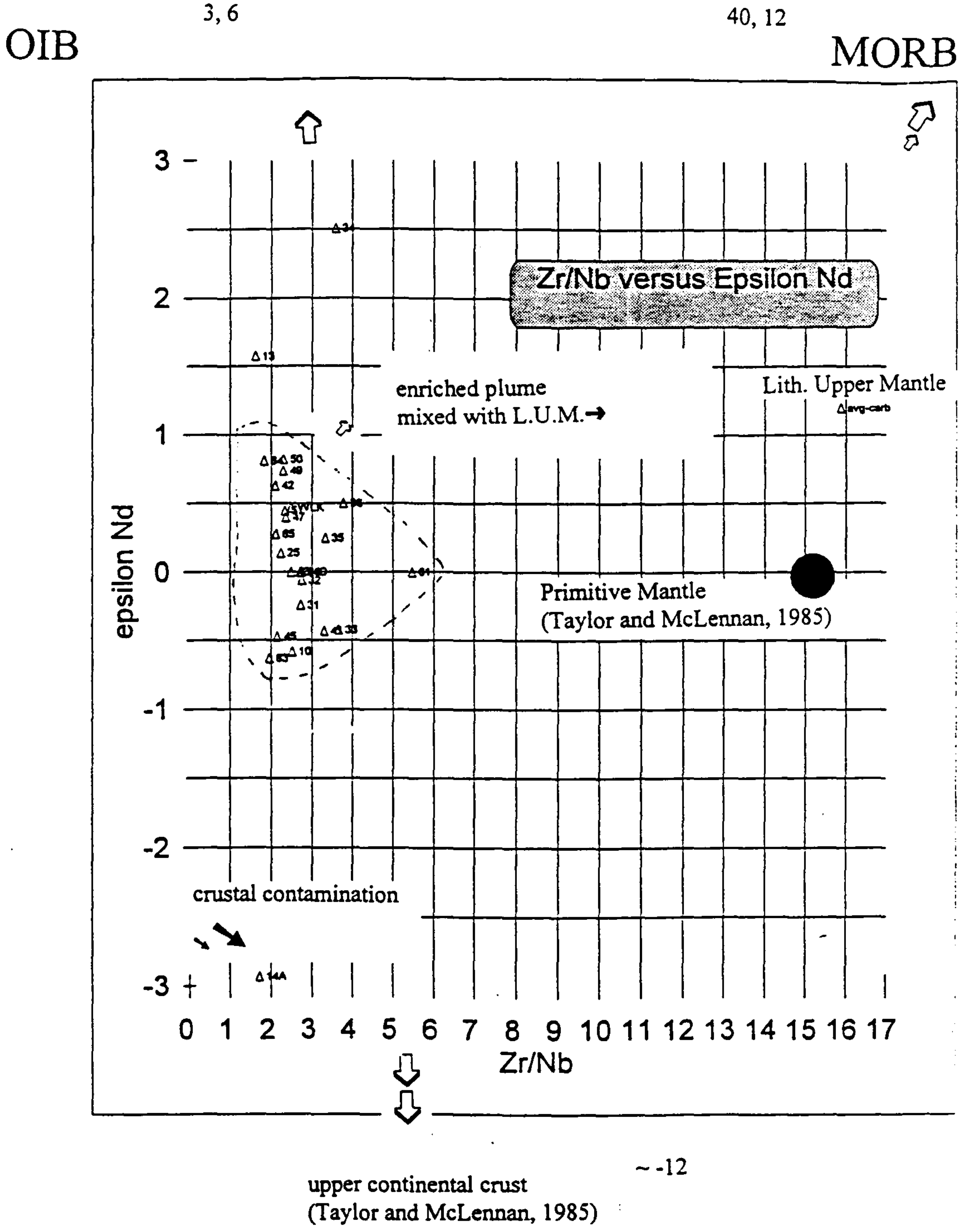


Figure 5.2.2.3.3: Zr/Nb vs. εNd for rocks of the Coldwell complex and end member magmas. Epsilon Nd data for the average Prairie Lake carbonatite is from Bell and Blenkinsop, (1987). OIB Nd data from Leat *et al.*, (1991).

5.2.2.4 Enrichment-depletion diagrams

Another useful tool available to geochemists is the major and trace element enrichment-depletion diagram which can be used to display element mobility in alteration zones and to illustrate evolution in related igneous rocks. Figure 5.2.2.4.1 is a bar graph denoting the difference in elemental abundances between sample 10 (Centre 3 quartz syenite) and sample 65, a Centre 1 gabbro. The elemental abundances of 10 was divided by the abundance of the corresponding element in 65. If the resulting number is greater than 1 sample 10 is enriched in that element relative to sample 65, if it is less than 1 sample 10 is depleted with respect to sample 65. The graph indicates that fractional crystallisation rather than other methods of elemental segregation such as alteration were responsible for the enrichment of the quartz syenites relative to the unaltered gabbro which is thought to be one of the earliest evolved rocks. This is especially evidenced by the series Ta-Zr which although relatively inert under alteration conditions are enriched in this case.

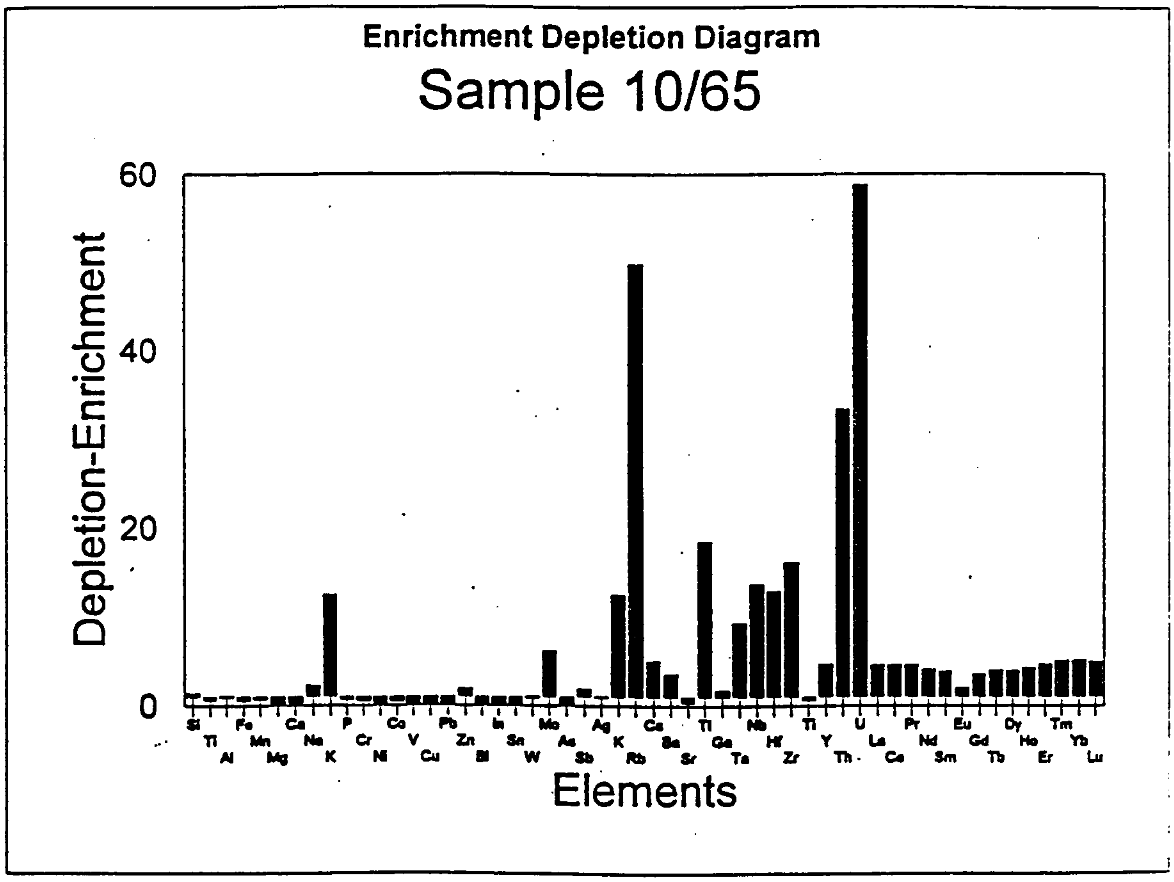


Figure 5.2.2.4.1: Enrichment-depletion diagram between sample 10 (quartz syenite, Centre 3) and sample 65 (gabbro, Centre 1).

5.2.3 Isotopic ratios versus elemental ratios

Because isotopic ratios cannot be fractionated by crystal-liquid equilibria so that they are representative of the magmatic source, correlation between isotopic ratios and major or trace elements can be indicative of major or trace element source composition (Rollinson, 1993). As is mentioned in section 3.1, two or more measured variables are required (Dickin, 1995), to discern between compositionally distinct sources in mixing environments with more than one degree of freedom. Ratios of highly incompatible trace or major elements are particularly useful, with correlations between the incompatible element ratio and the initial Nd ratio being indicative of crustal contamination. Figure 5.2.3.1 is a plot of K/Zr (a ratio between a highly incompatible and a moderately incompatible element) versus epsilon Nd. As can be seen from the diagram, a good correlation does not exist between the Nd isotopic ratio and the elemental ratio which returns a Pearson correlation coefficient of r= -0.22. If the two outliers (14A mineralised western gabbro, Centre 1; and 34 mineralised Two Duck Lake intrusion, Centre 1) are removed the coefficient of correlation does not significantly improve (r= -0.31). This further indicates that crustal contamination was not a significant factor in the genesis of the Coldwell complex magmas. A test for correlation between epsilon Nd and the following incompatible element ratios; Rb/Nb, Ba/La, Th/La, Zr/Nb was carried out and no significant correlation was found (see figure 5.2.3.2).

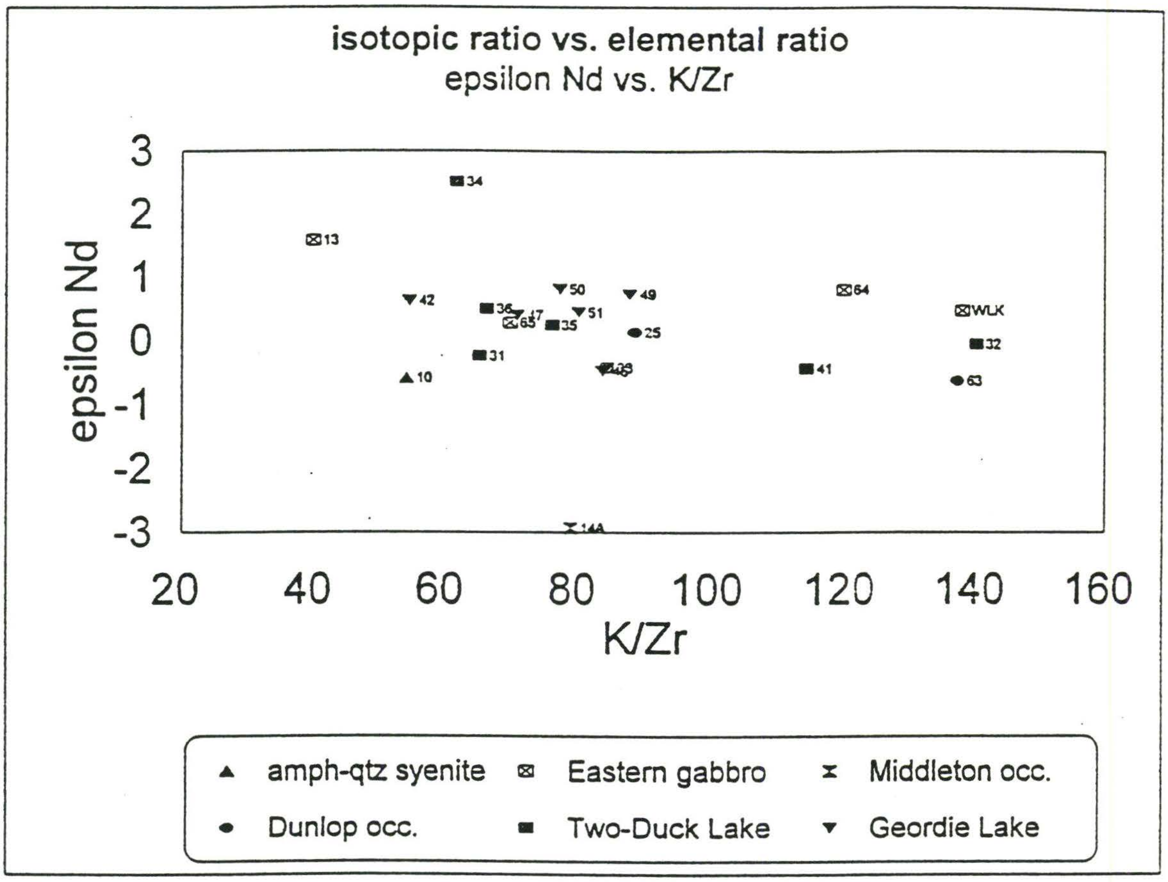


Figure 5.2.3.1: ϵNd versus K/Zr.

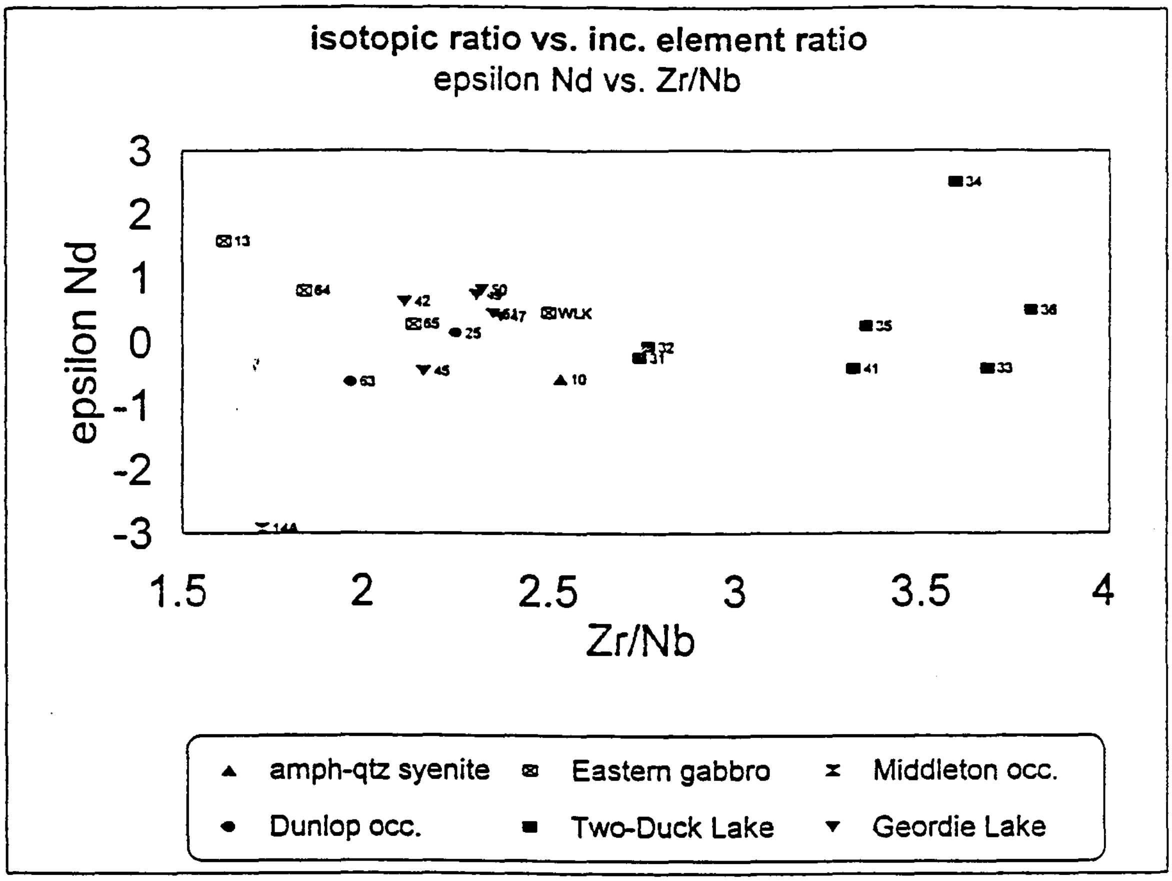


Figure 5.2.3.2a-d: εNd versus ratios of various incompatible elements (Zr/Nb, Ba/La, Rb/Nb, and Th/La respectively).

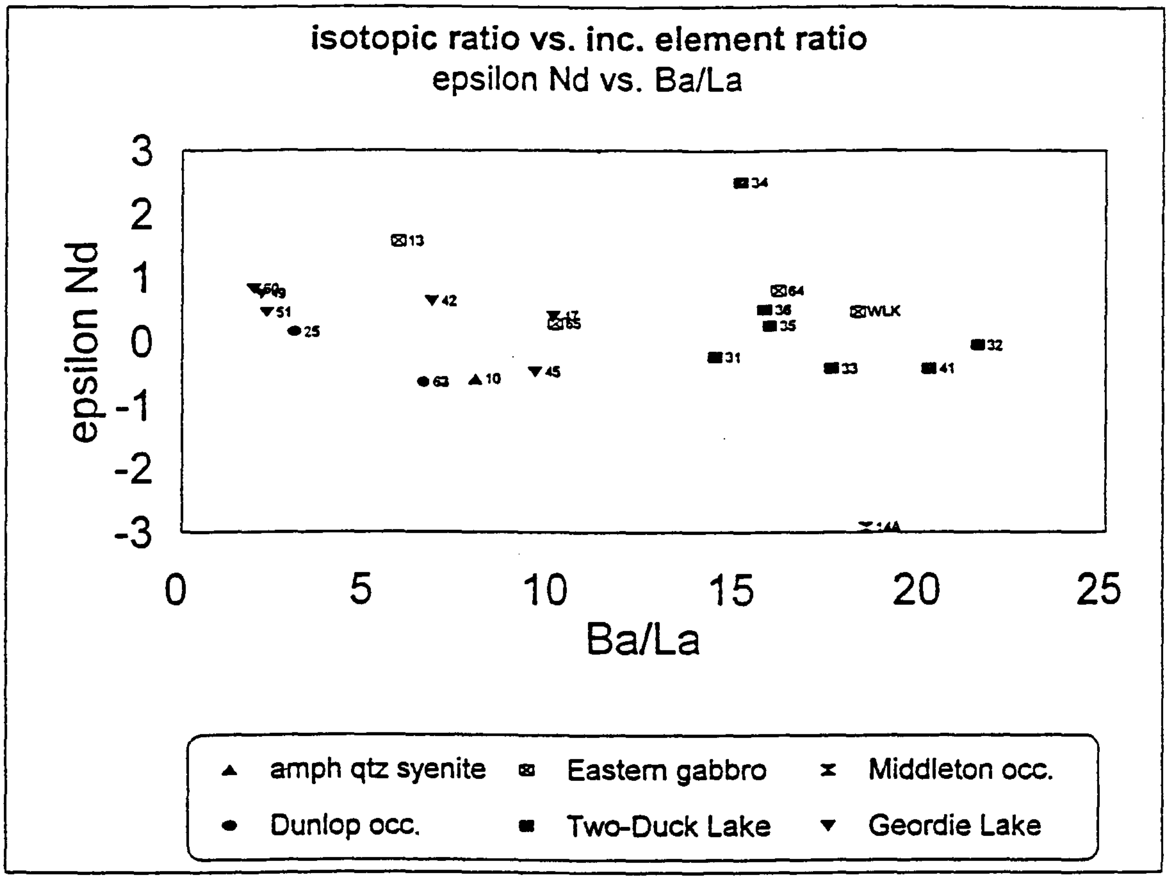


Figure 5.2.3.2b

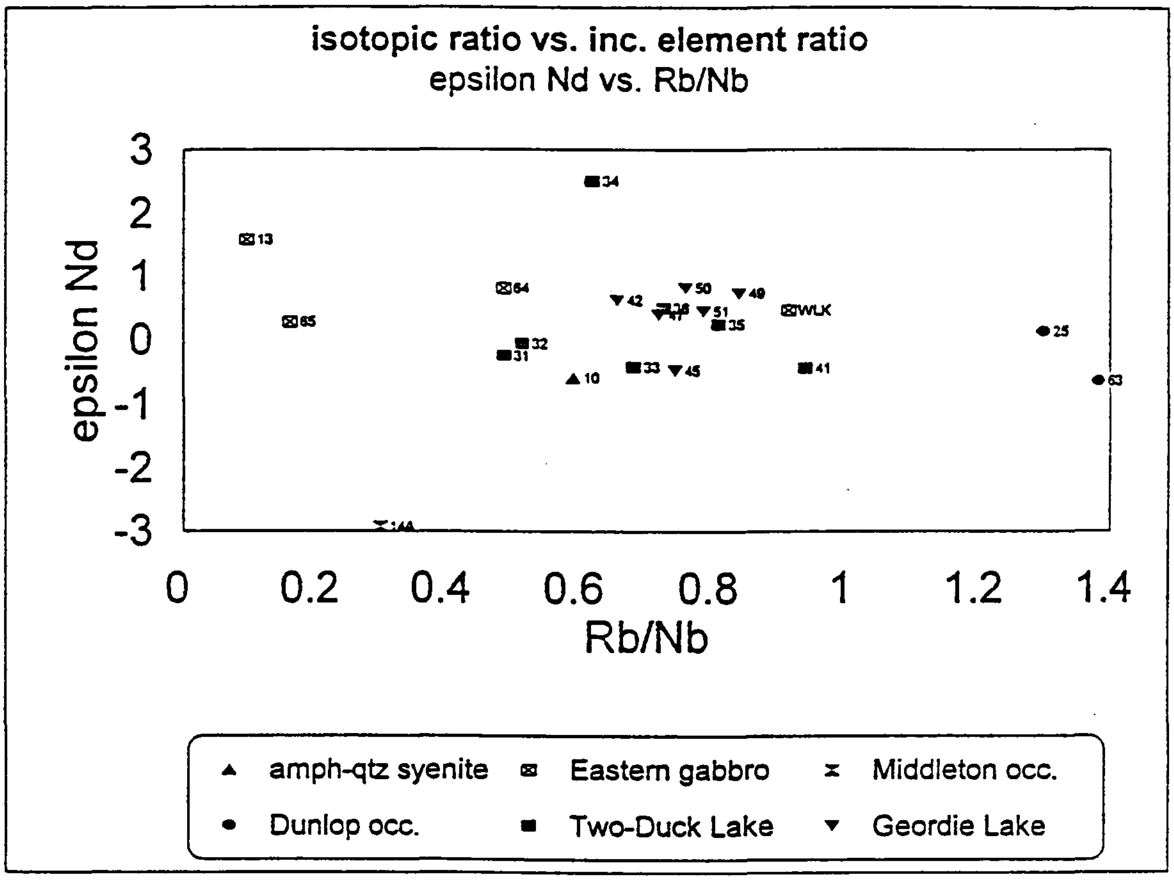


Figure 5.2.3.2c

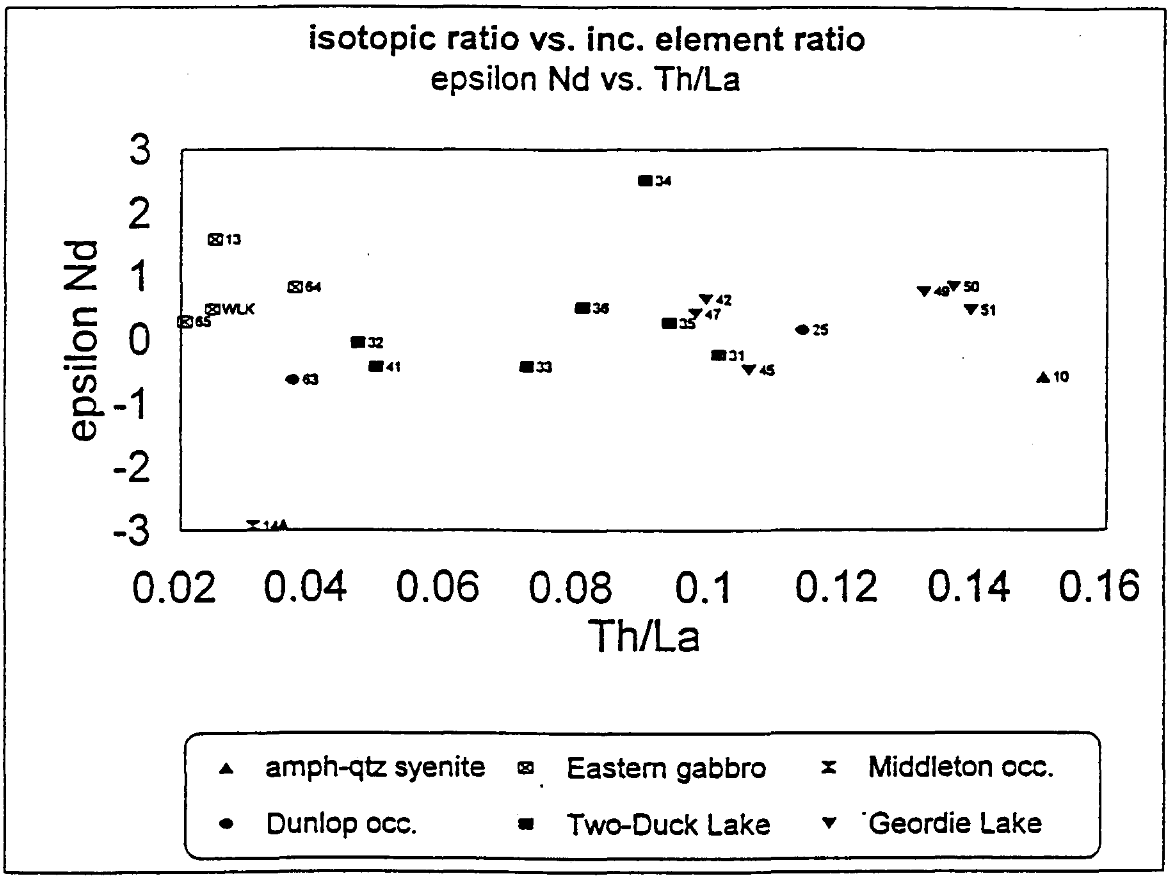


Figure 5.2.3.2 d

Tholeiitic lavas from the Portage Lake Volcanic group (PLV) investigated by Paces and Bell, (1989) indicate derivation from a LIL-enriched source. There is no exposed alkaline volcanic rock in the MCR, and therefore no intrusive analogue to the alkaline plutonic assemblages of the Coldwell complex, although Paces and Bell, (1989) point out that alkaline lavas may exist at the bottom of the stratigraphic pile.

5.3 STABLE ISOTOPE ANALYSES

Oxygen analyses was carried out on 25 whole-rock samples, analyses on 3 magnetite separates from whole-rock samples was also performed (see table 5.3.1 and figure 5.3.2). Igneous rocks and minerals exhibit a relatively restricted range of $\delta^{18}O$ in comparison to meteoric water. Figure 3.2.1 illustrates that most igneous rocks occur in the range between +5‰ and +11‰ (+15‰ if you include pegmatite). Variations from this range may indicate that a rock has been altered by interaction with meteoric water. Magnetite has the lowest tendency to incorporate heavy oxygen (ie: it has low $\delta^{18}O$ values), whereas quartz has the highest tendency to fractionate ^{18}O. Magnetite separates were analysed to try and determine the extent to which this oxide segregated ^{18}O and thereby contributed to the observed $\delta^{18}O$ signature. The gabbroic rocks of the Coldwell complex, especially the magnetite-rich Geordie Lake occurrence would be depleted in ^{18}O relative to some of the more evolved felsic rocks found in the west in Centre 3.

Martinez *et al.,* (1996), state that oxygen isotopes can be a useful tool in delineating crustal contamination due to the fact that the concentration of oxygen in magma and potential contaminants is more or less equal, whereas the elemental and isotopic ratios of contaminants are generally unknown. Unfortunately, low-temperature alteration processes can shift oxygen isotope ratios, and therefore one must be able to assess isotopic changes due to low temperature processes and look through the alteration in order to identify contamination-induced trends in the data. Petrographical and field observations are useful in determining if alteration has occurred, data is then collected from both visibly altered and seemingly fresh rocks.

As mentioned in section 3.2, correlation diagrams between radiogenic isotopes and oxygen isotopes are useful because the two systems vary independently of each other. Long exposure to the hydrosphere at low temperature tends to enrich crustal rocks in ^{18}O, while crustal reservoirs are depleted in ^{143}Nd/^{144}Nd in relation to mantle reservoirs (Rollinson, 1993; Faure, 1986). Bivariate plots between the two isotopic systems may indicate if mantle rocks were subjected to crustal contamination. Figure 5.3.2 is a bivariate plot of ϵNd versus δ^{18}O. A negative slope should result due to the fact that the most evolved and thereby felsic rocks should also have the highest δ^{18}O values. In fact there is no real observable trend in the data. Most samples tend to cluster in the range ϵNd=±1, and δ^{18}O +6‰ to +8‰. Samples 42 (magnetite-bearing eastern gabbro), 10 (amphibole-quartz syenite) and 14A (mineralised epidote-bearing western gabbro) define a nice negative trend. However, three samples out of 18 do not define a statistically valid trend, and sample 14A, being a gabbro should plot somewhere between 42 and 10. The fact that sample 14A appears, from this diagram, to be more evolved than the quartz syenite represented by sample 10 is an indication of the hydrothermal alteration of the western gabbro at the Middleton occurrence corroborated by the petrographical observations of alteration products in the form of allanite and epidote. The depressed ϵNd value yielded by 14A also indicates that some small-scale, local contamination may have occurred at this locality. Crustal contamination should shift δ^{18}O values to the right in figure 5.3.2, although in reality it appears that the oxygen isotope composition is shifted to the left which is attributable to hydrothermal alteration. Samples 10 and 14 show visible evidence of hydrothermal alteration (brick-red feldspars in 10, and abundant epidote and allanite in 14A), the low $\delta^{18}O$ observed in sample 42 can be attributed not to alteration, but to its high concentration of magnetite, which displays a proclivity for fractionating ^{16}O.

	14a	14d	25	53	56	61	63	31	32	33	34	35	36	41
$\delta^{18}O$	5.2	8.5	7.5	7.2	7.9	9.1	6.6	6.7	6.5	8.5	5.5	6.8	6.1	6.3
	64	67	42	44	45	47	49	50	51	10	43	32m	34m	42m
$\delta^{18}O$	7.1	7.4	1.4	2.4	5.9	5.8	7.3	7.0	6.7	3.4	5.0	1.9	0.9	-3.7

Table 5.3.1: Oxygen isotope data for rocks of the Coldwell complex, all data from whole-rock analyses except that which is denoted by an 'm' which indicates a magnetite separate.

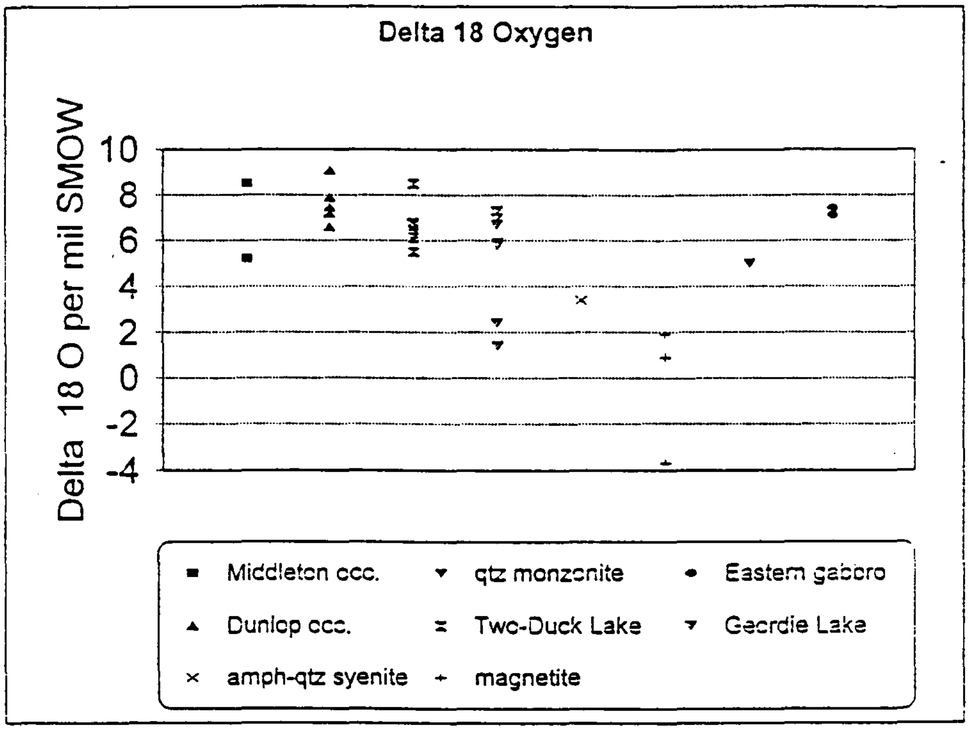


Figure 5.3.1: graph of the range of values for $\delta^{18}O$ for selected rock types and locales in the Coldwell complex.

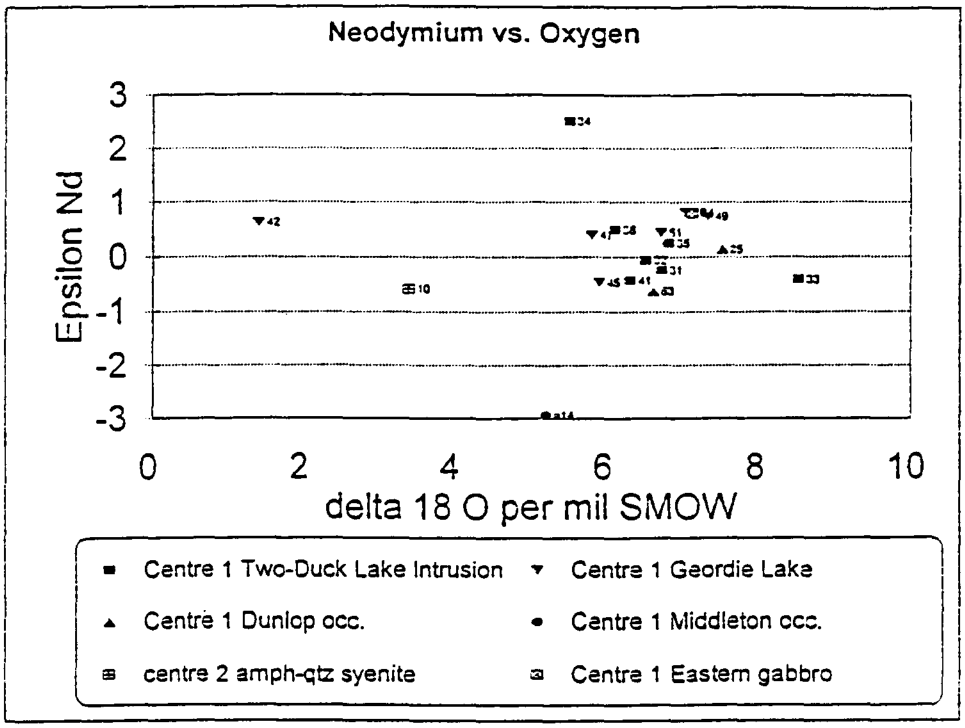


Figure 5.3.2: ϵNd vs. δ^{18}O ‰ SMOW, alteration will shift oxygen values to the left, while contamination will shift points down and to the right.

It is difficult to determine the true nature of the contamination and the extent of contamination without knowledge of the oxygen and neodymium isotopic composition of the country rock at depth. The Coldwell complex is believed to be a funnel-shaped intrusion and as such, a sample of the Archaean country rock at the present erosional level would not necessarily reflect the composition of the primary assimilant. Therefore it is only possible within the scope of this study to suggest that small, and varying amounts of crustal contamination likely occurred as evidenced by oxygen isotope analyses. It is important to note that interaction of the rock with water and the subsequent re-equilibration of oxygen due to this hydrothermal alteration likely acted to depress $\delta^{18}O$ values in the Coldwell complex rocks. While this fact can be used to argue for a late hydrothermal overprint in effect masking a contamination signature, it must be noted that samarium-neodymium isotopic evidence and trace and major element data do not suggest that contamination was a significant factor in the genesis of the Coldwell complex. Thus the oxygen isotope data is probably best interpreted as indicating that hydrothermal alteration of the Coldwell complex occurred, this alteration is variable, and may mask a shift to higher oxygen isotope values caused by local small-scale contamination with the Archaean country rock.

5.4 MICROPROBE ANALYSES

Samples from the Western Gabbro and the Two-Duck Lake Intrusion were analysed by Dr. C.J. Shaw at the University of Western Ontario to determine if the same Ba-enrichment of mica observed by Shaw and Penczak, (1996) and attributed by them to metasomatism associated with late pegmatites, or crystallisation of interstitial fluids, was also present in the mineralised Fleck deposit (TDLI) and Middleton occurrence (Western Gabbro). These sites did not show appreciable Ba enrichment. The TDLI micas, however, displayed extreme F-enrichment (see table 5.4.1).

sample	31	34	14a
location	TDLI	TDLI	WG
SiO_2	37.74	38.45	35.89
TiO_2	5.11	1.41	5.53
Al_2O_3	13.86	10.54	13.94
Cr_2O_3	.01	.04	.02
FeO	13.27	22.88	13.47
MnO	.06	.59	.05
MgO	15.96	11.04	15.56
CaO	.01	.10	.04
BaO	.21	.11	.41
Na_2O	.32	.08	1.17
K_2O	9.37	8.98	7.10
F	1.09	3.66	.05
Cl	.17	.28	.02
-O=F+Cl	.50	1.60	.03
Total	96.67	96.52	93.20

Table 5.4.1: Selected electron microprobe data on micas from the Two-Duck Lake intrusion and the Western Gabbro, Coldwell complex.

Fluorine enrichment in mica is often attributed to the chemical composition, thus Mg-biotites can incorporate more F than Fe-biotites (Speer, 1984). This concept is referred to as Fe-F avoidance (Ekström, 1972 as cited in Munoz, 1984), enhancement of halogens can also be ascribed to hydrothermal alteration. In view of the importance of halogens in ore genesis, the observed F-enrichment of the PGE-bearing Two Duck Lake Intrusion may well be significant to unravelling the genesis of the Fleck deposit. High F/Cl ratios like those observed in the Fleck deposit are in fact attributable to magmatic fluids, as opposed to hydrothermal fluids.

Watkinson and Ohnenstetter (1992) as cited in Good and Crocket (1994) interpreted a number of petrographical observations including the association of PGE-bearing minerals with halogens to mean that a chloride solution interacted with and refined primary sulphides with respect to Pd and Cu. Good and Crocket (1994) suggest that a hydrothermal origin is not consistent with their data which suggests that Ir and Ni correlate well, although hydrothermal alteration should fractionate Ni with respect to Ir since Ni is far more volatile. The correlation between S and chalcophile elements which is characteristically magmatic also refutes the hydrothermal genetic model for this particular deposit (Good and Crocket, 1994).

The micas occur in clusters or ‘balls’ in the pegmatitic lower TDLI and appear to be a late crystallisation phase. They do not appear to be the product of hydrothermal alteration, as they do not exhibit any of the classic replacement textures one might expect to see in a hydrothermally altered rock. The feldspars, especially prone to alteration by hydrothermal fluids are fresh, yielding further evidence that large-scale hydrothermal alteration did not occur. Good and Crocket (1994) specify that had hydrothermal alteration been responsible for the PGE emplacement in this reducing environment, it would have had to have occurred pervasively, since the concentrations of Pt and Pd in acidic, oxidising chloride solutions at low temperature is only on the order of ppb. The PGE emplacement is instead thought to have resulted from the migration of elements in a deuteric fluid (Good and Crocket, 1994). It is this method which is thought to have crystallised the F-rich mica balls in the lower Two-Duck Lake intrusion. Crystallisation from a remnant interstitial fluid is also invoked by Shaw and Penczak (1996) as the method whereby moderately Ba enriched micas were crystallised in the Eastern and Western Gabbros.

6.0 CONCLUSIONS

Analysis of samples predominantly from mineralised occurrences in the Coldwell complex has been undertaken to try to ascertain what role crustal contamination played, if any in the genesis of the complex, especially in the context of the Ni-Cu-PGE bearing sulphides. Samples were analysed for Sm-Nd isotopic composition, oxygen isotope composition, and major and trace element composition. Data from these analyses was then interpreted, both alone and in combination with other data types to try and determine the geochemical nature of the Coldwell complex, especially with respect to the mineralised occurrences. The data from this geochemical survey was then applied specifically to the question of crustal contamination of the magmas, as well as to the question of the specific source of the magmas which generated the complex.

Due to the fact that Os isotopic data suggests that crustal contamination is a key factor in the genesis of many Cu-Ni-PGE deposits, it was decided to try and undertake an isotopic study of the Coldwell complex with focus on the know occurrences of Cu-Ni-PGE sulphides as well as non-mineralised rock assemblages to try and ascertain whether or not crustal contamination payed a role in the genesis of the Coldwell complex. This data could then be used to assess the mineralisation potential of other alkalic complexes with respect to Ni-Cu-PGE sulphides. Radiogenic isotopes, such as Sm-Nd are effective geochemical tools which can discern a great deal of information about the magmatic genesis of an igneous body, and as such was utilised in this study. Sm-Nd analyses were performed on barren and mineralised rocks of the complex, and it was determined that crustal contamination was not a significant factor in relation to any of the mineralised rock of the Coldwell complex.

Sm-Nd data from the complex clusters around CHUR, with the more evolved Centre 3 rocks exhibiting average ϵNd values of -0.9 and Eastern gabbros from Centre 1 having average values of +0.5. These ϵNd values do not imply evidence for contamination by continental crust which at the time of emplacement (1108 Ma) would have had values between -12 and -17. Contamination of depleted mantle (ϵNd=+5.0) with Archaean crust should result in a significant depression of the ϵNd values for the resultant magmas. This is not the case, and as such is evidence for crustal contamination playing only a minimal role or no role whatsoever in the genesis of the Coldwell complex. Also indicative of a lack of crustal contamination is the fact that the compositionally distinct Centre 1 and 2 rocks display nearly identical ϵNd values. It is highly unlikely that contamination could have occurred such that mixing between the crust and two separate magma sources could result in similar isotopic values. Further evidence for a lack of crustal contamination in the Coldwell complex comes from the examination of whole-rock geochemical analyses.

Major and trace element information can be used on its own and in conjunction with radiogenic isotope evidence to strengthen or corroborate conclusions drawn from isotopic data alone. Ratios of incompatible elements to Nd isotopic ratio indicate that crustal contamination was not a significant factor in the genesis of the Coldwell complex. Contamination did, however, occur locally to a small extent. The data collected was used to try and define geochemical fields which would represent the possible source end members of the magma which formed the complex. The isotopic data alone, indicates that the source consists of enriched mantle with an OIB-like signature, indicative of the involvement of a mantle plume. The compositional fields defined by the available geochemistry indicate that an enriched mantle plume (OIB-like signature) did likely contribute significantly to the genesis of the complex. Also evident is the fact that crustal contamination played a role in the formation of at least some of the rock types in the rift, specifically the Partridge Lake layered intrusion and the slightly more evolved rocks from Centre 3. The incompatible element versus Nd isotopic ratio diagram yields some interesting results in that it appears that while a definite plume signature exists, some amount of incorporation of lithospheric upper mantle also occurred. This is based on the average carbonatite composition which has been suggested by Bell and Blenkinsop (1986), to represent lithospheric upper mantle. It should be duly noted that other researchers such as Sage, (1991) indicate that the carbonatites are enriched. It should also be noted that carbonatites represent a very specialised type of magma which generally should not be construed to be representative of the mantle composition.

Also integral to defining the nature of contamination in the Coldwell complex magmas was a study of the $\delta^{18}O$ of various rocks in the area. Oxygen isotope values indicate that alteration was prevalent in the Centre 2 and Centre 3 rocks. Observed values for $\delta^{18}O$ indicates that some slight amount of contamination with continental crust occurred in order to shift oxygen isotopic ratios to higher values for the rocks of the Centre 1 eastern gabbros. Oxygen isotope data also indicates that samples from the Western gabbro were subjected to intense hydrothermal alteration making it difficult to ascertain whether the observed trace element values for these rocks are due to the alteration or assimilation of country rock.

The oxygen isotope data is also crucial in supporting the hypothesis of Good and Crocket, (1994) which suggests that the PGE enrichment of the Two-Duck Lake intrusion was due to magmatic fluids and not hydrothermal fluids. This is further proven by a microprobe study of biotite from the Two-Duck Lake intrusion. The microprobe survey found that the biotite possesses high F-Cl ratios which are attributable to enrichment by a deuteric fluid.

In conclusion; this geochemical and isotopic survey undertaken on the Coldwell complex has helped to elucidate on the genesis of the magma which formed the complex. Nd isotope ratios suggested that an enriched source, likely a mantle plume contributed to the formation of the Coldwell complex and the MCR. Trace element geochemistry, helped to corroborate this theory, as well as define the individual trace element characteristics, and thus the history with respect to alteration and contamination, of the various economic mineral showings in the complex. Major element geochemistry, oxygen isotope analyses and microprobe analyses helped to further validate the theory that the primary constituent of the Coldwell magma was plume-derived with some influence from the upper crust and the lithospheric upper mantle. All followed by subsequent hydrothermal alteration of certain lithologies.

Basically, because the contribution of crustal contamination to the chemical character of these rocks is variable and relatively insignificant, it is not recommended that contamination be used as a major criteria for PGE-enrichment in alkaline intrusions in rift settings. Re-Os isotope analyses, while sensitive to crustal contamination in the context of sulphide mineralisation would not likely yield too much relevant information in the case of the Coldwell complex since the complex seems to be primarily plume-oriented.

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APPENDIX 1: ANALYTICAL INFORMATION

1.1 SAMPLE COLLECTION AND PREPARATION

All samples were collected from the Coldwell Alkaline complex by T. Bohay with the assistance of C. Boerboom, with the exception of sample WLK from Wullie Lake which was collected by Mark Smyk and Bernie Schneiders of the Ontario Geological Survey. Large fresh samples of rock at least 1 kilogram in weight were collected using a sledge hammer, certain samples from the Fleck property at Two-Duck lake were collected from blast test pits (samples number 34 and 36). Samples 14a at the Middleton Occurrence and 64 and 65 from the Dunlop Occurrence are from exploration trenches. Samples were stored in separate plastic sample bags and returned to McMaster University for preparation by Boerboom and Bohay.

Samples were checked to ascertain that they were fresh and homogeneous, all weathered surfaces were further trimmed using a hydraulic splitter and a hammer, and all pieces containing visible alteration or veining were discarded. The fresh pieces were then crushed to approximately 1 cm^2 in a jaw crusher and put through a sample splitter four times, this remaining material was further reduced in size to a fine powder (<200 mesh-210μm) in a tungsten-carbide swing mill and the resultant powder was stored in a small new plastic bottle. To prevent cross contamination between samples, the entire rock crushing facility was thoroughly vacuumed and then cleaned with water. New disposable latex gloves, lubricated with corn starch, rather than talc were used for each sample and during cleaning procedures. All equipment was cleaned thoroughly before and after each successive sample was processed. Cleaning consisted of disassembling equipment where possible and in the case of the jaw crusher, scouring the jaws with a wire brush. All surfaces were then vacuumed, wiped with disposable paper towels, and rinsed with acetone or ethyl alcohol. Prior to using the jaw crusher, a small portion of the rock to be crushed was run through the apparatus and discarded in a pre-contamination step.

1.2 Sm-Nd ISOTOPIC ANALYSES

1.2.1 CHEMICAL PREPARATION

The author followed standard protocol during the chemical preparation of the samples for Sm-Nd mass spectrometry, as outlined by Dr. A.P. Dickin. Chemical separation of LREE was carried out in the “ultraclean” chemical preparation laboratory at the Department of Geology, McMaster University.

Chemical dissolution was performed on the <200 mesh homogenous rock powder, between 70 and 150 mg of said powder was weighed into a static-free teflon bomb of known weight on an analytical balance. After approximately 100 mg of powder was weighed out, about 10 mL of concentrated HF (48%) was added and the bombs sealed, placed in a protective jacket and heated in an oven at 120°C for 72 hours. After heating, the resultant slurry was evaporated down to dryness on a hotplate at which time approximately 5 mL of 16N HNO_3 was added and the solution was again evaporated on a hotplate. Five mL of 6N HCl is then added and the solution is returned to the oven for 24 hours. After this last episode of heating, the solution is inspected to ascertain that no undissolved material remains. If the powder has been completely dissolved, the solution is diluted with 5mL of triple-distilled, deionised water (Milli-Q water) and then split into two fractions. Splitting involves weighing the solution and bomb and then pouring off about half of the solution into a 15 mL beaker for spiking with ^{149}Sm/^{150}Sm, the bomb and remaining solution is re-weighed to determine the amount of solution to be spiked.

The aliquot to be spiked has a weighed amount of ^{149}Sm/^{150}Sm spike added (5 drops, which constitute between 150-250 mg of spike solution). This spiked aliquot is for the purpose of isotope dilution analyses. After spiking both the spiked and unspiked solutions are evaporated to dryness, and then redissolved in 2 mL of 2.5N HCl. Both solutions are then poured into polystyrene tubes and centrifuged for ten minutes. The solutions are then both ready for cation exchange column chemistry.

Synthetic high-molecular weight organic polymers possessing a large amount of ionogenic groups can act as ion exchange resins in that divinylbenzene (DVB) bridges between the polymer chains of the resin form a three-dimensional matrix which swells in response to contact with a solvent. Ion exchange is fascilitated by ionogenic groups such as $-SO_3H$ (Korkisch, 1989). REE are strongly adsorbed on strong acid cation exchange resins from dilute HCl solutions (Korkisch, 1989).

Columns and resin are first prepared by running through 10mL of Milli-Q water followed by 60 mL of 6 N HCL. They are then conditioned by running through 20 mL of 2.5 N HCl. The quartz columns are packed with Bio-Rad® AG 50W 200-400 mesh resin. The columns are 195mm×10mm and are packed to 125mm high with resin. Flow rate is dictated by gravity. Samples were diluted with 1 mL of 2.5 N HCl and loaded into the columns. Elution with a total of 46 mL of 2.5 N HCl removed the major elements and Sr. Ba and other impurities were removed by elution with 30 mL of 2 N HNO_3, and the REE were collected with 14 mL of 7.5 N HNO_3. After the REE were collected, the solution was evaporated down to dryness under heat lamps, then dissolved in 1 mL of 0.2 N HCl in preparation for the next step which involves the reverse phase REE columns.

Quartz columns (195mm×10mm) loaded with 100-200 mesh teflon powder coated with Di-2-ethyl-hexyl-orthophosphoric acid (HDEHP) resin to a height of 85mm were used in the separation of Sm and Nd (Guo, 1995). Again these columns were gravity-feed columns.

After cleaning these columns and resin with 60 mL of 6 N HCl, followed by standardisation by 30 mL of 0.2 N HCl, the samples were loaded. Twenty one mL of 0.2 N HCl were added in sequential steps to collect Nd (from both the spiked and unspiked samples) for isotope dilution analysis and isotope ratio analyses respectively. A further elution of 4 mL of 0.5 N HCl resulted in the collection of spiked Sm in 6 mL of 0.5 N HCl. All three samples were evaporated down under heat lamps then redissolved in 2 drops of a 100:1.3 solution of 3 N HNO_3 and 0.3 M H_3PO_4 in preparation for mass spectrometry.

1.2.2 MASS SPECTROMETRY (Sm-Nd)

One to 1.5 μmL of H_3PO_4 is added to approximately 1.5 μmL of the sample, 1.5 μmL of this solution is then loaded onto the Ta side filament of a triple-filament bead (to which a Re filament and one Ta filament have been welded). The solution is then evaporated to dryness by the application of a small electric current (1.5-2.0 amperes) to yield a salt. This procedure is the same for both isotope ratio and isotopic dilution analyses.

A VG® ISOMASS 354 solid source thermal ionisation mass spectrometer with a 27 cm radius and a 90° magnetic sector was utilised in this study. The Sm and Nd concentrations were determined by isotopic dilution analyses in the single collector mode. Nd isotopic ratios were derived by using a four collector multidynamic mode, $^{145}Nd/^{144}Nd$ metal analyses are then corrected for fractionation using the international value of 0.7219 for $^{146}Nd/^{144}Nd$ (Dickin, 1995). The international standard La Jolla was analysed in every run for a total of 7 analyses which produced an average value of 0.511864 ± 0.0000455, 2σ-population.

1.3 OXYGEN ISOTOPE ANALYSES

1.3.1 PHYSICAL PREPARATION

Preparation of rocks for analyses of oxygen isotopes is similar to preparation for Sm-Nd isotopic analyses, essentially the same very fine powder (<200 mesh) was used, no form of sieving was actually performed, so as not to preferentially concentrate soft minerals such as apatite and thereby skew the results of both oxygen and Sm-Nd analyses. The rock chips were swingmilled for a sufficient time, such that it could be ascertained that all of the powder passed through a 200 mesh sieve. A test of this was performed to ascertain that all of the powder was indeed finer than 210 microns (the size of the openings in an analytical grade 200 mesh polypropylene Spectra/Mesh® polymer filter). This powder was then used for whole-rock oxygen isotope analyses. A separate aliquot of the same powder had the magnetite along with other heavy minerals separated out by passing the sample through diiodomethane (CH_2I_2) twice. The sample was further purified with a hand magnetite, and finally by hand-picking while utilising a binocular microscope in order that an analyses could be performed on a magnetite separate from selected powders.

1.3.2 CHEMICAL PREPARATION

Oxygen analyses was performed by Hong Li at the Department of Geology stable isotope research facility, MCMaster University. Oxygen in whole rock and mineral samples was released by reacting the samples with a strong oxidising agent, in this case the oxidant was bromine pentafluoride (BrF_5) in a nickel vessel at temperatures between 550-650°C (Clayton and Mayeda, 1963). Typically about 8-15 mg of sample and 10-15 millimol of O^2 were used for each run, with approximately five times the excess BrF_5 required stoiciometrically. Fluorides are frozen in liquid N^2 traps to purify the oxygen which has been extracted. This oxygen is then converted to CO_2 by passing it through a heated graphite furnace (~550-600°C) in a reduction reaction.

1.3.3 MASS SPECTROMETRY ($\delta^{18}O$)

The analyses was performed by H. Li on a VG® dual inlet-triple collecting mass spectrometer according to the procedure outlined by Taylor and Epstein (1962). The oxygen yield was routinely measured for all samples, with the criteria for for a satisfactory yield established at 2% of stoichiometric yield. Samples with unsatisfactory yields were repeated and the results of repeat unsatisfactory yields diacarded. The standard NBS-28 was routinely analysed along with the samples, and average $\delta^{18}O$ of 9.5 ‰ and a precision of 0.14 ‰ was obtained. (All of the above from Hong Li, pers. comm., 1997).

1.4 WHOLE ROCK ANALYSES

Again, the same powder used in the Sm-Nd and oxygen experiments was submitted for whole-rock analyses. Analyses was performed by ACT-Labs, Ltd. Ancaster, Ontario and by J. McAndrew, McMaster University, Department of Geology XRF facility. Some duplicate samples were sent to both institutions, and these do differ slightly, this is a function, both of the fact that two different analytical techniques were utilised (ICP, and ICPMS at ACT-Labs, and XRF at McMaster), and may also be due to the fact that the McMaster lab did not heat the samples to ~100°C prior to forming the fusion discs and pressed pellets in order to drive off advected moisture. This caused the anomalously high total exhibited by the data from McMaster University.

1.5 MICROPROBE ANALYSES OF MICAS

Dr. C.J.S. Shaw analysed biotite samples from the Coldwell complex at the University of Western Ontario's Jeol®-JXA-8600 electron microprobe, utilisting a wave dispersive spectrometer. An accelerating voltage of 1 kV and a beam current of 10 nA were used. Samples were analysed with a defocussed 5 μm electron beam. The above is from Dr. C.J.S. Shaw (pers. comm., 1996).

APPENDIX 2.0 DATA

APPENDIX 2.1 TRACE ELEMENT DATA (ACT-Labs)

All data reported in ppm; negative values indicate that the amount of the element in question existed in amounts below detection levels.

Sample	Cr	Ni	Co	V	Cu	Pb	Zn	Bi	In	Sn	W	Mo	As	Sb	Ag
10	14	-5	33.6	22	33	18	100	-0.05	0.1	4.2	112	3.92	-5	0.49	-0.5
13	15	-5	84.8	222	14	-5	74	-0.05	-0.1	-0.2	101	0.76	-5	0.81	-0.5
14A	13	174	119.7	363	3910	14	87	0.2	-0.1	0.3	55	0.63	24	0.35	-0.5
14D	-10	-5	27.1	76	81	-5	24	-0.05	-0.1	-0.2	116	0.38	-5	0.43	-0.5
25	-10	-5	51.6	16	15	22	111	-0.05	0.1	2.5	92	1.64	-5	0.63	-0.5
28	-10	6	56.5	254	133	14	39	0.09	0.1	1.4	73	2.46	-5	0.52	-0.5
31	165	523	76	180	8540	7	72	0.16	-0.1	0.6	61	0.51	-5	0.35	4.2
32	28	103	82.1	209	179	9	64	-0.05	-0.1	-0.2	163	0.34	-5	0.31	-0.5
33	197	62	46.2	201	418	-5	31	-0.05	-0.1	-0.2	138	0.4	-5	0.39	-0.5
34	119	599	96.1	306	10800	7	78	-0.05	-0.1	-0.2	91	0.33	-5	0.46	5.5
35	134	82	72.3	309	327	-5	35	-0.05	-0.1	-0.2	138	0.41	-5	0.23	-0.5
36	128	163	63.9	147	2100	-5	40	-0.05	-0.1	-0.2	112	0.53	6	0.28	1.2
41	176	357	73.9	218	6320	10	66	0.08	-0.1	0.5	85	0.55	-5	0.2	2.8
43	-10	-5	20.2	20	55	42	190	0.09	0.1	6.9	88	3.69	-5	0.66	-0.5
42	10	157	108.1	434	6850	12	166	-0.05	-0.1	1.5	77	1.93	16	0.45	2.2
45	-10	34	69.5	629	239	5	81	-0.05	-0.1	0.6	80	1.54	-5	0.23	-0.5
47	-10	23	58.5	449	184	23	96	-0.05	-0.1	1.5	74	1.57	-5	0.35	-0.5
49	-10	-5	26.6	-5	19	18	120	-0.05	0.1	3.4	165	4.19	-5	0.37	-0.5
50	-10	-5	26.5	-5	17	16	126	-0.05	0.1	4.1	189	4.74	-5	0.25	-0.5
51	-10	-5	22.1	-5	17	19	122	-0.05	0.1	3.5	187	4.67	-5	0.41	-0.5
61	318	33	20.9	188	299	17	26	-0.05	-0.1	-0.2	111	0.49	-5	0.47	-0.5
63	17	34	33.2	422	391	-5	108	-0.05	-0.1	-0.2	30	0.56	-5	0.13	-0.5
64	-10	-5	49.2	79	28	8	63	-0.05	-0.1	-0.2	242	1.98	-5	0.27	-0.5
65	30	57	74.2	481	409	-5	52	0.28	-0.1	-0.2	124	0.64	15	0.26	-0.5
WLK	194	88	79.5	557	1820	20	76	0.18	-0.1	-0.2	62	0.24	-5	0.23	0.5

K	Rb	Cs	Ba	Sr	Tl	Ga	Ta	Nb	Hf	Zr	Ti	Y	Th	U	La	Ce
38352	166.74	1.22	1804.26	229.17	0.37	31	13	282.34	16.8	710.87	5695	73.9	34.12	10	226.99	399.53
2573	3.85	0.53	809.09	2655.67	0.05	20	2.7	40.11	1.6	64.71	13189	33.6	3.48	1.02	138.25	285.88
2075	4.6	0.53	819.28	987.42	0.06	19	0.97	15.36	0.76	26.34	15407	18.4	1.38	0.31	44.46	94.9
7720	41.12	3.58	1656.85	1920.79	0.07	22	1.3	13.89	0.86	37.59	4077	7.7	2.21	0.62	27.29	50.02
41839	274.35	3.44	601.1	112.38	1.29	29	8.1	211.46	10.8	473.14	3177	74.6	22.56	4.97	198.46	348.55
21251	138.89	4.5	1246.25	573.64	0.48	24	4.7	94.41	6.4	259.54	9532	41.1	12.36	3.47	108.47	206.99
3154	8.63	0.41	280.41	556.78	0.15	15	0.91	17.73	1.4	48.41	4556	13.3	1.97	0.47	19.47	40.19
3487	4.64	0.56	411.86	729.17	0.03	18	1.3	9.03	0.75	24.87	4256	9.5	0.9	0.22	19.2	38.35
3902	8.57	0.23	324	642.51	0.02	19	1.2	12.6	1.3	46.2	5455	12.9	1.34	0.33	18.5	37.69
2822	7.91	0.28	279.4	555.91	0.08	16	0.88	12.79	1.3	45.78	4556	11.9	1.67	0.45	18.53	38.31
3819	12.15	0.46	334.81	667	0.03	17	1.4	15.05	1.4	50.28	4556	12.9	1.98	0.55	21.12	43.92
3736	10.8	0.36	392.72	689.79	0.25	18	1.1	14.9	1.6	56.44	3477	13.5	2.02	0.56	25	49.4
4234	10.52	0.57	429.97	706.48	0.12	17	0.83	11.22	1.1	37.09	4556	12.2	1.06	0.3	21.33	42.29
40925	207.27	2.65	1804.74	396.32	1.38	28	13	262.07	16.3	651.29	4856	65.9	33.87	9.34	216.7	377.92
7886	45.19	4.97	626.26	609.07	0.45	20	3.7	68.96	3	144.86	10791	35.9	9.18	2.32	92.58	181.06
15108	62.19	2.24	878.96	454.39	0.22	21	4.5	83.85	4	180.4	14748	36.1	9.7	2.61	91.85	180.42
16354	70.24	2.5	1167.12	539.34	0.25	22	4.9	97.99	5	231.06	13309	42.4	11.31	2.98	115.88	221.93
41839	174.35	3.8	424.38	57.06	0.57	29	10.8	208.09	11.6	476.89	4496	66.7	26.66	7.47	201.88	369.19
40261	171.21	3.74	409.13	53.69	0.54	29	11.5	226.05	12.6	521.38	4616	70.2	29.18	8.05	213.61	386.33
40842	171.35	3.32	465.12	60.8	0.62	29	11.3	218.38	12.4	510.55	4736	66.9	28.51	7.83	204.76	375.43
3736	12.04	1.57	860.46	770.26	0.18	19	0.64	11.31	1.8	61.78	3477	21.5	2.74	0.7	35.03	74.73
6475	33.43	3.34	580.21	575.95	0.03	12	1.5	24.19	1	47.21	11690	33.5	3.28	0.88	88.6	183.77
17184	38.18	0.94	1778.15	1280.13	0.07	23	4.7	78.55	3.3	143.52	6535	24.5	4.13	1.12	110.59	211.91
3071	3.34	0.24	501.62	638.13	0.02	17	1.4	20.72	1.3	44.04	9772	16	1.02	0.17	49.48	87.4
4151	11.03	1.66	670.84	755.13	0.23	19	0.74	12.09	0.94	30.08	15887	19	0.91	0.24	36.83	81.52

Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
35.989	136.34	24.6	5.19	15.6	2.4	14.34	2.84	8.48	1.186	8.29	1.408
29.393	131.26	24.6	7.19	14.7	1.7	8.49	1.36	3.22	0.325	2.11	0.358
9.747	45.11	8.9	2.99	6.4	0.8	3.98	0.7	1.76	0.19	1.25	0.212
4.543	19.3	3.5	2.78	2.3	0.3	1.61	0.3	0.76	0.087	0.57	0.102
34.11	134.49	26.8	3.93	18.5	2.8	15.59	2.88	8.19	1.2	7.95	1.395
18.923	77.61	14.7	3.47	9.9	1.4	8.11	1.56	4.33	0.589	3.99	0.691
3.973	17.74	4.1	1.41	3.3	0.5	2.71	0.52	1.5	0.198	1.34	0.213
3.821	16.87	3.6	1.81	2.7	0.4	1.96	0.37	1.03	0.123	0.85	0.143
3.709	17.11	3.9	1.64	3.4	0.5	2.71	0.53	1.46	0.182	1.2	0.192
3.826	17.33	4	1.34	3	0.4	2.49	0.47	1.34	0.171	1.2	0.199
4.309	19.47	4.3	1.59	3.4	0.5	2.79	0.52	1.5	0.198	1.37	0.23
4.688	20.32	4.4	1.71	3.4	0.5	2.82	0.53	1.52	0.191	1.25	0.223
4.112	18.56	4	1.77	3.2	0.4	2.59	0.49	1.39	0.171	1.23	0.206
33.403	124.01	22.2	4.8	13.7	2.2	12.98	2.57	8	1.109	8.07	1.375
17.101	72.04	13.7	3.75	9.7	1.3	7.33	1.37	3.94	0.513	3.4	0.577
16.801	69.64	13.3	3.44	9	1.3	7.25	1.4	4.02	0.536	3.68	0.644
20.756	84.6	15.8	4.06	10.3	1.5	8.58	1.64	4.82	0.625	4.35	0.742
33.668	129.32	23.3	4.35	14.9	2.3	13.56	2.65	8.11	1.156	8.14	1.461
35.531	135.41	24.6	4.48	15.4	2.4	14.13	2.78	8.3	1.193	8.52	1.509
34.216	129.6	23.9	4.52	14.8	2.3	13.52	2.7	8.25	1.188	8.48	1.518
7.708	35.62	8.2	2.39	6.2	0.8	4.32	0.83	2.43	0.329	2.27	0.398
18.34	82.08	15.9	4.08	10.8	1.3	7.18	1.3	3.35	0.387	2.28	0.398
19.584	80.43	14.6	5.16	8.2	1.1	5.54	0.97	2.58	0.298	2.15	0.376
7.855	33.09	6.4	2.52	4.5	0.6	3.61	0.67	1.82	0.234	1.62	0.284
8.645	40.64	8.7	2.91	6.5	0.8	4.35	0.77	2.05	0.231	1.45	0.238

APPENDIX 2.2 TRACE ELEMENT DATA (McMaster Geology XRF Lab)

Sample No.	Nb	Zr	Y	Sr	Rb
7	10	78	18	632	53
42	59	190	43	706	45
14D	16	96	7	2104	38
10	234	682	78	209	140
43	250	745	77	410	198
34	7	68	14	597	7
JG-1A	12	114	32	176	178
JB-1A	25	153	26	448	42

All values in ppm, JG-1A and JB-1A are standards.