OXYGEN AND HYDROGEN ISOTOPE STUDIES OF METAMORPHIC ROCKS

OXYGEN AND HYDROGEN ISOTOPE STUDIES
OF METAMORPHIC ROCKS
IN THE WAWA-KAPUSKASING CRUSTAL TRANSECT
ONTARIO, CANADA

BY

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This work is dedicated to the memory of Nuo Li, my father, and to Shuying Qin, my mother, for their support and encouragement throughout my education.

ABSTRACT

Oxygen and hydrogen isotopic distributions have been studied for rocks from a 100 km transect in the central Superior Province of Ontario, Canada. The transect represents progressively deeper terrains of the Michipicoten Greenstone Belt (MGB), the Wawa Gneiss Terrane (WGT), and the Kapuskasing Structural Zone (KSZ), which correspond to an increase of metamorphic grade and are interpreted as an oblique section through approximately 20 km of crustal thickness. The rocks in the terrains range in age from ~2.76 to ~2.60 Ga, with fewer later intrusions.

Equivalent lithologic types have similar $\delta^{18}O$ range at middle and lower crustal levels (WGT and KSZ). Tonalitic to granodioritic rocks range from 6.4‰ to 9.5‰; Dioritic and anorthositic rocks range from 5.5‰ to 7.6‰; a majority of the mafic gneisses (group 1) range from 5.7‰ to 7.1‰, while group 2 mafic gneisses range from 8.1‰ to 9.5‰. $\delta^{18}O$ values of the rocks exhibit a remarkable correlation with SiO_2 values, similar to that observed in unaltered plutonic rocks of equivalent composition. Paragneisses have significantly higher $\delta^{18}O$ values, 9.3‰ to 12.2‰. Low-grade metavolcanic and metasedimentary rocks of the MGB are ^{18}O-enriched compared to their high-grade equivalents in the KSZ and WGT, 7.4‰ to 13.3‰ for mafic to felsic metavolcanic rocks and 11.4‰ to 14.7‰ for clastic metasediments.

Coexisting minerals from high-grade rocks exhibit ^{18}O-fractionation closely consistent with isotopic equilibrium, suggesting that the isotopic system has not been grossly disturbed. Isotopic thermometers give uniform apparent temperatures, about 553°C to 584°C, across the entire transect, which are lower than the inferred metamorphic temperatures in the highest-grade (KSZ) terrane.

The lack of distinctive isotopic differences between equivalent rock types in the KSZ and WGT suggests that there is no significant gradient in $\delta^{18}O$ with depth in the crust or with metamorphic grade. The majority of mafic gneisses (Group 1) have $\delta^{18}O$ values similar to fresh basalts and appear to have been emplaced either as subaerial extrusives, intrusive sills, or, less likely, as submarine extrusives that were hydrothermally altered at high temperatures. The less abundant Group 2 mafic gneisses have $\delta^{18}O$ values typical of greenstones that were altered at low temperature by sea-water, and isotopically resemble low-grade rocks in the Michipicoten and Abitibi belts. In general, no major changes in whole-rock isotopic composition appear to have occurred during granulite facies metamorphism, implying limited flux of water or CO_2.

The continuous linear gradient in $\delta^{18}O$ vs SiO_2 in the high-grade rocks cannot be due to differentiation of a mafic source magma. A model involving an association between mantle-derived mafic magma and ^{18}O-enriched crustal materials is more consistent with the oxygen isotopic data.

Hydrogen isotope composition of hornblende and biotite has been analyzed from selected rocks. Mafic and anorthositic rocks from the KSZ have δD values from -58 to -62‰, suggesting a possible mantle-derived origin of fluid in the system. Two mafic gneisses, which are ^{18}O-enriched, show lower δD values, -89 and -101‰. The depletion of deuterium is consistent with the model of low temperature alteration with seawater in a submarine environment. Mafic and tonalitic gneisses from the WGT are also depleted in deuterium, -87 to -109‰. Since these rocks intruded into relatively higher level of the crust and commonly contain secondary alteration minerals, it is possible that hydrothermal alteration took place at late- or post-metamorphism stage, and the source of the fluid is likely meteoritic water, The a mount of water involved in the exchange was restricted, and was not enough to disturb the oxygen isotopic system in the rocks.

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CHAPTER ONE

INTRODUCTION

There is currently an increase of international interest in studying the middle and lower crust of the Earth. This is not only because to understand the nature and the history of middle and lower continental crust will enhance our knowledge of the geological evolution of the Earth, but partly due to the development of modern technology, for instance, seismic imaging and gravity modelling, making it is possible to map the structure of the deep crust (Percival et al., 1989). However, fully understanding and interpreting fundamental crustal construction and evolution still require a knowledge of geology, such as field geology, petrology, geochemistry, geophysics and so on. The difficulty of the geological investigation of the middle and lower crust often arises from being unable to directly sample the rocks, unless deep drilling has been done in some terrane. Fortunately, there are some terrains, which locally expose the deeper levels, which have been eroded and uplifted by structural events. The Wawa-Kapuskasing transect is one of these terrains and currently it attracts a lot of interest.

The Wawa-Kapuskasing transect is located in the central Superior Province of the Canadian Shield. The region is underlain by rocks of Archean age, cut by several Proterozoic carbonatitic complexes and diabase dyke swarms. The transect has been recently interpreted as an oblique section through about 20 km of Archean crust, thrust upward along the west dipping Ivanhoe Lake Cataclastic Zone. The transect reveals a 120 km continuous transition, eastward from the low-grade Michipicoten Greenstone Belt (MGB) to the high-grade Kapuskasing Structure Zone (KSZ), which represents a gradual increase of crustal depth. This transect provides a good opportunity to study the middle and lower crust.

It is useful to study various geochemical trends across a crustal section in order to evaluate the degree of internal differentiation with depth. In this study oxygen and hydrogen stable isotope geochemistry have been carried out on rocks in the Wawa-Kapuskasing transect.

Oxygen is a very interesting chemical parameter because it is the dominant chemical component of most common minerals, such as silicates, carbonates, oxides and so on, which form many igneous, sedimentary, metamorphic rocks and some economically important ore deposits as well. The oxygen isotopic ratio ($^{18}O/^{16}O$) determined from minerals or rocks can provide important evidence about the source of crustal materials and their evolutionary history. Oxygen is also an important component of water, and the $^{18}O/^{16}O$ ratio of water is typically different from the ratios of most rocks. Isotopic exchange between rock and water might be indicated by change in the oxygen isotopic ratio of the rocks, and the degree of the exchange is largely dependent on the temperature and the amount of water involved. For these reasons, study of oxygen isotopes has become an important tool in petrology studies since the early 60's and many investigations have been carried out in various kind of geological terrain (e.g. Taylor and Epstein, 1962; Shieh and Schwarcz, 1974; Valley and O'Neil, 1984).

Hydrogen is always of minor content in various rock types, but is often an important component of fluid phases. The hydrogen isotopic ratio ($^2H/^1H$) of hydroxyl-minerals or rocks, together with oxygen isotopic ratio may provide constraints on the source of fluids involved in formation of rock and the path of fluid migration during or after the formation. Hydrogen isotopic ratio is very sensitive to the isotopic exchange since hydrogen is a minor component. It is possible that a very small amount of fluid might significantly change the hydrogen isotopic ratio of the minerals, while keeping the oxygen isotopic ratio unchanged. Some studies have been done in igneous and low- to medium-grade metamorphic rocks (e.g. Sheppard and Epstein, 1970; Rye et al., 1976; Wickham and Taylor, 1985), however, only few data of high-grade rocks have been reported (Taylor, 1977; Taylor and Forester, 1979).

This study is a geochemical contribution to the investigation of the Wawa-Kapuskasing transect, as part of the LITHOPROBE project. The term LITHOPROBE is derived from "probing the lithosphere" and the project is designed to study the outmost 100 km of the Earth whose dynamics control the geological development of the Earth crust. The Kapuskasing Structural Zone is one of the areas which LITHOPROBE focuses on.

The oxygen isotopic ratios of rocks from different crustal levels have been determined, as well as the ratios for coexisting minerals and the hydrogen isotopic ratios for hydroxyl-minerals. Our purpose is (a) to provide general oxygen isotopic characteristics of the major lithologic units across the transect, (b) to examine the isotopic relationships within the rocks and coexisting minerals, and (c) to infer the possible origins of the rocks, the possible protolith of the high-grade metamorphic rocks and their metamorphic processes. The hydrogen isotopic ratios were studied to determine the role of fluids during high-grade metamorphism and provide insight into the possible source of the fluids.

CHAPTER TWO

GEOLOGY OF THE WAWA-KAPUSKASING TRANSECT

2.1 INTRODUCTION

The Superior Province of the Canadian Shield is the largest Archean terrain in the world. Like many Archean terrains, the Superior Province is characterized by two distinct types of belts (subprovinces), alternating low-grade greenstone belts and high-grade gneiss belts, which generally show east-west trends (Figure 2.1). In the central Superior Province, the continuity of the east-west structural trends is transected by north-east striking Kapuskasing Structural Zone (KSZ) (Thurston et al., 1977), distinguished by lithologically heterogeneous and high-grade metamorphic rocks accompanying the positive gravity and aeromagnetic anomalies (Percival and Card, 1985).

The KSZ extends over 300 km in length, from the north at James Bay to the south near Lake Superior (Percival, 1981). Three distinct geological-geophysical blocks have been divided: from south to north, the Chapleau,

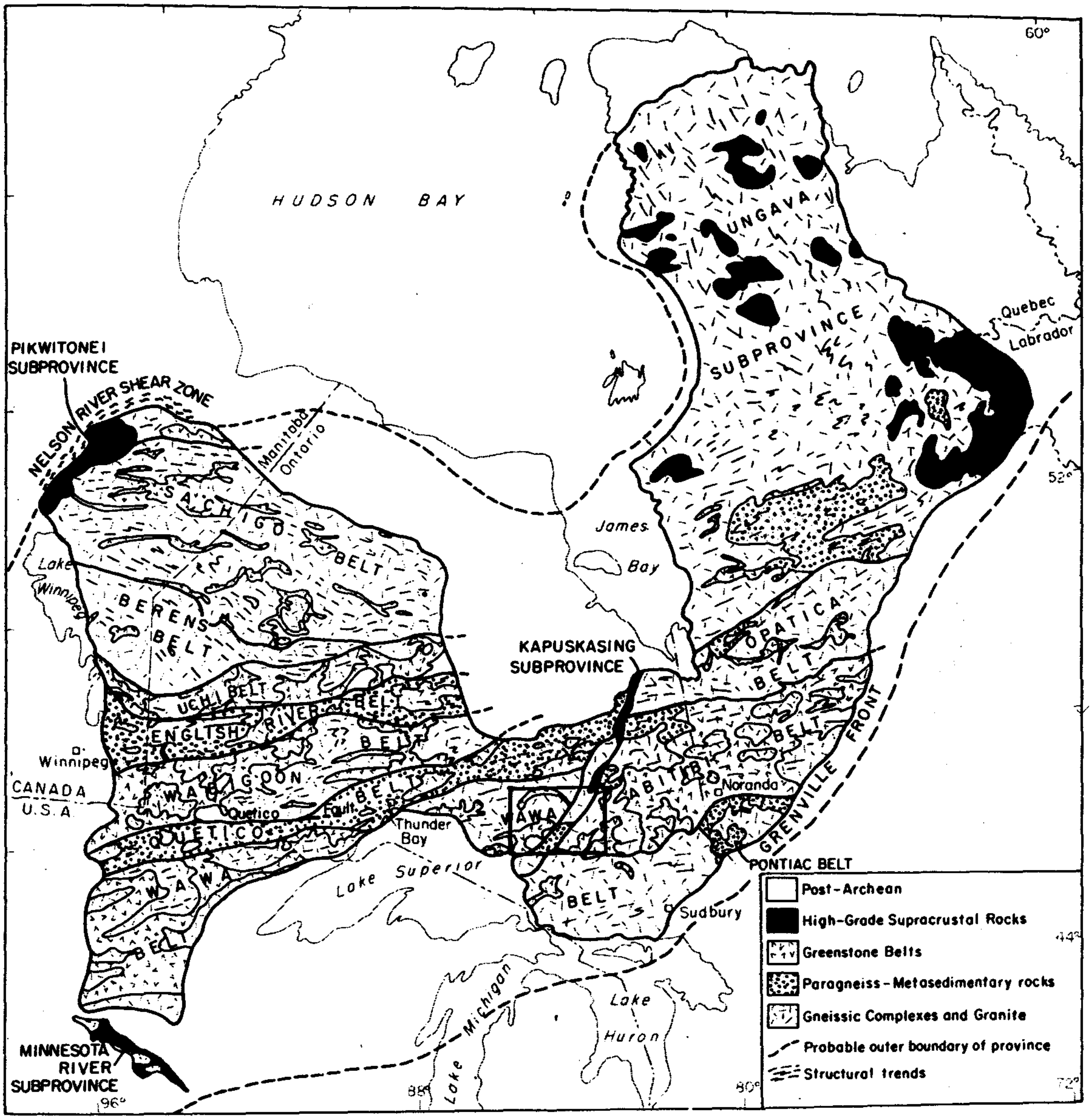

Figure 2.1 Geologic map of the Superior Province, Canada and U.S.A. (after Condie, 1981). The central box is the study area shown in the Figure 2.2.

Groundhog River, and Fraserdale-Moosenee blocks (Percival and McGrath, 1986). Among them, the Chapleau block has been well studied, in the fields of geology, geophysics and geochemistry.

In the Chapleau region a complete and continuous transect is exposed, eastward from the low-grade Michipicoten Greenstone Belt (MGB), through the intermediate Wawa Gneiss Terrane (WGT) into the high-grade Kapuskasing Structural Zone (KSZ), over about 120 km distance. The Ivanhoe Lake Cataclastic Zone (ILCZ) bounds the transect on the east, separating the high-grade KSZ with the low-grade Abitibi Greenstone Belt (AGB) (Figure 2.2).

The Kapuskasing structure was originally interpreted as a thinning granitic crust based on the gravity information (Garland, 1950) and as a rift-related structure associated with the central American Rift (Innes, 1960, Burke and Dewey, 1973). More recently, the structure has been interpreted as an oblique section through about 20 km of Archean crust, representing progressively deeper crustal levels, thrust upward along the west dipping ILCZ and overlying the AGB (Thurston et al, 1977, Percival and Card, 1985, Percival and McGrath, 1986).

This study is focusing on the Chapleau region, including the southern part of the KSZ, the adjacent WGT, and the central and eastern parts of the MGB (Figure 2.1 and 2.2).

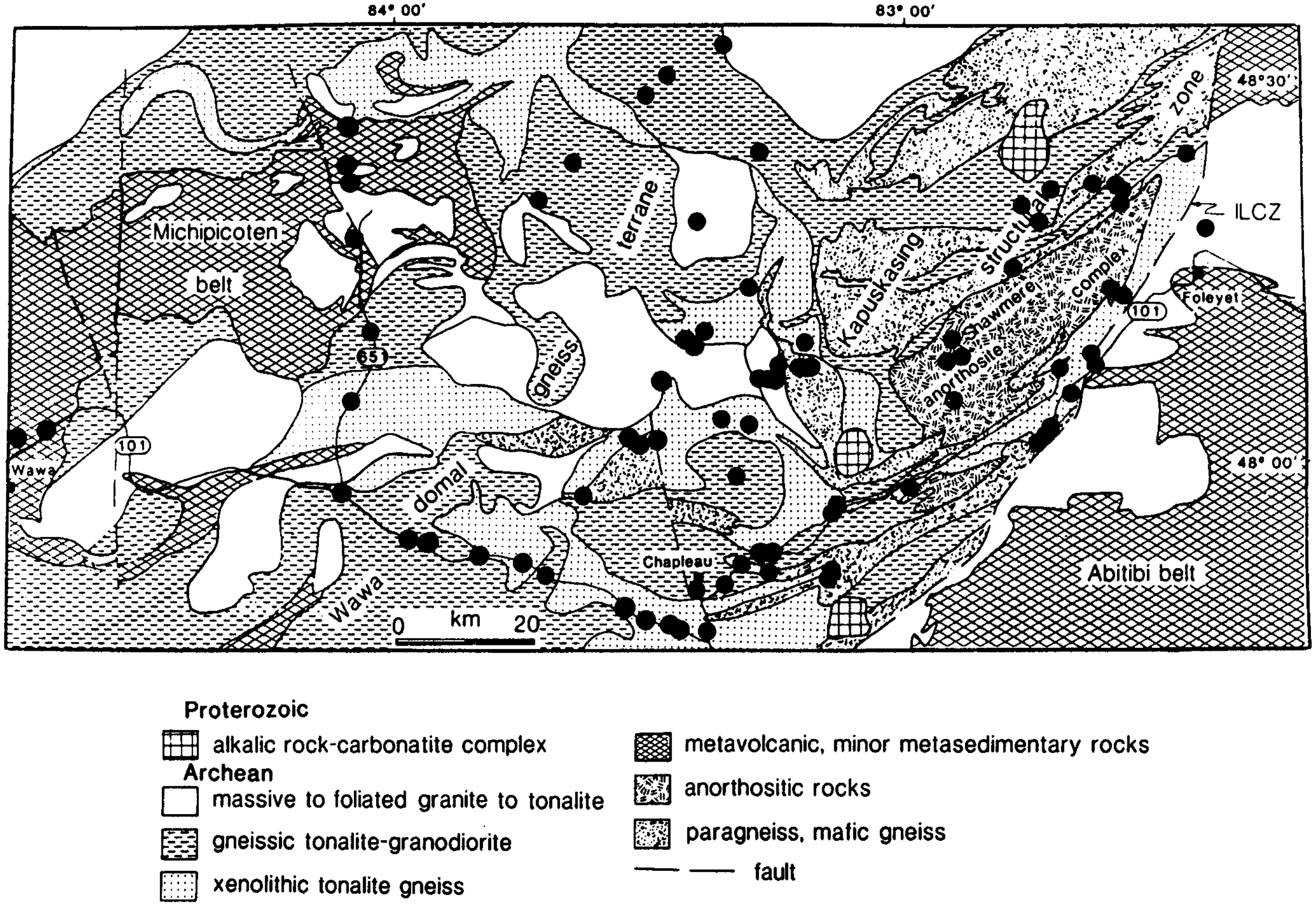

Figure 2.2 Map of study area, including the south part of the Kapuskasing Structural Zone (KSZ), adjacent Wawa Gneiss Terrain (WGT) and the east part of the Michipicoten Greenstone Belt (MGB) (after Percival and Card, 1983). Black dots show sample locations. A few sample locations from the central MGB are not shown on the map.

2.2. GEOLOGICAL SETTING

2.2.1. KAPUSKASING STRUCTURAL ZONE

The Kapuskasing Structural Zone, a northeast-striking belt, is composed of heterogeneous and interlayered high-grade gneissic rocks, predominantly paragneiss, mafic gneiss, gneissic and xenolithic tonalite and anorthositic rocks (Percival and Card, 1983, 1985). The paragneiss, together with associated mafic gneiss, is commonly referred to as a supracrustal sequence in the KSZ. Several small carbonatitic complexes of Proterozoic age are associated with the KSZ.

Paragneiss is a widespread but volumetrically minor component in the KSZ, commonly associated with mafic gneiss. The paragneiss is recognized chemically by its Si, Al-rich composition (58-80% SiO_2 and 16-18% Al_2O_3) and locally by the presence of graphite and relics of conglomeratic texture. Major element discriminant functions (Shaw, 1972) calculated for the rocks give negative values, supporting their interpretation as metasedimentary rocks. The paragneiss is composed of garnet-rich, biotite-rich and quartz-rich layers; and commonly shows migmatitic texture, with concordant tonalitic leucosome.

Mafic gneiss is characterized by garnet-clinopyroxene-hornblende-plagioclase-quartz mineral assemblages. They are chemically similar to basalt, but slightly higher in calcium (9-16% CaO) and alumina (14-17% Al_2O_3). There are concordant tonalitic layers in the mafic gneiss, possibly of migmatitic origin.

Tonalitic and granodioritic rocks are gneissic and foliated. The rocks have hornblende-biotite-plagioclase-quartz mineral assemblages, and contain xenoliths of paragneiss, mafic gneiss and ultramafic bodies.

The Shawmere Anorthosite Complex consists of two discrete bodies: a main northern body and a small southern body. They are gabbroic to anorthositic rocks in composition, with garnet, pyroxene and hornblende as major mafic minerals. The margins of the body often show gneissic texture, whereas the interior has preserved primary igneous texture.

Intermediate rocks, mostly diorite in composition, are volumetrically minor components. They have hornblende-biotite-plagioclase-quartz mineral assemblages, show foliated to gneissic texture, and occur dominantly within the paragneiss units.

The rocks of the KSZ have been metamorphosed to upper amphibolite to granulite facies, varying systematically across the region. Two metamorphic zones have been distinguished: a garnet-clinopyroxene-plagioclase bearing zone and an orthopyroxene bearing zone (Percival, 1983). Pressure and temperature conditions of metamorphism are in the range 7 to 9 Kbar and 700 to 800°C, based on garnet-pyroxene-biotite mineral geobarometers and geothermometers (Percival, 1983).

The KSZ is sharply separated from the AGB to the east by the northeasttrending and west-dipping ILCZ, while the western boundary with the WGT is gradational, in structure, lithology and also metamorphic grade (Figure 2.2).

2.2.2. WAWA GNEISS TERRAIN

The Wawa Gneiss Terrain is dominated by tonalitic gneiss and monzonitic to granitic plutons. Tonalitic gneisses have hornblende-biotite-plagioclase-quartz assemblages, containing various amounts of xenoliths of mafic gneiss and paragneiss. The plutonic rocks are intruded into the older gneissic rocks, and are foliated and strongly deformed. Mafic xenoliths have similar bulk composition with the mafic gneisses in the KSZ, and commonly have clinopyroxene-hornblende-biotite-plagioclase-quartz assemblages. The region is also cut by a few diabase dyke swarms (Halls and Palmer, 1990).

Metamorphic grade of the rocks is amphibolite to upper amphibolite facies in the WGT and increasing eastward. Three metamorphic zones have been defined: from the west to the east, a hornblende-plagioclase zone; a hornblende-clinopyroxene-plagioclase zone; and a garnet-clinopyroxene-plagioclase zone (Percival, 1983). Pressure and temperature conditions of the metamorphism are in the range of 5 to 6 kbar and 600 to 700°C.

2.2.3. MICHIPICOTEN GREENSTONE BELT

The Michipicoten Greenstone Belt consists of mafic to felsic metavolcanic rocks, divided into lower, middle and upper metavolcanic sequences and interstratified with clastic and chemical metasedimentary units (Attoh, 1980). In the central part of the MGB, the volcanic sequence is dominantly basalt and rhyolite in composition, while dacite and andesite are less abundant. The sedimentary units contain mainly marine type sediments, dominantly greywacke, shale, conglomerate, and locally iron formation. The supracrustal sequences are intruded by plutons, diorite to granodiorite in composition.

Most of the rocks in the MGB were metamorphosed to greenschist facies, with pressure and temperature conditions of 2 to 3 kbar and 325 to 450°C (Studemeister, 1983).

2.3. GEOCHRONOLOGY

Uranium-lead radiometric techniques have been applied to date the rocks in the Wawa-Kapuskasing transect, providing some constraints on the crustal history of the region.

The metavolcanic rocks from the MGB have been dated using the zircon U-Pb method (Turek et al., 1982), yielding ages of 2696 Ma for the upper volcanic sequence and 2749 Ma for the lower volcanic sequence, which give a minimum time period of 53 Ma for the evolution of the MGB.

Two sets of plutonic rocks associated with the supracrustal sequences exist in the MGB: older intrusions have U-Pb zircon ages of 2747-2737 Ma, which are possibly coeval with the lower sequence of the volcanics; and younger plutons have U-Pb zircon ages in the range 2685-2668 Ma (Krogh and Turek, 1982; Krogh et al., 1982), which intruded later than the development of volcanic sequences.

Tonalitic gneiss from the WGT has a minimum Pb-Pb zircon age of 2707 Ma (Percival and Krogh, 1983).

Foliated to gneissic tonalite in the Shawmere anorthosite complex of the KSZ has been dated (Percival and Krogh, 1983), giving a minimum Pb-Pb zircon age of 2765 Ma. This is thought to represent the development of the Kapuskasing supracrustal sequence and Shawmere anorthosite.

The metamorphic and tectonic events in the Wawa-Kapuskasing transect took place in the time period of 2700-2685 Ma for the upper crustal level (MGB) and 2650-2627 Ma for the lower level (KSZ), recorded by the zircon U-Pb system of the rocks (Percival and Krogh, 1983). Significantly younger ages of the lower crust are interpreted by Percival and Krogh (1983) as the results of slow post-metamorphic cooling at depth, and later is argued by Corfu (1987) as reflecting independent metamorphism from that of the upper level crust.

A time framework for the regional evolution can be reconstructed based on these geochronological data: the Kapuskasing supracrustal sequence and Shawmere anorthosite (>2765 Ma) developed first, followed by the main Wawa volcanic sequence (2749-2696 Ma). The syn- to post-volcanic tonalites (2707-2668 Ma) were subsequently intruded into the two earlier sequences. The region may have experienced more than one stage of metamorphic and tectonic effects (from 2700 to 2627 Ma).

2.4. DISTRIBUTION OF SAMPLING

Sample localities for the investigation are shown as black dots in Figure 2.2, and the rock units and their brief descriptions are summarized in Tables 4.1, 4.2 and 4.3. All samples were collected between the period of 1983-1989, and cover most lithological and structural units in the region. The samples prefixed P were provided by J. Percival and those prefixed WW were donated by K. Attoh.

The sample set has been used for parallel geochemistry studies in the LITHOPROBE program (Shaw et al., 1988, Truscott and Shaw, 1990), which provided a complete data base for both major and many trace elements.

CHAPTER THREE

STABLE ISOTOPES AND ANALYTICAL METHOD

3.1. STABLE ISOTOPES

3.1.1. OXYGEN AND HYDROGEN ISOTOPES

Isotopes are defined as atomic species whose nuclei contain the same number of protons but different number of neutrons. Isotopes of one element occupy the same position in the Periodic Table. Stable isotopes are those that are not radioactive and their abundances in nature are not a function of time. Most elements have more than one stable isotope.

Oxygen has three stable isotopes in nature: ^{16}O, ^{17}O and ^{18}O, which have average abundance 99.735%, 0.0375% and 0.1995%, respectively (Hoefs, 1980). Among the three isotopes, ^{18}O, ^{16}O and their isotopic ratio, $^{18}O/^{16}O$, are mostly interesting to geologists because of their higher abundance and the greater mass difference between them, which often result in large variations in oxygen isotopic compositions of many natural materials.

Hydrogen has two stable isotopes in nature: hydrogen ^1H and deuterium ^2H (usually represent as D). ^1H has average abundance 99.9844% and ^2H has 0.0156% (Way et al., 1950). In addition, there is a radioactive hydrogen isotope occurring naturally, tritium ^3H, with a half-life of approximately 12.5 years. In this study, only the two stable isotopes are of concern.

3.1.2. TERMINOLOGY

Following are the terminologies and expressions commonly used in the stable isotope studies.

The stable isotopic compositions of oxygen and hydrogen are conventionally reported in δ notation, which is the difference in isotopic ratio between a sample and a standard, with units of parts per thousand or permil (‰):

$$\delta^{18}O(‰) = \left(\frac{R_{sample}-R_{standard}}{R_{standard}}\right)\times 10^3 \tag{3-1}$$

$$\delta D(‰) = \left(\frac{R_{sample}-R_{standard}}{R_{standard}}\right)\times 10^3 \tag{3-2}$$

where R_{sample} and $R_{standard}$ are the atomic ratios of the heavy to the light isotope in sample and standard, for example, $R={}^{18}O/{}^{16}O$ and $R=D/H$ for oxygen and hydrogen isotopes, respectively.

The isotope fractionation factor, $\alpha_{x\text{-}y}$, between two mineral phases x and y is defined as:

$$\alpha_{x\text{-}y}=\frac{R_x}{R_y} \tag{3-3}$$

The fractionation factor α can also be expressed related to δ values:

$$\alpha_{x\text{-}y}=\frac{1+10^{-3}\delta_x}{1+10^{-3}\delta_y} \tag{3-4}$$

Δ is the difference of δ values between two mineral phases (some people also call is the isotopic fractionation), and defined as:

$$\Delta_{x\text{-}y}=\delta_x-\delta_y \tag{3-5}$$

mathematically, α can be very well approximated as:

$$10^3\ln\alpha_{x\text{-}y}\cong\Delta_{x\text{-}y}=\delta_x-\delta_y \tag{3-6}$$

for $|\Delta_{\text{oxygen}}| \leq 10$ ‰; or $|\Delta_{\text{hydrogen}}| \leq 80$ ‰

Theoretical studies show that the fractionation factor α is a linear function of T^{-2}, where T is in Kelvin. A general relation can be expressed by the equation (Bottinga and Javoy, 1973):

$$10^3\ln\alpha= A\ T^{-2}+ B \tag{3-7}$$

where A and B are equilibrium coefficients, depending on the phases in equilibrium. The fractionation factor α is generally not a function of pressure.

3.2. ANALYTICAL METHOD

3.2.1. SAMPLE PREPARATION

Rock samples were crushed and ground to grain size less than 200 mesh by using a tungsten carbide shatterbox. Great care was taken in order to avoid any contamination during the operation. The powdered samples were used for bulk chemical analyses and whole rock oxygen isotope analyses.

Rock powder with grain size of 100 to 150 mesh was used for mineral separation. Magnetite was separated initially from rock powder by using a hand magnet. Hornblende and biotite were magnetically separated by using the Franz Isodynamic Magnetic Separator. Quartz and feldspar, from coarse tonalitic rocks, were hand picked under a binocular microscope. The mineral separates were cleaned using dilute HCl and distilled water (except biotite which was only washed using water). The purity of the mineral samples was checked under a binocular microscope and was better than 95%. For oxygen isotope analyses, the minerals were further ground into fine powder of less than 200 mesh.

3.2.2. CHEMICAL ANALYSIS

Major and trace elements of whole rock samples were analyzed by X-ray Fluorescence Spectrometry (XRF)[a], using fused disc and pressed pellet methods.

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[a]: XRF and INAA were performed at McMaster University.

Chemical compositions of hornblende and biotite were determined by Electron Microprobe Analysis (EMA)[b].

3.2.3. STANDARDS IN STABLE ISOTOPE ANALYSIS

Standard Mean Ocean Water (SMOW) as a universal standard for both oxygen and hydrogen isotope was defined by Craig (1961), and the δ value of SMOW is 0 ‰. Consequently, samples with positive $\delta^{18}O$ or δD value indicate enrichment in ^{18}O or D compared to SMOW, whereas one with negative value implies depletion in these isotopes.

A pure silica sand (NBS-28) is used as a reference standard for oxygen isotope analysis and its $\delta^{18}O$ values have been reported in a range 9.0 to 10.0 ‰ (Friedman and Gleason, 1973 and Lipman and Friedman, 1975). A biotite (NBS-30) is used as a reference standard for hydrogen isotope analysis and its δD value is recommended as -64 ‰ by IAEA[c].

The precision of the isotope analysis is usually indicated using a standard deviation, expressed as:

$$S=\sqrt{\frac{\sum_{i-1}^{n}(X_i-\overline{X})^2}{n-1}} \qquad (3-8)$$

---

[b] EMA was performed by B. Barnett at University of Western Ontario.

[c] IAEA: International Atomic Energy Agency.

where *S* is standard deviation, *n* is number of duplication, and X_i and $\overline{X}$ are the *i*th δ value and mean δ value, respectively. It has been stated in many articles that the standard deviation of oxygen isotope analyses is 0.1 to 0.2 ‰ and that of hydrogen isotope analyses is 1 to 2 ‰.

The accuracy of the isotope analysis is checked by running the standards and comparing the results with recommended values.

Two internal standards have been used as reference for mass spectrometric analyses. GCS is a calcite sample used for oxygen isotope analyses and DTAP is distilled water for hydrogen isotope analyses. All samples were determined relative to the references and calibrated relative to SMOW standard.

3.2.4. OXYGEN ISOTOPE ANALYSIS

Oxygen in whole rock and mineral samples was released by reacting samples with a strong oxidizing agent, bromine pentafluoride (BrF_5), in nickel vessels at 550-650°C (Clayton and Mayeda, 1963). A typical reaction of bromine pentafluoride with a silicate can be illustrated as:

$$KAlSi_3O_8 + 8BrF_5 \rightarrow KF + AlF_3 + 8BrF_3 + 4O_2 + 3SiF_4 \qquad (3\text{-}9)$$

The sample weights corresponding to 10-15 mmol O_2 were used for each run, with an approximately five-fold excess of oxidizing reagent (BrF_5) over stoichiometric requirements. Oxygen gas can be separated from other products by trapping the fluoride in a series of liquid-N_2 traps. The extracted oxygen was converted to carbon dioxide by passing a hot graphite (550-600°C) by the reaction:

$$C + O_2 \rightarrow CO_2 \tag{3-10}$$

The detailed procedures have been described by Taylor and Epstein (1962).

Mass spectrometric analyses of carbon dioxide were carried out using a dual inlet, triple collecting VG mass spectrometer. The oxygen isotope composition is reported conventionally in δ notation relative to SMOW. The standard NBS-28 was routinely analyzed along with unknown samples, giving an average $\delta^{18}O = 9.6$ ‰ and a precision of 0.16 ‰ (1σ) (Table 3.1). Among the various types of rocks and minerals about 20% of the analyses have been duplicated and the results are in agreement within the expected precision, with few exceptions.

3.2.5. HYDROGEN ISOTOPE ANALYSIS

Hydrogen in hornblende and biotite exists as the hydroxyl groups. An important concern about hydrogen isotope analysis in hydroxyl minerals is to completely release the hydroxyl water from the minerals. Hornblende samples, their weights corresponding to about 10 mmol of H_2O, were loaded in vycor tubes and connected to a vacuum line opened to the diffusion pump. The samples were preheated at about 100°C in order to remove absorbed moisture. Then, hornblende and biotite were heated up to their melting points by using a gas torch

Table 3.1 $\delta^{18}O$ (‰) OF NBS-28 STANDARD ANALYSES

9.79	9.83	9.29	9.76	9.66	
9.67	9.61	9.59	9.37	9.73	
10.02*	9.65	9.50	9.65	9.65	
9.90	9.65	9.36	9.37	9.32	
10.28*	9.57	9.63	9.40	9.69	
9.66	9.67	9.06*	9.83	9.61	
9.58	9.61	9.55	10.05*	9.42	
9.77	9.53	9.50	9.35	9.42	
9.61	9.71	9.64	9.31	9.49	
9.54	9.47	9.77	9.80	9.66	
9.98	9.56	9.42	9.49	9.78	AVE=9.59
9.75	9.56	9.49	9.33		S=0.16
9.59	9.41	9.44	9.61		N=59

Note: 1) All results in the table have satisfactory yields (see text). 2) the numbers with (*) were eliminated from the precision calculation, since they fall at outside 2σ range. 3) AVE: average of the results; S: standard deviation; N: numbers of analyses.

to release the hydroxyl water. The vycor tubes were opened to a liquid-N_2 cold finger which can trap condensed gases and lower the internal pressure, therefore, encouraging the release reaction.

The released hydroxyl water is mainly in the form of H_2O and trapped in the cold finger. The extracted water was passing through a uranium furnace at 750°C (Bigeleisen et al., 1952 and Craig, 1961), reduced to H_2 by the reaction:

$$U + 2H_2O \rightarrow UO_2 + 2H_2 \tag{3-11}$$

A small portion of hydroxyl water is liberated in the form of H_2 gas directly, which, if ignored, may cause isotopic fractionation as high as 30 ‰. In our experiments this small portion of hydrogen was collected in a charcoal-filled tube at liquid-N_2 temperature and later analyzed together with the hydrogen gas from the H_2O conversion.

Mass spectrometric analyses of hydrogen were performed on the VG mass spectrometer. The hydrogen isotope composition is also reported in δ notation relative to SMOW. The precision is 1 ‰ (1σ) based on replicate analyses of SMOW (Table 3.2). The standard NBS-30, run under the same conditions as the unknown samples, gave an average $\delta D = -65$ ‰ and a precision of 0.6 ‰ (1σ) (Table 3.2). Some duplicate analyses of samples showed poor agreement, which is probably caused by the presence of impurities in the mineral samples, especially when the impurities are also hydroxyl-bearing minerals, such as chlorite and sericite.

Table 3.2 δD (‰) OF SMOW AND NBS-30 STANDARD ANALYSES

SMOW:	72.60		NBS-30:	-64.74	
	71.87			-65.94	
	70.73			-64.58	
	73.79			-64.80	
	73.26				
	72.14				
	73.09				
	73.93				
	72.39	AVR=72.31			AVR=-65.02
	70.47	STD=1.18			STD=0.54
	71.13	N=11			N=4

Note: 1)SMOW is reported relative to DTAP reference. 2)NBS-30 is reported relative to SMOW.
3)AVE: average results; S: standard deviation; N: numbers of analyses.

CHAPTER FOUR

OXYGEN ISOTOPIC COMPOSITIONS OF WHOLE ROCKS

4.1. INTRODUCTION

Oxygen isotope geochemistry has been applied to igneous and metamorphic petrology studies for near three decades. Many oxygen isotopic data have been produced and interpreted for igneous and metamorphic rocks from various places. These studies have provided a useful data base of general oxygen isotopic characteristics for different types of rocks and their isotopic variations due to magmatic and metamorphic processes. Oxygen isotope geochemistry has helped to solve many petrological problems, especially regarding the origin of the igneous and metamorphic rocks, their conditions of formation and the involvement of fluid phase during these processes (Taylor, 1968, 1970; Shieh and Schwarcz, 1974, 1977; Bottinga and Javoy, 1975; Muehlenbachs and Clayton, 1976; O'Neil, Shaw and Flood, 1977; Longstaffe, 1979; Wilson, 1981; Chivas et al., 1982; Valley and O'Neil, 1984; Sheppard and Harris, 1985; and Jiang et al., 1988).

In this study, oxygen isotopic geochemistry has been applied to the unique Wawa-Kapuskasing transect, a metamorphic terrain with increasing metamorphic grade. The purpose is to present the isotopic data of different crustal rocks, to discover whether the oxygen isotopic composition of these rocks varies systematically with increasing crustal depth or metamorphic grade, and to determine the origin of the protoliths of the metamorphic rocks, the metamorphic conditions and possible fluid effects during high-grade metamorphism.

4.2. OXYGEN ISOTOPE GEOCHEMISTRY IN CRUSTAL ROCKS

Many studies indicate that rocks formed in different environments are generally characterized by different isotopic composition ranges. There are two distinctive categories: igneous rocks which formed in high-temperature environment; and sedimentary rocks which formed in low-temperature environment.

Igneous rocks have relatively restricted $\delta^{18}O$ values (Figure 4.1, after Taylor, 1974). For instance, lunar basalts and fresh oceanic basalts have very uniform $\delta^{18}O$ values of 5 to 7 ‰. Very similar $\delta^{18}O$ values are also observed in ultramafic rocks. The oceanic basalts and ultramafic rocks are believed to be of mantle origin and their $\delta^{18}O$ values indicate that there probably is a uniform ^{18}O reservoir in the upper mantle. Intermediate rocks and more felsic volcanic rocks, such as anorthosite, andesite, dacite and rhyolite flows have a slightly larger $\delta^{18}O$

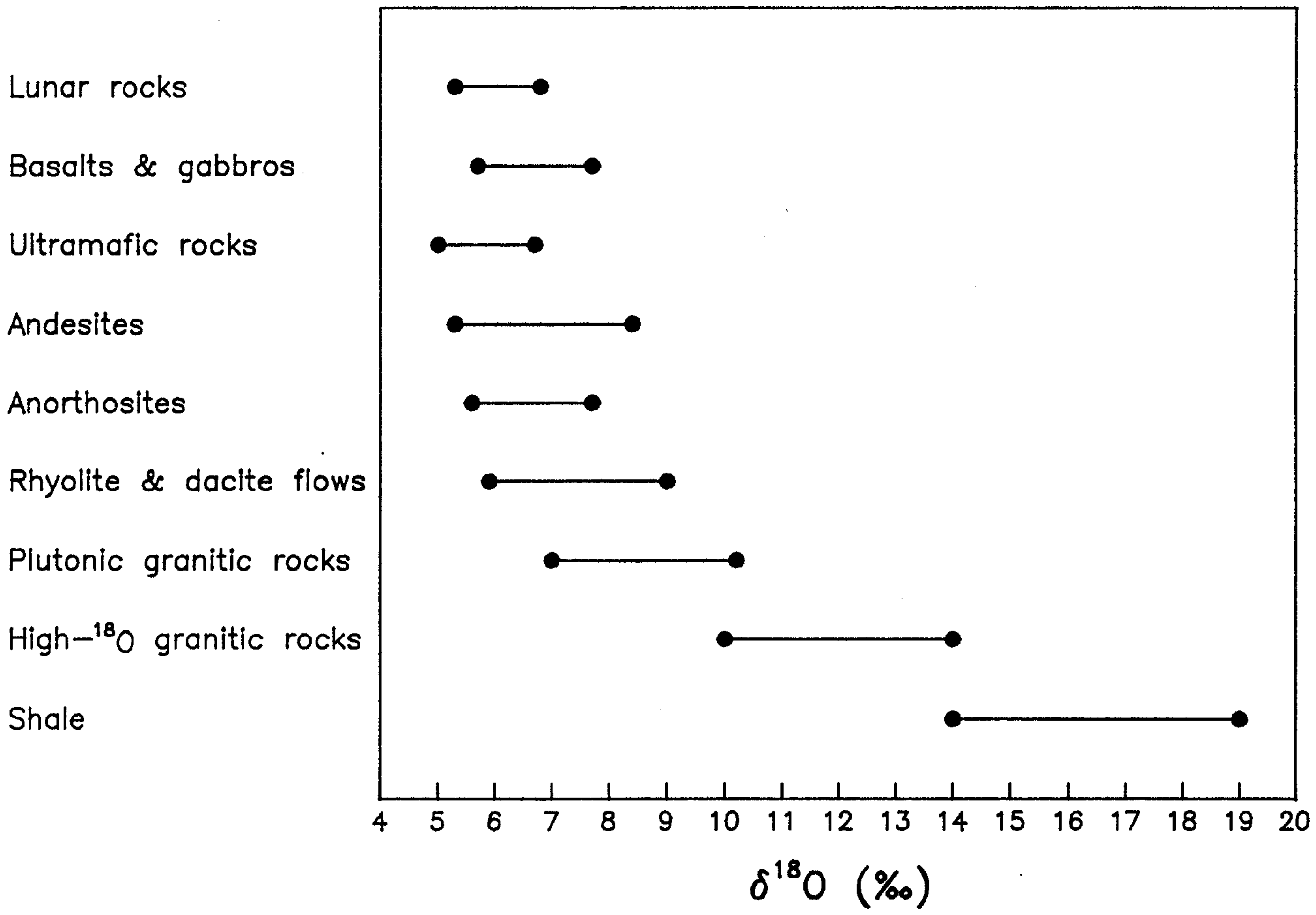

Figure 4.1 δ^{18}O range for common igneous and sedimentary rocks. Original data are from Savin and Epstein (1970), Taylor (1974), Taylor and Magaritz (1975), Longstaffe and Schwarcz (1977), Harmon et al. (1984), Wickham and Taylor (1985) and Debon et al. (1986).

range, 5.6 to 8.7 ‰. Most intrusive granitic rocks have $\delta^{18}O$ range of 7.8 to 10.2 ‰. During the last fifteen years, however, many studies show that there are granitic plutons having higher $\delta^{18}O$ values of 10 to 14 ‰ (Figure 4.1). Most of these ^{18}O-enriched granitic rocks are middle Palaeozoic to Cenozoic in age, and are volumetrically important in many orogenic zones, such as the Himalayan, Hercynian and Caledonian. The $\delta^{18}O$ data indicate that magmas producing these rocks contain a large proportion of crustal materials, which have undergone surface weathering processes (see below) (Harmon et al., 1984; Wickham and Taylor, 1985 and Debon et al, 1986)

Sedimentary rocks have a relatively large $\delta^{18}O$ range. The bulk oxygen isotopic composition of detrital sedimentary rocks is mainly controlled by the mineral and rock particles of which they are composed and affected by the degree of weathering and transportation that the detritals have undergone. Normally, weathering involves large amounts of water, such as meteoric water. At the surface temperature, there are large isotopic fractionations between mineral and water (Savin and Epstein, 1970), resulting in ^{18}O-enrichment of the mineral phases, typically clay minerals. For instance, Longstaffe and Schwarcz (1977) reported immature clastic metasediments, which contain large proportion of unweathered felsic volcanic detritals, having $\delta^{18}O$ values of 8.0 to 13.3 ‰. Magaritz and Taylor (1976) reported greywacke having $\delta^{18}O$ values of 10.3 to 15.3 ‰. Shales have higher $\delta^{18}O$ values of 14 to 19 ‰ (Savin and Epstein, 1970). Chemical sediments have an even higher $\delta^{18}O$ range, for example, 28 to 30 ‰ for recent marine limestones and ≥30 ‰ for chert (Faure 1986).

These distinctive characteristics of whole rock $\delta^{18}O$ values provide a powerful index which could help us to distinguish the origins of the igneous rocks and protoliths of the metamorphic rocks, and to estimate the relative portion of mantle and crust materials involved in magmatic processes. Using the oxygen isotopic composition as an index is especially important to identify the origin of the high-grade metamorphic rocks, in which the bulk chemical composition is possibly either igneous or sedimentary. In some amphibolites, for instance, their original mineralogical assemblages, pre-metamorphic texture and structure have been completely destroyed during high-grade metamorphism.

In addition, many rocks show anomalous $\delta^{18}O$ values while the bulk chemical compositions are normal. For example, some igneous and metamorphic rocks have very low ^{18}O contents, which can be shown to have been altered by meteoric water at high temperature. Studying the oxygen isotopes of these rocks can help to understand the geological process which are attributed to these unusual $\delta^{18}O$ values (Taylor, 1969; Valley and O'Neil, 1982,1984).

4.3. METAMORPHIC EFFECTS ON THE OXYGEN ISOTOPES

Before we discuss the oxygen isotopic composition of metamorphic rocks, it is necessary to review some of the important metamorphic processes which would have effects on their oxygen isotopic composition.

The distribution of oxygen isotopes in metamorphic rocks, in fact, depends on the combination of many complex effects. Of many effects, however, there are four controlling factors: 1) the isotope composition of the protolith; 2) the effects of volatilization during metamorphism; 3) exchange with fluid; and 4) the metamorphic temperature.

4.3.1. OPEN AND CLOSED SYSTEM

Two extreme metamorphic situations have to be considered: ***closed system*** and ***open system***. If metamorphism takes place in a closed system, in which rocks neither exchange with exterior materials nor do fluids escape from the system, the metamorphosed rocks should preserve their original isotope compositions (Valley and O'Neil, 1984; Valley, 1986; and Wickham and Taylor, 1987). In many terrains, however, metamorphism has taken place in an open system, in which either external materials were introduced into, or volatile components escaped from, the rock system (see below). The external materials could be an intrusive magma (e.g. the situation of contact metamorphism) or other fluid phases, such as water, which may have different isotope compositions from the original rocks (e.g. meteoric water depleted in both ^{18}O and D).

The isotopic exchange with foreign materials might modify the oxygen isotopic compositions of the rocks and the scale of the exchange would be controlled by the features of the original rocks, the external materials, and as well as the metamorphic condition (Taylor, 1969; Wilson and Baksi, 1983). In some kind of metamorphism the rocks have been isotopically exchanged with a large reservoir, for instance, with permeating water, and the original isotope difference of the rocks could be smoothed out by an external oxygen dominated reservoir on a very large scale (Shieh and Schwarcz, 1974). In this kind of situation, the $\delta^{18}O$ values of the metamorphic rocks would be controlled by the reservoirs.

4.3.2. VOLATILIZATION

The effects of volatilization on isotope compositions of metamorphic rocks have been studied by many people. The most common types of volatilization are dehydration, and decarbonation in some carbonate-bearing lithologies. The volatilization reactions usually increase the volume of the system, therefore fluids produced tend to escape from the system towards a low pressure direction, generally upwards. The liberated metamorphic fluids generally have different isotopic compositions than the rocks because of the isotopic fractionation between fluid and solid phases at a certain temperature. This can have a profound effect on the isotope content of the residual rocks.

The volatilization reaction can be described by two extreme models (Broecker and Oversby, 1971). ***Batch*** volatilization is a process where all fluids equilibrate with the rocks before any is permitted to escape (also some people refer to this as "closed system". ***Rayleigh*** volatilization is a process where each small aliquot of fluid is immediately isolated from the system before the next volatilization, which is close to an "open system". In nature, however, volatilization might proceed in a way between these two extreme models.

The Batch fractionation reaction can be described by the equation:

$$\delta_f = \delta_i + 10^3 \ln\alpha\,(1-F) \qquad (4\text{-}1)$$

and the Rayleigh fractionation reaction can be described by the equation:

$$\delta_f = (\delta_i + 10^3)\,F^{(\frac{1}{\alpha}-1)} - 10^3 \qquad (4\text{-}2)$$

where δ_f and δ_i are the final and initial isotopic values of the rocks (e.g. $\delta_f^{18}O$ or $\delta_f D$); α is the equilibrium fractionation factor between mineral and volatile (Equ. 3-3); and F is the mole fraction of the element that remains in the rock after volatilization. The δ_f can be determined experimentally. For most cases, the exact pre-metamorphic isotopic compositions (δ_i) and the volatile contents of a rock are impossible to know and can only be assumed, based on the "normal" values of such rocks. Since fractionation factor α is a function of metamorphic temperature

(Equ. 3-7), the effect of the volatilization to δ_f is also dependent on the temperature.

Valley (1986) has calculated the effects of both models of volatilization on the oxygen isotopic compositions of the metamorphic rocks. For example, he assumed that a rock original contains 5 wt% H_2O (e.g. shale), which is driven off during the dehydration, and a value of $F \approx 0.9$. Even if a relative large fractionation factor is assumed (e.g. $\alpha = 1.006$, at $T = 300°C$), the change of δ values, $\delta_f - \delta_i$, is only about 0.6 ‰. This hypothetical calculation indicates that metamorphic volatilization, in general, does not significantly affect oxygen isotope composition of the rocks, so the changes of the $\delta^{18}O$ values are usually less than 1 ‰. This is because the rocks themselves are the major reservoirs of oxygen compared with the fluid phases. However, the influences of volatilization on other stable isotopes may be very large due to the relatively small amount of these elements in the rocks, for instance, hydrogen isotopes. The change of δD values by dehydration during metamorphism and the comparison with oxygen isotopes will be further discussed in Chapter 6.

4.3.3. WATER-ROCK INTERACTION

In addition to releasing fluids during metamorphism, rock may also interact with fluids already present. Such rock-fluid interaction is an important process, which might significantly modify the stable isotopic compositions of the rocks

(Wilson et al., 1983; Valley and O'Neil, 1984). Stable isotopic study of metamorphic rocks, therefore, can be a very useful tool to discover the source of fluids, the nature of the fluids and the scale of fluid migration in the system.

Two situations can be defined, regarding the movements of the fluids in the rock system. A ***Pervasive*** fluid is defined as one that moves independently of the structure and lithology, and equally permeates through all rocks. The pervasive fluids often tend to homogenize the isotopic compositions of the rocks. A ***Channelized*** fluid only moves along vein systems, contact zones or some permeable lithologic units. Channelized fluids may cause some rocks to dramatically change their isotopic compositions, while others remain unaffected (Valley, 1986).

In most metamorphic terrains, water is the most important component of the fluid phase. The CO_2 is also found to be important in the fluid phase in many high-grade terrains. Many studies have been carried out in recent years about carbon isotopes in fluid phases (e.g. Vry et al., 1988), however, isotopic compositions of CO_2-rich fluids are not the subject of this study.

There are several possible sources of metamorphic waters: 1) metamorphic fluid liberated by volatilization reactions; 2) magmatic fluid derived from deep levels; 3) meteoric water derived from the earth's surface; 4) sea water; and 5) connate formation water. The oxygen isotopic compositions of these source waters have been well studied. For instance, most common meteoric waters generally have relatively low $\delta^{18}O$ values ranging from 0 ‰ to -10 ‰ and seawater has relatively a constant $\delta^{18}O$ value about 0 ‰. These waters might leave their signature in the rocks, especially when large amounts of water were present and interacted with the rock at high temperature.

Hydrogen isotopes can also provide useful information about the nature of the fluids. In many situations, hydrogen isotopes are more sensitive than oxygen isotopes, because most minerals and rocks contain a minor amount of hydrogen, so their hydrogen isotopic compositions are more easily modified, even only with a small amount of water added to the system. Since oxygen and hydrogen are both present in water and their isotopic compositions are related to each other, it is necessary to consider them together. For convenience, we will discuss the oxygen and hydrogen isotopic compositions of the fluids probably involved in the metamorphism in Chapter 6, with emphasis on the hydrogen isotopes.

4.3.4. TEMPERATURE

The temperature is critical for all metamorphic processes discussed above because the isotopic fractionation between coexisting materials is a function of temperature (Equ. 3-7). The effect of the temperature on the isotopic fractionation and the isotopic compositions will be considered regarding the individual processes throughout this and following chapters.

4.4. OXYGEN ISOTOPE STUDY OF ARCHEAN METAMORPHIC ROCKS: A REVIEW

4.4.1. GRANITOIDS IN ARCHEAN HIGH-GRADE TERRAIN

Granitoids are the major components of many Archean high-grade terrains, which, in a broad sense, refer to holocrystalline quartz-bearing rocks including granite, tonalite, granodiorite and monzonite; some paragneisses with similar chemical compositions are also included. The rocks are usually massive, schistose and gneissic in structure, corresponding to igneous and low-grade to high-grade metamorphism; the metamorphic grade can be up to amphibolite to granulite facies. In many terrains, the rocks have been migmatized and strongly foliated.

Oxygen isotope studies of Archean granitic rocks have been carried out by many people. For instance, Taylor and Magaritz (1975) have studied the granitic rocks from Swaziland and the Rhodesian craton of Africa; Perry et al.(1976) have reported oxygen isotopic data on rocks in the Isua supracrustal belt of West Greenland; Shieh and Schwarcz (1977) and Longstaffe (1979) have made intensive survey of Archean granitic rocks in the Superior province of Canadian Shield and Wilson (1981) has studied the granitoids in Yilgarn Block of Western Australia.

There are several important observations on the oxygen isotopic compositions of Archean granitoids. Firstly, many of the granitoids in Archean high-grade terrains show oxygen isotopic homogeneity. For instance, the $\delta^{18}O$ values of the granitic rocks in the Superior province display a narrow range from 7.6 ‰ to 8.6 ‰ (Figure 4.2), with an average value of 8.1 ‰ (Shieh and Schwarcz, 1977), and a survey of granitoids from the Yilgarn Block show a range of $\delta^{18}O$ values from 7.0 ‰ to 9.5 ‰ (Figure 4.2), with an average value of 7.9 ‰ (Wilson, 1981).

Accompanying large scale isotopic homogenization, significant depletion of ^{18}O contents is often observed in these high-grade terrains. For example, Longstaffe (1979) reported the Footprint gneisses of the Superior province having $\delta^{18}O$ values from 5.9 ‰ to 7.0 ‰ (Figure 4.2). Some unusually low $\delta^{18}O$ values have been reported, such as some granulites in the Strangways Range of Australia which have $\delta^{18}O$ values as low as 0.1 ‰ (Wilson and Baksi, 1983), if this is not erroneous.

Based on the mass balance principle, such large scale isotopic homogeneity and depletion of ^{18}O needs a large reservoir with low $\delta^{18}O$ value and good communication between rocks and the reservoir. Shieh and Schwarcz (1974,1977) have suggested that deep-seated mafic or ultramafic bodies are the possible low $\delta^{18}O$ reservoir for those granitic rocks in the Grenville and Superior province. The volume of the mafic reservoir is probably large compared to the volume of the granitic rocks in the lower crust which commonly have $\delta^{18}O$ values

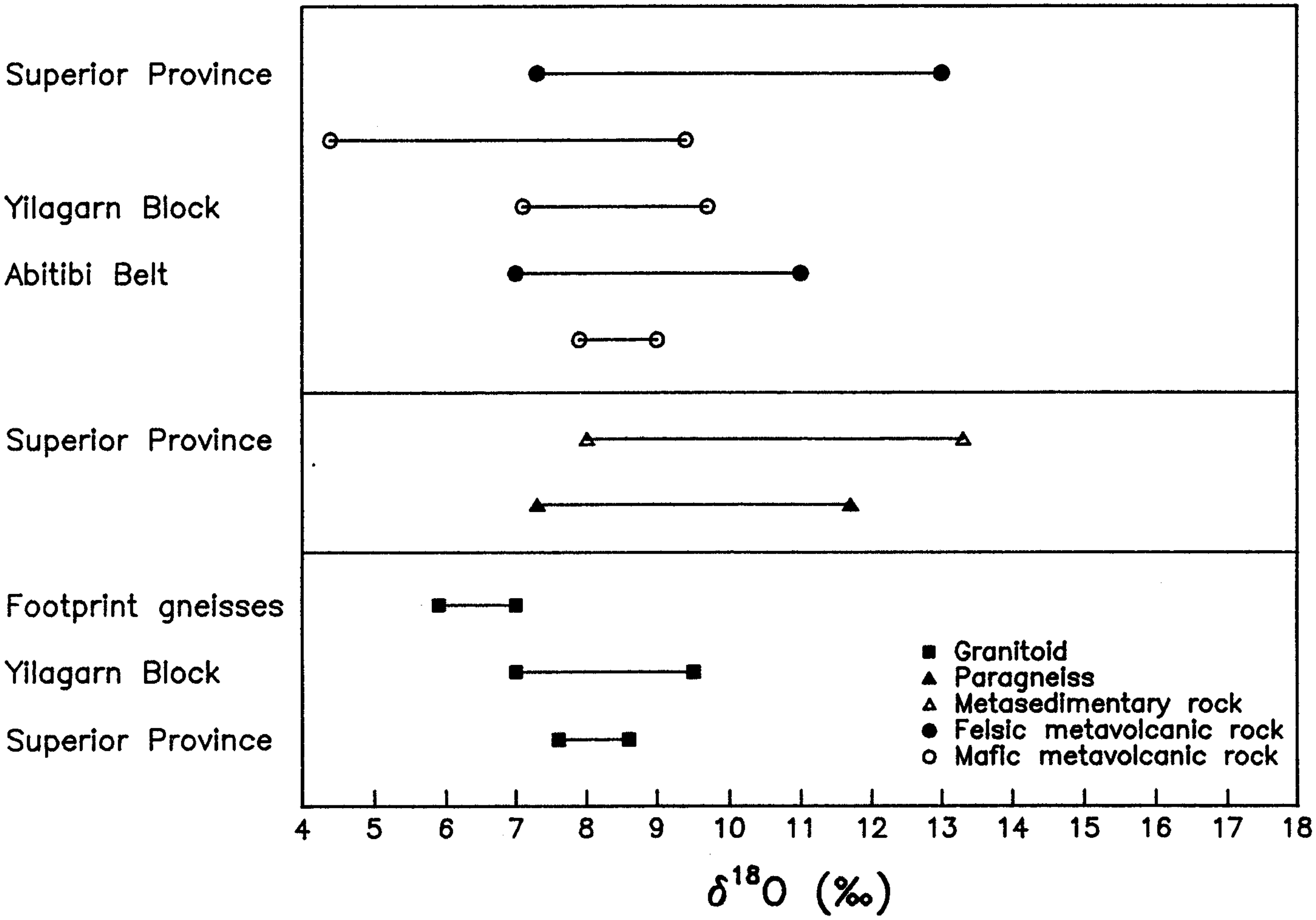

Figure 4.2 Summary of $\delta^{18}O$ data of Archean rocks. Original data are from Longstaffe and Schwarcz, 1977; Shieh and Schwarcz, 1977,1987; Hoefs and Binns, 1978; Longstaffe 1979; Beaty 1980 and Wilson, 1981.

about 6 ‰ (Figure 4.1). Furthermore, the authors have pointed out that the isotopic homogeneity of the high-grade granitoids is often associated with partial melting (migmatization) due to high-grade metamorphism, therefore either metamorphic fluid or silicate melt could serve as the isotopic exchange medium. CO_2-flow from mantle outgassing was also suggested as the exchange medium, especially in an area lacking large scale partial melting (Fourcade and Javoy, 1973). However, direct evidence supporting this hypothesis is speculative.

Another possible low ^{18}O reservoir is aquatic fluid which is relatively easy to circulate in a large area under a heat gradient. Seawater or meteoric water are most likely, such as in the Trois Seigneurs Massif, Pyrenees (Wickham and Taylor, 1985) and in the Strangways Range of Australia (Wilson and Baksi, 1983). Interaction with such external waters is specially attractive for those rocks having very depleted $\delta^{18}O$ values less than 5.5 ‰.

A second important feature is that the $\delta^{18}O$ values of many unaltered Archean granitoids are generally lower than those of chemically equivalent rocks of younger ages. For instance, Archean granitoids in the Swaziland and Rhodesian have relatively lower $\delta^{18}O$ values and no samples analyzed have $\delta^{18}O$ values greater than 9.0 ‰ (Taylor, 1977 and Taylor and Magaritz 1975); in the Superior Province have $\delta^{18}O$ of 7.6 to 8.6 ‰ (Figure 4.2) (Shieh and Schwarcz, 1977); and in the Yilgarn Block have $\delta^{18}O$ of 7.0 to 9.5 ‰ (Figure 4.2) (Wilson, 1981). While the younger granitic plutons often have $\delta^{18}O$ values from 10 to 14 ‰, for instance, rocks in the Tuscan province of Italy (Taylor and Turi, 1976); in Northern Britain (Harmon et at., 1984) and in the High and "Lesser Himalayas" belts (Debon et al., 1986). This may indicate the Archean granitic rocks are more juvenile than the younger ones, which implies that less crustal material was involved in the Archean granitic magma genesis.

4.4.2. ARCHEAN SEDIMENTARY ROCKS

Archean metasediments are present in both high-grade gneiss belts and low-grade greenstone belts. The metasediments in greenstone belts are commonly clastic sediments, low-grade metamorphosed and contain large percentages of recognizable volcanic rock fragments. The paragneisses in the gneiss belts are often metamorphosed to amphibolite to granulite facies. Most of these Archean metasediments show considerably lower $\delta^{18}O$ values than the values of most Phanerozoic and late Proterozoic metasediments of comparable metamorphic grades (e.g. Garlick and Epstein, 1967; and Magaritz and Taylor, 1975). For example, the clastic sediments in the Superior province have $\delta^{18}O$ values in a range of 8.0 ‰ to 13.3 ‰ (Figure 4.2) (Longstaffe and Schwarcz, 1977; and Shieh and Schwarcz, 1978), and some paragneisses from the Superior province show $\delta^{18}O$ values in the range from 7.3 ‰ to 11.7 ‰ (Figure 4.2). Longstaffe and Schwarcz (1977) observed that increasing $\delta^{18}O$ values correlate with decreasing volcanic rock fragment contents. The study suggests that the low

$\delta^{18}O$ values of the Archean sediments can be attributed to the high percentage of unaltered igneous rock detritus in the sediments.

4.4.3. ARCHEAN METAVOLCANIC ROCKS IN GREENSTONE BELTS

The oxygen isotopic composition of low-grade metavolcanic rocks has been studied from several Archean greenstone belts. For instance, felsic metavolcanic rocks of the Superior province have $\delta^{18}O$ values ranging from 7.3 ‰ to 13.0 ‰ and mafic metavolcanic rocks have $\delta^{18}O$ values from 4.4 ‰ to 9.4 ‰ (Figure 4.2) (Longstaffe and Schwarcz, 1977). The metamorphosed tholeiites from the Yilgarn greenstone belt of Australia have $\delta^{18}O$ values of 7.1 ‰ to 9.7 ‰ (Figure 4.2) (Hoefs and Binns, 1978).

The most intensive study of oxygen isotopes in Archean greenstone belts has been carried out by Beaty (1980) in the Abitibi greenstone belt (AGB). Metabasalts in the AGB have $\delta^{18}O$ values about 7 ‰ to 9 ‰ and metarhyolites have $\delta^{18}O$ values about 7 ‰ to 11 ‰ (Figure 4.2). It appears that nearly all metavolcanic rocks from the greenstone belts are ^{18}O-enriched relative to fresh volcanic rocks by 0 ‰ to 4 ‰. Beaty has calculated the $\delta^{18}O$ shifts of the volcanic rocks and the $\delta^{18}O$ values of the fluid responsible for the alteration, by assuming an open system and using temperatures, about 200°C-300°C, calculated from the metamorphic assemblages. The results suggest that the hydrothermal fluid had $\delta^{18}O$ values of

0±2 ‰ and alteration took place under conditions of high water/rock ratio. Beaty concluded that the ^{18}O-enrichment in these metavolcanic rocks resulted from low temperature alteration with seawater soon after they were extruded onto the seafloor, in the same fashion that modern oceanic crust interacts with seawater on a massive scale (Gregory and Taylor, 1981).

4.5. OXYGEN ISOTOPIC COMPOSITIONS OF WHOLE ROCKS

4.5.1. δ^{18}O DATA OF KAPUSKASING STRUCTURE ZONE

A total of fifty whole rock samples from the KSZ have been analyzed for their oxygen isotopic compositions, including granitic, anorthositic and dioritic rocks, mafic gneisses, ultramafic plutons, paragneisses and one lamprophyre.

Granitic rocks in the KSZ include the high-grade tonalitic and granodioritic gneisses, less metamorphosed monzonitic to tonalitic plutons and one granodioritic pegmatite. The δ^{18}O values of the gneissic rocks range from 6.6 ‰ to 9.5 ‰ and the δ^{18}O values of the plutonic rocks range from 7.7 ‰ to 8.4 ‰ (Table 4.1). All these are plotted as one group in Figure 4.3-I. The high-grade gneissic rocks and the igneous rocks have similar chemical compositions, with SiO_2 contents ranging from 64.3% to 75.6% (Table 4.1). The oxygen isotopic compositions are comparable, except the gneissic rocks have a relatively larger δ^{18}O range.

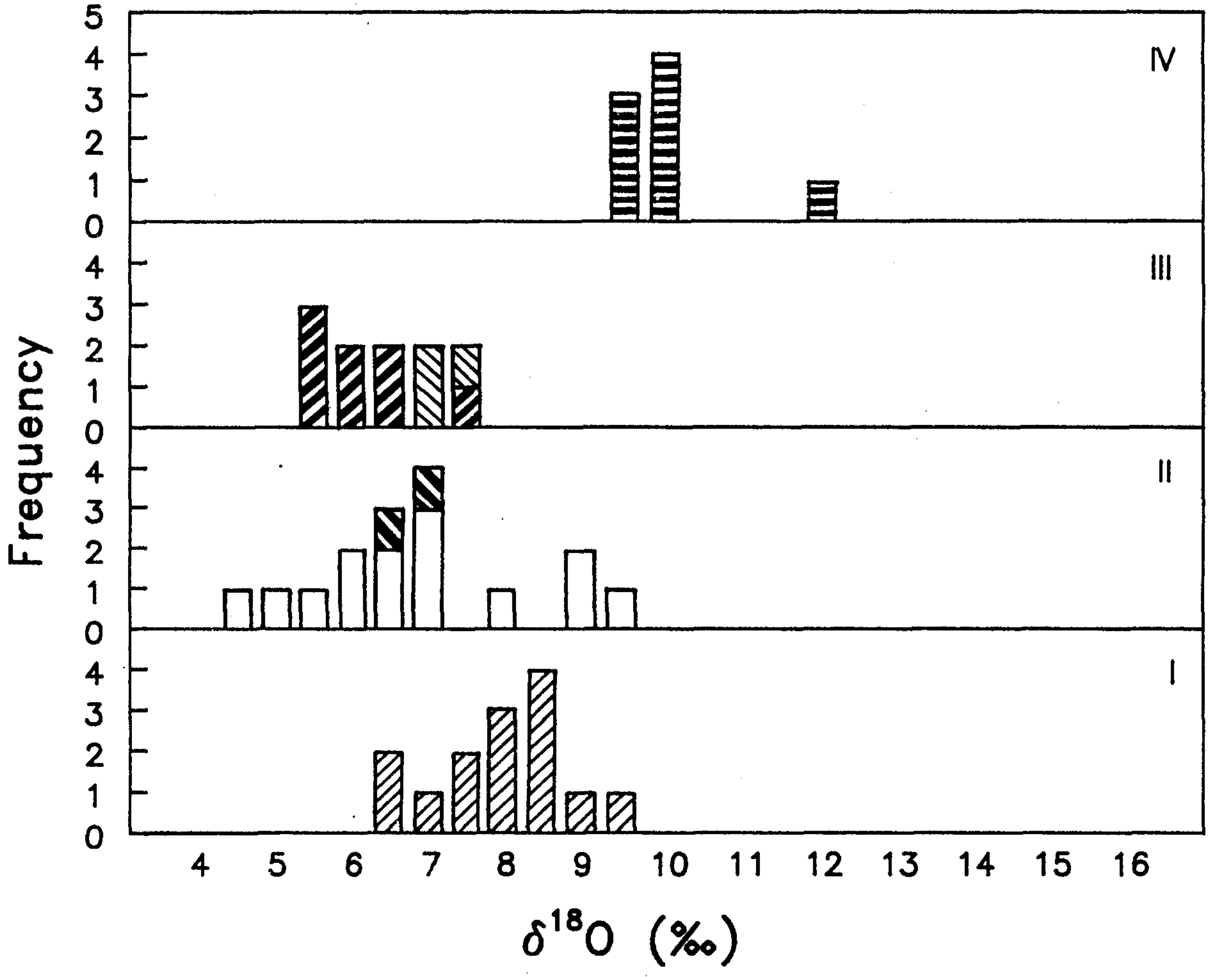

Figure 4.3 $\delta^{18}O$ values of whole rocks from the KSZ. I: tonalitic rocks ▨; II: mafic ☐ and ultramafic rocks ▧ ; III: anorthositic ▨ and dioritic rocks ▧ ; IV: paragneiss ▤.

Table 4.1 Names of rock units*, brief descriptions for granitic rocks from the KSZ, and their $\delta^{18}O$ whole rock values and SiO_2 contents

Sample	Rock Unit	Rock Type Description	$\delta^{18}O$ (‰)	SiO_2 (%)
870818-1	7A	bio leucotonalite	9.5	66.3
870818-12	7A	sheared tonalite (leucosome)	9.1	67.7
L880816-7N	7B	sheared tonalite	8.4	69.0
840715-1	7B	gar+hb+bio tonalite gneiss	6.6	64.8
P564	7B	bio+hb tonalite gneiss	6.7	65.9
840715-3	7C	gar+bio tonalite gneiss	8.7	71.8
840715-4	7C	gar+bio tonalite gneiss	8.5	64.3
870818-10	7H	hb+bio granodiorite	7.2	69.1
870818-11	7H	leucogranodiorite pegmatite	7.7	75.6
P45A	10A	bio tonalite	7.8	72.8
P850	10A	hb+bio granodiorite	8.4	74.1
P006	10B	bio granodiorite	8.2	73.2
P402	10C	bio+qtz monzonite	8.2	73.3
P869C	10C	bio granodiorite	8.3	73.3

*: names of the rock units are taken from Percival (1981), with minor modification.

Notably, the $\delta^{18}O$ range of the high-grade gneisses and the less metamorphosed igneous rocks are within the range of normal igneous granitic rocks (Figure 4.1).

The mafic gneisses in the KSZ have a relatively large range of $\delta^{18}O$ values from 4.7 ‰ to 9.5 ‰ (Table 4.2 and Figure 4.3-II). We know from many studies that fresh basaltic rocks have very uniform $\delta^{18}O$ values about 5.5 ‰ to 7.0 ‰ (Figure 4.1). Based on this knowledge, the mafic gneisses from the KSZ have been separated into two groups. Group 1 have a $\delta^{18}O$ range of 5.7 ‰ to 7.1 ‰, similar to normal igneous basalts. Four mafic gneisses in Group 2 have $\delta^{18}O$ values from 8.1 ‰ to 9.5 ‰, which are considerably higher than fresh basalts. The mafic gneisses in both groups, however, show no significant differences in their major element compositions: for instance, the SiO_2 contents are in the normal range of 44.5% to 53.8% (Table 4.2), and their mineral assemblages and some trace element compositions are rather similar (Li et al., 1991).

Sample 870819-1 (Table 4.2) is a garnet-epidote-hornblende gneiss, which has a lower $\delta^{18}O$ value of 4.7 ‰. The hydrous minerals in this sample, such as epidote, probably indicate that the rock has undergone late retrograde alteration, and the lower $\delta^{18}O$ value could have resulted from interaction with hydrothermal water of possible meteoric origin.

Two ultramafic plutonic rocks in the KSZ have $\delta^{18}O$ values of 6.4 ‰ and 6.8 ‰ and are also plotted in Figure 4.3-II. Their oxygen isotopic compositions are comparable with fresh igneous basalts. One lamprophyric rock has a $\delta^{18}O$ value

Table 4.2 Names of rock units*, brief descriptions for mafic rocks from the KSZ, and their $\delta^{18}O$ whole rock values and SiO_2 contents

Sample	Rock Unit	Rock Type Description	$\delta^{18}O$ (‰)	SiO_2 (%)
L880816-8B	2	skarn or calc-magn-silicate rock	6.3	49.8
PBA2	2A	amphibolite	9.0	53.8
890824-1	2A	amphibolite	9.5	50.0
P812	2C	gar+hb gneiss	6.9	50.9
870818-2	2C	gar+hb gneiss	7.1	51.5
870818-8	2C	gar+hb gneiss	5.8	48.0
870819-1	2C	gar+epid+hb gneiss	4.7	51.9
840714-6	2D	clz+gar hornblendite	6.1	44.8
840714-7	2D	gar amphibolite	5.2	48.4
840715-2	2D	gar+cpx+hb granulite	8.1	47.0
840715-7	2D	chlor amphibolite (sheared)	5.6	50.4
830814-2	2E	gar+cpx+hb granulite (altered)	6.6	47.3
870818-13	2E	gar+opx granulite (melanosome)	6.8	47.9
870819-2	2E	scap+gar+cpx granulite	9.0	48.4
P814	4G	bio+cpx+hb hornblendite	6.8	46.5
P445	4G	cpx+plag hornblendite	6.4	44.5
840715-6	14D	lamprophyre	4.0	38.0

*: names of the rock units are taken from Percival (1981), with minor modification.

of 4.0 ‰ (not shown in the histogram). The $\delta^{18}O$ value of the lamprophyre is the lowest value observed in the region and remains unexplained.

The anorthositic samples were collected from the main body of the Shawmere anorthosite complex (see Chapter 2). They are anorthosite to gabbro in composition and have SiO_2 contents ranging from 43.0% to 51.4% (Table 4.3), and $\delta^{18}O$ values ranging from 5.5 ‰ to 7.6 ‰ (Figure 4.3-III). These results are nearly identical to those of anorthosite in the Adirondack Mountains, 5.8 ‰ to 7.6 ‰ (Figure 4.1), which are considered typical of this type of rock (Taylor, 1970), and are close to the value resulted from plagioclase in equilibrium with a basaltic magma with $\delta^{18}O$ value about 5.5 ‰. This supports the general belief that the anorthosite complex is igneous in origin.

Dioritic rocks from the KSZ show a narrow range of $\delta^{18}O$ values, from 6.8 ‰ to 7.5 ‰ (Figure 4.3-III), intermediate between the Group 1 mafic gneisses and the granitic rocks, as are their SiO_2 contents, from 51.0% to 59.4% (Table 4.3).

Paragneisses were collected from various localities across the KSZ. The $\delta^{18}O$ values range from 9.4 ‰ to 12.2 ‰ (Table 4.4); seven of eight samples fall in a narrow range of 9.4 ‰ to 10.2 ‰ (Figure 4.3-IV). Notably, the $\delta^{18}O$ values of the paragneisses are generally higher than the metaigneous rocks. On the other hand, the $\delta^{18}O$ values of the high-grade paragneisses are significantly lower than

Table 4.3 Names of rock units*, brief descriptions for anorthositic and dioritic rocks from the KSZ, and their $\delta^{18}O$ whole rock values and SiO_2 contents

Sample	Rock Unit	Rock Type Description	$\delta^{18}O$ (‰)	SiO_2 (%)
830814-4	3B	gar+opx+cpx+hb gabbro (coronite)	5.5	45.6
840714-9	3B	gar+hb+plag granulite	5.8	46.0
840715-10	3B	gar+opx+hb gabbro (coronite)	5.6	43.0
870818-9	3B	gar+hb gabbroic anorthosite	6.2	44.7
L880816-4	3B	hornblende anorthosite	5.7	48.2
840714-8	3C	qtz+hb anorthosite (altered)	6.4	51.4
L880816-5	3C	hornblende gabbro	6.4	49.6
830814-1	3E	opx+gar+hb melagabbro	7.6	47.2
P807	4B	opx+bio+hb diorite gneiss	7.5	59.4
P444A	4C	bio+hb diorite	6.8	51.1
P792	4C	bio+hb diorite gneiss	7.2	58.7

*: names of the rock units are taken from Percival (1981), with minor modification.

Table 4.4 Names of rock units*, brief descriptions for paragneisses from the KSZ, and their $\delta^{18}O$ whole rock values and SiO_2 contents

Sample	Rock Unit	Rock Type Description	$\delta^{18}O$ (‰)	SiO_2 (%)
840715-5	1B	gar+bio paragneiss	10.1	63.5
P443	1B	hb+bio+gar paragneiss	10.1	64.6
P527	1B	gar+bio+hb paragneiss	10.2	63.3
L880816-1	1B	gar+hb+bi paragneiss	9.4	58.1
L880816-7S	1B	gar-bio-qtz-plag rock	9.5	63.8
890824-2	1B	musc-gar-bio paragneiss	12.2	79.8
830814-3	1E	gar+bio paragneiss	10.0	63.0
840715-9	1H	graph+gar+bio paragneiss	9.4	62.6

*: names of the rock units are taken from Percival (1981), with minor modification.

those of younger metasediments at equivalent metamorphic grade, but are comparable with many other Archean metasediments (Figure 4.2).

4.5.2. $\delta^{18}O$ DATA OF WAWA GNEISS TERRAIN

In the WGT, the granitic rocks are volumetrically the major component, which, as in the KSZ, include tonalitic to granodioritic gneisses and less metamorphosed monzonitic to granitic plutons. Forty of these rocks have been analyzed for oxygen isotopes, and the $\delta^{18}O$ results, along with the SiO_2 contents and simple rock descriptions are summarized in Table 4.5. The $\delta^{18}O$ values are plotted as one group in a histogram (Figure 4.4-I). The $\delta^{18}O$ values of these granitic rocks vary from 6.7 ‰ to 10.4 ‰ and most samples are in a range of 6.7 ‰ to 9.3 ‰, with the single exception of one porphyritic gneiss having a $\delta^{18}O$ value of 10.4 ‰. This range is essentially identical to the equivalent rock types in the KSZ (6.6 ‰ to 9.5 ‰).

The mafic rocks in the WGT are minor components, and include mafic gneisses, diabase dykes and ultramafic plutons. The mafic gneisses in the WGT often occur as xenoliths in the tonalitic gneisses. The $\delta^{18}O$ values of the mafic gneisses range from 6.2 ‰ to 7.0 ‰, and are summarized in Table 4.6, with their SiO_2 contents and rock descriptions, and illustrated in Figure 4.4-II. The oxygen isotopic compositions are similar to the Group 1 mafic gneisses in the KSZ and as

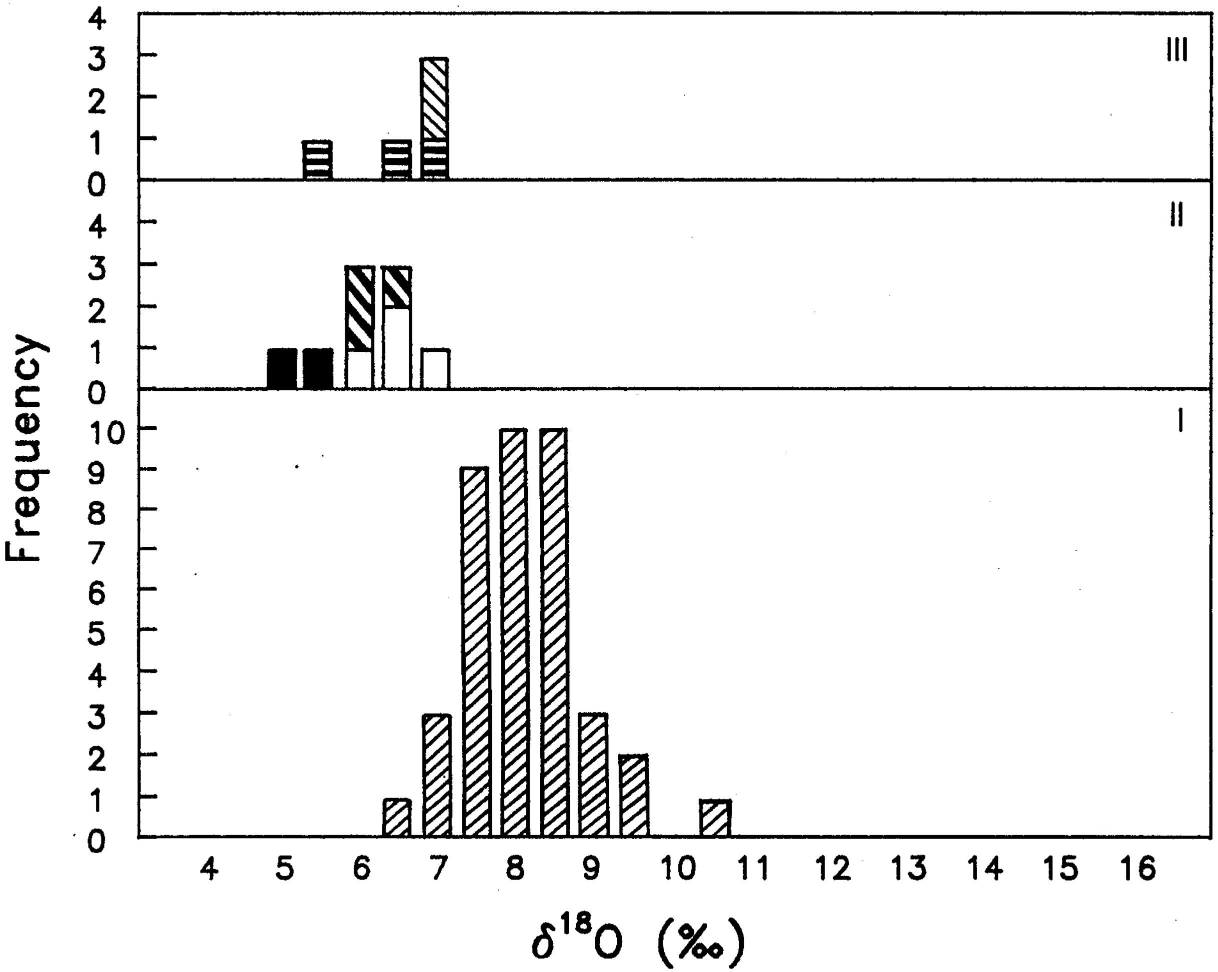

Figure 4.4 $\delta^{18}O$ values of whole rocks from the WGT. I: tonalitic rocks ▨; II: mafic ☐ ultramafic ▧ and diabase ■ ; III: dioritic ▧ and metavolcanic rocks ▤.

Table 4.5 Names of rock units*, brief descriptions for granitic rocks from the WGT, and their $\delta^{18}O$ whole rock values and SiO_2 contents

Sample	Rock Unit	Rock Type Description	$\delta^{18}O$ (‰)	SiO_2 (%)
840713-5	7A	epid+chlor tonalite gneiss	7.3	67.1
840715-11	7A	musc+bio tonalite	7.8	72.4
840715-12	7A	bio tonalite gneiss	8.2	69.1
870819-5	7A	leucotonalite pegmatite	9.3	76.7
870819-11	7A	epid+bio tonalite gneiss	8.2	70.3
870820-16	7A	leucotonalite gneiss (leucosome)	8.8	77.1
870820-20	7A	chlor tonalite (sheared, altered)	9.0	62.9
870820-20A	7A	chlor tonalite (altered)	7.5	63.4
870820-23	7A	bio tonalite gneiss	8.3	68.1
870820-25	7A	bio tonalite	7.9	66.6
L880817-6m	7A	bio tonalite gneiss	6.9	64.7
P627	7B	bio+hb tonalite gneiss	7.4	65.7
840715-14B	7B	leucogranodiorite pegmatite	8.0	66.7
L880817-5	7B	epid-hb-bio tonalite gneiss	7.1	63.8
L880817-6v	7B	tonalite vein in L880817-6m	7.8	71.4
870820-17	7B	epid+hb gneiss (melanosome)	8.2	64.8
870820-19	7B	bio+hb tonalite gneiss	7.3	63.2
870820-22A	7C	gar+hb+bio gneiss	9.3	57.1
870820-22B	7C	gar+bio+chlor gneiss	8.3	70.4

Table 4.5 continue

840713-2	7H	chlor granodiorite (altered)	8.6	75.1
840713-4	7H	bio monzonite gneiss	7.2	62.7
840715-13	7H	bio leucogranodiorite	8.4	73.4
870819-4	7H	leucogranodiorite (altered)	8.4	71.6
870819-6	7H	leucogranodiorite pegmatite	8.9	72.1
870819-9	7H	bio leucogranodiorite	7.7	71.1
870819-10	7H	bio leucogranodiorite	8.6	75.3
870819-12	7H	leucogranodiorite vein	8.5	71.5
870820-24A	7H	epid granodiorite gneiss	8.6	71.2
870820-24B	7H	granodiorite gneiss (porphyritic)	10.4	75.6
L880817-1	7H	epid-bio granodiorite	7.8	70.6
P860F	7H	gar+hb+bio+qtz granodiorite	6.7	68.9
P883D	7H	cpx+bio+qtz granodiorite	8.6	73.4
P799B	8B	bio granodiorite	7.4	68.3
840714-1	9E	bio+cpx granodiorite	7.6	73.2
L880817-7	10A	leucogranite vein	8.5	71.2
P797B	10A	bio granodiorite	7.4	68.4
P364	10B	bio granodiorite	8.2	71.3
P804	10C	bio+qtz monzonite	7.6	74.4
P860M	10C	gar+hb+bio+qtz monzonite	7.8	66.6

*: names of the rock units are taken from Percival (1981), with minor modification.

Table 4.6 Names of rock units*, brief descriptions for mafic and intermediate rocks from the WGT, and their $\delta^{18}O$ whole rock values and SiO_2 contents

Sample	Rock Unit	Rock Type Description	$\delta^{18}O$ (‰)	SiO_2 (%)
870819-8	2B	bio+hb gneiss	6.5	53.8
840713-1	2D	hb gneiss	7.0	49.7
840713-3	2D	cpx+hb gneiss	6.5	48.1
870819-3	2J	cpx+hb gneiss	6.2	49.6
P805I	4A	cpx+hb+qtz dioritic gneiss	6.8	59.4
840714-3	4A	cpx+bio+hb dioritic gneiss	6.8	58.5
L880817-2	5A	epidote amphibolite	6.5	50.1
L880817-3	5A	epidote amphibolite	6.8	50.8
L880817-4	5A	magnetite silicate rock	5.7	41.4
840714-2	9F	bio+cpx meladiorite	6.2	45.7
840714-4	9F	cpx+bio hornblendite	6.4	46.5
840714-5	9F	hb pyroxenite	6.2	50.7
870820-18	11	diabase (altered)	4.8	51.7
870820-21	11	opx+cpx diabase (fresh)	5.7	51.3

*: names of the rock units are taken from Percival (1981), with minor modification.

well as the fresh igneous basalts.

Two diabase dykes have been collected from the WGT. One fresh diabase dyke has a $\delta^{18}O$ value of 5.7 ‰ (Table 4.6 and Figure 4.4-II), which is similar to fresh basalt. Another diabase dyke (870820-18) is altered, with a hydrothermal mineral assemblage, and has been depleted in ^{18}O, with a $\delta^{18}O$ value of 4.8 ‰ (Table 4.6 and Figure 4.4-II). Again, the ^{18}O-depletion is likely the result of the hydrothermal alteration by meteoric water.

Three ultramafic rocks in the WGT have $\delta^{18}O$ values from 6.2 ‰ to 6.4 ‰ (Table 4.6), which are illustrated together with the mafic gneisses and the diabase dykes in Figure 4.4-II. The oxygen isotopic compositions of these ultramafic rocks are normal compared with fresh igneous basalt.

Two dioritic gneisses have been collected from the WGT, and have identical $\delta^{18}O$ values of 6.8 ‰ (Table 4.6 and Figure 4.4-III), which are within the $\delta^{18}O$ range of the same type of rocks in the KSZ.

Three mafic rocks of lower amphibolite facies were collected from near the boundary between the WGT and MGB. For convenience, these samples are grouped into the WGT. The $\delta^{18}O$ results of these amphibolites range from 5.7 ‰ to 6.8 ‰ (Table 4.6 and Figure 4.4-III).

4.5.3. $\delta^{18}O$ DATA OF MICHIPICOTEN GREENSTONE BELT

Low-grade metasediments from the MGB are metamorphosed shale and carbonaceous chert. One greywacke from the Abitibi Greenstone Belt is included with these rocks. The oxygen isotopic results, their SiO_2 contents and brief sample descriptions are summarized in Table 4.7. The $\delta^{18}O$ values of the metasediments range from 11.4 ‰ to 14.7 ‰ (Figure 4.5-I), which are in agreement with values observed for many similar rock types in other Archean terrains (Figure 4.2).

Low-grade metavolcanic rocks are from the central part of the MGB. Mafic metavolcanics include tholeiitic basalts, calcalkaline basalts and andesite, which have SiO_2 contents from 48.4% to 55.3% (Table 4.7), and $\delta^{18}O$ values from 7.4 ‰ to 9.1 ‰ (Table 4.7 and Figure 4.5-II). Notably, the oxygen isotopic results are higher than either fresh, mafic igneous equivalents or the Group 1 mafic gneisses in the adjacent KSZ and the WGT. However, these values are comparable with the Group 2 mafic gneisses in the KSZ and similar rocks in the AGB (Beaty, 1980).

Felsic metavolcanics of the MGB are dacite to rhyolite in composition, with SiO_2 content from 62.2% to 78.4% (Table 4.7). The felsic metavolcanics display a wide range of oxygen isotopic compositions, from 6.0 ‰ to 16.0 ‰, with most between 8.9 ‰ and 13.3 ‰ (Table 4.7 and Figure 4.5-II). These metavolcanic rocks are very enriched in ^{18}O compared to fresh rhyolite obsidians and rhyolite flows (Figure 4.1) and to the granitic rocks in the KSZ and the WGT (Figure 4.3 and 4.3).

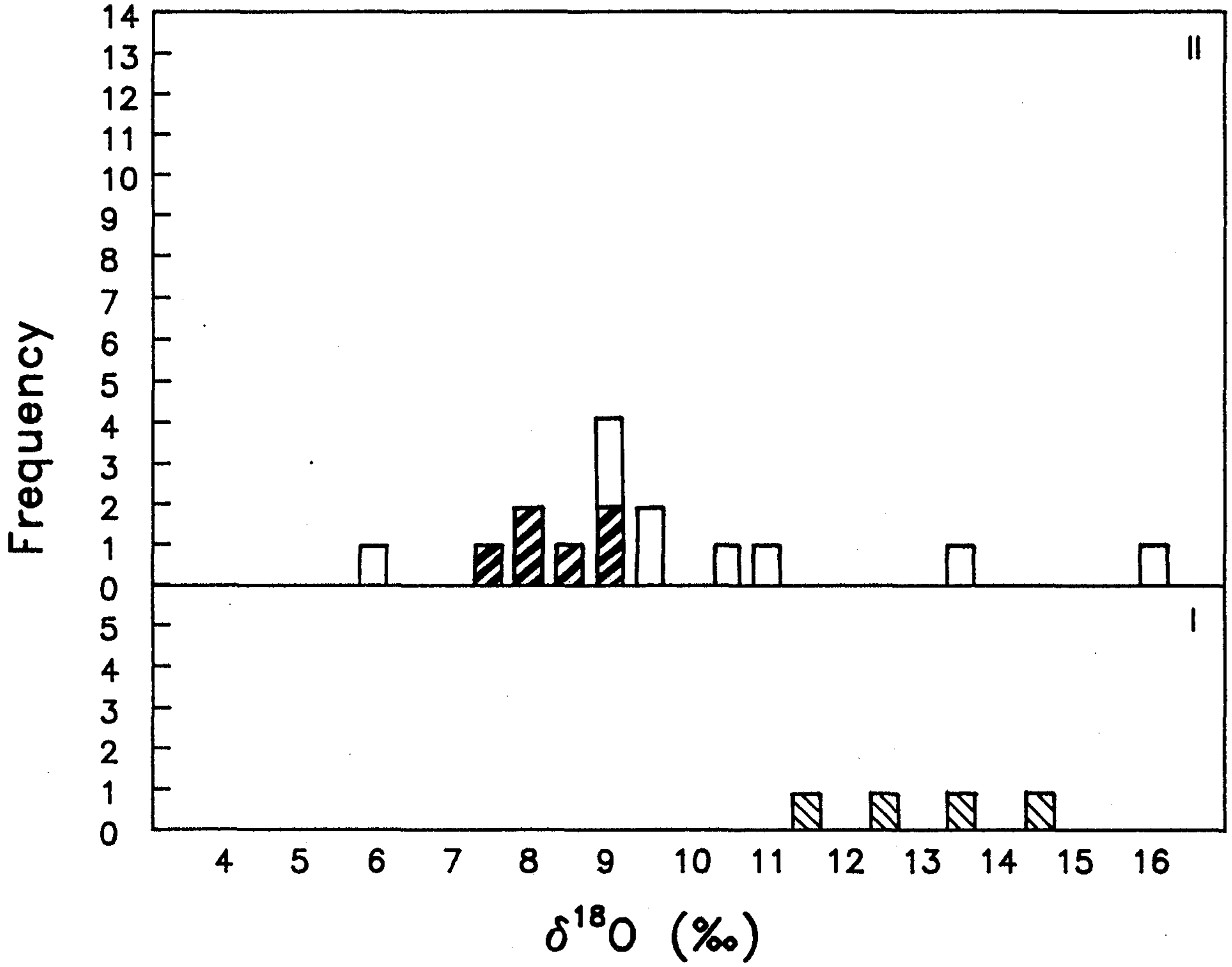

Figure 4.5 δ^{18}O values of whole rocks from the MGB. I: metasediments ▧ ; II: metabasaltic ▨ and metarhyolitic rocks ☐.

Table 4.7 Names of rock units*, brief descriptions for metasediments and metavolcanics from the MGB and AGB, and their $\delta^{18}O$ whole rock values and SiO_2 contents

Sample	Rock Unit	Zone#	Rock Type Description	$\delta^{18}O$ (‰)	SiO_2 (%)
830815-1	6A	(A)	greywacke (Abitibi)	12.1	64.9
830812-2	6A	(M)	carbonaceous chert	14.7	88.4
KC 84-1	6C	(M)	shale (Michipicoten belt)	11.4	66.0
KC 84-2	6C	(M)	shale (Michipicoten belt)	13.5	74.7
WW 19B	MV-1	(M)	tholeiitic basalts and andesites	8.3	48.4
WW 324	MV-1	(M)	tholeiitic basalts and andesites	8.1	51.0
WW 197A	MV-1	(M)	tholeiitic basalts and andesites	8.2	51.3
WW 329	MV-1	(M)	tholeiitic basalts and andesites	7.4	55.3
WW 151	MV-1	(M)	calcalkaline basalt and andesite	9.1	52.3
WW 138	MV-1	(M)	calcalkaline basalt and andesite	8.9	52.7
WW 132	MV-1	(M)	HREE-depleted dacite	11.0	63.2
WW 144A	MV-1	(M)	rhyolite	13.3	72.5
WW 26	FV-1	(M)	dacite	9.1	62.2
WW 45	FV-1	(M)	dacite	9.6	66.6
WW 422	FV-1	(M)	low-si rhyolite	6.0	69.8
WW 38	FV-1	(M)	low-si rhyolite	10.5	72.7
WW 250	FV-1	(M)	high-si rhyolite	16.0	76.2
WW 415	FV-1	(M)	high-si rhyolite	9.2	75.7
WW 416c	FV-1	(M)	high-si rhyolite	8.9	77.4
WW 106	FV-1	(M)	high-si rhyolite	9.3	78.4

*: names of the rock units are taken from Percival (1981) and Attoh (1980). #: A-AGB; M-MGB.

The ^{18}O-enrichment of metavolcanic rocks has been observed from many other greenstone belts (figure 4.2) and attributed to the hydrothermal alteration of the volcanic rocks by seawater at low temperature.

4.6. THE SIGNIFICANCE OF WHOLE ROCK $\delta^{18}O$ DATA

4.6.1. REGIONAL VARIATIONS

The oxygen isotope distributions of the whole rocks in the KSZ, WGT and MGB have been summarized in Figure 4.6. The solid lines in the Figure 4.6 represent the ranges of the $\delta^{18}O$ values for each rock type, while the solid diamonds and the numbers mark the average $\delta^{18}O$ values.

In general, no systematic variation in oxygen isotopic composition is evident for equivalent rock types within the high-grade terrains. Granitic rocks in the KSZ range from the less metamorphosed plutons and amphibolite to granulite facies gneisses. In spite of the relatively large $\delta^{18}O$ range for gneissic rocks, the gneisses and plutons have very similar $\delta^{18}O$ averages, 8.2 ‰ and 8.0 ‰ (Figure 4.6). In the adjacent WGT, granitic plutons are relatively abundant, and the metamorphic grade of the gneissic rocks generally tends to be lower compared with the KSZ, mostly amphibolite facies. The granitic plutons in the WGT have an average $\delta^{18}O$ value of 7.8 ‰, and the gneissic rocks have an average of 8.2 ‰ (Figure 4.6). An average $\delta^{18}O$ value of all samples in the granitic categories of the high-grade terrain is 8.0

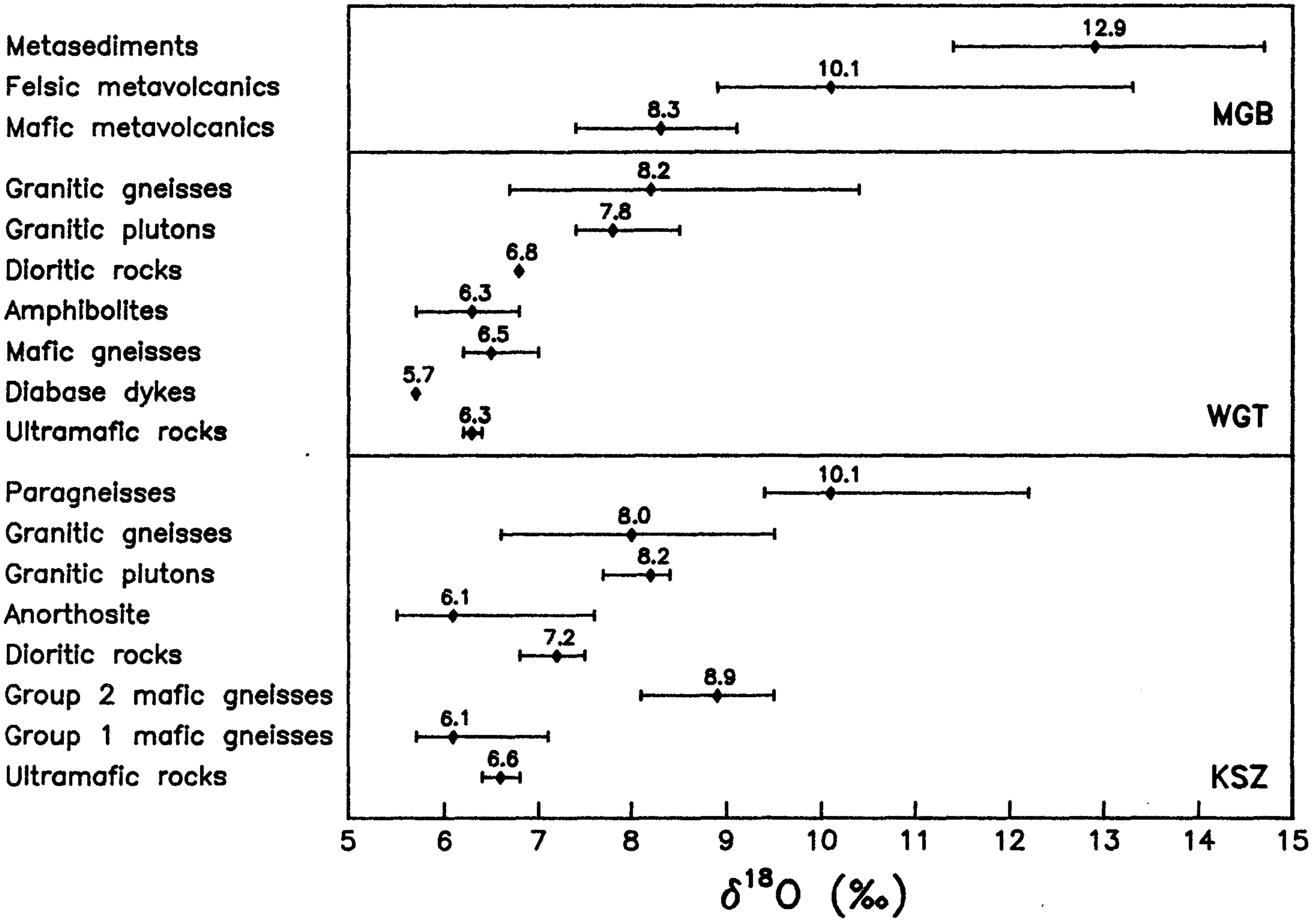

Figure 4.6 Summary of $\delta^{18}O$ data in the Wawa-Kapuskasing transect. Solid lines represent the $\delta^{18}O$ ranges for each rock type, while solid diamonds and numbers mark the average $\delta^{18}O$ values.

‰ (σ=0.8), which is comparable with many other Precambrian granitoids (see section 4.4.1.).

The intermediate and mafic rocks (excluding group 2 mafic gneisses) from both KSZ and WGT also have similar $\delta^{18}O$ ranges (Figure 4.6). The results from the KSZ and the WGT show no significant difference in both distribution ranges and averages of the $\delta^{18}O$ values, which suggest no systematic variation of the oxygen isotopic distributions as a function of metamorphic grade or depth in the crust.

On the other hand, felsic and mafic metavolcanic rocks of the greenstone belts are significantly ^{18}O-enriched compared to chemically equivalent rocks in the high-grade terrane (Figure 4.6). The $\delta^{18}O$ data suggest two distinct geological environments involved in development of the low-grade and high-grade belts, although they show a continuous trend of increasing metamorphic grade.

4.6.2. $\delta^{18}O$ VALUE AND SiO_2 CONTENT

Figure 4.7 is a plot of $\delta^{18}O$ values versus SiO_2 contents for the rocks in the KSZ. The gneissic and plutonic rocks in the bottom envelope include ultramafic to granitic rocks and are assumed to be of igneous origin. These rocks display a trend of increasing $\delta^{18}O$ value with the SiO_2 content, and their correlation is given by the regression equation:

$$\delta^{18}O(‰)=0.078SiO_2(wt\%)+2.58 \qquad (4\text{-}3)$$

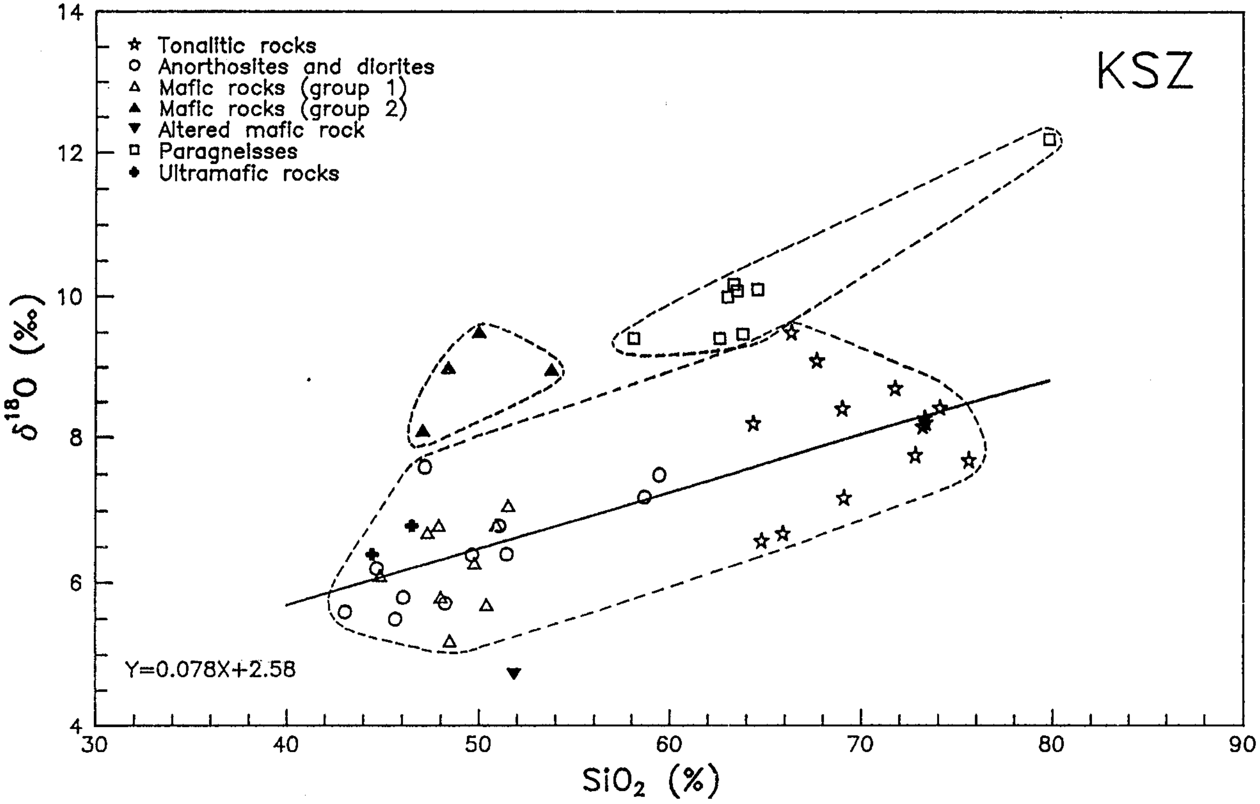

Figure 4.7 $\delta^{18}O$ value vs. SiO_2 content for rocks from the KSZ.

which gives an approximate gradient of 0.8 ‰ per 10 wt% increase in SiO_2 content. The paragneisses (open square) and Group 2 mafic gneisses (solid triangle) are ^{18}O-enriched, and their fields are clearly separated from the trend of the igneous and metaigneous rocks.

A similar and more obvious trend can be seen for the rocks in the WGT (Figure 4.8), and the corresponding regression equation is:

$$\delta^{18}O(‰) = 0.082 SiO_2 (wt\%) + 2.29 \qquad (4-4)$$

which results in a similar gradient of 0.8 ‰ per 10 wt% increase in SiO_2 content. Again, nearly identical correlations between $\delta^{18}O$ value and SiO_2 content for samples from both the KSZ and the WGT indicate that the metamorphic grade and increasing depth of the crust are not controlling factors for the oxygen isotope distribution of the rocks in the region.

Figure 4.9 is a plot of $\delta^{18}O$ value versus SiO_2 content for the rocks in the MGB. The high-grade field at the bottom is the field of the mafic to felsic rocks in the KSZ and the WGT, taken from Figure 4.7 and 4.8. Most of the low-grade metavolcanic rocks and metasedimentary rocks are ^{18}O-enriched with respect to the high-grade rocks. The felsic metavolcanic rocks occupy a large field, and overlap the field of metasediments. Some of the former may be volcaniclastic rocks whose high $\delta^{18}O$ values may reflect the admixture of an ^{18}O-rich component precipitated at lower temperature.

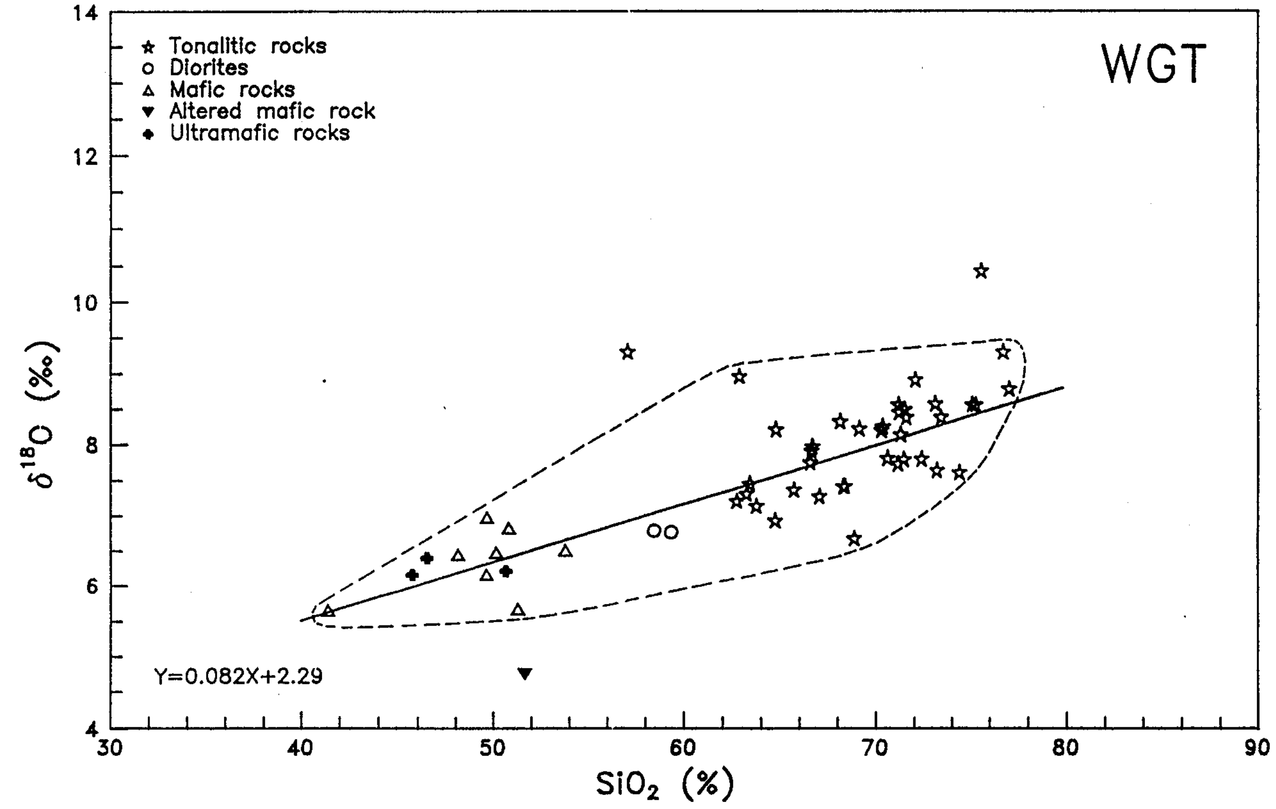

Figure 4.8 $\delta^{18}O$ value vs. SiO_2 content for rocks from the WGT.

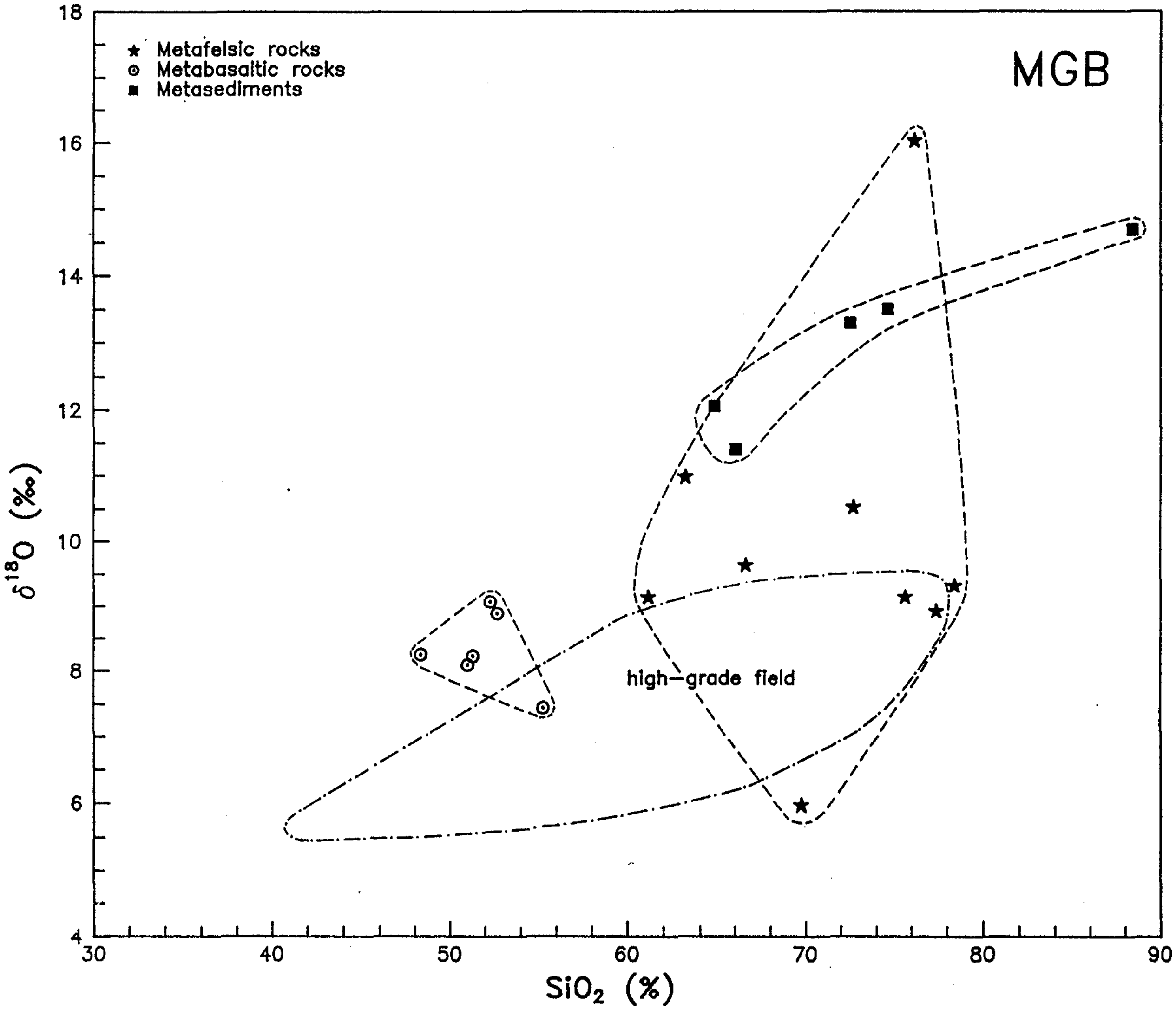

Figure 4.9 $\delta^{18}O$ value vs. SiO_2 content for rocks from the MGB. Envelope at bottom is from Figure 4.8.

The well-defined correlations of $\delta^{18}O$ value versus SiO_2 content for the high-grade rocks in the KSZ and the WGT do not necessarily suggest a single fractionation or partial melting process generating both mafic and granitic magmas.

The effects of crystal fractionation or partially melting on the oxygen isotope composition have been demonstrated both theoretically and experimentally. Sheppard and Harris (1985) have examined Ascension Island lavas, which include fresh alkali basalt, hawaiite, trachyandesite, trachyte and comendite. They have semi-quantitatively calculated a trend of isotope variation during crystal fractionation, starting from a basaltic magma with initial $\delta^{18}O$ value of 6.0 ‰ and ending at comendite with $\delta^{18}O$ value about 6.9 ‰. The study demonstrated that crystal fractionation leads to an ^{18}O-enrichment of about 0.4‰ per 10 wt% increase in SiO_2 content. Chivas et al. (1982) observed a similar variation of $\delta^{18}O$ values versus SiO_2 contents from the Solomon islands plutonic complex, and argued that this plutonic suite formed by crystal fractionation from a mantle-derived basaltic source with initial $\delta^{18}O$ value of 5.5‰. Kalamarides (1984) has studied the Kiglapait layered intrusion and the results illustrate that little change (less than 1 ‰) occurs in the $\delta^{18}O$ values of a high-alumina basic magma which undergoes extreme fractionation. All these studies indicate that crystal fractionation of basaltic magma, with typical SiO_2 content and $\delta^{18}O$ value about 5.5‰, would not produce igneous rocks with $\delta^{18}O$ values greater than 7‰. Any ^{18}O-enrichment higher than this must be the result of processes other than or additional to crystal fractionation. This interpretation is also true for partial melting.

The observed slopes in the KSZ and WGT are higher than that produced through model fractionation from a basaltic parent. In addition, the large volume of granitoid rocks and relatively smaller amounts of mafic rocks in the region also suggest that fractional crystallization can not account for the origin of the granites, because of the apparent absence of the abundant ultramafic cumulates (although there might be some unexposed at depth) that would have been produced during such fractionation. In any case, there is no geological evidence that all the rocks are genetically related.

The $\delta^{18}O$-SiO_2 gradient observed in the Kapuskasing transect, however, may possibly represent the following processes: 1) mantle-derived mafic rocks associated with felsic rocks formed by melting of ^{18}O-enriched crustal rocks; 2) assimilation of such crustal rocks by mantle-derived mafic magma (Taylor, 1980); or c) some more complex process.

The model of mantle-derived mafic rocks associated with crust-derived materials can also interpret the important observation that $\delta^{18}O$ values of Archean granitoids are generally lower than those of the equivalent rocks of younger age (see section 4.4.1.). Archean granitic rocks contain relatively a large proportion of the mantle materials, since less crustal rocks are available at the time, while younger granitoids probably contain a larger proportion of fused continental crust.

Some rocks which are apparently excluded from the $\delta^{18}O$-SiO_2 trend, such as paragneisses, Group 2 mafic gneisses (Figure 4.7) and greenstones (Figure 4.9), are affected by processes other than magmatic processes (see below).

4.6.3. PARAGNEISSES

Paragneiss in the KSZ is commonly granulite facies migmatite, and has $\delta^{18}O$ values varying from 9.4 ‰ to 12.2 ‰, which are higher than associated rocks of igneous origin (Figure 4.6) and also higher than other migmatitic paragneisses in the Superior province (Shieh and Schwarcz, 1974; Longstaffe, 1979), which generally have $\delta^{18}O$ values less than 8.5 ‰ and are associated with large scale oxygen isotopic homogeneity. On the other hand, the $\delta^{18}O$ values of the paragneisses in the KSZ are generally comparable to those of low-grade Archean metasediments with similar chemical composition, such as clastic sediments in the Superior province, with $\delta^{18}O$ values of 8.0 ‰ to 13.3 ‰ (Figure 4.2).

We have discussed metamorphic effects on oxygen isotopic compositions (section 4.3.). High-grade metamorphism alone does not significantly influence the oxygen isotope composition of whole rocks, unless a fluid phase is present or widespread anatexis occurs. If channelized fluid is present, it will only change the oxygen isotopic composition on a very small scale (e.g.locally), while a pervasive fluid tends to homogenize the $\delta^{18}O$ values on a regional scale. Shieh and

Schwarcz (1974) have indicated that anatexis (or migmatization) during high-grade metamorphism could facilitate the oxygen isotopic exchange, which might decrease and homogenize the $\delta^{18}O$ values over a large region. For instance, they observed that granitic rocks, including migmatitic paragneisses and other gneissic rocks, along a 200 mile traverse from the northwest Grenville Province have $\delta^{18}O$ values in a narrow range from 6.5 ‰ to 8.4 ‰. Similar observations have also been reported for equivalent rocks in the Superior province (Shieh and Schwarcz, 1977).

The $\delta^{18}O$ values of the paragneisses in the KSZ are apparently comparable to those of low-grade Archean metasediments, suggesting that these paragneisses have inherited their ^{18}O-enriched composition from a low-grade metasedimentary protolith and have not been disturbed by high-grade metamorphism. This leads to the conclusion that the metamorphism in the KSZ took place under relatively dry conditions, with no infiltrating fluid present to act as a carrier medium for isotopic exchange, even though the rocks are migmatized. These data suggest that intensive migmatization, which is believed to be necessary to produce isotope exchange, might not be a sufficient driving force in itself.

It must be considered whether the metasediments were originally even richer in ^{18}O, like younger sedimentary rocks (Savin and Epstein, 1970), and then isotopically exchanged oxygen with a low $\delta^{18}O$ reservoir during high-grade metamorphism. The paragneisses are commonly associated with the mafic gneisses in the field (Chapter 2), but have much higher $\delta^{18}O$ values, even higher than the Group 2 mafic gneisses (Figure 4.9). The large contrast in $\delta^{18}O$ values between paragneiss and nearby mafic gneiss, makes it unlikely that widespread isotope exchange has occurred in the region.

4.6.4. MAFIC GNEISSES

There are two groups of mafic gneisses distinguished by their oxygen isotopic compositions (Figure 4.3), as already discussed. Most mafic gneisses from the KSZ and WGT have $\delta^{18}O$ values comparable to fresh igneous basalt and much lower than those in mafic volcanic rocks of adjacent greenstone belts. The enrichment in ^{18}O of mafic metavolcanic rocks in greenstone belts, relative to fresh basalt, has been interpreted as the effect of low-temperature interaction between submarine basaltic extrusive and seawater (section 4.4.3.). It appears, therefore, that the Group 1 mafic gneisses in the KSZ and WGT did not develop in environments like those of the MGB and AGB.

There are several possible explanations for this. 1) the protoliths of the mafic gneisses may have been emplaced as intrusions at sufficient depth in an oceanic crust, to prevent hydrothermal interaction with circulating seawater; 2) the mafic rocks may originally have been emplaced as sills or flows in or on a stabilizing continental crust (mini-craton); or 3) they could have been extruded as lava or tuff in a marine environment, but equilibrated with seawater at a relatively high temperature. The last model is the least likely, because there is only a relatively narrow temperature range at which all these rocks could have fortuitously equilibrated with seawater of $\delta^{18}O$ = 0‰ (or any other uniform value) and arrived at whole rock compositions equal to their starting values. Equilibration at lower or higher temperatures would have generated higher or lower $\delta^{18}O$ values, respectively. The association between mafic gneiss and clastic metasediments in the KSZ suggests that the mafic rocks are probably derived from supracrustal flows or shallow sills. Therefore a subaerial or intracratonic origin seems most likely for the Group 1 mafic gneisses in the KSZ.

Group 2 mafic gneisses have high $\delta^{18}O$ values comparable with those in greenstone belts. Two rocks collected near Borden Lake, 10 km southeast of Chapleau, show possible relict pillow structures (Moser, 1989): one of them is in direct contact with paragneiss, which has a $\delta^{18}O$ value of 12.2‰, the highest observed in KSZ paragneisses. This evidence is consistent with derivation of the mafic rocks in a marine environment. Therefore, the protoliths of the Group 2 mafic gneisses appear to have been extruded as submarine basaltic flows which were hydrothermally altered by seawater at low-temperature, which enriched their ^{18}O contents. The altered mafic rocks (equivalent greenstones) with associated sediment have been buried later at sufficient depth and metamorphosed to the upper amphibolite to granulite facies without significant fluid present. Therefore, the rocks are able to preserve their pre-metamorphic oxygen isotopic compositions.

CHAPTER FIVE

OXYGEN ISOTOPIC DISTRIBUTION AMONG COEXISTING MINERALS

5.1. INTRODUCTION

It has been discussed in Chapter Four that oxygen is an important component of most rock-forming minerals in igneous and metamorphic rocks. In addition to whole rock samples, oxygen isotopic data of coexisting minerals and fractionation between mineral pairs can provide important information about the equilibrium or disequilibrium character of mineral assemblages in rocks, the temperature of formation and the source of fluids probably involved in magmatic or metamorphic processes. For these reasons, the study of oxygen isotopes in coexisting minerals has become an important tool in igneous and metamorphic petrology (Taylor, 1962; Garlick and Epstein, 1967; Bottinga and Javoy, 1973, 1975; and Valley and O'Neil, 1984).

In this chapter, oxygen isotopic data for quartz, feldspar, biotite and magnetite from selected granitic rocks have been provided. The rock samples are distributed across the Wawa-Kapuskasing transect and range widely in metamorphic grade. The isotopic data from the mineral phases are used to test isotopic equilibrium of the rock system and to calculate the isotopic temperatures.

5.2. OXYGEN ISOTOPIC DATA OF COEXISTING MINERALS

5.2.1. ISOTOPIC EQUILIBRIUM

Common rock-forming minerals in most igneous and metamorphic rocks have a consistent tendency to concentrate ^{18}O. Epstein and Taylor (1967) have observed the following ranking in order of decreasing ^{18}O-content in the minerals: quartz, dolomite, alkali feldspar, calcite, intermediate plagioclase, muscovite, anorthite, pyroxene, hornblende, olivine, garnet, biotite, chlorite, ilmenite and magnetite. It is believed that the sequence of decreasing ^{18}O-content is closely related to crystallography and chemical composition of the minerals. For instance, the more highly polymerized the silicate, the greater is the tendency to concentrate ^{18}O (Taylor, 1967). In general, Si-O-Si bonds are the most ^{18}O-enriched, followed by Si-O-Mg and Si-O-Fe bonds, and Si-O-Al bond is more depleted in ^{18}O (Garlick, 1966; O'Neil and Taylor, 1967). Therefore, quartz has the greatest tendency to concentrate ^{18}O.

The highly consistent tendency of ^{18}O-enrichment of these minerals suggests that igneous and metamorphic rocks tend to be in isotopic equilibrium during their formation. The order of oxygen isotopic values for a suite of coexisting minerals, therefore, can be used as an indicator of isotopic equilibrium of the rock system. Reversed order of the $\delta^{18}O$ values for coexisting minerals has been observed in nature (isotopic reversals) and indicates isotopic disequilibrium of the rock system.

The order of ^{18}O-enrichment of coexisting minerals is a necessary test of isotopic equilibrium, but is not sufficient. In many cases, the isotopic shift of minerals by alteration is not so large as to result in isotopic reversal, but will vary the isotopic fractionation between mineral pairs. Isotopic fractionation between coexisting mineral pairs, therefore, can be used as another test of isotopic equilibrium.

For a rock which attained isotopic equilibrium, the isotopic fractionation between coexisting minerals is a function of temperature, expressed by the equation (3-7):

$$10^3 \ln\alpha = A\,T^{-2} + B$$

where $10^3\ln\alpha$ is approximated as $\Delta_{x\text{-}y}=\delta_x-\delta_y$ (Equ. 3-6). For a given mineral pair, for instance quartz and magnetite, their isotopic fractionation α should be in a small range at a given temperature, regardless of modal abundance and isotopic compositions. Unusually large or small isotopic fractionations between coexisting minerals indicate isotopic disequilibrium of the rock system. The isotopic fractionation decreases with increasing temperature.

5.2.2. OXYGEN ISOTOPIC RESULTS

Quartz, feldspar, biotite and magnetite have been separated from ten granitic rocks. The rocks are generally coarse grained, massive to gneissic, and have been metamorphosed from amphibolite to granulite facies.

The $\delta^{18}O$ values of mineral separates, their whole rock $\delta^{18}O$ values and fractionation between mineral pairs are summarized in Table 5.1 and are illustrated in Figure 5.1. The samples are arranged in approximate east-west order across the transect from top to bottom in Table 5.1 and from left to right in Figure 5.1, which corresponds to increasing metamorphic grade from amphibolite to granulite facies and increasing depth of crustal level.

Most minerals show relatively uniform $\delta^{18}O$ values (Table 5.1). Quartz has $\delta^{18}O$ values of 9.1 to 10.7 ‰, feldspar[d] has 6.2 to 8.2 ‰ and magnetite has -0.0 to 1.7 ‰. These results are consistent with the narrow $\delta^{18}O$ range observed from the whole rocks, 7.7 to 9.3 ‰. Biotite has a relatively large range of $\delta^{18}O$ values among the analyzed minerals, 2.0 to 4.4 ‰.

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[d] Feldspar includes both alkali feldspar and plagioclase. The difference of $\delta^{18}O$ values between these feldspar is usually from 0 to 1.5 ‰ (Taylor,1967).

Table 5.1 δ^{18}O values of minerals, fractionation of mineral pairs and isotopic temperatures

	δ^{18}O (‰)					Fractionation (‰)					Temperature(°C)[3]	
Sample[1]	WR[2]	Qtz	Fel	Bi	Mt	Qtz-Fel	Qtz-Bi	Qtz-Mt	Fel-Mt	Fel-Bi	Qtz-Bi	Qtz-Mt
870818-11	7.67	9.10	6.21	2.91	-0.01	2.90	6.20	9.11	6.22	3.30	464	558
840715-3	8.68	9.95	7.80			2.15						
840715-4	8.45	10.73	7.99			2.73						
840715-14B	7.98	9.23	7.54	3.62	0.01	1.69	5.61	9.22	3.92	7.53	498	553
870819-5	9.31	9.56	8.01	1.97		1.55	7.59			5.58	398	
870819-6	8.92	9.74	8.19	4.04		1.55	5.70			4.15	492	
870819-12	8.50	9.26	8.20	4.41		1.06	4.85			3.79	550	
870820-16	8.79	10.26	7.85		1.69	2.41		8.57	6.16			584
870819-10	8.57	9.21	7.26		0.02	1.95		9.19	7.24			554
870820-24B	8.57	9.31	7.46			1.85						

1: The samples are arranged from top to bottom in approximate east-west order across the transect.
2: WR–whole rocks; Qtz–quartz; Fel–both alkali feldspar and plagioclase; Bi–biotite; Mt–magnetite.
3: Quartz-magnetite isotopic thermometer calculation is based on the equation of Chiba et al. (1989);
Quartz-biotite isotopic thermometer calculation is based on the equation of Bottinga and Javoy (1975).

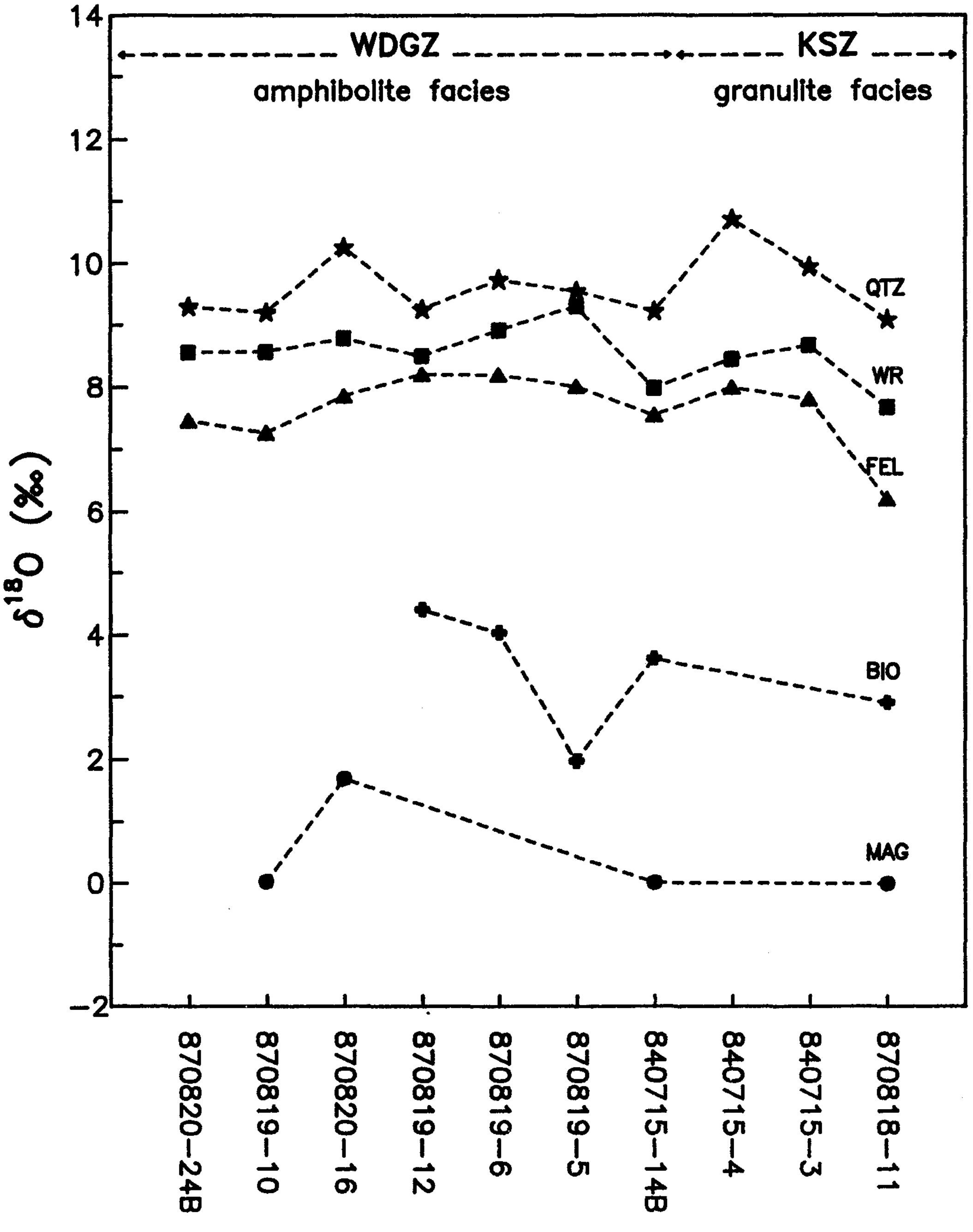

Figure 5.1 $\delta^{18}O$ values of whole rocks and coexisting minerals from the KSZ and the WGT. The samples are arranged in order of their approximate position across the transect from west to east (see Fig. 2.2). WR: whole rock; QTZ: quartz; FEL: feldspar; BIO: biotite and MAG: magnetite.

In Figure 5.1 no coexisting minerals from all analyzed rocks show isotopic reversal. The results suggest that the mineral phases from these metamorphic rocks are not grossly out of isotopic equilibrium.

Isotopic fractionations between analyzed mineral pairs are listed in Table 5.1 and illustrated in Figure 5.2. The fractionation between mineral pairs of quartz-feldspar and quartz-biotite vary from 1.06 to 2.90 ‰ and 4.85 to 7.59 ‰, respectively, and showed no regular pattern of change with increasing metamorphic grade. These results suggest that the isotopic system has been disturbed, possibly by late alteration. The alteration has also been evidenced by the petrographic observation that many feldspar are sericitized in thin section. The fractionation between quartz and magnetite is relatively constant, 8.57 to 9.22 ‰, suggesting that they are virtually unaffected by late alteration reactions.

5.3. OXYGEN ISOTOPIC GEOTHERMOMETRY

5.3.1. GENERAL FEATURES OF ISOTOPIC THERMOMETRY

The basic principle of isotopic thermometry is that isotopic fractionation between two coexisting mineral phases is a function of temperature. From equation (3-7) we know that the isotopic fractionation ($10^3\ln\alpha_{x-y}$, or δ_x-δ_y) between a mineral pair is linearly related. Plotting $10^3\ln\alpha_{x-y}$ vs. T^2 will yield a straight line, with a slope A. If equilibrium coefficients A and B have been calibrated, isotopic temperature can be calculated by using determined δ_x-δ_y values.

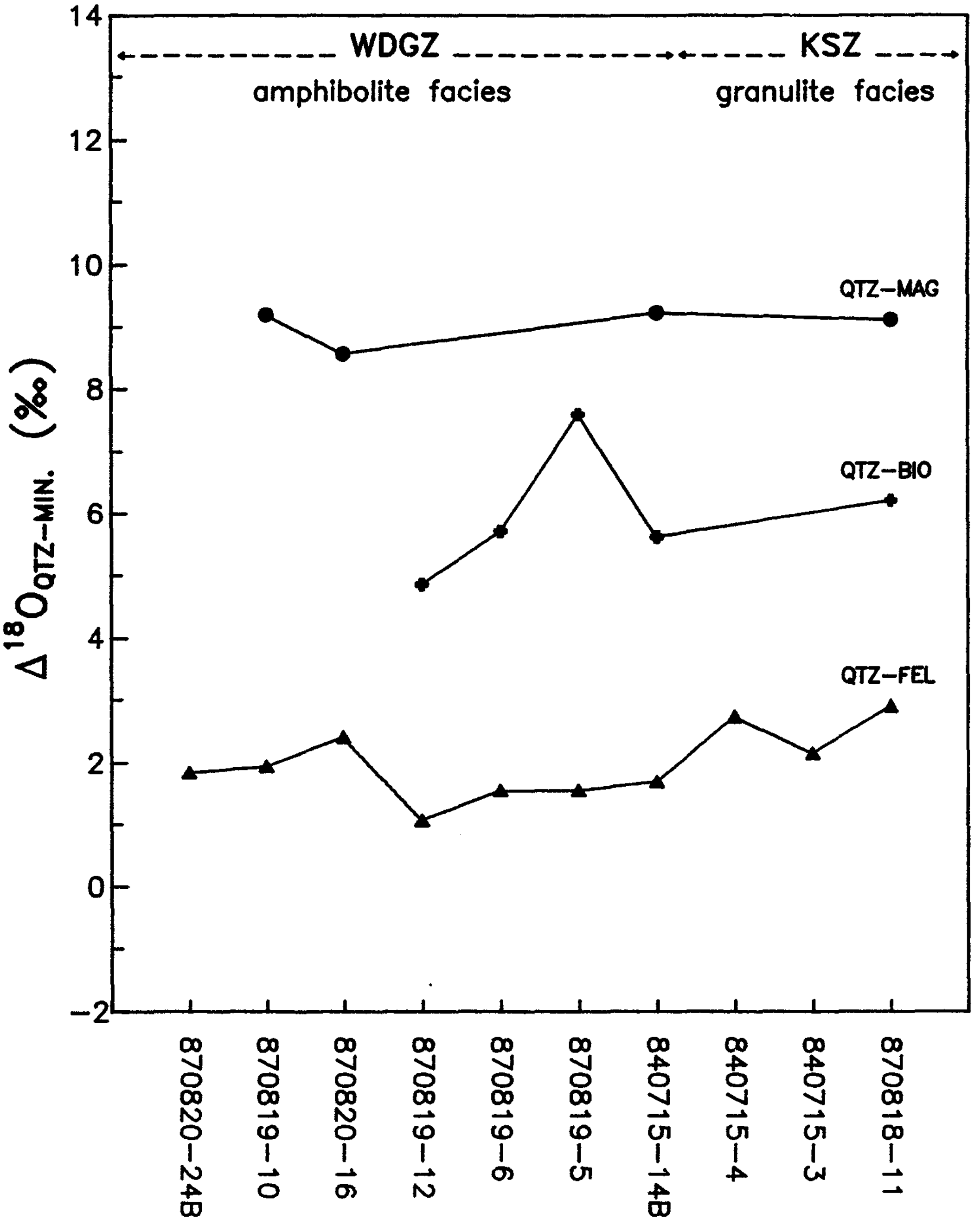

Figure 5.2 $\Delta^{18}O$ values of quartz-feldspar, quartz-biotite and quartz-magnetite pairs. The samples, their arrangement and abbreviation are same to the Figure 5.1.

Many studies have shown that isotopic fractionation between common coexisting mineral pairs is large relative to analytical error, even among high temperature mineral phases, and that isotopic fractionation is basically pressure independent. These features give isotopic thermometry a great advantage relative to many other geothermometers. Though hydrogen, carbon and sulphur isotopes are all useful thermometers, the oxygen isotope thermometer is the commonest choice in practice, especially for high temperature igneous and metamorphic rocks.

A good isotope thermometer should have following features: 1) the temperature coefficient of the fractionation factor (A in Equ. 3-7) is large, so that the plot of $10^3\ln\alpha$ vs. T^{-2} has large slope, which increases the precision of the calculation; 2) the isotopic fractionation between mineral pairs (δ_x-δ_y) is large relative to experimental errors of isotopic analysis; and 3) the minerals in the pair are not subject to isotopic exchange by late geological events (O'Neil, 1986). As already mentioned, quartz and magnetite form a good isotopic thermometer, because both are refractory minerals. Quartz is the most ^{18}O-enriched mineral and magnetite is very ^{18}O-depleted in most igneous and metamorphic rocks, so they usually have the largest isotopic fractionation among common mineral pairs. Feldspar, on the other hand, would not form a good thermometer with quartz, since both have a similar tendency to concentrate ^{18}O, and feldspar is less resistant to late stage alteration reactions.

5.3.2. CALIBRATION OF ISOTOPIC THERMOMETERS

The use of isotope thermometers is strongly depend on accurately calibrating the fractionation factor α and the equilibrium coefficients A and B in equation 3-7. Three methods have been used: 1) theoretical calculation; 2) experimental determination in the laboratory; and 3) calibration on an empirical basis.

The theoretical calculation is based on quantum principles and requires knowledge of vibration, translation and rotation of a molecule (Kieffer, 1982). The method is specially suitable for gas reactions, but is exceedingly difficult for solid phases due to the lack of thermodynamic data, such as vibration frequencies of molecules in crystal lattices.

In experimental determination a mineral of interest is chosen as starting material, and equilibrated with a large amount of water (as exchange medium) at a series of temperatures. When isotopic exchange approaches equilibrium, final δ values of mineral and water are determined, and the isotopic fractionation factor α can be calculated by using equation (3-4):

$$\alpha_{x-y} = \frac{1 + 10^{-3}\delta_x}{1 + 10^{-3}\delta_y}$$

where x is the mineral phase and y is water phase, respectively. Several techniques have been employed in different laboratories, for instance, two-direction approach, partial exchange technique, three-isotope method and so on (Matsuhisa et at., 1978; Downs et al., 1981; Matthews et al., 1983; and Chiba et al. 1989).

The idea of empirical calibration is to calculate the formation temperature of a rock (e.g. using x-y mineral pair, whose equilibrium coefficients are already known), with which another mineral z is also coexisting. The coefficients for mineral pair x-z can be calibrated using the calculated temperature and measured fractionation (Bottinga and Javoy, 1973, 1975). The assumption is that all minerals were at isotopic equilibrium. However, this is not always the situation.

In practice, experimental methods and empirical calibration are often chosen to determine the equilibrium fractionation factors. Faure (1986) has summarized some calibrations of oxygen isotope thermometers for common mineral pairs. Lately, Chiba et al. (1989) have provided some new calibration data, which were experimentally determined by new techniques, in which mineral-mineral fractionations were obtained by using carbonate as the exchange medium instead of using water.

Attempts have been made in this study to calculate isotope temperature using the quartz-magnetite and quartz-biotite thermometers. The quartz-magnetite isotopic thermometer calculation is based on the equation given by Chiba et al. (1989):

$$10^3 \ln\alpha_{quartz\text{-}magnetite} = 6.29 \times 10^6 T^{-2} \tag{5-1}$$

where B=0 (Equ.3-7). The quartz-biotite isotopic thermometer calculation is based on the equation derived from the data of Bottinga and Javoy (1975):

$$10^3\alpha_{quartz\text{-}biotite} = 3.69\times 10^6 T^{-2} - 0.60 \tag{5-2}$$

5.3.3. ISOTOPIC TEMPERATURES

Isotope temperatures calculated from the available data are summarized in Table 5.1. The quartz-magnetite isotopic thermometer gives apparent temperatures in the range from 553°C to 584°C, while the quartz-biotite thermometer gives apparent temperatures from 398°C to 550°C.

The temperatures calculated for two rocks from both thermometers are discordant. For instance, sample 870818-11 recorded a temperature of 464°C from the quartz-biotite thermometer and 558°C from the quartz-magnetite thermometer. The large discordances of isotopic temperatures reflect internal isotopic disequilibrium of the rock system.

One effective way to examine the isotopic equilibrium is to use a $\Delta^{18}O$ diagram (Deines, 1977). For three coexisting minerals, x, y and z to be in isotopic equilibrium, the equation (3-7) can be rewritten for mineral pairs x-y and y-z :

$$\Delta_{x\text{-}y} = A_{x\text{-}y}T^{-2} + B_{x\text{-}y} \tag{5-3}$$

$$\Delta_{y\text{-}z} = A_{y\text{-}z}T^{-2} + B_{y\text{-}z} \tag{5-4}$$

Combining the equations (5-3) and (5-4):

$$\Delta_{x-y} = A'\Delta_{y-z} + B' \qquad (5-5)$$

where A' and B' are the coefficients calculated from the equations (5-3) and (5-4). Plotting Δ_{x-y} versus Δ_{y-z} defines a straight line (concordant line). If coexisting minerals are in isotopic equilibrium, the fractionations between mineral pairs would be on or close to the line.

Figure 5.3 and 5.4 are the $\Delta^{18}O$ diagrams of coexisting quartz, feldspar and biotite or magnetite. Data for calculations are from Bottinga and Javoy (1975); Matsuhisa et al. (1979); and Chiba et al. (1989). The concordant lines for An contents and temperature contours are plotted in diagrams. In Figure 5.3, coexisting quartz, feldspar and magnetite are obviously out of isotopic equilibrium, since they all depart from the concordant lines. The coexisting quartz, feldspar and biotite plotted in Figure 5.4 also show isotopic disequilibrium. Isotopic disequilibrium can be caused either by an alteration reaction or by different isotopic exchange rates of minerals during or after metamorphism.

The temperatures from the quartz-biotite thermometer are generally much lower than those from quartz-magnetite and are more variable (Table 5.1). This again may be due to the different resistance of minerals to retrograde isotopic exchange. In general, quartz and magnetite are usually refractory minerals, which tend to retain their original isotopic compositions, while feldspar and biotite are less

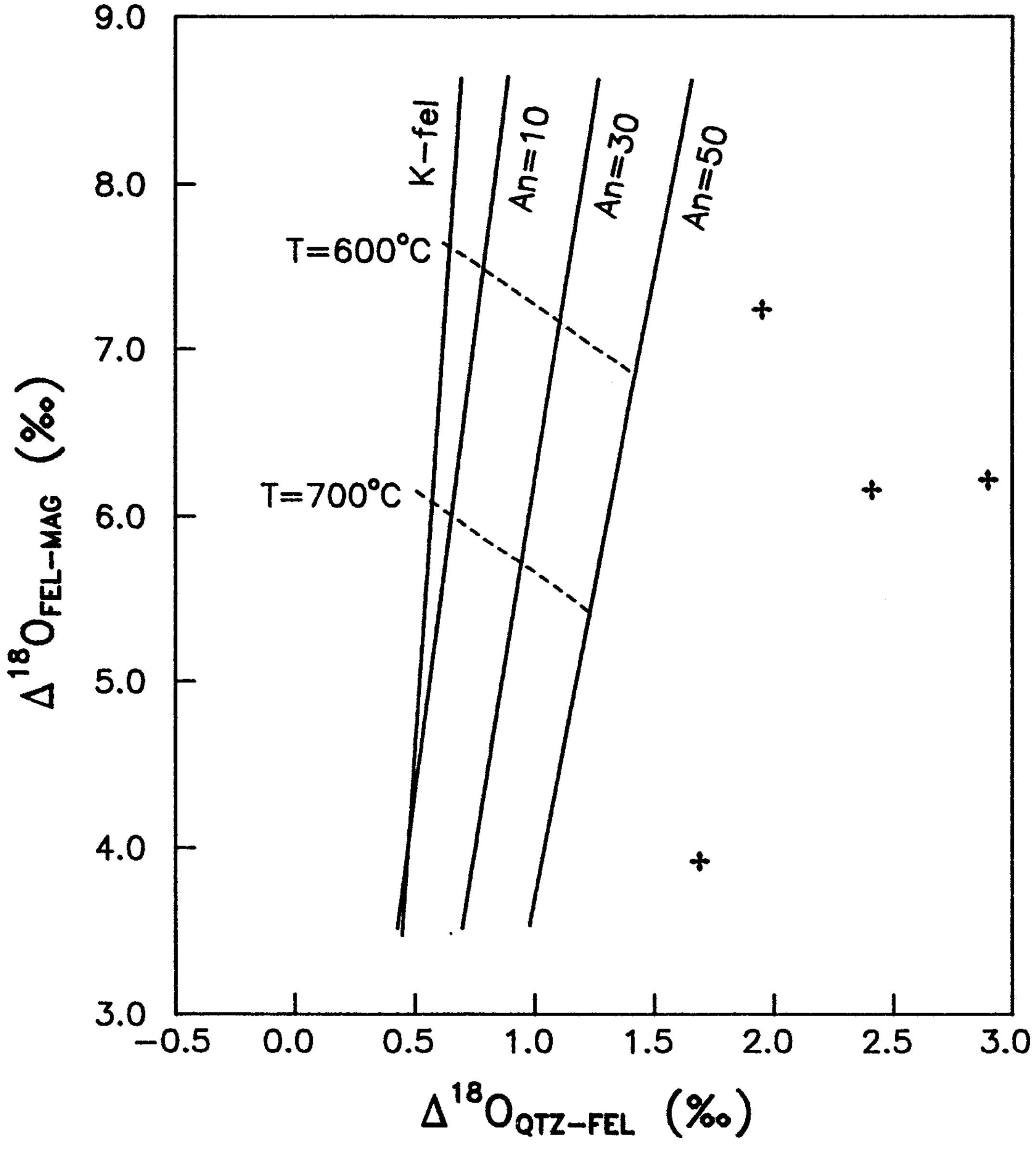

Figure 5.3 $\Delta^{18}O_{\text{Fel-Mag}}$ vs. $\Delta^{18}O_{\text{Qtz-Fel}}$. The concordant lines are calculated from the data of Matsuhisa et al. (1979) and Chiba et al. (1989). "An" is the anorthite content of the feldspars. The abbreviations are same as in Figure 5.1.

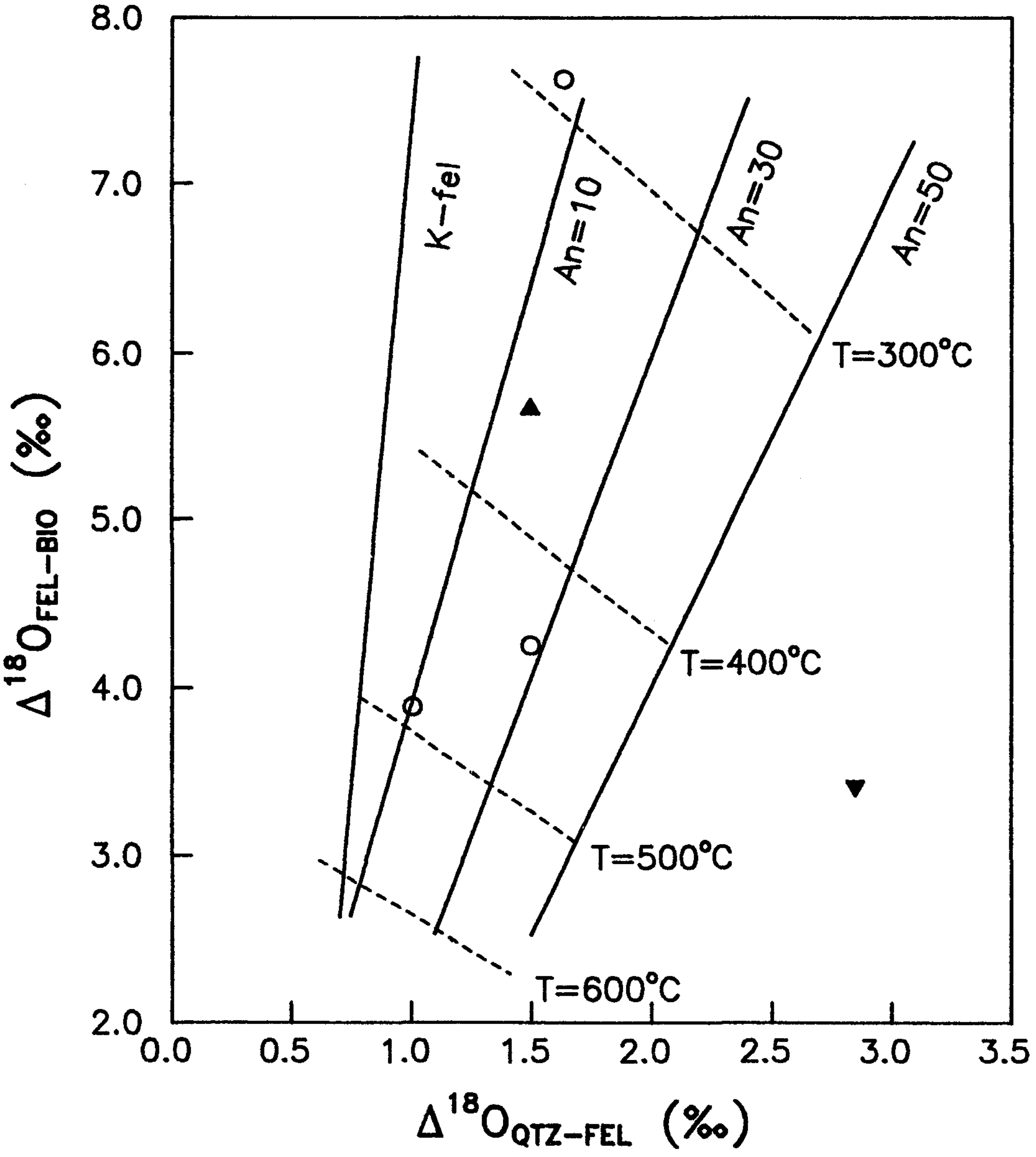

Figure 5.4 $\Delta^{18}O_{Fel-Bio}$ vs. $\Delta^{18}O_{Qtz-Fel}$. The concordant lines are calculated from the data of Bottinga and Javoy (1975) and Matsuhisa et al. (1979). "An" is the anorthite content of the feldspars. ▾: Plag An_{24}; ▴: Plag An_{30}; and ○: K-fel. The abbreviations are same as in Figure 5.1.

resistant, are easily altered and change their isotopic compositions during retrograde exchange (Garlick and Epstein, 1967).

Percival (1983) has calculated metamorphism temperatures using cation-exchange geothermometers. Across the Wawa-Kapuskasing transect, metamorphism temperatures vary from about 600°C to 800°C, increasing eastward. Comparing the isotopic temperatures with cation-exchange temperatures, the former are generally much lower. This phenomenon has been observed in other metamorphic terrains (Bottinga and Javoy, 1975; Giletti, 1986), and is attributed to a continued isotope exchange by oxygen diffusion after peak metamorphism.

Giletti (1986) has studied the influence of closure temperature (or blocking temperature) of oxygen isotope diffusion on the isotope temperature. In a rock containing several coexisting minerals, a mineral with a relatively high closure temperature will stop isotope exchange at a higher temperature, which will be recorded by the isotopic composition of the mineral. A mineral with lower closure temperature will continue to exchange until it also reaches its closure temperature, which would be recorded in the isotopic ratio. Giletti (1986) has calculated closure temperatures of minerals for oxygen diffusion: magnetite has a higher closure temperature (580°C at cooling rate 80°C/m.y.), followed by quartz (544°C), and K-feldspar has much lower closure temperature (~300°C). Therefore, quartz-magnetite isotopic temperatures likely represent the closure temperatures of oxygen exchange at equilibrium.

Giletti has also demonstrated that the cooling rates as well as the closure temperatures are related to the oxygen diffusion rates. For a rock cooling slowly, a lower isotopic temperature will be recorded than with fast cooling. This can explain the usually low isotopic temperature in most metamorphic terrains. So the low apparent isotopic temperature of the Wawa-Kapuskasing rocks suggests that the rocks underwent slow cooling, which is in accord with their deep crustal source.

The last feature indicated in this study is that the oxygen isotope temperatures across the transect are nearly constant (Table 5.1). This is in contrast with the observations that metamorphic grade and metamorphic temperatures increased eastward (Percival, 1983). Because no obvious gradient in isotopic fractionation is evident across the transect, the blocking of oxygen exchange or oxygen diffusion must have occurred everywhere at approximately same temperature, although not necessarily at the same time. Therefore, there is no evidence for significant differences in uplift and cooling rates across the Wawa-Kapuskasing transect from the oxygen isotope information.

CHAPTER SIX

HYDROGEN ISOTOPE GEOCHEMISTRY

6.1. INTRODUCTION

Hydrogen isotope geochemistry provides valuable information about the source of water present in igneous and metamorphic rocks and about rock-water interactions during magmatic and metamorphic processes. Many studies have been carried out on igneous rocks, regarding the origins of magmas, seawater alteration, meteoric-hydrothermal systems and other related processes (e.g. Sheppard and Epstein, 1970; Taylor and Forester, 1979; Kyser and O'Neil, 1984). Most hydrogen isotopic data of metamorphic rocks are from low- to medium-grade terrains (e.g. Hoernes and Friedrichsen, 1978, 1980; and Wickham and Taylor, 1985). Hydrogen isotopic data of high-grade metamorphic rocks (upper amphibolite to granulite facies) are rare in the literature, and data for Archean high-grade terrains are especially scarce.

In this study, hydroxyl minerals from Archean rocks in the Kapuskasing transect have been analyzed. The purpose is to obtain hydrogen isotope data from deeper crustal rocks and to supplement these with the oxygen isotopic data, in order to better understand the water-rock system in this high-grade metamorphic terrain.

6.2. HYDROGEN ISOTOPE GEOCHEMISTRY

6.2.1. CHARACTERISTICS OF HYDROGEN ISOTOPES

Hydrogen isotopes have interested many geochemists because they have a large relative mass difference between the two isotopes, which results in large variations in hydrogen isotope ratios (D/H) in natural materials, and also because they occur in simple forms of H_2O, OH^-,H_2 and CH_4 throughout the Earth and the Solar system. Hydrogen in igneous and metamorphic rocks is mainly as OH^- in hydroxyl minerals and also as H_2O or trace amounts of CH_4 in fluid inclusions, whose isotopic compositions are closely related to the water present during the rock formation. In addition, hydrogen is restricted to certain hydroxyl minerals, such as mica, amphibole and some secondary alteration minerals, while oxygen is a major component for most rock-forming minerals. These characteristics, together with oxygen isotopic ratios, make the hydrogen isotopic ratios a very useful tool in igneous and metamorphic petrology, providing some constraints on the origins of water involved in metamorphism and on the nature of water-rock interactions.

An important difference between hydrogen and oxygen isotopes is that the amount of hydrogen is very small in many rocks. For instance, typical basalt contains average 45.0 wt% or 59.5 atom% oxygen and 0.1 wt% or 2.2 atom% hydrogen; and granite contains average 48.8 wt% or 62.2 atom% oxygen and 0.07 wt% or 1.5 atom% hydrogen (calculated from Le Maitre's chemical composition data, 1976). Therefore, the D/H ratios of minerals or rocks are much more sensitive to the rock-water interaction. Especially, when the water/rock ratio is very low, only hydrogen isotopic data can provide evidence for the rock-water exchange and for the source of waters, because very small amounts of water will change D/H ratios significantly, while they may be not enough to affect $^{18}O/^{16}O$ ratios appreciably (Taylor,1978).

6.2.2. METHOD OF STUDY

As already mentioned, the main application of the hydrogen isotope study is to determine the nature of water, which has interacted with rocks. Two methods can be utilized to determine δD values of water involved in magmatic and metamorphic processes (Taylor,1979):

1) It is to directly measure the water itself, which has been trapped as primary fluid inclusions in igneous rocks when the minerals crystallized. If fluid inclusions in non-hydroxyl minerals are chosen, such as in quartz, post-formation hydrogen isotopic exchange with the host mineral is restricted. This is in contrast to the $^{18}O/^{16}O$ ratios of fluid inclusions which is strongly buffered by the host

minerals. δD values obtained by this method, therefore, likely represent the original hydrogen isotopic composition of the water, which was present at the time of rock formation. In many cases, however, secondary fluid inclusions may contaminate the primary ones and modify the isotopic compositions.

2) More commonly, water cannot be sampled directly from the geological samples, since it is no longer present. In this case, the δD value of water can be obtained by analyzing the hydrogen isotopic composition of hydroxyl minerals, and calculating the isotopic composition of water in equilibrium with the mineral assemblage at the temperature of formation. This method is commonly used, since it can be applied to most igneous, metamorphic rocks and other hydrothermal rocks. A similar technique has been successfully applied to oxygen isotope studies for many igneous and metamorphic rocks (see summary by Criss and Taylor; Muehlenbachs; Valley, 1986).

6.2.3. MINERAL-WATER FRACTIONATION

In order to calculate the hydrogen isotopic composition of water, which now has been removed from the system, it is necessary to know the isotopic fractionation factor between a hydroxyl mineral and water as a function of temperature, expressed by equation (3-7):

$$10^3 \ln\alpha = A\ T^{-2} + B$$

and in some case, as a function of composition of the minerals. The hydrogen isotopic fractionation factors between many hydroxyl minerals and water (α_{M-W}) have been determined experimentally (e.g. Suzuoki and Epstein, 1976; Graham et al. 1980, 1984). The patterns of hydrogen fractionation curves are very complex compared to those for oxygen (e.g. Bottinga and Javoy, 1975; Matthews et al. 1983b). Some of the results from different laboratories are not consistent.

Suzuoki and Epstein (1976) have demonstrated important linear relationships between mineral-water fractionation factor and $1/T^2$ for micas and amphiboles in the temperature range from 450 to 800° C, and have also proposed correlation between the fractionation factor and molar fractions of octahedrally coordinated cations. The equation (3-7) is thus modified as follows:

$$10^3 \ln\alpha_{M-W} = -22.4(10^6 T^{-2}) + 28.2 + (2X_{Al} - 4X_{Mg} - 68X_{Fe}) \qquad (6-1)$$

where α_{M-W} is the fractionation factor between a mineral and water; X is the molar fraction of the octahedrally coordinated cations in the mineral structure; and T is absolute temperature in Kelvin. The relationships are not only helpful to calculate the isotopic composition of fluid phases, but also to explain some natural phenomena, for instance, most muscovite is enriched in deuterium with respect to coexisting biotite, since it contains less Mg and Fe in its octahedral sites.

Graham et al. (1984), however, argued that these relationships are not universal among the hydroxyl minerals, even for some amphiboles. Instead, they observed that fractionation factors of some minerals are temperature independent in similar temperature ranges. For instance, there is a constant fractionation factor $10^3\ln\alpha_{M\text{-}W}$=-23.1 ‰ at 350°C to 950°C for hornblende and a fractionation factor $10^3\ln\alpha_{M\text{-}W}$=-21.7 ‰ at 350°C to 650°C for tremolite. They observed that only at higher temperatures do the fractionation factors become temperature dependent.

At low temperatures ($<$400°C), hydrogen isotope fractionation factors are not well estimated due to slow isotopic exchange. The patterns of fractionation curves are more variable and some of them show an opposite relationship to that observed for high temperatures (Graham et al. 1980). For instance, kaolinite-water fractionation at $T \leq 400$°C has a positive slope ($A>0$ in Equ. 3-7), while most fractionations at higher temperature have a negative slope ($A<0$). Therefore, one must be cautious in extrapolating high temperature calibration to estimate fractionation factors at low temperature, as this may result in large errors. Because of these uncertainties and the limited experimental data available, calculated δD values for water may only be semi-quantitative.

In this study, hydrogen isotopic fractionation factors defined by Suzuoki and Epstein (Equ. 6-1) have been used because it is to be expected from theoretical principle that the isotopic fractionation is a function of temperature. Chemical compositions of minerals have been analyzed by EMA (Chap. 3). Molar fractions of aluminum, magnesium and iron have been estimated by assuming an ideal chemical formula for the hornblende: $X_{2\text{-}3}Y_5Z_8O_{22}(OH)_2$, where Z is the tetrahedral site, occupied by silicon and aluminum atoms; Y is the octahedral site, occupied by aluminum, magnesium and iron; and X is composed of potassium, sodium and calcium atoms.

6.2.4. HYDROGEN ISOTOPES IN IGNEOUS AND METAMORPHIC ROCKS

The hydrogen isotopic composition of most igneous rocks (volcanic and plutonic) is within a range of -85 to -50 ‰, often referred to as "igneous" values (Sheppard and Epstein, 1970; Taylor, 1977). Metamorphic rocks have a wider range of δD values, typically -100 to -40 ‰ for metasediments, -70 to -35 ‰ for metabasalts and associated rocks from the ocean crust and ophiolite complexes (Sheppard, 1986a), and -85 to -35 ‰ for regional metamorphic rocks (e.g. muscovite, biotite and hornblende, Taylor, 1979).

6.2.5. WATER SOURCES AND THEIR ISOTOPIC COMPOSITIONS

In order to identify water sources by using their isotopic fingerprint on rocks, it is necessary to know the initial hydrogen and oxygen isotopic ratios of the water which was possibly present during igneous and metamorphic processes. In nature the following are most likely the water sources available:

Meteoric Waters Meteoric water includes all cycled continental surface waters, such as rain, snow, ice, rivers, groundwater and so on. The isotopic compositions, both oxygen and hydrogen, for today's meteoric waters vary systematically with the latitude and elevation. Generally, the higher the latitude or elevation, the lower the δ values. $\delta^{18}O$ and δD values of all meteoric waters are strongly correlated, approximately in a linear relationship (Craig, 1961),

$$\delta D \approx 8\delta^{18}O + 10 \ (‰) \qquad (6\text{-}2)$$

which is often referred to as the "Meteoric Water Line" (Figure 6.1). Ancient meteoric waters probably followed a similar relation, though we expect some shift (Sheppard, 1986a). In nature the $\delta^{18}O$ and δD values of meteoric water vary largely from place to place, however, the volumetrically most important meteoric waters have $\delta^{18}O$ values at 0 to -10 ‰ and δD at +10 to -70 ‰ (Sheppard, 1986a).

Ocean Waters Present-day seawater has relatively constant $\delta^{18}O$ and δD values in most part of the oceans, both close to zero (Figure 6.1), except in areas where evaporation and fresh water dilution are significant and have resulted in isotopic enrichment or depletion, respectively (Craig, 1966; Epstein and Mayeda, 1953). Many studies indicate that the isotopic composition of ocean water probably fluctuated within a small range throughout most of Phanerozoic time, for instance, the $\delta^{18}O$ value from +1.8 ‰ to -1‰, largely limited by glaciation (Shackleton, 1968; Taylor, 1979). Back to the Precambrian, however, there are major uncertainties about the isotopic composition of ocean water. There is some evidence showing roughly similar oxygen isotopic composition of ancient seawater

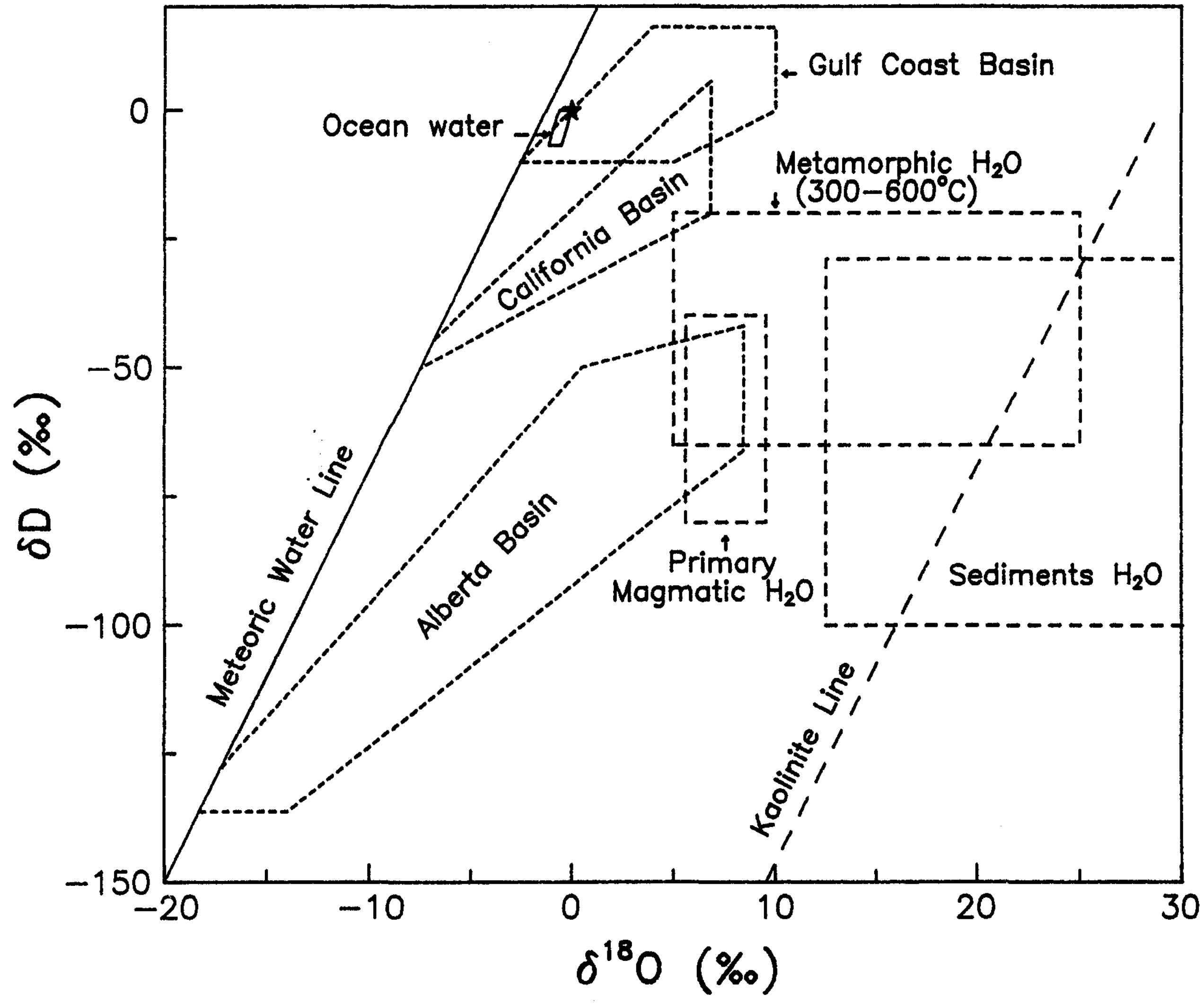

Figure 6.1 Oxygen and hydrogen isotopic compositions and fields for important source waters (after Sheppard, 1986). ★: SMOW.

(Knauth and Epstein, 1976; Beaty and Taylor, 1982), whereas others suggest that ancient seawater was depleted in ^{18}O (Perry, 1967; Becker and Clayton, 1976) and became progressively enriched throughout time (see summary by Sheppard, 1986a). There is very little evidence of any change in hydrogen isotopes overtime.

Magmatic Waters Magmatic water is physically dissolved in and has equilibrated with magma at high temperature. Calculated δD values from the measurements of hydroxyl minerals in the rocks are in a range of -85 to -40 ‰ (Taylor, 1979), which, together with oxygen isotopic compositions of 5.5 to 9.5 ‰ are plotted in Figure 6.1 as "primary magmatic water" field. Although magmatic water is often referred to a deep-seated source, it should not be confused with "juvenile water", which, by definition, came from the mantle of the Earth and has never been involved within the hydrosphere. It has been suggested that the normal δD values of -85 ‰ to -40 ‰ arise in part by melting of subducted seafloor, which was hydrothermally altered by seawater (Taylor, 1977). Recent hydrogen and helium isotope studies of oceanic basalts indicate that magmatic water may alternatively have a mantle origin with δD values of -85 to -80 ‰ (Poreda et al, 1986).

Metamorphic waters Metamorphic waters are present in rocks when metamorphism takes place. The $\delta^{18}O$ and δD values of metamorphic waters are dependent on their precursor parent rocks, metamorphic temperature and fluid phases introduced into the rocks during metamorphism. The δD value of metamorphic water can be measured in fluid inclusions, or calculated from analysis of minerals or rocks. The $\delta^{18}O$ value, however, can only be calculated from analysis of minerals, since the oxygen in fluid inclusions isotopically exchanges with the host mineral during the cooling. The typical δD values for regional metamorphic water appear relatively narrow, -20 to -65 ‰ (Taylor, 1979), whereas the $\delta^{18}O$ values are very large, from 5 to 25 ‰ (Figure 6.1). Deuterium-rich metamorphic waters, with δD values up to 0‰ were probably derived from the dehydration of oceanic crust (Sheppard, 1981). Deuterium-depleted waters may result from interaction of heated meteoric water or equilibrium with iron-rich minerals.

Connate waters Connate waters are fossil seawaters trapped in the sediments, whose original isotopic composition would be identical to contemporary seawater. The δD and $\delta^{18}O$ values of connate waters have a very wide range (e.g. basins in Figure 6.1), and generally have tendency to increase with decreasing latitude and increasing salinity (Taylor,1979).

In addition, there may be other types of water involved in igneous and metamorphic processes, such as sediment water and geothermal water. However, these waters basically are modified and recycled from the waters just described above. Isotopic values for different water types show some overlap and are commonly present together in many geological terrains. Therefore, there may not be simple and prompt solutions obtained from stable isotopic studies regarding the origin of the fluids and in many cases other geological and geochemical information is helpful.

6.3. HYDROGEN ISOTOPE RESULTS

6.3.1. δD VALUES IN HYDROXYL MINERALS

Seven hornblende and two biotite separates have been analyzed for their hydrogen and oxygen isotopic compositions. Hornblendes are from five mafic gneisses, an anorthosite and an ultramafic pluton. The biotites are from a tonalitic gneiss and a paragneiss.

The δD values obtained in this study, along with the mineral and whole rock $\delta^{18}O$ are summarized in Table 6.1. The δD values of the minerals are plotted against the $\delta^{18}O$ values of the whole rocks in Figure 6.2. For comparison, the fields of most primary igneous biotite and hornblende and whole rocks are also plotted in Figure 6.2, along with some data from Precambrian gneisses (Taylor, 1977; Taylor and Forester, 1979).

The hydroxyl minerals display a large δD range, from -109 to -58 ‰. In general, there is no regular correlation between δD and $\delta^{18}O$ values. Several important features have been noticed from these data:

Table 6.1 δD values of hornblende and biotite and $\delta^{18}O$ values of the minerals and rocks.

Sample	Min. Type	$\delta^{18}O$ (‰)		δD (‰)	Zone	Rock Type
		WR	MIN			
PBA2	Hornblende	9.0	7.8	-102.6	K	amphibolite
890824-1	Hornblende	9.5	8.3	-88.7	K	amphibolite
84-715-9	Biotite	9.3	5.7	-75.4	K	graph-gar-bio paragneiss
840714-9	Hornblende	5.8	5.0	-58.0	K	gar-hb-plag granulite
840714-7	Hornblende	5.2	4.5	-58.3	K	gar amphibolite
840714-5	Hornblende	6.2	6.0	-61.5	W	hb pyroxenite
840713-1	Hornblende	7.0	6.1	-87.3	W	hb gneiss
840713-5	Biotite	7.3	2.8	-88.5	W	ep-chlo tonalitic gneiss
840713-3	Hornblende	6.5	5.8	-108.6	W	cpx-hb gneiss

WR: whole rocks; MIN: mineral separates; K: Kapuskasing Structural Zone; W: Wawa Gneiss Terrain.

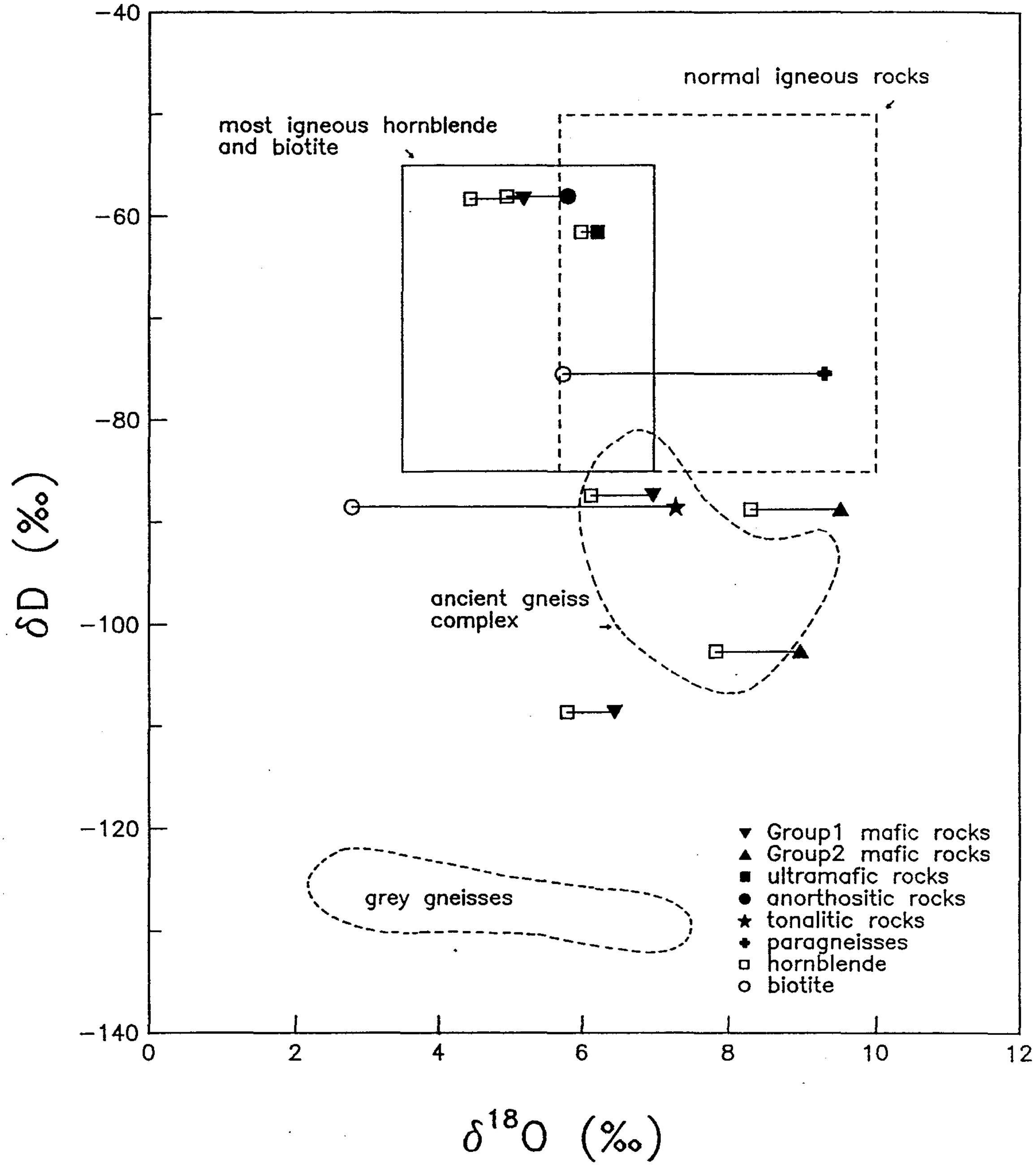

Figure 6.2 Hydrogen and oxygen isotopic data of selected rocks from the Wawa-Kapuskasing transect. The normal igneous rocks and ancient gneiss complex fields are from Taylor, 1977. The igneous hornblende and biotite and grey gneisses fields are after Taylor and Forester, 1979. The gneissic rocks in both fields are Precambrian in age.

1) Samples 840714-9, 840714-7 and 840714-5, which are all in the KSZ, have δD values from -58 to -62 ‰, compatible with those of "normal" igneous rocks (Table 6.1 and Figure 6.2). Sample 840714-9, which was collected from the interior of the Shawmere complex, is a garnet-hornblende-plagioclase granulite and contains about 50% hornblende. The rock is generally structureless and has preserved the primary igneous minerals and texture. It is undoubted that the anorthosite complex is of igneous origin, though it has been metamorphosed to upper amphibolite to granulite facies. Sample 840714-7 is a garnet amphibolite, with about 55% hornblende, which is generally massive, without strong gneissosity. Sample 840714-5 is an ultramafic intrusive, hornblende pyroxenite, and the hornblende makes up about 45% of the rock. All these samples show "normal" whole rock $\delta^{18}O$ values and hornblende $\delta^{18}O$ values as well. The δD values, -58 to -62 ‰, of the hornblende are typical of unaltered igneous rocks. Since hornblende is the major hydroxyl mineral (>90%) in these rocks, the hydrogen isotopic compositions determined on hornblende approximately represent the whole rock values.

In addition to the normal $\delta^{18}O$ and δD values of these hydroxyl minerals, there is another feature in common: the rocks do not contain significant amounts of secondary alteration minerals. Therefore, it is possible that these samples inherit the hydrogen isotopic compositions from their unmetamorphosed parent rocks, and the fluid incorporated with the rocks is deep-seated magmatic water.

Dehydration during the high-grade metamorphism may have had effects on these rocks, which will be discussed in section 6.2.4.

Sample 840715-9 is a paragneiss from the KSZ. Biotite is the only hydroxyl mineral and makes up about 15% of the rock. The paragneiss has relatively higher whole rock $\delta^{18}O$ value (9.3 ‰), while the biotite from the rock has $\delta^{18}O$ (5.7 ‰) and δD (-75 ‰) values within the "normal" igneous field (Figure 6.2). From the early discussion (section 4.6.3.), we believe that unweathered volcanic rock fragments are the major components of the paragneisses, which account for their relative low $\delta^{18}O$ values and might also explain the igneous δD value of the paragneiss.

2) Samples PBA2 and 890824-1 are ^{18}O-enriched mafic gneisses (Group 2) from the supracrustal belt of the KSZ, which were metamorphosed to amphibolite facies and have hornblende-plagioclase-quartz mineral assemblages, with trace amounts of biotite. Hornblendes separated from both samples have δD values of -89 and -103 ‰, one of which is markedly depleted in deuterium, and have $\delta^{18}O$ values of 7.8 and 8.3 ‰, which are enriched in ^{18}O compared with "normal" igneous rocks (Figure 6.2).

The field structures and the whole rock oxygen isotopic data of these mafic gneisses suggest that they are the equivalents of metabasalts in greenstone belts, which interacted with seawater at low temperature. It is known that at low temperature, minerals tend to be enriched in heavy oxygen ^{18}O and depleted in deuterium, because of fractionation factors $\ln\alpha_{(oxygen)} > 0$ and $\ln\alpha_{(hydrogen)} < 0$ (Beaty, 1980; Kyser and O'Neil, 1984). Therefore, it is possible that low temperature alteration with seawater would lead to ^{18}O-enrichment and D-depletion of the basalts.

It must be considered, however, that dehydration during high-grade metamorphism would also deplete deuterium in the rocks. The magnitude of the isotope composition change depends on the amount of water in the rocks, the amount of water lost and the temperature of the metamorphism. The possible effect of dehydration will be calculated in section 6.2.4.

3) Samples 840713-5, 840713-1 and 840713-3, from the WGT, are gneissic rocks and have relatively lower δD values, -87 to -109 ‰ (Figure 6.2). Sample 840713-5 is a tonalitic gneiss, in which biotite and hornblende are the primary hydroxyl minerals, making up about 15% of the rock. There are significant amounts of secondary hydroxyl minerals present (epidote-clinozoisite and chlorite), making up about 5% of the rock. The whole rock displays a "normal" δ^{18}O value (Table 6.1). The δD value (-89 ‰) and δ^{18}O value (2.9 ‰) of the biotite are somewhat lower, compared with most biotite from igneous rocks (Figure 6.2). Samples 840713-1 and 840713-3 were collected from the same outcrop near the boundary between the WGT and the MGB. Both samples are mafic gneisses, associated with tonalitic gneisses in the field and containing about 60% and 40% of hornblende, respectively. Sample 840713-1 has a hornblende-plagioclasesphene assemblage with accessary pyrite, and 840713-3 has a clinopyroxe-hornblende-plagioclase assemblage and chlorite, clinozoisite and sericite secondary alteration is widespread. The $\delta^{18}O$ values of the whole rocks are normal, as well as the values of hornblende. The hydrogen isotopic compositions are lower, especially sample 840713-3 (-108‰).

Because there are several hydroxyl minerals present in the rocks (e.g. samples 840713-5 and 840713-3), the contributions of each to the whole rock δD value has to be considered. Hornblende is usually found to have identical hydrogen isotopic composition with coexisting biotite (Suzuoki and Epstein, 1976). Epidote has fractionation factor $10^3 \ln\alpha = -36$, at temperature 300-600°C (Graham et at., 1980), which is lower than the fractionation factors of hornblende (Table 6.2). The fractionation of chlorite has not been well estimated due to a very slow exchange rate. However, it is similar to hornblende on the basis of an empirical calibration in the same temperature range (Taylor, 1974). Therefore, the δD values for these whole rocks should either resemble or be slightly lower than the δD value determined on hornblende or biotite.

The δD results are generally compatible with the observations on an Archean gneiss complex from southern Africa (Figure 6.2, marked as ancient gneiss complex). Several explanations for these D-depleted Archean gneisses have been put forward: a) Taylor (1977) suggested that the lower δD values from

Archean gneisses might reflect Archean "juvenile" water, because the early upper mantle may not yet have been contaminated by hydroxyl minerals from subducted oceanic crust; b) it was also suggested that the lower δD values of Archean gneisses might come from a hydrothermally altered oceanic crust by D-depleted Archean seawater (Sheppard, 1986b), because subducted oceanic crustal hydroxyl minerals are the basic controls of the "normal" δD values for most younger igneous rocks (Taylor, 1977); c) some have also argued that meteoric water could penetrate downward to depths of 6 to 10 km, and hydrothermally alter deeply buried rocks, producing in D-depletion, such as grey gneisses in East Greenland (Figure 6.2, Taylor and Forester, 1979).

Models (a) and (b) only can apply to unaltered rocks, in which the fluid is basically of magmatic origin. In the WGT, rocks were obviously hydrated either at later- or post-regional metamorphism. There are two types of water sources for hydration: surface meteoric water penetrating downward or dehydration water released from the deeper crustal rocks which rose up to the WGT. The possible water source will be further discussed in next two sections.

6.3.2. DEHYDRATION REACTION DURING HIGH-GRADE METAMORPHISM

It has been proposed that dehydration during high-grade metamorphism may have effects on the isotopic composition of the rocks (section 4.3.2.). However, the change of δ^{18}O values is always small, since oxygen is a major component of most rocks. In contrast to oxygen, the effect of dehydration on δD may be very large because rocks contain only small amounts of hydrogen. In this section possible hydrogen isotopic changes due to dehydration will be calculated, based on available data.

Equations (4-1) for ***Batch*** dehydration and (4-2) for ***Rayleigh*** dehydration models are recalled here:

$$\delta_f=\delta_i+10^3\ln\alpha\,(1-F) \tag{6-3}$$

$$\delta_f=(\delta_i+10^3)\,F^{\left(\frac{1}{\alpha}-1\right)}-10^3 \tag{6-4}$$

Fractionation factors, calculated based on Suzuoki and Epstein's equation (1976) at temperature 600 and 700°C, are summarized in Table 6.2. The temperature range is based on the mineral phase geothermometer (Chapter 2). Notice that most samples have similar chemical composition, resulting in similar fractionation factors. Average fractionations ($10^3\ln\alpha$) equal to -30.3 ‰ (T=600°C) and -24.6 ‰ (T=700°C) are used in modelling. Two initial δ_i values of rocks are assumed: -80 and -60 ‰, which are typical of unaltered igneous; -80 ‰ is close to the value of the mantle and -60 ‰ is about the average of unaltered metaigneous rocks in the KSZ (section 6.2.4.).

Table 6.2 Calculations of the molar fractions and the fractionation factor

$$10^3\ln\alpha_{e\ (\text{min.-water})} = -22.4(10^6T^{-2}) + 28.2 + (2X_{Al}-4X_{Mg}-68X_{Fe})^*$$

Sample	X_{Al}	X_{Mg}	X_{Fe}	A#	$10^3\ln\alpha_e$				
					600°C	700°C	200°C	250°C	300°C
PBA2	0.13	0.40	0.47	-5.10	-34.49	-28.76	-105.2	-87.0	-73.3
890824-1	0.12	0.42	0.45	-3.84	-33.23	-27.50	-104.0	-85.7	-72.1
840714-7	0.12	0.43	0.45	-3.88	-33.27	-27.54			
840714-5	0.07	0.57	0.36	1.58	-27.81	-22.08			
840714-9	0.14	0.57	0.28	7.16	-22.23	-16.50			
840713-3	0.11	0.48	0.41	-1.38	-30.77	-25.04			

*: the equation is defined by Suzuoki and Epstein (1976).

#: $A = 28.2 + (2X_{Al}-4X_{Mg}-68X_{Fe})$.

Figure 6.3 is a plot of δ_f vs. F (mole fraction of hydrogen that remains in the rock after dehydration), based on the two end-member models. Straight lines are the Batch fractionation and curves are the Rayleigh fractionation. Both models show a decrease of δD values by dehydration. When F is large (≥0.9), most of the water is still in the rock and only small amounts have been released; the δD value of the rock is slightly lower and the amount of decrease ΔδD is <5 ‰. For F≥0.6, Batch and Rayleigh fractionation have similar effects on the δD values,and the decrease in δD values is less than 15 ‰. When F<0.6, two models show significantly different effects on the δD values, especially when dehydration nears completion and when F is close to 0, the decrease in the δD value could be larger than 100 ‰ by Rayleigh fractionation.

Mafic gneisses collected from the KSZ and the WGT have an average 0.91% H_2O content[e]. If the rocks originally were fresh basalt or gabbro containing 0.95% H_2O, an average basalt (Le Maitre, 1976), there was only about 0.05% H_2O is lost during the metamorphism. In this situation F is larger than 0.9, and metamorphic dehydration reactions would only slightly change δD values of the rocks. The three metaigneous rocks, with normal igneous δD values (Figure 6.2), likely developed in such a situation, so their δD values approximately represent

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e: The H_2O contents are based on the analyses of loss on ignition. It might include other volatile elements, such as C or S. For most analyzed samples, however, these elements are trace components. The results of the loss on ignition approximately represent the H_2O contents in the rocks.

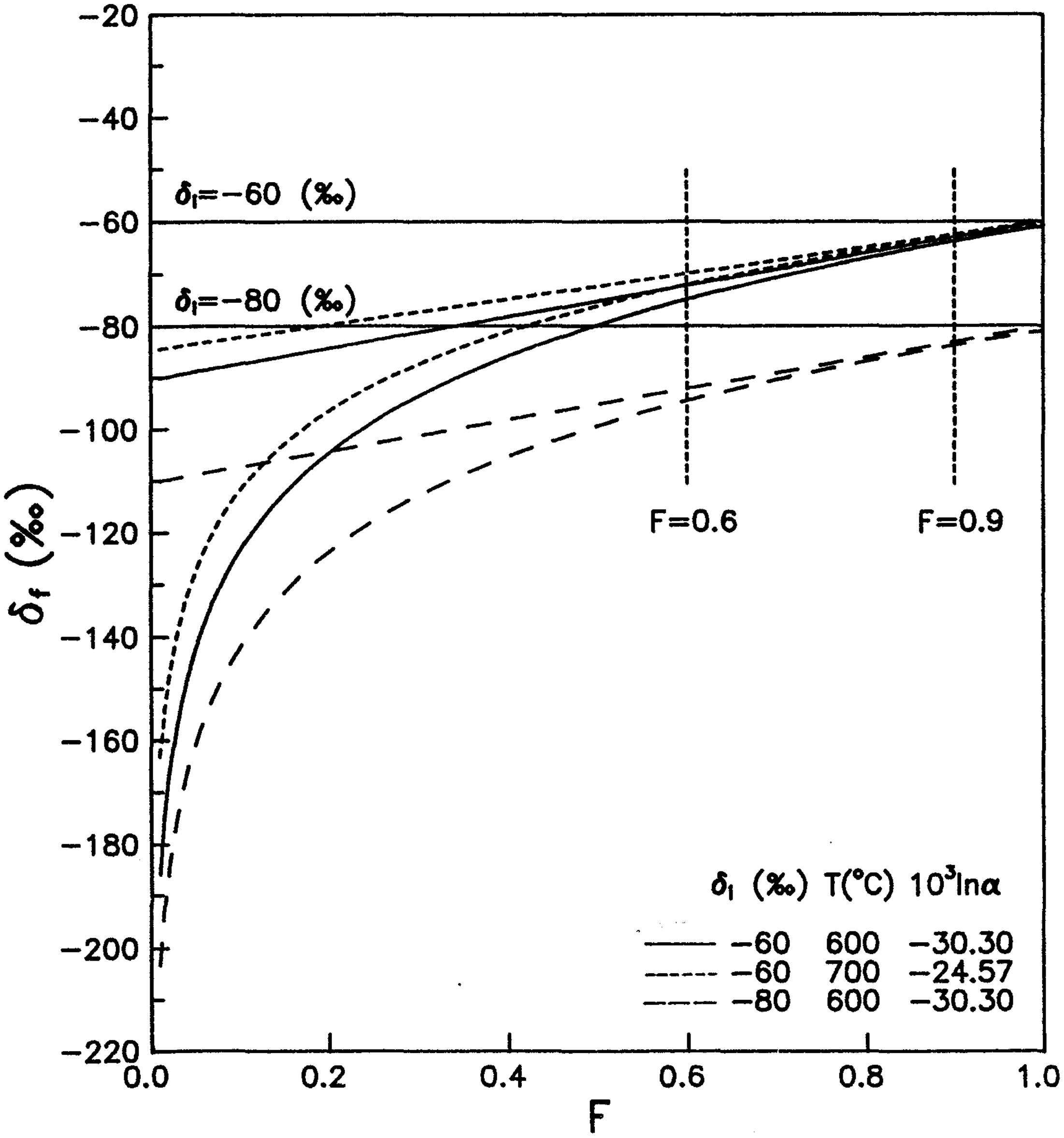

Figure 6.3 Calculated effects of dehydration reactions on δD values of rocks. Straight lines result from ***Batch*** dehydration and curves result from ***Rayleigh*** dehydration reactions. F is the mole fraction of hydrogen remaining in the rocks. δ_I is assumed initial δD values of rocks. Fractionation factors are the average values from Table 6.2.

their pre-metamorphic values.

If mafic gneisses were originally the metabasalt of greenstone belts, like Group 2 mafic gneisses, the parent rocks may contain higher H_2O contents from seawater alteration (Kyser and O'Neil, 1984). Metabasalts from the MGB have a wide range of H_2O contents, 0.90 to 2.70% (Sylvester, et al., 1987). Taking the average (2.13%) as the original H_2O content of the metabasalt, and again 0.91% as the final H_2O content of the mafic gneisses, about 57% of the water was released during the metamorphism and F is about 0.43. If metamorphism in the KSZ took place at $T \geq 700°C$, the δD values of the rocks could be 15 to 20 ‰ lower than their parent rocks (Figure 6.3).

One result of dehydration is to release D-enriched water, which may rise upward or be trapped in the original rock system, depending on the permeability. This water could be the source of a subsequent hydration reaction, either for upper level rocks during the metamorphism if the overlying rocks are permeable, or for the original source rock itself during retrograde metamorphism if surrounding rocks are impermeable. In either case, the secondary hydroxyl minerals formed by hydration reaction would be enriched in deuterium content.

In the KSZ, no significant retrograde metamorphism has been observed. In the WGT, hydration reactions do occur, however, the δD values of the rocks tend to decrease (e.g. samples 840713-3 and 840713-5). Therefore, it is unlikely that dehydration water from depth (KSZ ?) accounts for the lower δD values of these Archean gneisses.

There is another possibility to explain the absence of D-enriched water: the original metabasalts contained less water, for instance, about 1%, at the low end of the H_2O range of metabasalts of greenstone belt. If this is so, the dehydration reaction will be not significant and the δD values of the mafic gneisses could be close to the original δD values of unmetamorphosed marine basalts. However, at the current stage, the possibility that the D-depletion of the Group 2 mafic gneisses, at least partially, resulted from dehydration during the high-grade metamorphism, can not be ruled out.

6.3.3. WATER-ROCK INTERACTION

The basic principles about the isotopic effects of water-rock interaction have been discussed in Chap. 4. In this section, a quantitative calculation is presented.

Based on mass-balance, Taylor (1977) has derived relations between δ values of rock and water, rock and water isotopic fractionation and water/rock ratios (W/R) for the oxygen isotopic system. The same principles can also be applied to the hydrogen system. There are two end-member models. A *closed* system, in which water is continuously circulated and equilibrated with the rocks, is described by:

$$W/R = \frac{\delta_{f(rock)} - \delta_{i(rock)}}{\delta_{i(water)} - \delta_{f(rock)} + \Delta} \qquad (6\text{-}5)$$

An *open* system, in which water will only make one pass through the rock and escape from the system without re-equilibrating with the rocks, is described by:

$$W/R = \ln \left[\frac{\delta_{i(water)} - \delta_{i(rock)} + \Delta}{\delta_{i(water)} - \delta_{f(rock)} + \Delta}\right] \qquad (6\text{-}6)$$

Where δ_f and δ_i are the final and initial isotopic values (oxygen or hydrogen) of rock and water; W and R are the atom percentage of the element in water and rock relative to the entire water-rock system, W+R=100; isotopic fractionation factor $\Delta \approx 10^3 \ln\alpha$, when $|\Delta_{oxygen}| < 10$ ‰ and $|\Delta_{hydrogen}| < 80$ ‰.

Five variables, $\delta_{f(rock)}$, Δ, $\delta_{i(rock)}$, $\delta_{i(water)}$ and W/R, in the above equations have to be evaluated. $\delta_{f\,(rock)}$ value can be experimentally measured if the rock has not been isotopically disturbed by later geological events. Δ could be estimated from knowledge of isotopic equilibrium relations between the minerals and water. In many cases, however, lacking fractionation data for all minerals present in the rock will make the estimation difficult. In practice a convenient approximation is often employed for the oxygen isotopic system, using a single mineral to represent the average whole rock. For instance, $\delta^{18}O_{(rock)}$ of a basalt at equilibrium is equal to the $\delta^{18}O$ value of plagioclase (e.g. An_{30}), therefore, fractionation factor $\Delta_{feldspar\text{-}water}$ can be used to represent the whole rock (Taylor, 1977). The situation for hydrogen isotopes is simpler since there are few hydroxyl minerals present. $\delta_{i\,(rock)}$ value can be assumed from "normal" values of similar rocks, for instance, fresh basalt might originally have δD value -60 ‰. These approaches may introduce uncertainty in the modelling, which is often difficult to estimate.

Two variables then remain unknown: W/R and $\delta_{i\,(water)}$. In general, they have to be treated together, for instance, their relationship can be illustrated graphically, or two equations relevant to a set of rocks can be solved. In either case the solutions may only give relatively broad limits to the combined values of W/R and $\delta_{i\,(water)}$. In certain circumstances, however, one of the two variables can be estimated. For example, if plenty of water is available, e.g. where volcanic rock is extruded into the ocean, W/R approaches infinity, and then the $\delta_{i\,(water)}$ value can be calculated directly from equations (6-5) or (6-6).

Two types of fluid involved in water-rock interactions will be tested for their initially isotopic compositions: 1) fluid incorporated in the Group 2 mafic gneisses of the KSZ, probably during seawater alteration, resulting in higher $\delta^{18}O$ values and lower δD values; and 2) fluid involved in the secondary alteration of the gneissic rocks in the WGT, resulting in normal $\delta^{18}O$ values and lower δD values.

Group 2 mafic gneisses in the KSZ were probably once extrusive basalts and the water-rock interaction likely took place in a submarine environment. It is apparent that a large amount of water is available and the hydrothermal system could be recharged continuously with fresh seawater during the interaction. This situation is close to an open system described by equation 6-6. For this reason, an open system model is used.

The temperature of alteration is difficult to estimate from the gneisses themselves, since the original temperature record has been completely erased by later high-grade metamorphism. A temperature range of 200°C to 300°C is assumed based on the mineral assemblage of metabasalts in the Abitibi greenstone belt, which is a well preserved Archean greenstone belt (Beaty, 1980). Calculated fractionation factors at this temperature range are listed in Table 6.2. The initial hydrogen isotopic composition, $\delta_{i\,(rock)}$, is assumed as -60 ‰ because it is typical of igneous rocks and is close to the average of unaltered metamorphic rocks in the region. Assuming these mafic gneisses have not been disturbed after seawater alteration, the measured δD values -102 ‰ and -89 ‰ (Table 6.1) are used as final hydrogen composition, $\delta_{f\,(rock)}$, in the model calculations. Calculated δ values of the initial fluid as function of the W/R ratios at different temperatures are plotted in Figure 6.4.

Figure 6.4 indicates that at very low W/R ratio, D-depleted initial water is required to lower the δD values of the rocks from -60 ‰ to -102 or -89 ‰. At higher W/R ratio, for instance W/R ratio is greater than 3, the hydrogen in the water dominates the system; isotopic exchange tends to be controlled by the isotopic composition of the initial water and is essentially independent of the W/R ratio. If

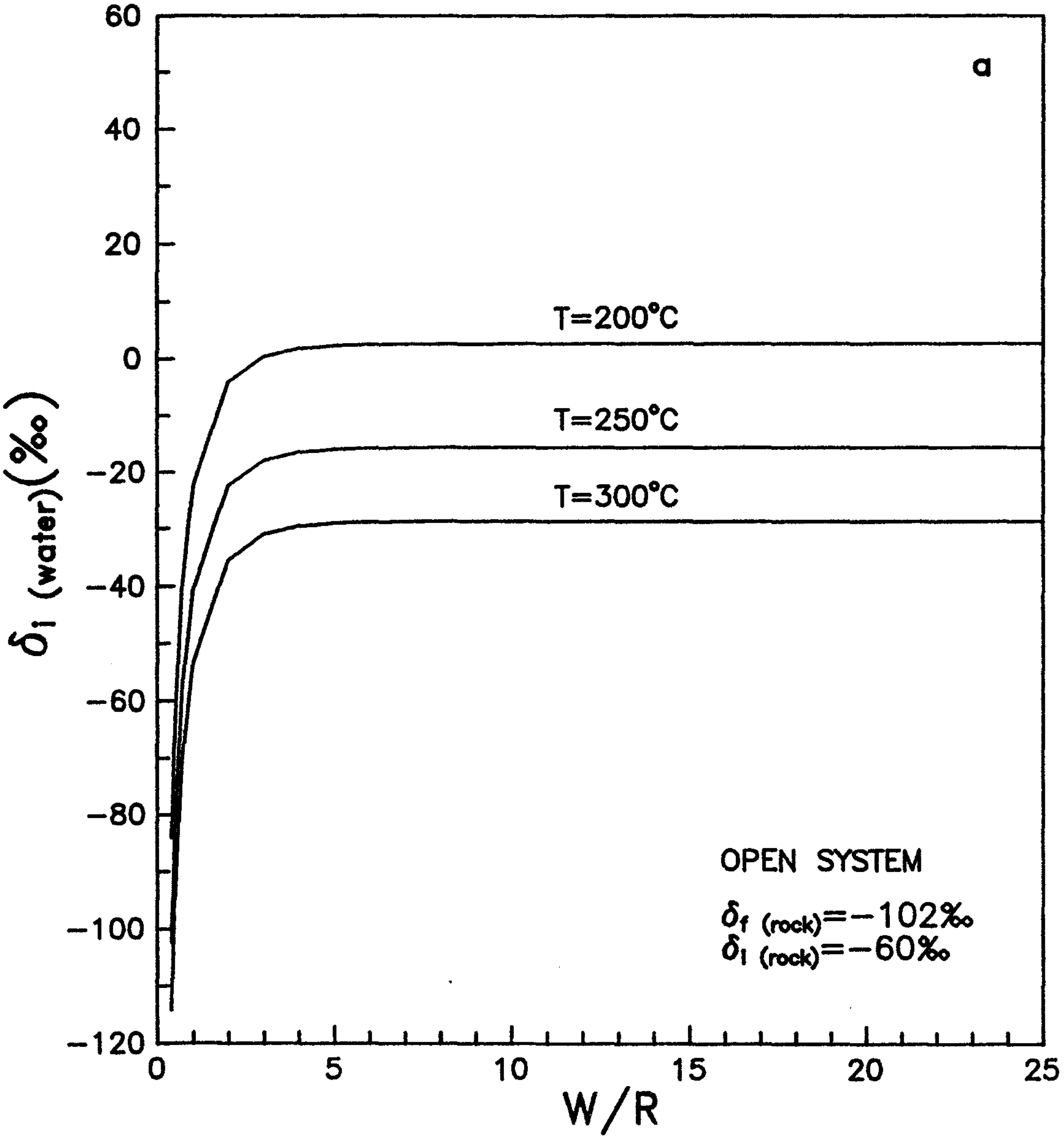

Figure 6.4a Calculated hydrogen isotopic composition of initial water versus W/R ratios for an open system at temperature 200°C to 300°C. Data are from sample PBA2;

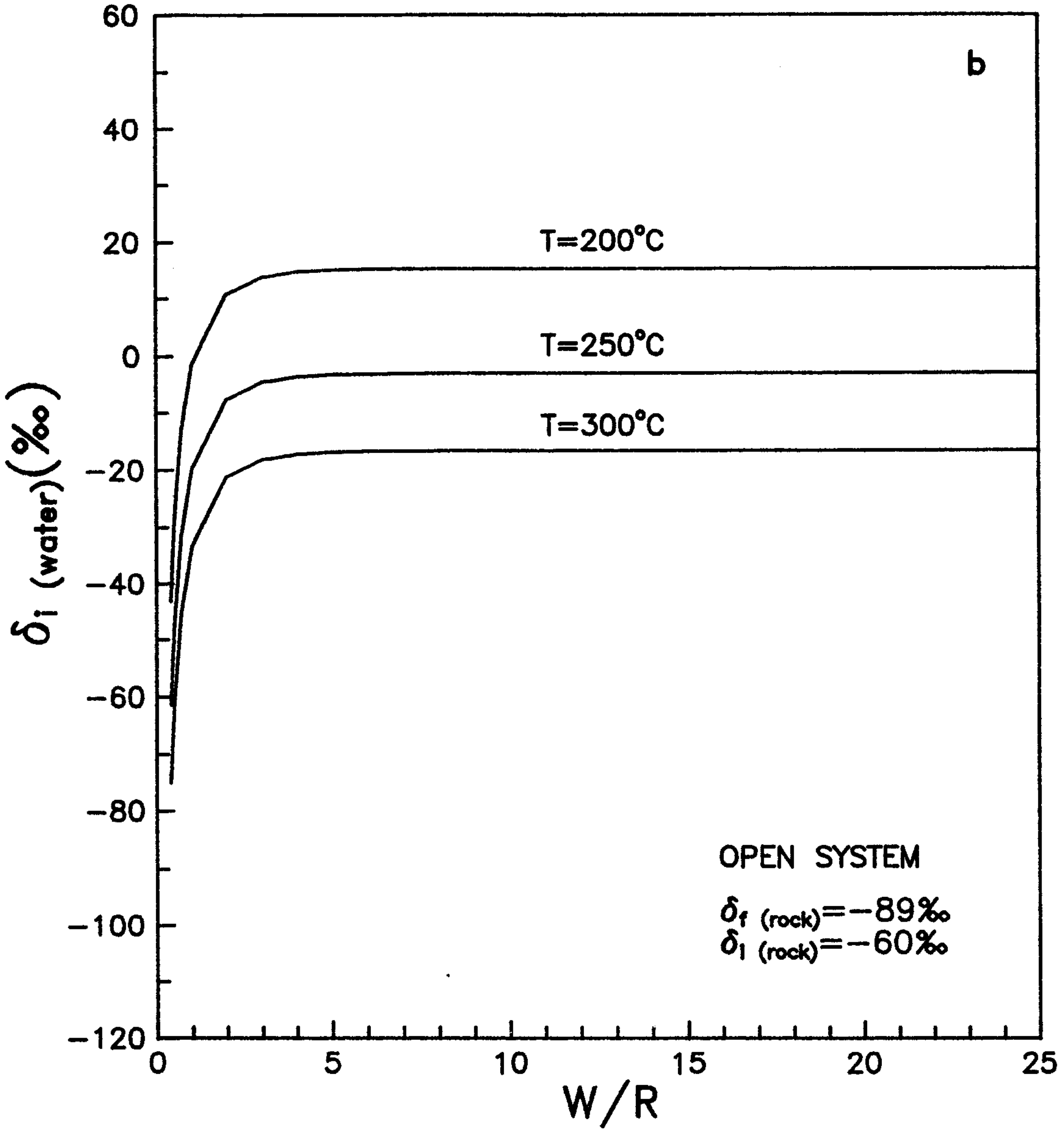

Figure 6.4b: Calculated hydrogen isotopic composition of initial water versus W/R ratios for an open system at temperature 200° C to 300° C. Data are from sample 890824-1.

W/R approaches to infinity, δ value of water will keep constant; $\delta_{f\,(water)}$ is equal to $\delta_{i\,(water)}$. Based on Equu. (3-4) and (3-6):

$$\delta_{i(water)} \cong \delta_{f(rock)} - \Delta \qquad (6\text{-}7)$$

There is only one unknown in this equation, and $\delta_{i\,(water)}$ can be calculated directly. The results computed from equations 6-5 and 6-6 are consistent within the experimental limits. Therefore, when W/R ration is larger than 3, the equation 6-7 is a good approximation to the equation 6-5.

The isotopic exchange is temperature dependent. Low temperature enhances the isotopic fractionation between rock and water, consequently less D-depleted initial water is demanded to lower the δD value of the rocks. A range of δD from 2.6 ‰ to -29 ‰ for the initial water is obtained for sample PBA2, corresponding to alteration temperatures from 200° C to 300° C (Figure 6.4a). For sample 890824-1, a more positive range is obtained, from 17 ‰ to -15 ‰ at same temperature range (Figure 6.4b). It is unfortunate that no certain value can be justified as the δD value of initial water from the currently available information. However, a very important feature indicated by these calculations is that the hydrogen isotopic compositions of the initial water (though in a wide range) are all enriched in deuterium. This fact supports the conclusion based on the oxygen isotope and other geological studies that the origin of the water is likely seawater, which either had a δD value close to today's ocean (e.g. 2.6 ‰), interacted with basalts at a lower temperature (200°C), or which had a lower δD value (e.g. -29 ‰), and interacted with basalt at higher temperature (300°C). A δD value much higher than 10 ‰ (as indicated by rock 890824-1) is not realistic, since no evidence, so far, suggests that the ancient ocean was very enriched in deuterium.

If D-depletion of sample PBA2 is partially caused by the dehydration reaction, for instance resulting in a 15 ‰ lower δD value, the δD value of unmetamorphosed marine basalt could have been about -88 ‰. If this value is then used as $\delta_{f\,(rock)}$, the calculated seawater alteration will show similar pattern illustrated in Figure 6.4b. This suggest a two stage evolution for the hydrogen isotopic composition of the mafic gneiss: fresh basalt first has been altered by seawater, leading a D-depletion from -60 to -88 ‰, and following by a dehydration during high-grade metamorphism, leading further D-depletion to -102 ‰, which is the value we observed today. It is difficult to distinguish the effects on the δD values of the rocks by seawater alteration and dehydration. The D-depletion of the mafic gneisses might be accounted by both processes.

Previous discussion has ruled out that the dehydration water from the depth is the water source for hydration in the WGT. What about the surface water? It is noticed that metamorphic alteration decreases from the WGT to the KSZ, corresponding to increasing depths of the crust, except near the ILCZ. Therefore, it is possible that surface meteoric water penetrated down and provided the source for the hydration.

Similar treatment for water-rock interaction is applied to sample 840713-3. The chosen temperature range of 600°C to 700°C is based on the mineral thermometer (see Chap.2). the $\delta_{i\,(rock)}$ value is again assumed to be -60 ‰, with a measured δD value of -109 ‰ as $\delta_{f\,(rock)}$. The calculated results for both end-member models are plotted in Figure 6.5. True curves for the actual system would lie between these two extremes, probably nearer to the closed system, since at the deeper crustal levels, a one pass process is very unrealistic. Figure 6.5 indicates that at low W/R ratio, very D-depleted water is required to lower the δD value of the rock. When the W/R ratio is higher ($\geq$3), the value of $\delta_{i\,(water)}$ tends to be constant. The closed system demands less D-depleted water than open system does.

A reasonable constraint on the $\delta_{i\,(water)}$ and W/R ratio is that they must satisfy two observations: depleted deuterium but nearly unchanged δ^{18}O in the rock. This requires very small amount of water, which is only sufficient to modify the hydrogen isotopic composition, but not enough to affect the oxygen isotope system of the rock.

Assuming that the whole rock δ^{18}O value change is less than 0.5 ‰ during the interaction with a meteoric water having $\delta_{i\,(water)}$ at -12.5 ‰, and utilizing a fractionation factor of plagioclase[f] (An_{40}) to represent the whole rock, the maximum W/R atomic ratio, calculated from a closed system model at 600 to 700°C, should

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f: $10^3\ln\delta_{plag.-water}=(3.13-1.04\beta)(10^6/T^2)-3.70$, where β is An content in the plagioclase. The equation is based on Bottinga and Javoy's calibration (1975).

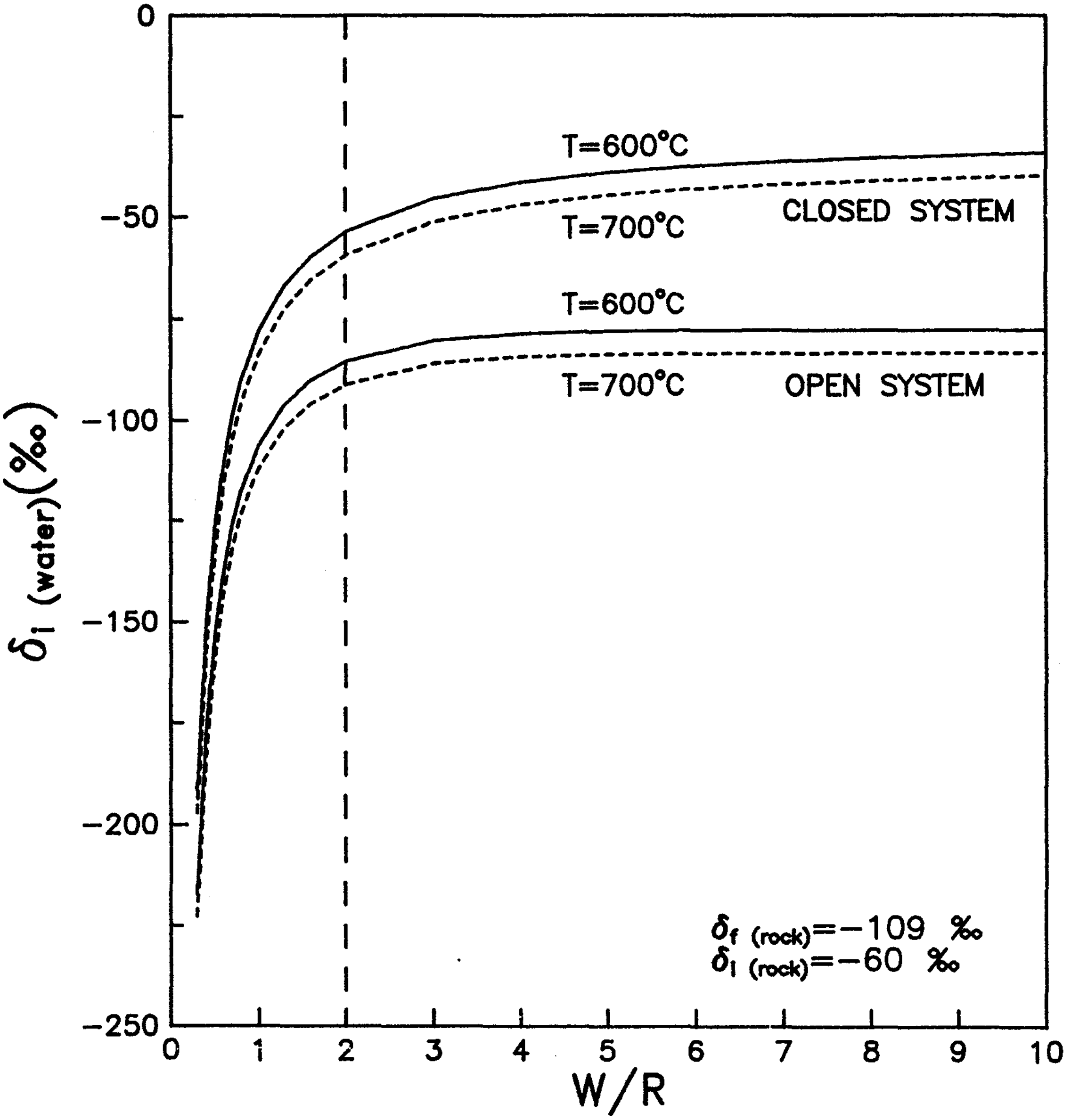

Figure 6.5 Calculated hydrogen isotopic composition of initial water versus W/R ratios for both open and closed systems, at temperature 600° C and 700° C. Data are from sample 840713-3.

be less than 0.03. The mafic rock contains about 45 wt% of oxygen and water contains 89 wt% of oxygen, therefore, the water/rock ratio in weight unit is equal to about 0.5W/R in oxygen atom ratio. The maximum oxygen W/R ratio of 0.03 corresponds to about 0.015 water/rock ratio in weight unit. The same type rock contains about 0.1 wt% of hydrogen and water contains 11 wt% hydrogen, therefore, 0.015 water/rock ratio in weight unit is converted to hydrogen W/R atom ratio about 2. Using this value as the limit of the amount of water involved, a range of δD values of initial water is obtained from -50 to -90 ‰ (Figure 6.5), which, for a meteoric water, corresponds to a $\delta^{18}O$ range -7.5 to -12.5 ‰. These results are higher than today's meteoric water in the region (located at the contour of δD=-90 ‰ and $\delta^{18}O$=-12.5 ‰, Taylor, 1977). Palaeomagnetism and palaeoclimatology studies indicate that in ancient times, the latitude of North America was close to the equator and the climate of the Precambrian was generally warmer than today's. Combining all the information, a range of δD value from -50 ‰ to -90 ‰ for meteoric water is quite reasonable.

CHAPTER SEVEN

CONCLUSIONS

In this study, oxygen and hydrogen isotopic composition for rocks from the Wawa-Kapuskasing transect have been reported.

Most high-grade gneisses have $\delta^{18}O$ values in the range 5.7 to 9.5‰, similar to fresh igneous rocks of equivalent chemical composition, from which they were derived. The $\delta^{18}O$ values are positively correlated with their SiO_2 content. The higher $\delta^{18}O$ values and the large gradient of $\delta^{18}O$ versus SiO_2, relative to a model fractionation trend, suggest that the rocks cannot have been derived directly from the mantle by fractional crystallization. A model involving an association between mantle-derived mafic magma and ^{18}O-enriched crust materials is more likely.

Most mafic gneisses have $\delta^{18}O$ values from 5.6 to 7.1‰, and are often associated with paragneisses, suggesting that they are supracrustal in origin, either as subaerial extrusives or less likely as submarine flows, which interacted with sea-water at high temperatures. A few mafic rocks which show ^{18}O-enrichment, are probably the result of low-temperature alteration of extrusive basalt by seawater, similar to low-grade metavolcanic rocks in adjacent greenstone belts.

Paragneisses in the KSZ have preserved the ^{18}O-enrichment of their sedimentary protoliths. The large contrast of δ^{18}O values between associated paragneiss and mafic gneiss implies that no infiltrating fluid was present and isotope exchange was limited during high-grade regional metamorphism.

Generally, there is no systematic change in whole-rock δ^{18}O values across the variable metamorphic grade and crustal levels of the transect. The oxygen isotopic data imply that bulk oxygen isotopic compositions of the high-grade rocks represent the original composition of their protoliths and were only slightly affected by the high-grade metamorphism.

Coexisting minerals phases show no isotopic reversal. Isotopic fractionations between quartz-feldspar and quartz-biotite are various, indicating internal isotopic disequilibrium, probably due to alteration of less resistant feldspar and biotite phases after metamorphism. Quartz-magnetite mineral pairs have relative constant fractionations and their isotopic temperatures are higher than the quartz-biotite pairs, because of their higher closure temperature. Isotopic thermometers give nearly constant apparent temperatures across the transect, indicating cessation of oxygen diffusion at approximately the same temperature for each mineral pair.

The hydrogen isotope data in this study are very limited and some of the interpretations are only tentative at the current stage.

Three unaltered metaigneous rocks, including two mafic rocks and one anorthositic rock from the KSZ have δD values compatible with "normal" igneous values, which are likely inherited from their pre-metamorphic parent rocks.

Group 2 mafic gneisses from the KSZ have lower δD values. The D-depletion probably resulted both from seawater alteration at low temperature and from dehydration during the high-grade metamorphism. Water-rock interaction calculations suggest that seawater alteration is responsible for the major part of the D-depletion. From an open system model, a range of δD values, from 2.6 to -29‰, for the initial fluid was obtained, consistent with seawater having interacted with the basalt at 200°C to 300°C.

The two groups of rocks with distinctive hydrogen isotopic compositions, "normal" igneous values and low δD values, coexist with each other in the KSZ. These results, once again, suggest that no infiltration of water was involved on a regional scale and high-grade metamorphism took place in approximately closed system conditions, supporting the conclusions from the oxygen isotope data.

Gneissic rocks from the WGT also have lower δD values, which probably resulted from post-metamorphic secondary alteration. The source of the water is likely meteoric water, which penetrated down from the surface of the Earth. The

δD values of the alteration water are calculated to be in the range -50 to -90 ‰, which are a reasonable prediction for meteoric water present at Precambrian time. The water involved in the alteration is very small, less than 1.5 wt% of W/R ratio, which has only affected the hydrogen isotopic ratio, but leaved the original oxygen isotopic ratio unchanged.

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