



**ECONOMIC GEOLOGY
RESEARCH UNIT**

University of the Witwatersrand
Johannesburg

**THE USES OF STABLE ISOTOPES
IN MINERAL EXPLORATION:
AN OVERVIEW**

P.A. DE GROOT

INFORMATION CIRCULAR No. 310

UNIVERSITY OF THE WITWATERSRAND
JOHANNESBURG

**THE USES OF STABLE ISOTOPES IN MINERAL
EXPLORATION: AN OVERVIEW**

by

P.A. DE GROOT
*(Economic Geology Research Unit, Department of Geology,
University of the Witwatersrand, P/Bag 3,
WITS 2050, South Africa)*

**ECONOMIC GEOLOGY RESEARCH UNIT
INFORMATION CIRCULAR No. 310**

May, 1997

THE USES OF STABLE ISOTOPES IN MINERAL EXPLORATION: AN OVERVIEW

ABSTRACT

The aim of this circular is to provide an overview of the use of stable isotopes in mineral exploration. Fluids are involved in most ore forming processes, and the application of stable isotope techniques in the study of hydrothermal systems is stressed in this circular. Fluid - rock interaction occurs at levels extending from the Earth's surface to more than 10 to 12 km depth into the crust. These circulating fluids leach ore metals from the rock and transport them to other crustal levels where they are concentrated into ore bodies. Stable isotope analysis provides an important tool, either to determine the extent of rock alteration, or to obtain information about the source(s) and conditions of the ore deposition. In this circular, emphasis is placed on O, H, C, S, and Cl isotopes and their applications are discussed.

A basic understanding of stable isotopes as well as some historical aspects of the subject are provided, together with a review of developments involving modern analytical techniques, including laser- and ion probes.

The use of stable isotopes in ore exploration can be subdivided into two major categories:

- 1) a direct exploration method, where rasterlike sampling and the construction of an isotopic contouring map results in locating anomalous isotopic zones, that are generally linked to ore mineralization; and
- 2) by modelling: a regional study, using stable isotope analysis and other methods, (the latter providing information on temperature, water/rock ratios, fluid sources, sulphur sources, oxygen fugacity, pH, grades and types of rock alteration, and the environment in which a mineral was formed), leads to a general model of the ore mineralization. This model may be applied to detect additional ore mineralization in other areas. It may also provide information on extensions to specific types of ore mineralization, as well as the volumes of such mineralization.

A combination of stable isotope and radiogenic isotope analysis may provide further information about sources of host rocks of specific ore mineralization types.

Lastly, some less well established stable isotope applications are discussed, including aspects such as palaeoclimate and the environment. These applications are restricted to (sub-)surface weathering and oxidation zones of the crust where bauxite, laterite and gossans may be developed.

—oOo—

THE USES OF STABLE ISOTOPES IN MINERAL EXPLORATION: AN OVERVIEW

CONTENTS

	Page
INTRODUCTION	1
HYDROTHERMAL PROCESSES	1
STABLE ISOTOPE SYSTEMATICS AND ANALYTICAL METHODOLOGY	2
Basic Stable Isotope Systematics	2
Analytical Techniques	3
<i>Analytical apparatus available at EGRU</i>	3
USE OF STABLE ISOTOPES IN ORE EXPLORATION	4
Contouring of Stable Isotope Ratios	5
<i>Three dimensional contouring</i>	6
Modelling of Ore-Forming Processes - Descriptive Methods	9
<i>Stable isotope thermometry</i>	9
<i>Water-rock ratio determination</i>	11
Specific Stable Isotope Applications	12
<i>O and H isotopes in fluid-rock interaction</i>	12
Fluid inclusions	13
<i>Carbon isotopes</i>	14
<i>Sulphur isotopes</i>	18
<i>Sulphur and oxygen isotopes: sulphates</i>	22
<i>Cl isotopes as an exploration tool</i>	23
Combined Stable and Radiogenic Isotopes	23
Palaeoclimatic - Environmental Methods	24
ACKNOWLEDGEMENTS	25
REFERENCES	25

____ oOo ____

Published by the Economic Geology Research Unit
Department of Geology
University of the Witwatersrand
1 Jan Smuts Avenue
Johannesburg 2001
South Africa

ISBN 1 86838 170 6

THE USES OF STABLE ISOTOPES IN MINERAL EXPLORATION: AN OVERVIEW

INTRODUCTION

Additions to the sulphur isotope facilities in the stable isotope laboratory of the Economic Geology Research Unit at the University of the Witwatersrand, Johannesburg and the development of a laser oxygen isotope analytical facility have stimulated the need for an overview of the use of stable isotopes in ore exploration.

The aim of this review is to present a summation of methods using stable isotope techniques in ore exploration. These methods combine different stable isotope applications, comprising direct and indirect approaches. Besides the use of stable isotopes in direct ore exploration, information about ore mineralization related to alteration zones and the physical and chemical conditions of specific types of ore mineralization also can be obtained by these methods. The involvement of fluids in most ore forming processes, and the application of stable isotope techniques in such systems is stressed.

The important role of fluids circulating through the crust in the majority of ore mineralizing processes is now widely accepted. Hydrothermal fluids are the perfect media to leach elements from minerals in the rocks they react with during their circulation through the crust. They transport these leached elements, generally in solution as simple- or as complex-ions. Metals are subsequently precipitated at sites where these ions, dissolved in the fluid, become unstable or occur at concentrations above their solubility limits for the ambient conditions. Magmatic intrusions are the most effective "engines" to drive hydrothermal processes, whereas tectonic and seismic processes may trigger fluid flow and create conduits for fluid flow in the crust. Ground water circulation generally operates at low temperature ranges and at shallow levels in the crust. Evidence for deep fluid circulation in the Earth's crust, to levels of at least 5 - 10 km, is provided by numerous examples such as: the Skaergaard hydrothermal system (Taylor and Forester, 1979), the Samail ophiolite, Oman (Gregory and Taylor, 1981), the oceanic crust (Stern et al., 1976; Lawrence and Gieskes, 1981; Cocker et al., 1982), and the Idaho batholith (Criss and Taylor, 1983). Direct evidence for deep fluid circulation has been obtained from the >12km deep borehole on the Kola peninsula (Kerr, 1984; Pavlenkova, 1992) and the ~9km deep KTP-borehole, Bavaria, (Kerr, 1993; Simon and Hoefs, 1993).

HYDROTHERMAL PROCESSES

Systems of hydrothermal fluid circulation may be divided into:

- 1) zones of rock leaching (chemical interaction between rocks and circulating fluids);
- 2) zones of material transport (where fluids are in equilibrium with the rocks through which they are passing); and
- 3) zones of mineral deposition (either by reaction between rocks and fluid, by mixing of different fluids, or by rapid fluid decompression).

Although the latter zone is the most relevant in any economic context, the other zones are also important in understanding the transport of the ore-forming components and the origins of ore mineralization.

Hydrothermal alteration zones are generally connected to ore mineralized sites and are therefore important targets for ore mineral exploration.

The statement by Criss and Taylor (1986) that: "*Application of the techniques of stable isotope geochemistry over the past 30 years has shown that virtually all rocks of the Earth's crust have undergone some type of interaction with an aqueous fluid*", shows that stable isotope analysis is one of the most important tools in the understanding of hydrothermal alteration and related ore-mineralizing processes. The fluids involved in ore-forming processes consists mostly of water or carbon dioxide, but may also contain smaller volumes of methane, organic compounds and sulphide/sulphate ions. These solutions contain oxygen, hydrogen, carbon and/or sulphur, for which the stable isotope compositions can be measured.

STABLE ISOTOPE SYSTEMATICS AND ANALYTICAL METHODOLOGY

Basic Stable Isotope Systematics

The stable isotopes which are most pertinent to mineral exploration are: oxygen ($^{16}\text{O} = 99.763\%$; $^{17}\text{O} = 0.0375\%$; $^{18}\text{O} = 0.1995\%$), hydrogen ($^1\text{H} = 99.9844\%$; ^2H or D = 0.0156%), carbon ($^{12}\text{C} = 98.89\%$; $^{13}\text{C} = 1.11\%$), sulphur ($^{32}\text{S} = 95.02\%$; $^{33}\text{S} = 0.75\%$; $^{34}\text{S} = 4.21\%$; $^{36}\text{S} = 0.02\%$), and chlorine ($^{35}\text{Cl} = 75.53\%$; $^{37}\text{Cl} = 24.47\%$). The isotopic ratios of interest are measured from gases extracted from minerals, whole rock samples, fluids, and organic matter, in a gas-source mass spectrometer. Stable isotopes are measured either directly or in a carrier gas; oxygen is measured from CO_2 or O_2 , hydrogen from H_2 , carbon from CO_2 , sulphur from SO_2 or SF_6 , and chlorine from CH_3Cl . Stable isotopes are measured in a relative, rather than in an absolute way and values or ratios are reported relative to a fixed standard.

Notation of stable isotope values is made with reference to the standard delta notation in per mil (‰):

$$\delta (\text{\textperthousand}) = \{(R_{\text{sample}}/R_{\text{standard}}) - 1\} \cdot 10^3$$

Isotopic fractionation is the partitioning of stable isotopes between two different phases with different isotope ratios. These fractionations are primarily caused by isotope exchange reactions or by kinetic processes, which depend principally on differences in reaction rates of isotopic molecules.

Isotopic fractionation is given as:

$$\alpha_{A-B} = (R_A/R_{\text{standard}})/(R_B/R_{\text{standard}}) = (R_A/R_B)$$

where R = $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$, $^{34}\text{S}/^{32}\text{S}$, H/D, or $^{37}\text{Cl}/^{35}\text{Cl}$ and A and B are samples which are in isotopic equilibrium with each other.

The standards used in stable isotope analysis are: oxygen: V-SMOW (Vienna standard mean ocean water) or PDB (PeeDee belemnite), hydrogen: V-SMOW, carbon: PDB, and

sulphur: CDT (Canon Diablo Troilite), and chlorine: SMOC (standard mean ocean chlorine).

Bowen (1988), Hoefs (1973, 1987, 1997), Kyser (1987a), Taylor et al. (1991), and Valley et al. (1986), provide general information about the systematics of stable isotopes, the analytical techniques available and their applications.

Analytical Techniques

Stable isotope analytical techniques were developed in the early 1950's following the construction of a reliable mass spectrometer by Nier (1947) and Nier et al. (1947). This was later modified and improved by McKinney et al. (1950) at the University of Chicago.

Different analytical techniques, using oxidation, reduction, acid reaction or combustion, for transforming natural samples (including silicates, carbonates, sulphides, sulphates, phosphates, oxides, chlorides, graphites, organic compounds, waters, atmospheric and crustal gases), into measurable gases (such as: CO₂, O₂, H₂, SO₂, SF₆, CH₃Cl), are now standard procedures (Bigeleisen et al., 1952 (H); Friedman, 1953(H); Clayton and Mayeda, 1963(O); Holt and Engelkemeir, 1970(S); Puchelt et al., 1971(S); Robinson and Kusakabe, 1975(S); Coleman and Moore, 1978(S); Sasaki et al., 1979(S); Coleman et al., 1982(H); Yanagisawa and Sakai, 1983(S); Horita, 1988(H); Horita and Gat, 1988(H); Vennemann and Smith, 1990(O); Hoefs, 1997(General)).

Modern developments have introduced the use of laser probes in fluorination devices or for combustion of carbonates or phosphates (Franchi et al., 1986, 1989; Shanks and Criss, 1989; Sharp, 1990, 1992; Powell and Kyser, 1991; Elsenheimer and Valley, 1992; Smalley et al., 1989, 1992; Weichert and Hoefs, 1995; Sharp and Cerling, 1996; Hoefs, 1997), or sulphides (Crowe et al., 1990; Kelley and Fallick, 1990; Crowe and Valley, 1992; Crowe and Vaughan, 1996). High resolution ion probes (SIMS = secondary ion mass spectrometry)(Shanks and Criss, 1989; Eldridge et al., 1989; Giletti and Shimozu, 1989; Lorin, 1992; Hoefs, 1997), either of bulk samples, of thin sections, of single grains, or through single grains on microscopic scale, are now also available for stable isotope analysis. Development of helium-continuous flow inlet systems for mass spectrometry has reduced the sample volumes necessary for CO₂, O₂, and SO₂ (from around 10 µmol to the nanomol level), and the development of a new generation of dynamic measuring mass spectrometers has permitted the introduction of the GC-IRMS (gas chromatography-integrated ratio mass spectrometry) device, with which isotopic ratios of separate components in gas mixtures can be measured simultaneously.

Analytical apparatus available at EGRU

The stable isotope laboratory at EGRU in the Department of Geology, University of the Witwatersrand, has a classic sulphur isotope analytical device available. Sulphides are mixed with CuO and are placed in a high vacuum system. The mixture is oxidized into SO₂ by on-line combustion and the gases are purified cryogenically (e.g. Robinson and Kusakabe, 1975).

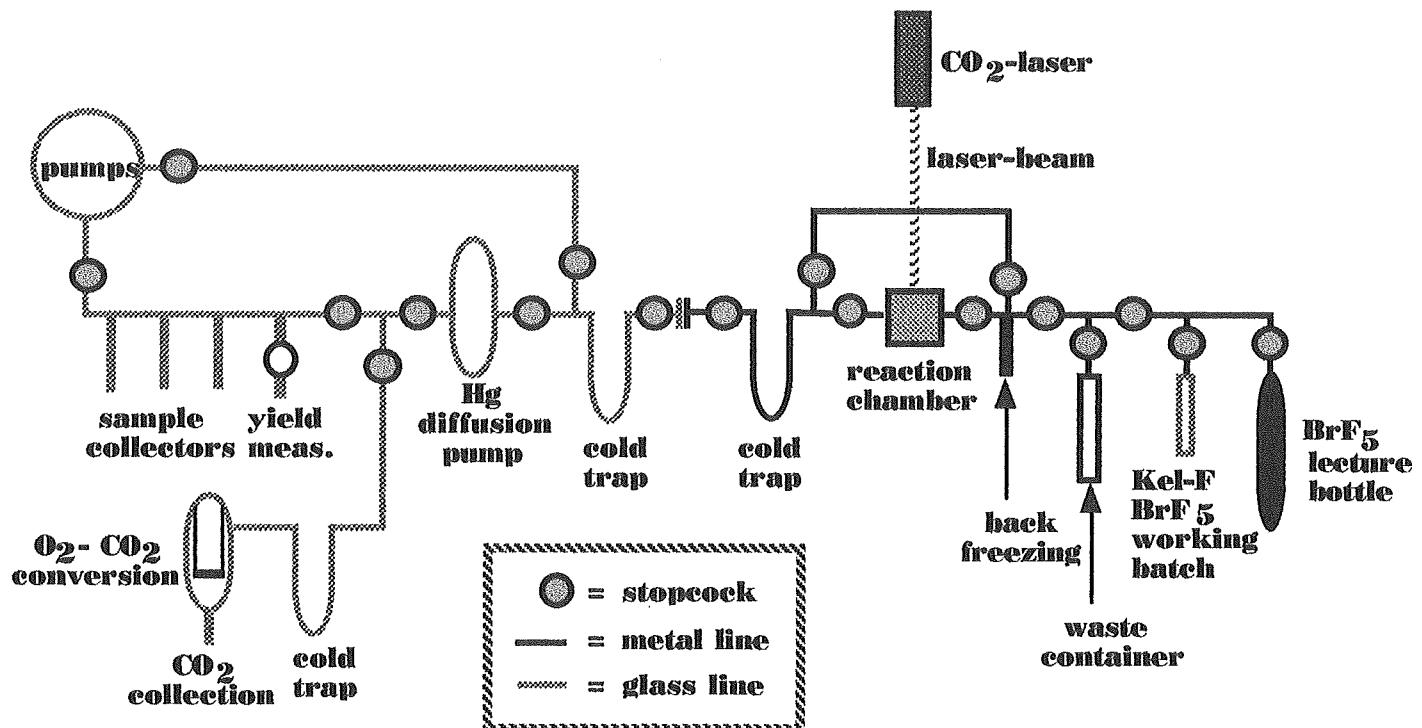


Figure 1: Schematic sketch showing the oxygen isotope - BrF₅ laser analytical facility at the Economic Geology Research Unit, University of the Witwatersrand, Johannesburg.

A laser-oxygen isotope apparatus for analysis of silicates and oxides is currently under construction (Fig. 1). In this device, a laser beam heats a sample in a strong oxidizing atmosphere of BrF₅, liberating all oxygen from the silicate. The oxygen gas either is converted into CO₂ by reacting with a hot carbon rod and measured on a mass spectrometer, or is measured directly as O₂ gas on a mass spectrometer (preferable for small samples).

Analytical facilities for the measurement of C and O isotopes in carbonates, hydrogen in powdered rocks, hydrous minerals, and fluids (i.e. fluid inclusions), and sulphur isotopes in sulphates are to be developed.

USE OF STABLE ISOTOPES IN ORE EXPLORATION

Different approaches in the use of stable isotopes in ore exploration are provided in the section that follows. A direct method is isotopic contouring in a selected area to pinpoint an ore occurrence. This method can be used in areas where rock alteration suggests the existence of (a blind) ore body, or where a still-undefined ore occurrence was discovered. Another general method is the construction of a genetic model of a specific type of ore occurrence to estimate the extent of the associated mineralization, and the use of the model to predict other, undiscovered mineralization.

Chlorine isotopes may be useful in detecting oxidized base metal deposits in arid to semi-arid regions and a combination of stable- and radiogenic isotopes may be used for the genetic interpretation of rocks, hosting mineralization or supplying ore forming metals.

Lastly there are some less well established methods involving palaeoclimatic and environmental studies, comprising detection of palaeoweathering zones, e.g. to locate gossans or laterite-bauxite horizons, or to define palaeo-climate conditions, particularly in relation to surface processes which may be useful, for example, in determining placer deposits in river beds.

Contouring of Stable Isotope Ratios

This method is based on sampling a selected area in a systematic, grid-like way. The samples collected are analysed for their isotopic (and chemical) composition and plotted on a map. The method was developed by Taylor (1971, 1973, 1974, 1979) and Sheppard and Taylor (1974). Contours can be constructed on a map by drawing lines between similar isotopic values (Figs. 2 and 3). Haloes of anomalously negative oxygen isotope values show, for example, a circular pattern around the General Custer Mine in the Yankee Fork district, Idaho (Fig. 2). Anomalously positive oxygen isotope anomalies ($> 14 \text{ ‰}$) define the ore deposits of the Kidd Creek Mine, Ontario. The formation of a negative or positive

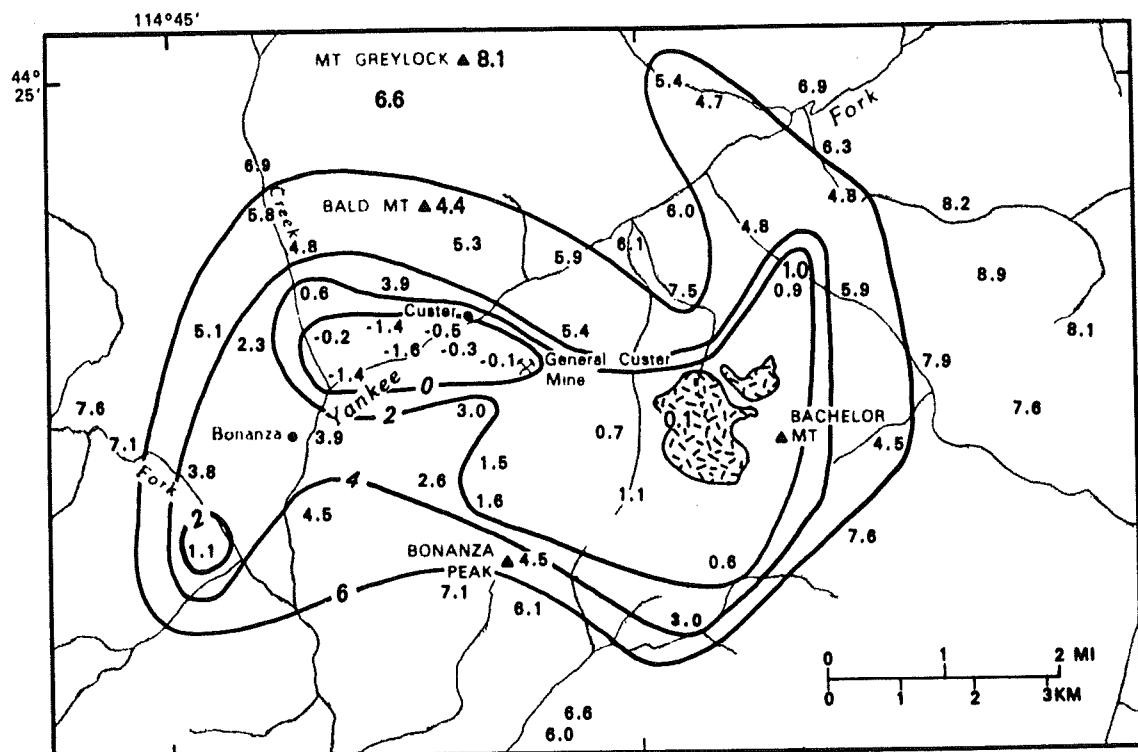


Figure 2: A whole-rock oxygen isotope contour map of the Yankee Fork district, Idaho. A small intrusion is shown by a dashed pattern. See text for explanation (from Criss and Taylor, 1986).

oxygen isotope anomaly depends on the oxygen isotopic compositions of both the fluids in the hydrothermal system and the original oxygen isotopic composition of the rocks in the hydrothermal alteration zone. If the oxygen isotopic composition of the fluid is lower or higher than the oxygen isotopic composition of the rock, a negative or positive anomaly will

form, respectively, by exchange between the fluid and the rock in the hydrothermal alteration zone. A weakly negative anomaly around the massive sulphide deposit in the Amulet Mine in the Noranda district in the Abitibi greenstone belt in Canada is shown in Figure 3. Anomalous negative oxygen isotope haloes, as seen around the General Custer and Kidd Creek Mines, are similar to low ^{18}O zones around the Kuroko (Japan) and Cyprus massive sulphide orebodies. In Figure 2 the small negative anomaly shown in the lower left corner might well represent an exploration target. The isotopic haloes generally show wider extent than the recognisable mineralogical alteration and for that reason may be a strong tool assisting in the detection of ore. Nesbitt (1996) reviewed the use of this method for different types of mineralization. Alternation of different rock types with different isotopic signatures may, however, complicate this method. For example, in Figure 2, the larger sized numbers represent rock types other than lavas of intermediate composition (area with smaller numbers). Areas with poor exposure may result in contouring uncertainty, and may even invalidate the method.

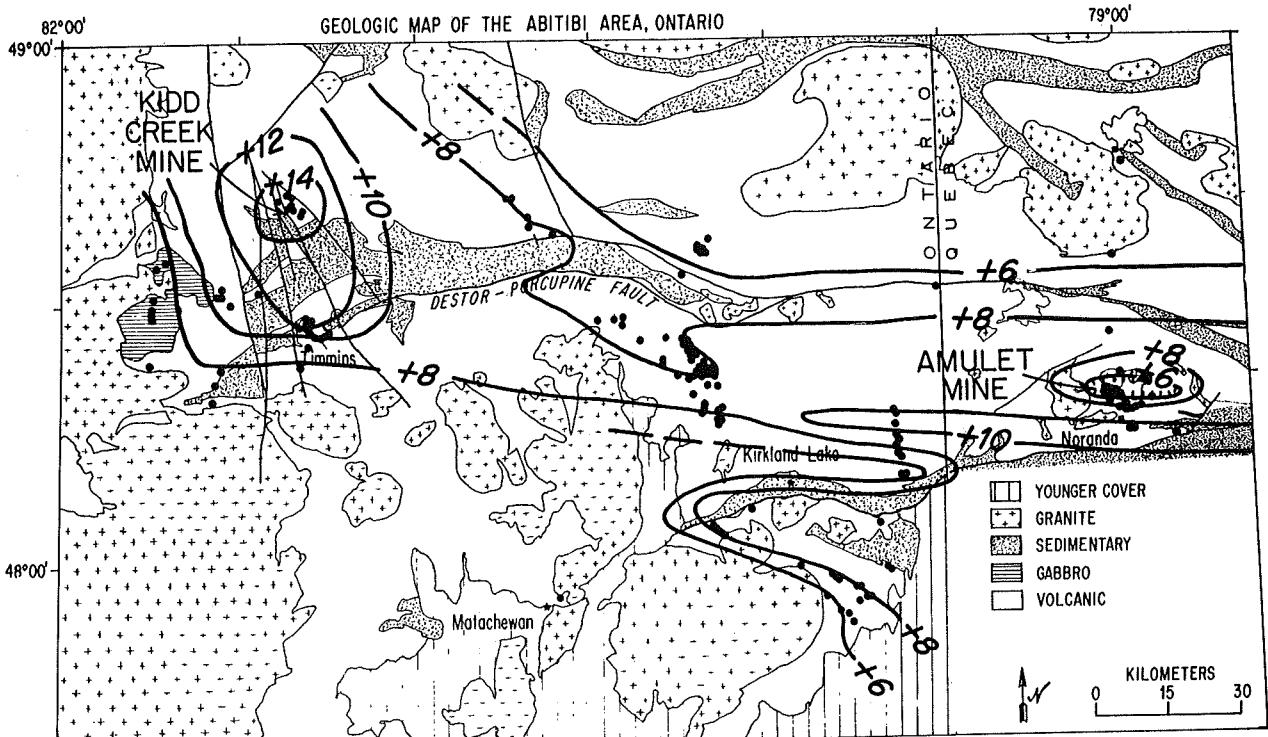


Figure 3: Geological map of the Abitibi greenstone belt, Canada, showing the distribution of whole-rock oxygen isotope values in the volcanic rocks and contour lines for similar ^{18}O values. See text for explanation (from Beaty et al., 1988).

Three dimensional contouring

This contouring method can be used on different levels of an existing mine (or from borehole intersections) to provide a three dimensional image of the alteration and related mineralization. An example of a mine-level sample map, compiled at the tin-tungsten Panasqueira Mine, Portugal (Fig. 4), shows isotopic data of samples from different levels in the mine.

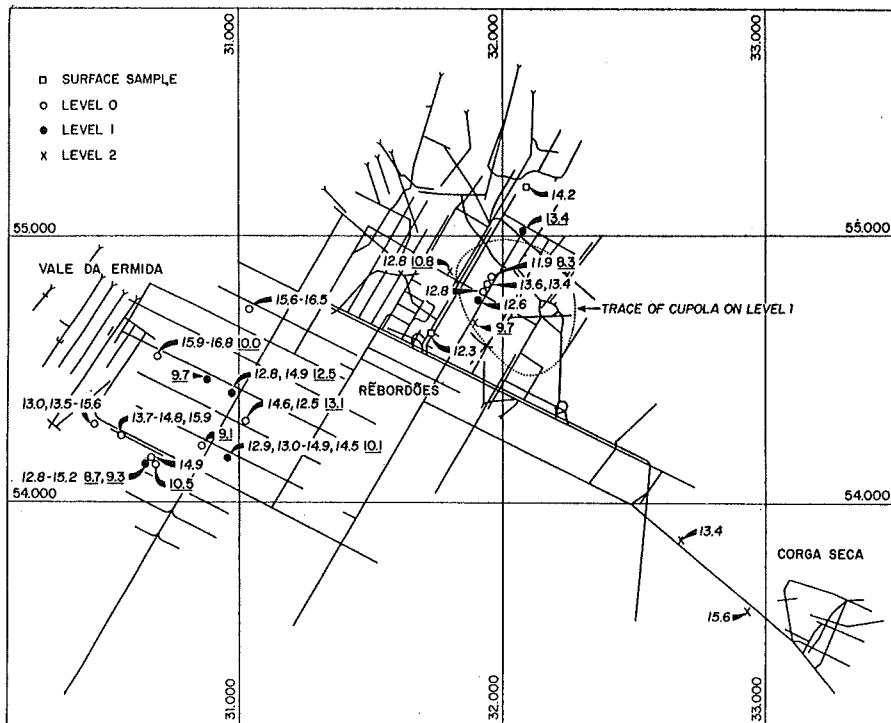


Figure 4: A composite map of the tin-tungsten Panasqueira Mine, Portugal. Isotopic data for muscovite (underlined) and quartz are shown for different mine levels. See text for explanation (from Kelly and Rye, 1979).

Although no contouring was applied to this example, it is possible, if sufficient sample points are available, to construct three dimensional spheres by connecting similar isotopic values (three dimensional contouring). A combination of several surface sections isotopically contoured, may provide a two dimensional impression of a specific area. Such a section may also provide information about alteration and the contact zones between different rock types. Figure 5 shows a section through the Birch Creek contact zone, near the California-Nevada border, which includes a skarn mineralization. The contact between the granite intrusion and the sediments and the skarn zone are clearly shown by the striking isotopic change. A smaller isotopic anomaly accompanies a schist xenolith in the granite (Fig. 5). Drill core samples may also contribute to a three dimensional impression. In Figure 6 drill hole J-628 (data from Coad, 1985) shows the stratigraphy (rhyolites and brecciated tuffs), relation to $\text{SiO}_2(\%)$, $\text{Cu}(\text{ppm})$, and $\delta^{18}\text{O}(\text{\textperthousand})$ values. Schematic enrichment in SiO_2 and Cu accompanied by a decrease in $\delta^{18}\text{O}$ with depth, is shown in Figure 6. Correlating drill core sections, surface contouring, and the use of different mine level, or surface sections, permits the construction of a three dimensional, sphere-like isotope contouring pattern for a hydrothermally altered or ore mineralized area.

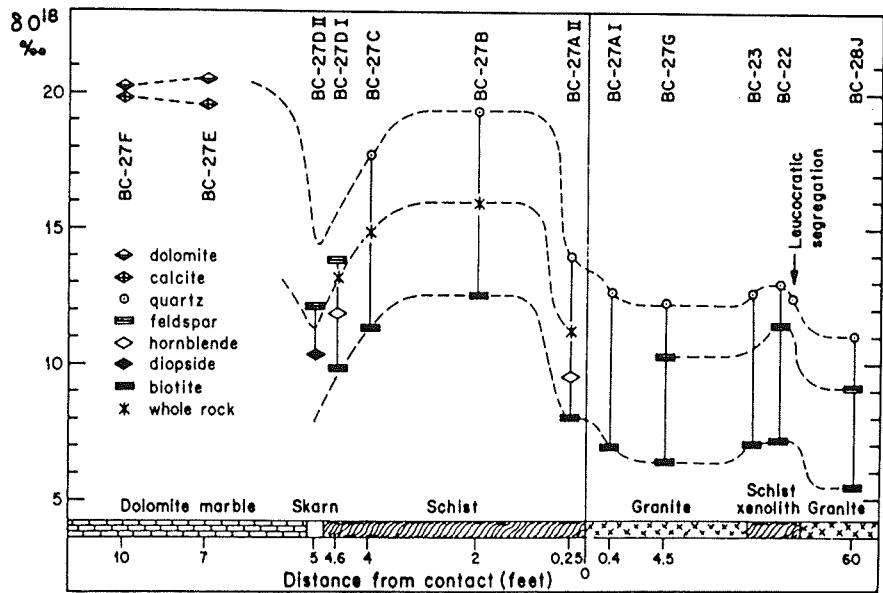


Figure 5: Geological section through the Birch Creek contact zone, on the California-Nevada border, with skarn mineralization. Isotopic values of minerals and whole-rock are plotted along the section. Low $\delta^{18}\text{O}$ values in the skarn are explained by volatilization processes (data from Shieh and Taylor, 1969). See text for explanation (from Valley, 1986).

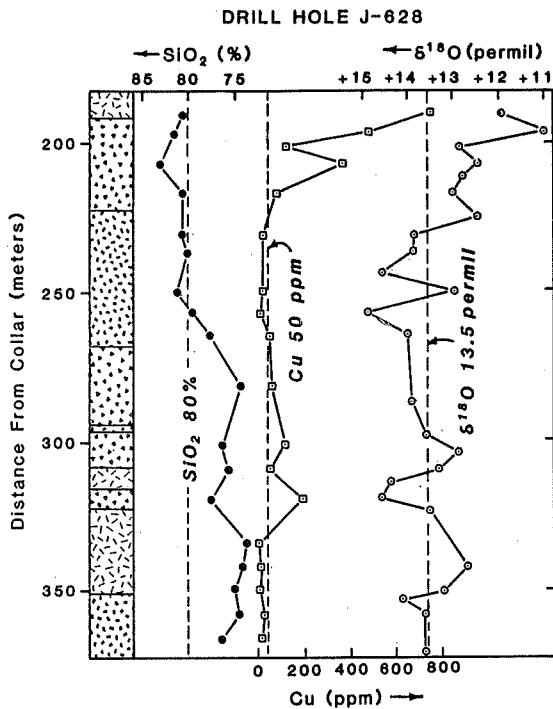


Figure 6: Plot of the geology, SiO_2 content, Cu content, and whole-rock oxygen isotope values as a function of position in the J-628 drill core. See text for explanation (from Beatty et al., 1988).

Modelling of Ore-Forming Processes - Descriptive Methods

Understanding the nature and genesis of a specific mineralization type from one locality may be useful in detecting similar types of ore mineralization at other locations. Additionally, a good understanding of an ore mineralizing process is an important factor in estimating the volume and grade of the ore mineralization. The uses of stable isotope(s), applicable to the modelling of ore forming processes, are discussed in the following sections.

Stable isotope thermometry

The fractionation of stable isotope ratios is generally dependent on temperature and therefore may be used to estimate temperatures of mineralizing processes. The method is based on the assumption that equilibrium exists between two minerals or a mineral and a fluid, and consequently, the attainment of equilibrium forms an important pre-requisite for the use of this geothermometer. The temperature estimate is also strongly dependent on the quality of the determination of the fractionation factor between the phases of interest. Fractionation factors are either obtained empirically, theoretically, or experimentally, and often show major inconsistencies and uncertainties. Figure 7 shows a diagram of Δ_{Qz-Mu} ($= \delta^{18}\text{O}_{\text{quartz}} - \delta^{18}\text{O}_{\text{muscovite}}$) versus $10^6 T^2$ (T in Kelvin). In the diagram curves represent fractionation of ^{18}O for the quartz-muscovite system against temperature, where different curves reflect the results of various methods. A wide scatter in isotopic fractionation is evident for the same quartz-muscovite system which stresses the inconsistency in temperature dependant fractionations for some mineral-water or mineral-mineral systems.

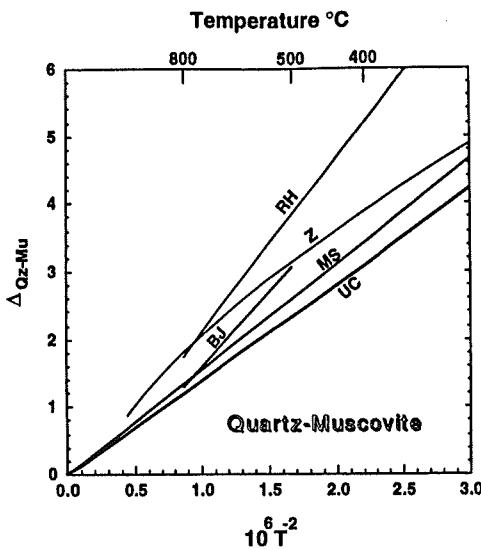


Figure 7: Temperature versus Δ_{Qz-Mu} plot. Comparison of various estimates of the quartz-muscovite oxygen equilibrium fractionation: RH, Z by the increment method, BJ by laboratory experiment and theoretical argument, MS by laboratory mineral-water exchange experiment, UC by laboratory mineral-calcite exchange experiment, combined with existing quartz-muscovite exchange data. See text for explanation. From Chacko et al., (1996).

A measure of this problem can be obtained by comparing fractionation factors in, *inter alia*, Clayton and Epstein (1961), O'Neil and Clayton (1964), Bottinga and Javoy (1973, 1975), Suzuki and Epstein (1976), Clayton (1981), Kieffer (1982), O'Neil (1986), Kyser (1987b), Blamart et al. (1988, 1989), Clayton and Kieffer (1991), O'Neil and Truesdell (1991), and Zheng (1991, 1993a, 1993b).

Thermometry should preferably be used for phases with a well-established fractionation factor, although others may be used, but could result in wide ranges of uncertainty in temperature. Compilations of fractionation factors have been published by Suzuki and Epstein (1976), Friedman and O'Neil (1977), Richet et al. (1977), O'Neil (1986), Hoefs (1987, 1997), and Kyser (1987b). A recent discussion on stable isotope thermometry is given by Ohmoto (1986).

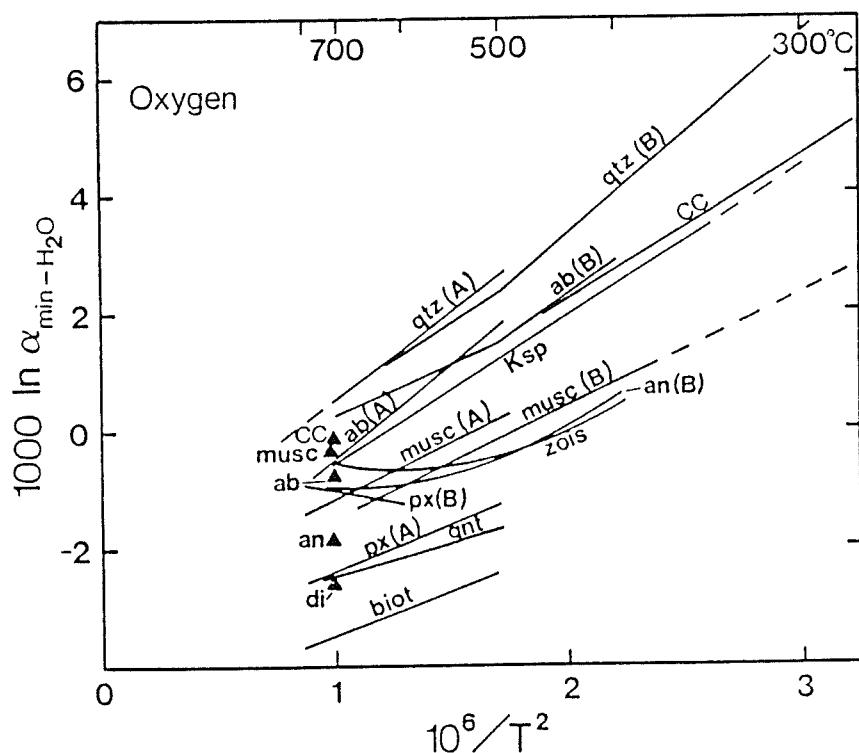


Figure 8: Example of a compilation of oxygen isotopic fractionations in the mineral-water system in a plot of temperature versus $10^3 \ln \alpha_{\text{min-water}}$. Broken lines are extrapolations. See text for explanation. From Kyser (1987a).

Examples of fractionation diagrams are shown in Figures 8 and 9. Figure 8 shows oxygen isotope fractionation curves in mineral-water systems in a $10^3 \ln \alpha_{\text{min-water}}$ versus $10^6/T^2$ (T in Kelvin) diagram. Different curves for similar systems show inconsistency in results for isotopic fractionations. Extrapolated values are shown by broken lines. A similar presentation is given in Figure 9 for hydrogen isotope fractionation curves in mineral-water systems. Horizontal lines are of no use for thermometry because of the independence of fractionation on temperature for that trajectory.

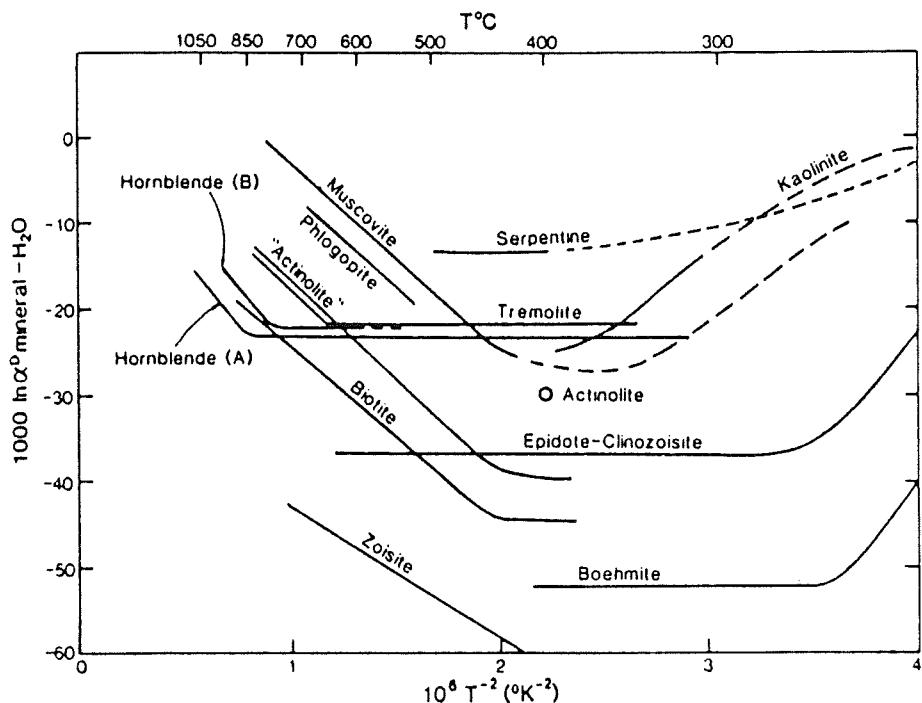


Figure 9: A compilation of hydrogen isotopic fractionations in the mineral-water system in a temperature versus fractionation diagram. See text for explanation. From Hoefs (1987).

Water-rock ratio determination

In hydrothermal deposits most of the ore-forming elements are transported by fluids. It therefore follows that the larger the volume of fluid in an ore-forming system, the larger the ore deposit might be. Determination of fluid-rock ratios is relevant in obtaining estimates of the potential size of any ore deposit.

Use of oxygen stable isotopes for fluid-rock ratio calculations results in minimum estimates. A distinction must be made between closed or open systems. Equations for such systems, published by Taylor (1977), are:

$$(1) \text{ w/r}_{\text{closed system}} = [\delta_f(\text{rock}) - \delta_i(\text{rock})] / [\delta_i(\text{fluid}) - \delta_f(\text{rock}) + \Delta]$$

$$(2) \text{ w/r}_{\text{open system}} = \ln [(\text{w/r})_{\text{cs}} + 1]$$

where w/r stands for fluid/rock ratios, and δ_i and δ_f for initial and final isotopic values, respectively, - all in the standard per mill (‰) notation, $\Delta = \delta_f(\text{rock}) - \delta_f(\text{fluid})$, $(\text{w/r})_{\text{cs}}$ and is the calculated w/r ratio for a closed system.

Calculations based on stable isotopes only represent reasonable estimates in the lower range of fluid/rock ratios. As soon as a fluid circulating through a rock is in (isotopic)

equilibrium with that rock, no further (isotopic) exchange between the fluid and the rock will occur. In higher w/r ratio systems, therefore, considerable volumes of fluids flow through the system without registering any exchange. In extreme cases this may lead to underestimation of several orders in the size of the actual fluid/rock ratio in a system (De Groot, 1997).

Specific Stable Isotope Applications

O and H isotopes in fluid-rock interaction

During interaction of fluids with rock-forming minerals, stable isotope exchange will occur. The change in the isotopic composition in both the minerals and fluids (= isotopic fractionation) is dependent on temperature, salinity (i.e. composition of the fluid), composition of the host rock, crystal structure of the minerals, water/rock ratios, and the time required to reach equilibrium between the components in the process. Determination of stable isotope signatures for rocks, or mineral separates, which have exchanged with a fluid, forms the basis for calculating isotopic compositions of the exchanging fluid at appropriate temperature, and provides information about the possible source(s) of the fluid. Different possible fluid sources are shown in Figure 10, which is an oxygen versus hydrogen isotope diagram. In the diagram, SMOW stands for Standard Mean Ocean Water, the international

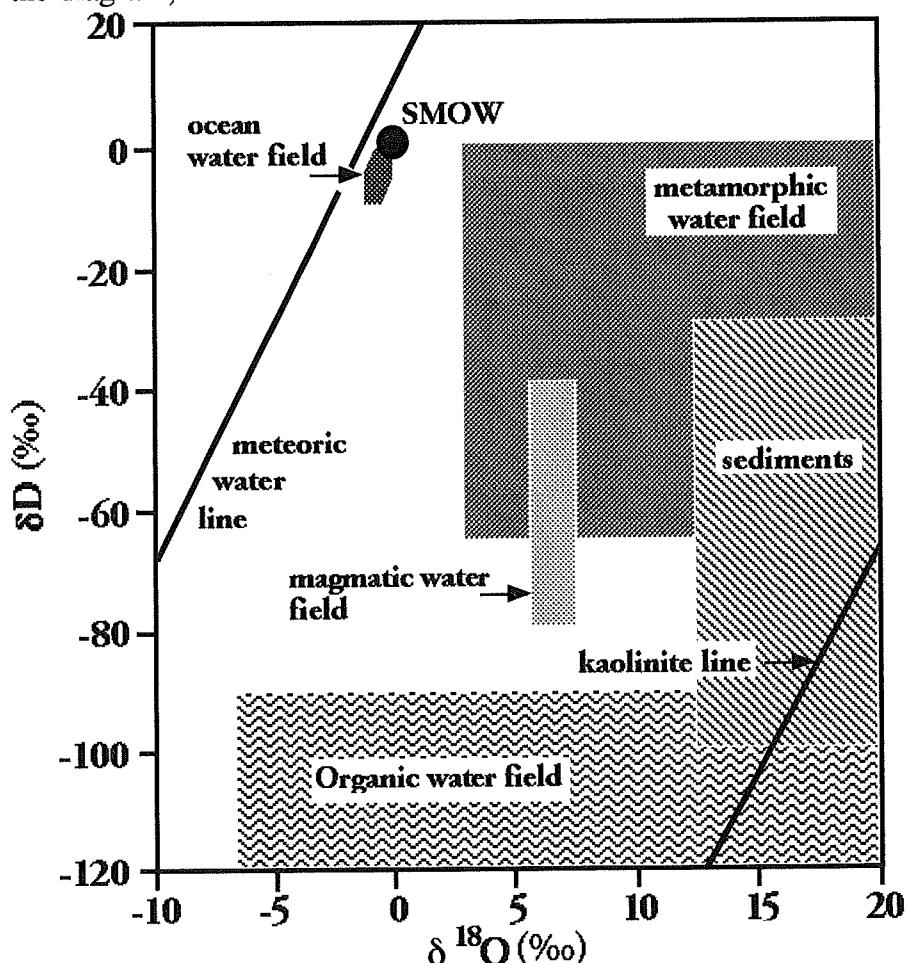


Figure 10: $\delta^{18}\text{O}$ versus δD diagram of major water sources in fluid-rock alteration systems. See text for explanation. After Sheppard (1986).

standard for both oxygen and hydrogen isotopes. The meteoric water line represents a generalised view of meteoric waters throughout the world, with equatorial latitudes at the higher end, and polar regions at the lower end of this line. The kaolinite line represents isotopic compositions of authigenic kaolinite (or clay close to and paralleling this line), formed at the Earth's surface in contact with meteoric waters. The boxes shown in the diagram (Fig. 10) represent the fields for most waters present in the Earth's crust.

Fluid-rock exchange, which is not in equilibrium, or different fluids interacting at separate stages with a rock, are complicating factors in the reconstruction of the fluid circulation history of a rock system.

Various minerals have different "closure" temperatures for isotopic exchange with other phases. Thus, given the same conditions in a mineralized site, some of the minerals might be closed for isotopic exchange while others are continuously exchanging with the fluid. If, in a fluid-rock exchange system, the fluid is cooling and only parts of the rock continue to exchange, there is a heterogeneous relationship between all the minerals and ore-forming fluid in an isotopic sense. This may hinder later fluid calculations, for there is a range of temperatures of preserved isotopic equilibrium. In many processes, no equilibrium is reached and this may cause isotopic ratios to fractionate relative to the equilibrium situation. Partly exchanged systems may be described by either closed or open *Rayleigh distillation* type fractionation processes, comparable with the Rayleigh fractional crystallization for magmatic melts (see: Taylor and Sheppard (1986) for an extended discussion of this process). For many low temperature (< 400°C) reactions, no thermodynamic equilibrium is reached and kinetic effects control isotopic fractionation (see: Cole and Ohmoto, 1986).

Isotope exchange is a special case of chemical equilibrium reactions, where at equilibrium a bi-directional isotopic exchange occurs. Under similar conditions a similar isotopic fractionation will occur between specified species. Kinetic isotope effects are associated either with incomplete and unidirectional processes (such as evaporation, dissociation reactions, biologically mediated reactions, and diffusion), or when the rate of a chemical reaction is sensitive to atomic mass at a particular position in one of the reacting species. For further information on this subject, refer to O'Neil (1986: pp. 1-5), Kyser (1987b), and Hoefs (1997: pp.5-15).

Fluid inclusions

Small inclusions of fluids may form in minerals when they grow in a fluid-containing system or when fluids pass along micro-fractures that occur within minerals. Isotopic measurements of these fluids constitute a useful addition to the methods described above for fluid-rock interacting systems. A combination of fluid inclusion thermometry-barometry and compositional determinations (by heating/cooling stage microscopy or by Raman-laser probe measurements; e.g. Poty et al., 1976; Roedder, 1972, 1979, 1984; Hollister and Crawford, 1981; Goldstein and Reynolds, 1994) with stable isotope analysis may provide useful information on the characteristics of ore fluids. These techniques have, in fact, become standard practice in ore-genetic studies, as clearly exemplified by the quantified nature of papers appearing in leading journals such as *Economic Geology*, *Geochimica et Cosmochim-*

ica Acta, Chemical Geology, Mineralogical Magazine, the Journal of Geochemical Exploration, the Journal of Volcanology and Geothermal Research, and Contributions to Mineralogy and Petrology.

Fluid inclusions generally contain one or more of the major fluid or gas phases such as water, carbon dioxide, and sometimes methane. These different fluids or gases can be collected by crushing or decripitation techniques (Hall and Friedman, 1963; Roedder et al., 1963; Hollister, 1981; Roedder, 1984), and after purification by cryogenic techniques, can be analysed for their hydrogen (water, methane), carbon (carbon dioxide, methane), or oxygen (carbon dioxide) isotopic compositions.

Limitations to the method, (in addition to the obvious constraints imposed by the existence of multiple inclusion generations and the generally small volumes of inclusion-hosted fluids and gases) include possible fluid leakage from the fluid inclusions after their formation (Crawford, 1981; Roedder, 1981, 1984), fluid circulation through the rock, changing the inclusion composition at later stages (e.g. Roedder, 1984; Jenkin et al., 1994; Goldstein and Reynolds, 1994), hydrogen diffusion through mineral crystals (Graham et al., 1987; Hall et al., 1991), adsorption or fractionation problems by crushing or decripitation isotopic value ranges in boxes, fields, and crossed lines (Archaean limestones) for most techniques respectively (Hall and Friedman, 1963; Roedder et al., 1963), and uncertainties in isotopic fractionation factors (see earlier under stable isotope thermometry).

The measured hydrogen isotopic composition of inclusion-water may be combined with the host mineral oxygen isotopic composition. Thus, the oxygen isotopic composition of water in equilibrium with the host mineral at the temperature measured by fluid inclusion thermometry, can be calculated.

Examples of combined fluid inclusion thermometry - stable isotope studies include: Kelly and Rye (1979), Charef and Sheppard (1988), Schöps and Herzig (1990), Santosh (1992), Golić and Spiro (1994), and Girard and Barnes (1995).

Stable isotope compositions of fluid inclusions may be used, in combination with stable isotope measurements of silicate- or oxide-minerals from ore deposits or host rocks, to determine the evolutionary history of the ore forming processes (i.e. the paragenetic sequence), as well as the genesis of the ore fluids (e.g. Robinson and Ohmoto, 1973; Landis and Rye, 1974; Ohmoto and Rye, 1974; Rye and Sawkins, 1974; Pollard et al., 1991; Suchchevskaya et al., 1991; Misra and Lu, 1992; Turner and Bowman, 1992).

Carbon isotopes

Carbon can be found in a wide range of naturally occurring phases, including carbonate minerals in limestones, marbles, cementing materials or in concretions in sediments, in vein fillings in fluid conduit zones, in gangue minerals associated with ore mineralization, and in graphite, diamonds, CO₂ and organic matter (e.g. coal, oil and natural gases). A compilation of different carbon reservoirs and their carbon isotopic compositions is shown in Figure 11. The upper part of the diagram shows carbonate carbon and oxygen isotopic value ranges in boxes, fields, and crossed lines (Archaean limestones) for most

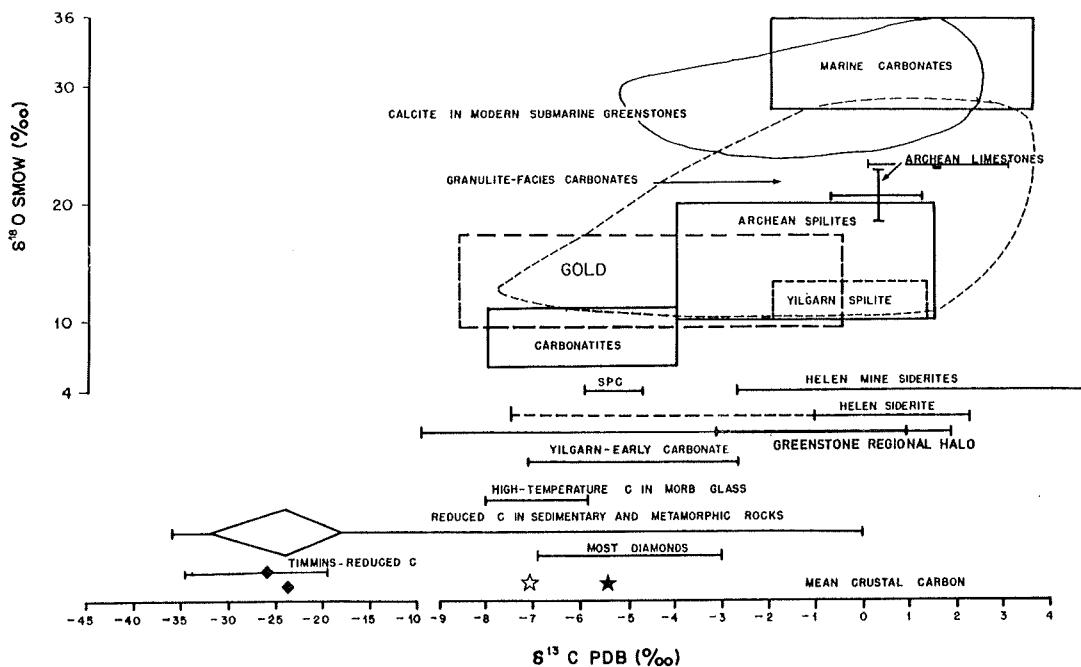


Figure 11: Compilation of oxygen and carbon isotope values of carbonates and for carbon isotopic values of carbon-containing phases from different settings. See text for explanation. From Kerrich (1987; see also for sources of data).

values of the particular carbonate occurrence. In the lower part of the diagram, lines show ranges of carbon isotopic values for particular mines, different rock materials, and diamonds as well as estimates for a mean crustal carbon isotopic value.

Carbon isotopes measured in carbonate minerals, or in graphite from mineralized occurrences, provide information about source(s) of carbon (i.e. sedimentary, magmatic, mantle, or organic) and other genetic implications (i.e. phases involved in a specific order), and are helpful in interpreting the nature of mineralized areas. Fluid inclusions in ore minerals may contain high percentages of carbon dioxide, from which carbon isotopic information may be obtained to provide similar types of information to that just described.

Marine carbonates are important carbon reservoirs. These sediments act as hosts to ore mineralization or they disintegrate, during subduction or when the sediments come into contact with magmatic intrusions. Some may dissolve in fluids with the carbon-containing compounds being brought to higher control levels by fluids or as gases, eventually stripping ore metals from rocks with which they react. They thus provide "building blocks" for ore mineralization into which these carbon compounds may also be deposited. Fluctuations in marine carbon isotopic composition with time during Earth's history is minimal, ranging between +2 and -1 % (traced back to ~ 800 Ma b.p. by Veizer et al., 1980), and does not overlap with the negative carbon isotopic values found in carbonates associated with ore forming processes.

Limestones or marbles may host a variety of mineralization types, the latter generally formed during secondary replacement processes. Some important carbonate-hosted ore occurrences include skarn-type mineralization (e.g. Einaudi et al. (1981) (Fig. 12), carbonate-hosted sulphide deposits (e.g. in Sangster, 1983), and Mississippi Valley Type (MVT) mineralization (e.g. Hall and Friedman, 1963; Roedder et al., 1963).

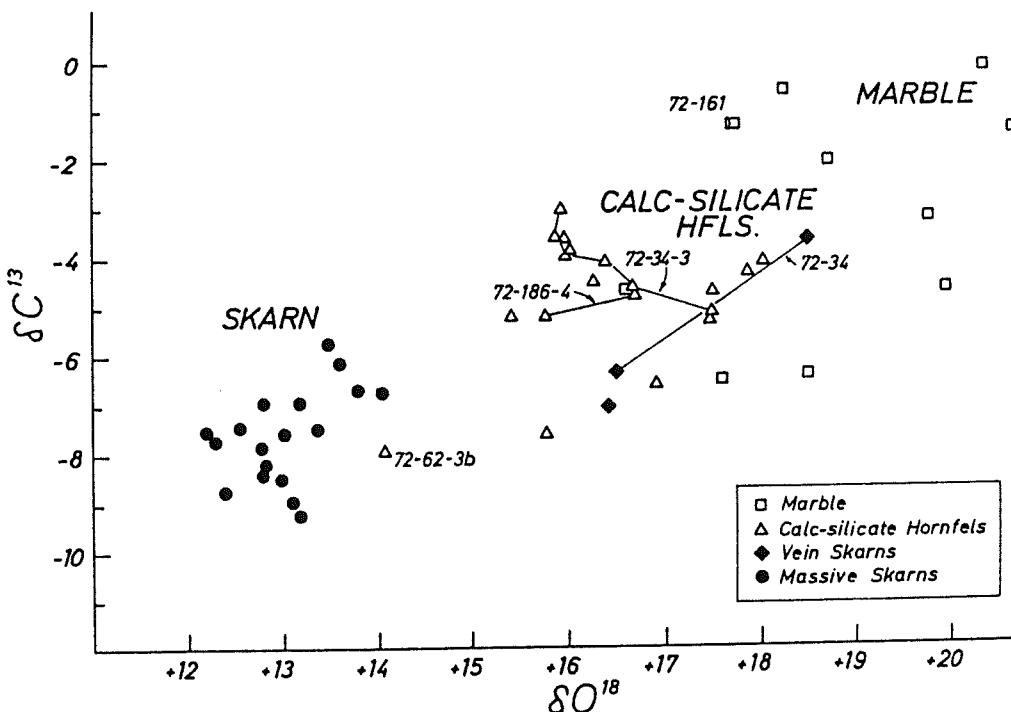


Figure 12: $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ diagram for calcite from marble, calc-silicate hornfels, massive skarn, and metasomatic veins and vein skarns. Samples from a single hand specimen are connected by a line. See text for explanation. From Taylor and O'Neil (1977).

Figure 12 shows the oxygen and carbon isotopic fractionation of a typical granite-related skarn. The marble has "normal" marine carbon isotope values and a slightly lower oxygen isotopic composition compared to isotopic values of carbonates deposited in a marine environment. The hornfelses are lower several permil for both carbon and oxygen isotopic values, and the skarn carbonates have the most depleted values. Carbon and oxygen isotopes in carbonates associated with ore mineralization generally deviate strongly from sedimentary formed carbonates, normally towards negative values. Carbonates related to mineralization show a carbon-oxygen isotopic trend comparable with deep (mantle?) isotopic signatures (e.g. Deines and Gold, 1969; Valley, 1986; Taylor, 1987), most probably representing recycled carbonate material from deeper parts of the crust (e.g. vaporisation of carbonate material by intruding magmas) or upper mantle regions (e.g. related to crustal subduction).

Fluids related to many mineralized occurrences are saline brines. In MVT deposits, fluids are often comparable with oil brine compositions (Hall and Friedman, 1963; Roedder et al., 1963) and sometimes contain petroliferous components (Roedder, 1984). Carbon and sulphur isotopic compositions of organic materials show low values, possibly inherited by carbon- (carbonates) and sulphur- (sulphides, sulphates) containing phases of the mineralized locality. The presence of depleted $\delta^{13}\text{C}$ values may identify the presence of such organic-related deposits.

The use of carbon isotope values of calcite or graphite, deposited in a fluid-controlled sulphide ore occurrence to determine pH and log $f\text{O}_2$ conditions of the system has been presented by Ohmoto (1972). Figure 13 shows a pH versus log $f\text{O}_2$ diagram in a carbon containing-fluid system. Stability fields at 250°C for calcite and graphite are shown for different total carbon concentrations in the fluid.

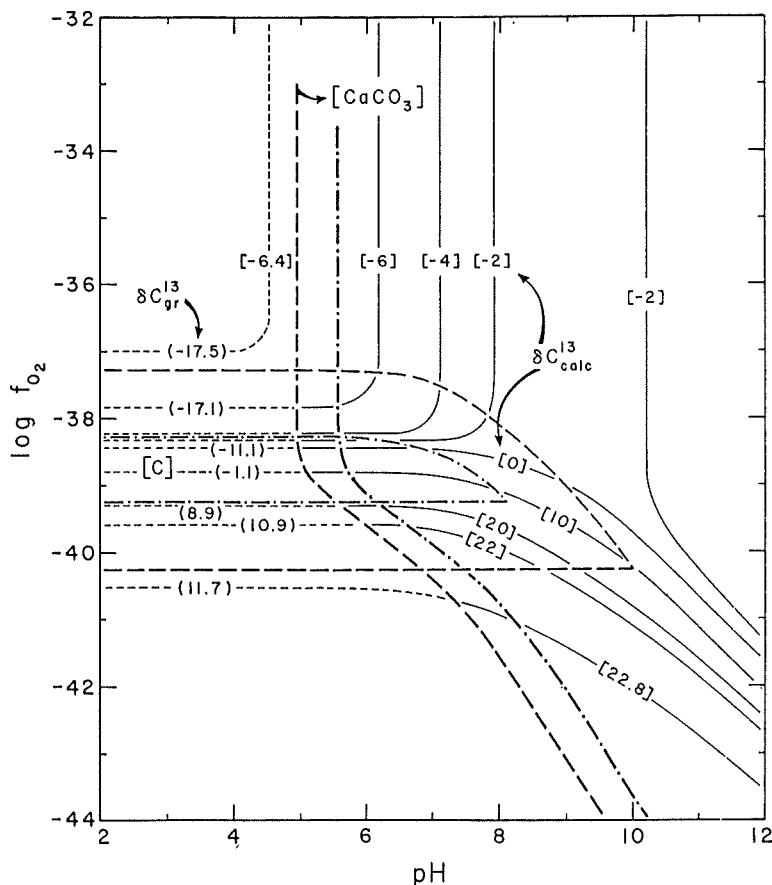


Figure 13: Comparison of the position of δC^{13} contours with the stability fields of calcite and graphite in a pH versus log $f\text{O}_2$ diagram. T = 250°C and I = 1.0. Solid lines: δC^{13} contours. Carbon isotope contours for calcite and graphite are shown by thin solid and broken lines; values in [] and () are, respectively, for calcite and graphite at $\delta\text{C}^{13\Sigma}\text{C} = 5\text{\textperthousand}$ (ΣC = total carbon), a probable value of carbon of juvenile origin. Broken lines: stability boundaries for calcite and graphite at $\Sigma\text{C} = 1 \text{ mole/kg H}_2\text{O}$. Dash-dot lines: stability boundaries for calcite and graphite at $\Sigma\text{C} = 0.1 \text{ moles/kg H}_2\text{O}$. See text for explanation. From Ohmoto (1972).

Application of carbon and oxygen isotopic analysis, in combination with sulphur (sulphides) and hydrogen (hydrous minerals, whole rock) isotopes may give important information about sources of fluids, sulphur and ore metals, as well as about physical conditions of the mineralization (e.g. temperature, pH, redox, $f\text{O}_2$).

Sulphur isotopes

Sulphide minerals are important constituents of most ore deposits. Sulphur isotope analyses of sulphides are used in thermometry, for constraining the origin of sulphur and in obtaining information of the physical conditions of the ore-forming system. A compilation of sulphur isotope compositions in different materials and settings is provided in Figure 14. The range of the sulphur isotopes is given by horizontal lines and the relative abundance of the isotopic values is illustrated by the width of these lines.

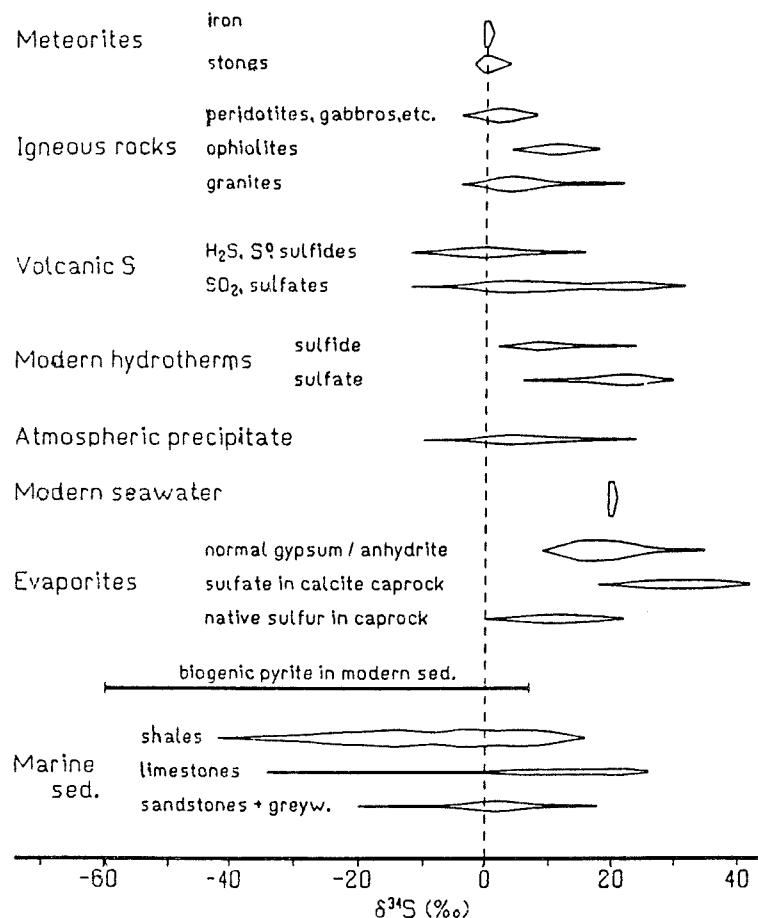


Figure 14: A compilation of $\delta^{34}\text{S}$ (‰) values for some natural materials of geochemical interest. See text for explanation. From Nielsen (1979).

Thermometry using stable isotopes has already been briefly discussed above. Specifically, sulphur isotope thermometry on sulphide minerals has been shown to be biased by isotopic disequilibrium situations between different coexisting sulphides and is also

dependent on local physical conditions of the fluid system (see: Ohmoto, 1986). The fractionation of sulphur isotopes in sulphide minerals in an ore system are generally different to the equilibrium fractionation values at ore deposition temperatures for that mineralization. Sulphur isotope thermometry on many sulphide-mineral pairs has led to low or unrealistic temperatures being determined for the deposition of the mineralization. Only if temperatures, obtained by sulphur isotope thermometry, are in accordance with temperatures obtained by other methods, (e.g. fluid inclusion thermometry), can they be considered reliable.

Sulphur isotopes are widely used for genetic interpretation (i.e. by determination of the sources of the sulphur, eventually providing constraints on the source of the ore metals, and the determination of different generations of sulphides. Suggestions for the interpretation of sulphur isotope compositions has been provided by Nielsen (1979), Faure (1986), and Hoefs (1987, 1997). In Figure 15 a compilation of $\delta^{34}\text{S}$ (in ‰) ranges for base metal sulphides, pyrites and sulphates from different types of intensely studied ore occurrences is shown. Sulphur isotopic values, determined for a particular mineral occurrence, can be compared with values shown in Figure 15 and a genetic interpretation can then be suggested.

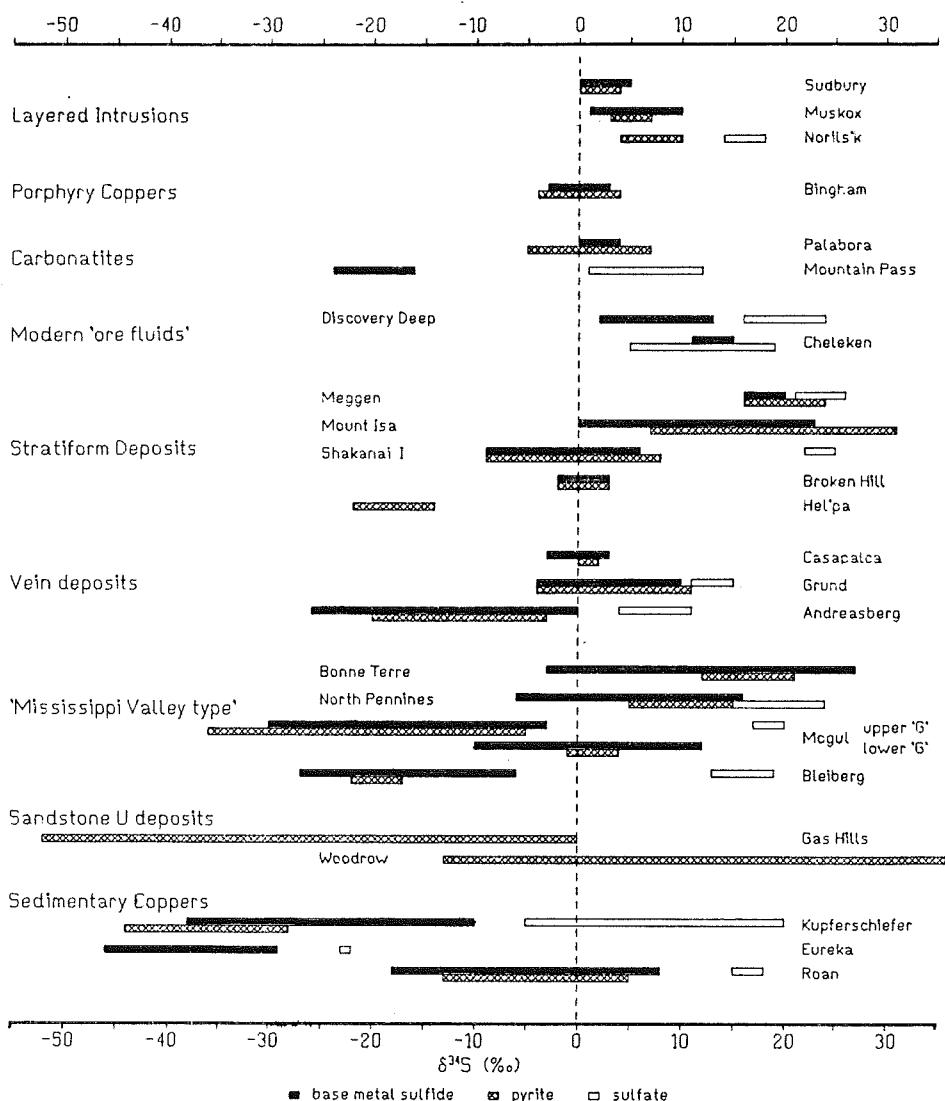


Figure 15: $\delta^{34}\text{S}$ ranges in sulphide and sulphate ore deposits of different genetic types.
From Nielsen (1979).

Sulphur isotopes from sulphides and sulphates may be used to determine combined pH and $\log f_{O_2}$, or pH and $\delta^{34}S_{H_2S}$ conditions in an ore mineralizing system (Ohmoto, 1972; Rye and Ohmoto, 1974). In Figure 16, the parameters pH and $\log f_{O_2}$ are related to $\delta^{34}S$ values of the stability fields of sulphides and barite in fluid-controlled sulphide deposits at fixed temperature and ionic strength, and for various ΣS_{fluid} (= total sulphur of fluid) compositions (Ohmoto, 1972). Alternatively, in Figure 17, the pH is related to $\delta^{34}S_{H_2S}$ for different $\log f_{O_2}$ situations in a sulphide mineralizing system.

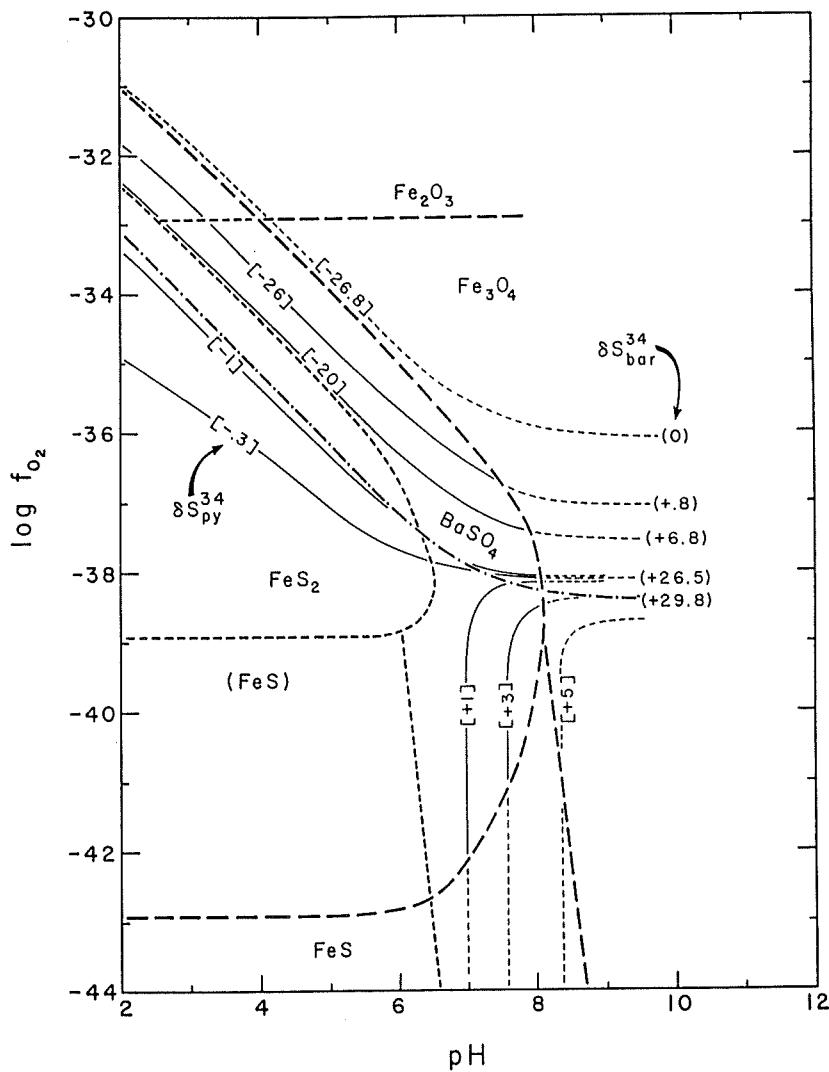


Figure 16: A pH versus $\log f_{O_2}$ diagram for comparison of the positions of $\delta^{34}S_i$ contours with the stability fields of Fe-S-O minerals and barite. $T = 250^\circ C$ and $I = 1.0$. Thin broken lines: $\delta^{34}S_i$ contours = values in [] and () are, respectively, for pyrite and barite at $\delta^{34}S_s = 0\text{\textperthousand}$. Bold broken lines: Fe-S-O mineral boundaries at $\Sigma S = 0.1 \text{ moles/kg H}_2\text{O}$. Median size broken lines: Fe-S-O mineral boundaries at $\Sigma S = 0.001 \text{ moles/kg H}_2\text{O}$. Dash-dot lines: barite soluble/insoluble boundary at $m_{Ba}2+ \cdot m_s = 10^4$. Under these T and I conditions, an increase of $m_{Ba}2+$ or m_s value by 1 order of magnitude drops the boundary by about 0.5 $\log f_{O_2}$ units. See text for explanation From Ohmoto (1972).

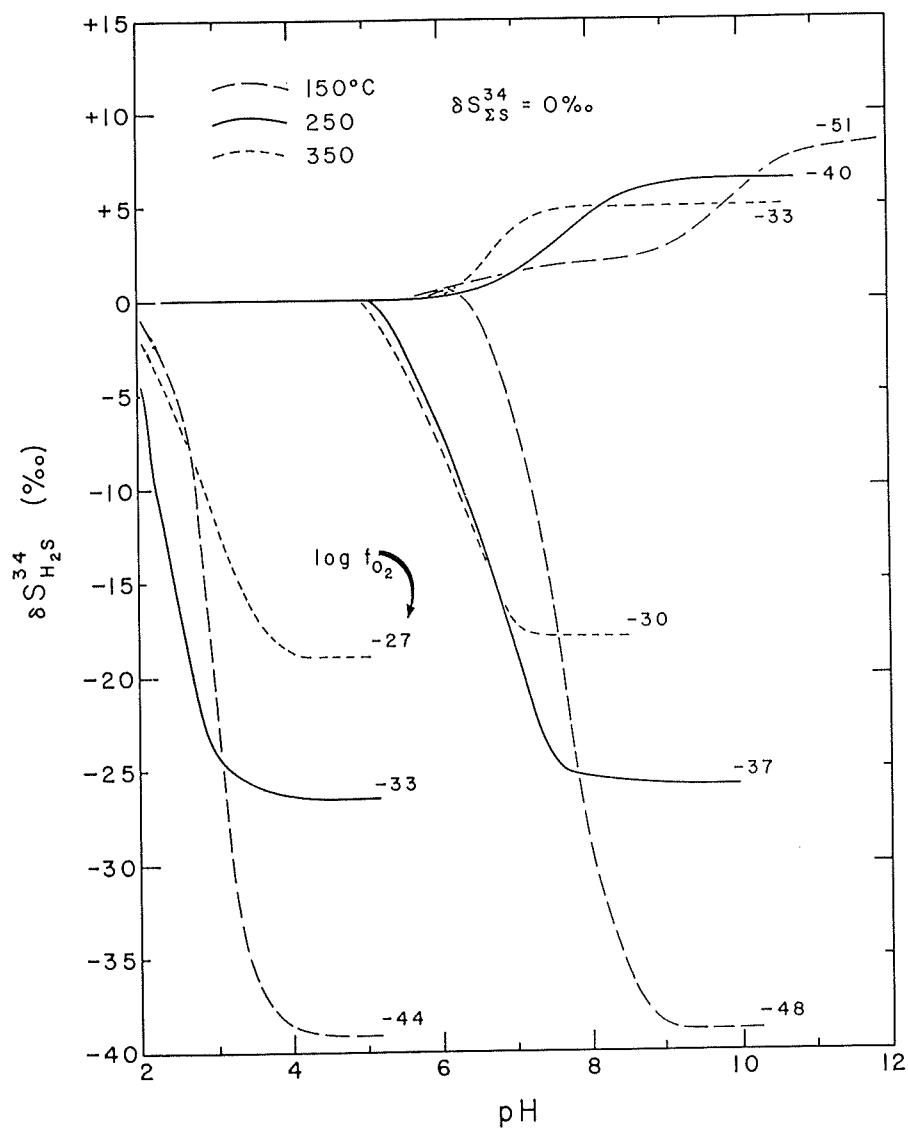


Figure 17: A pH versus $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ diagram for comparison of the effect of change in pH on the $\delta^{34}\text{S}_i$ values at different T and $\log f\text{O}_2$ of the fluids. $I = 1.0$. $\delta^{34}\text{S}$ values for H_2S are where $\delta^{34}\text{S}_s = 0\text{\%}$. See text for explanation. From Ohmoto (1972).

This type of diagram, reflecting different temperature scales (Ohmoto (1972), has the potential for providing limits to the physical conditions of a sulphide mineralizing system. If, for example, the sulphur isotopic composition of pyrite and the formation temperature of mineralization are known for a specific ore deposit, it is possible, with help of the diagrams shown in Figures 16 and 17, to obtain the pH, $\log f\text{O}_2$ and $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ for that particular system. These parameters will then assist in the interpretation of the depositional history of the ore minerals and the order in which they were formed.

Sulphur and oxygen isotopes: sulphates

Sulphates from evaporitic deposits or from cap-rock in salt diapirs have also been analysed for oxygen and sulphur isotopes. Evaporates are of economic importance mostly because they concentrate on different salts (e.g. potassium mines in the Alsace, France and the Zechstein deposits of the northern plains of the Netherlands, Germany and Poland).

Important occurrences of sulphates occur in the chimneys of smokers on the seafloor. Sulphates are deposited by mixing seawater with exhalative hydrothermal fluids, and are (partly) replaced by sulphides in chimneys showing advanced stages of development (e.g. James and Elderfield, 1996). The relationship of these sulphates to (massive) sulphides make them interesting for exploration purposes, and in tracing and interpreting seafloor type sulphide deposits.

Interpretation of sulphur isotopes of sulphates in marine evaporates must be related to the time of deposition, since sulphur isotopes from sulphates show a wide variation with time (Claypool et al., 1980). Figure 18 shows values of $\delta^{18}\text{O}$ (‰) and $\delta^{34}\text{S}$ (‰) against age in millions of years for sulphur isotope compositions of seawater sulphates. The oxygen isotope composition only changes slightly, while the sulphur isotopes show a considerable shift with time. This latter observation has important implications for the interpretation of marine sulphate deposits and their ages.

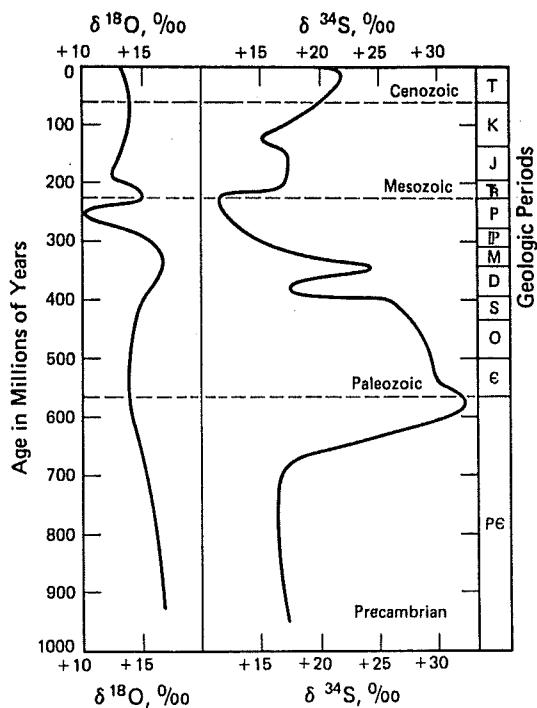


Figure 18: Variations of $\delta^{34}\text{S}_{\text{CDT}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$ of marine sulphate minerals from Late Precambrian to the present. The curves demonstrate that the isotopic compositions of both elements in marine sulphate minerals have varied in Late Precambrian and Phanerozoic time. The causes for the observed variations involve a complex interplay of inputs and outputs of S and O_2 in the oceans, but are not yet completely understood. See text for explanation. From Faure (1986).

Cl isotopes as an exploration tool

Chlorine shows only a small degree of isotopic fractionation and hence few chlorine isotopic systematics have been studied in detail, or applied to ore-genesis studies until very recently. Present techniques have vastly improved the precision of the isotopic analysis (near $\pm 0.1\text{\textperthousand}$ for repeated measurement) and it is now obvious that a range of about $15\text{\textperthousand}$ in different chlorine phases has been determined (Long et al., 1993; Eggenkamp, 1994; Hoefs, 1997). Figure 19 shows a compilation of the ranges of chlorine isotopes found in different reservoirs.

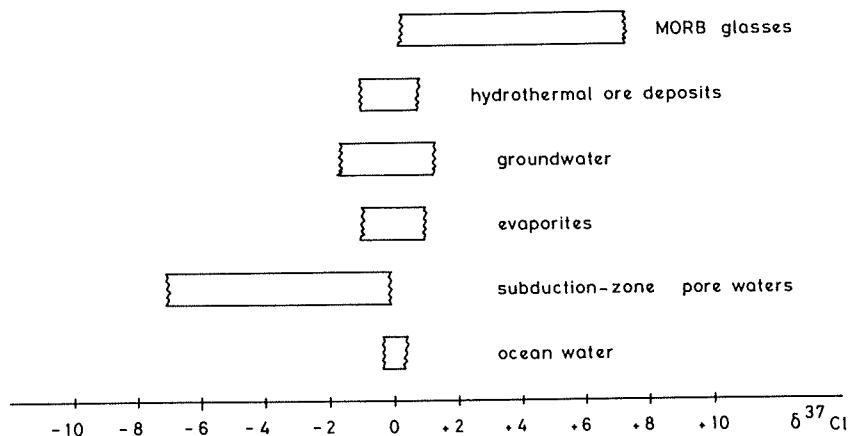
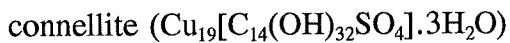


Figure 19: A compilation of different $\delta^{37}\text{Cl}$ values for different reservoirs. See text for explanation. From Hoefs (1997).

Eggenkamp and Schuiling (1995) proposed the use of chlorine isotopes for exploration purpose. Base metal sulphides, generally having $\delta^{37}\text{Cl}$ values around SMOC (Standard Mean Ocean Chloride, the chosen standard for chlorine), oxidise in arid to semi-arid regions with the formation of minerals such as:



which have strongly positive $\delta^{37}\text{Cl}$ values. If groundwater comes into contact with these minerals, a positive $\delta^{37}\text{Cl}$ signature may be imparted to the groundwater, providing a chlorine isotope tracer for exploration purposes.

Combined Stable and Radiogenic Isotopes

Oxygen isotope analysis may be used in combination with radiogenic isotopes, such as strontium (Taylor, 1980; Taylor and Sheppard, 1986) (Fig.20) or lead (Curti, 1987;

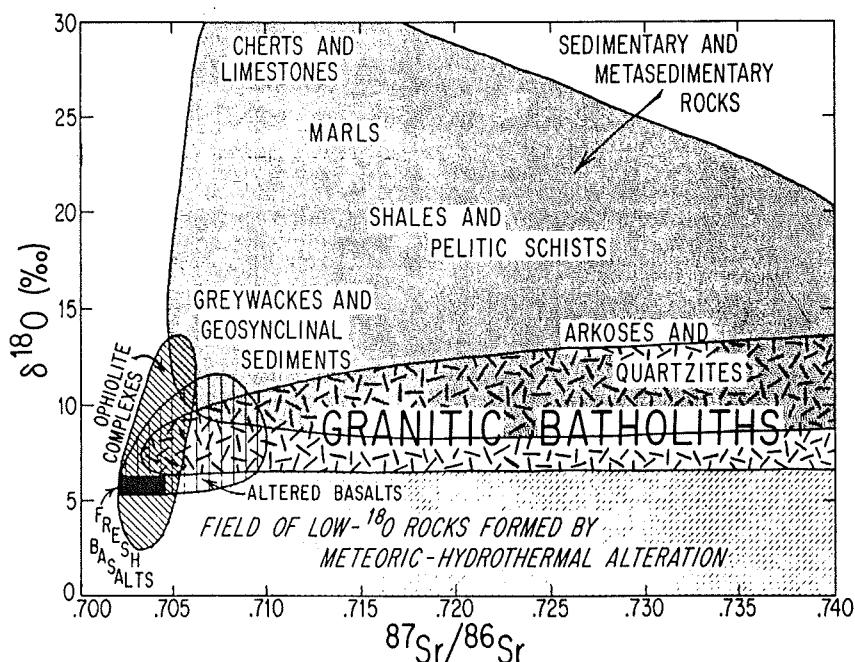


Figure 20: $\delta^{18}\text{O}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ diagram, modified after Taylor (1980), showing the range of isotopic compositions observed in a variety of terrestrial rocks, generalized from literature data sources. See text for explanation. From Taylor and Sheppard (1986).

Ayuso et al., 1996) in order to obtain here constraints on the sources of ore-forming components. Applied to magmatic rocks, this method provides information about eventual contamination of magmas and the source(s) of such contamination. The application in ore exploration is therefore limited to magmatic-related ore mineralization, and may provide useful information for formulating a genetic ore model. Consideration of Figure 20 and the Sr- (0.705 - 0.708) and O- (7 - 9 ‰) isotopic compositions of the Arequipa and Baoroso volcanics of Peru (Magaritz et al., 1978), indicate that they fit into the fields of altered basalt or granitic batholiths. If, on the other hand, consideration is given to the Maladeta Complex of the Pyrenees (Michard-Vitrac et al., 1980), with values of 0.708 to 0.716 for Sr and 8 - 12 ‰ for O, this occurrence fits the subfield (Fig. 20) of greywackes and the geosynclinal sediments (see also in: Taylor and Sheppard, 1986).

Palaeoclimatic - Environmental Methods

Less established applications in the use of stable isotopes, which may be useful in the fields of ore exploration or environmental studies are briefly mentioned below. These include low temperature surface processes, in which water and atmospheric oxygen and CO₂ play an important role. At low temperatures, oxygen isotope fractionations in silicates or oxides are large compared to higher temperature (ore forming) processes, and will lead to specific, high oxygen isotopic signatures. Hydrogen strongly reflects the water source in the newly formed minerals.

Weathering processes are related to climatological conditions on the Earth's surface. Near-surface ore mineralization, in the form of gossans, bauxite, or laterite or clay deposits (kaolinite), is related to weathering. The importance of gossans in concentrating specific metals (e.g. gold) is well known. Laterite and bauxite are important as ores of aluminium, iron, and manganese. Kaolinite and other clay minerals, are important products for the ceramic industry. They may be formed both by weathering or by hydrothermal alteration of felsic (granitic) rocks. Stable isotope studies of kaolinites in the Cornubian granites (e.g. Sheppard, 1977; Alderton and Harmon, 1991) provide an example of the application of stable isotopes to the understanding of clay formation. In this occurrence kaolinitization was interpreted as a low temperature hydrothermal alteration rather than surfacial weathering.

Palaeoclimate change was determined in East Greenland (Nevle et al., 1994) by analysis of oxygen and hydrogen isotopes of shallow level magmatic intrusions of Tertiary age which all exchanged with meteoric waters at different ages. Comparison of the stable isotope composition of these rocks with the calculated isotopic composition of the waters which exchanged with the intrusions, provided an estimate of the climate change with time.

ACKNOWLEDGEMENTS

Thanks are due to Carl Anhaeusser, Rudi Boer and Laurence Robb for their criticism and suggestions which helped improve earlier drafts of this manuscript.

REFERENCES

- Alderton, D.H.M. and Harmon, R.S. 1991. Fluid inclusion and stable isotope evidence for the origin of mineralizing fluids in south-west England: Mineralogical Magazine, v.55, p.605-611.
- Ayuso, R.A., Barr, S.M. and Longstaffe, F.J. 1996. Pb and O isotopic constraints on the source of granitic rocks from Cape Breton Island, Nova Scotia, Canada: American Journal of Science, v.296, p.789-817.
- Beaty, D.W., Taylor, H.P. Jr. and Coad, P.R. 1988. An oxygen isotope study of the Kidd Creek, Ontario, volcanogenic massive sulfide deposit: Evidence for a high ^{18}O ore fluid: Economic Geology, v.83, p.1-17.
- Bigeleisen, J., Perlman, M.L. and Prosser, H.C. 1952. Conversion of hydrogenic materials to hydrogen for isotopic analysis: Analytical Chemistry, v.24, p.1356-1357.
- Blamart, D., Pichavant, M. and Sheppard, S.M.F. 1988. D/H isotopic fractionation between tourmaline and water: The experimental calibration of tourmaline-mineral geothermometers at 50°C to 700°C: Chemical Geology, v.70, p.182.

- Blamart, D., Pichavant, M. and Sheppard, S.M.F. 1989. Détermination expérimentale du fractionnement isotopique D/H entre tourmaline et eau à 600, 500°C et 3 kbar: Compte Rendu Académie de Science de Paris, tome 308, p.39-44.
- Bottinga, Y. and Javoy, M. 1973. Comments on oxygen isotope geothermometry: Earth and Planetary Science Letters, v.20, p.250-265.
- Bottinga, Y. and Javoy, M. 1975. Oxygen isotope partitioning among the minerals in igneous and metamorphic rocks: Reviews in Geophysics and Space Physics, v.13, p.401-418.
- Bowen, R. 1988. Isotopes in the Earth Sciences, Elsevier Applied Science Publ. Ltd., 647p.
- Campbell, A., Rye, D. and Petersen, U. 1984. A hydrogen and oxygen isotope study of the San Cristobal Mine, Peru: Implications of the role of water to rock ratio for the genesis of wolframite deposits: Economic Geology, v.79, p.1818-1832.
- Chacko, T., Hu, X., Mayeda, T.K., Clayton, R.N. and Goldsmith, J.R. 1996. Oxygen isotope fractionations in muscovite, phlogopite, and rutile: Geochimica et Cosmochimica Acta, v.60, p.2595-2608.
- Charef, A. and Sheppard, S.M.F. 1988. The Malines Cambrian carbonate-shale-hosted Pb-Zn deposit, France: Thermometric and isotopic (H, O) evidence for pulsating hydrothermal mineralization: Mineralium Deposita, v.23, p.86-95.
- Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H. and Zak, I. 1980. The age curves of sulphur and oxygen isotopes in marine sulfate and their mutual interpretation: Chemical Geology, v.28, p.199-260.
- Clayton, R.N. and Epstein, S. 1961. The use of oxygen isotopes in high temperature geological thermometry: The Journal of Geology, v.69, p.447-452.
- Clayton, R.N. and Mayeda, T.K. 1963. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis: Geochimica et Cosmochimica Acta, v.27, p.43-52.
- Clayton, R.N. 1981. Isotopic thermometry, In: Newton, R.C., Navrotsky, A. and Wood, B.J., eds., Thermodynamics of minerals and melts, Springer, p. 85-109.
- Clayton, R.N. and Kieffer, S.W. 1991. Oxygen isotopic thermometer calibrations, In: Taylor, H.P. Jr., O'Neil, J.R. and Kaplan, I.R., eds., Stable isotope geochemistry: A tribute to Samuel Epstein, The Geochemical Society, p.3-10.
- Coad, P.R. 1985. Rhyolite geology at Kidd Creek - a progress report: Canadian Mining and Metallurgy Bulletin, v.78, no.874, p.70-83.

- Cocker, J.D., Griffin, B.J. and Muehlenbachs, K. 1982. Oxygen and carbon isotope evidence for seawater-hydrothermal alteration of the Macquarie Island ophiolite: Earth and Planetary Science Letters, v.61, p.112-122.
- Cole, D.R. and Ohmoto, H. 1986. Kinetics of isotopic exchange at elevated temperatures and pressures, *In*: Valley, J.W., Taylor, H.P. Jr. and O'Neil, J.R., eds., Stable isotopes in high temperature geological processes: Reviews in Mineralogy, Mineralogical Society of America, v.16, p.41-90.
- Coleman, M.L. and Moore, M.P. 1978. Direct reduction of sulfates to sulphur dioxide for isotopic analysis: Analytical Chemistry, v.50, p.1594-1595.
- Coleman, M.L., Shepherd, T.J., Durham, J.J., Rouse, J.E. and Moore, G.R. 1982. Reduction of water with zinc for hydrogen isotope analysis: Analytical Chemistry, v.54, p.993-995.
- Crawford, M.L. 1981. Phase equilibria in aqueous fluid inclusions, *In*: Hollister, L.S. and Crawford, M.L., eds., Fluid inclusions: Applications to petrology: Short Course Handbook, Mineralogical Association of Canada, v.6, p.75-100.
- Criss, R.E. and Taylor, H.P. Jr. 1983. An $^{18}\text{O}/^{16}\text{O}$ and D/H study of Tertiary hydrothermal systems in the southern half of the Idaho batholith: Geological Society of America Bulletin, v.94, p.640-663.
- Criss, R.E. and Taylor, H.P. Jr. 1986. Meteoric-hydrothermal systems, *In*: Valley, J.W., Taylor, H.P. Jr. and O'Neil, J.R., eds., Stable isotopes in high temperature geological processes: Reviews in Mineralogy, Mineralogical Society of America, v.16, p.373-424.
- Crowe, D.E., Valley, J.W. and Baker, K.L. 1990. Micro-analysis of sulphur-isotope ratios and zonation by laser microprobe: Geochimica et Cosmochimica Acta, v.54, p.2075-2092.
- Crowe, D.E. and Valley, J.W. 1992. Laser microprobe study of sulfur isotope variation in a sea-floor hydrothermal spire, Axial Seamount, Juan de Fuca Ridge, eastern Pacific: Chemical Geology (Isotope Geoscience Section), v.101, p.63-70.
- Crowe, D.E. and Vaughan, R.G. 1996. Characterization and use of isotopically homogeneous standards for in situ laser microprobe analysis of $^{34}\text{S}/^{32}\text{S}$ ratios: American Mineralogist, v.81, p.187-193.
- Curti, E. 1987. Lead and oxygen isotope evidence for the origin of the Monte Rosa gold lode deposits (Western Alps, Italy): A comparison with Archean lode deposits: Economic Geology, v.82, p. 2115-2140.
- De Groot, P.A. 1997. On the value of water/rock ratio calculations: European Union of Geosciences 9, Terra Nova, Abstracts Supplement No.1, v.9, p.547.

- Deines, P. and Gold, D.P. 1969. The change in carbon and oxygen isotopic composition during contact metamorphism of Trenton limestone by the Mount Royal pluton: *Geochimica et Cosmochimica Acta*, v.33, p.421-424.
- Eggenkamp, H.G.M. 1994. $d^{37}\text{Cl}$. The geochemistry of chlorine isotopes: Ph.D. thesis, University of Utrecht, Utrecht, *Geologica Ultraiectina - Mededelingen van de Faculteit Aardwetenschappen der Rijksuniversiteit te Utrecht*. No. 116, 149p.
- Eggenkamp, H.G.M. and Schuiling, R.D. 1995. $d^{37}\text{Cl}$ variations in selected minerals: a possible tool for exploration: *Journal of Geochemical Exploration*, v.55, p.249-255.
- Einaudi, M.T., Meinert, L.D. and Newberry, R.J. 1981. Skarn deposits, In: Skinner, B.J., ed., *Economic Geology, 75th Anniversary Volume*, p.317-391.
- Eldridge, C.S., Compston, W., Williams, I.S. and Walshe, J.L. 1989. Sulphur isotopic analyses on the SHRIMP ion microprobe, In: Shanks, W.C. III and Criss, R.E., ed., *New frontiers in stable isotopic research: Laser probes, ion probes, and small-sample analysis*: U.S. Geological Survey, Bulletin 1890, p.163-174.
- Elsenheimer, D. and Valley, J.W. 1992. In situ oxygen isotope analysis of feldspar and quartz by Nd:YAG laser micro probe: *Chemical Geology (Isotope Geoscience Section)*, v.101, p.21-42.
- Faure, G. 1986. *Principles of isotope geology*: Second edition, Wiley & Sons.
- Franchi, I.A., Wright, I.P., Gibson, E.K. Jr. and Pillinger, C.T. 1986. The laser microprobe: A technique for extracting carbon, nitrogen and oxygen from solid samples for isotopic measurements: *Journal of Geophysical Research*, v.91, p.D514-D524.
- Franchi, I.A., Boyd, S.R., Wright, I.P. and Pillinger, C.T. 1989. Application of lasers in small-sample stable isotopic analysis, In: Shanks, W.C. III and Criss, R.E., ed., *New frontiers in stable isotopic research: laser probes, ion probes, and small-sample analysis*: U. S. Geological Survey, Bulletin 1890, p.51-59.
- Friedman, I. 1953. Deuterium content of natural waters and other substances: *Geochimica et Cosmochimica Acta*, v.4, p.89-103.
- Friedman, I. and O'Neil, J.R. 1977. Data of geochemistry: Compilation of stable isotope fractionation factors of geochemical interest: Professional Paper 440-KK, U. S. Geological Survey.
- Giletti, B.J. and Shimizu, N. 1989. Use of the ion microprobe to measure natural abundances of oxygen isotopes in minerals, In: Shanks, W.C. III and Criss, R.E., ed., *New frontiers in stable isotopic research: laser probes, ion probes, and small-sample analysis*: U. S. Geological Survey, Bulletin 1890, p.129-136.

- Girard, J.-P. and Barnes, D.A. 1995. Illitization and palaeothermal regimes in the middle Ordovician St. Peter sandstone, central Michigan basin: K-Ar, oxygen isotope, and fluid inclusion data: AAPG Bulletin, v.79, p.49-69.
- Goldstein, R.H. and Reynolds, T.J. 1994. Systematics of fluid inclusions in diagenetic minerals: SEPM Short Course, Tulsa, Oklahoma, Society for Sedimentary Geology, v.31, 199p.
- Goliçe, A. and Spiro, B. 1994. Stable isotope study of antimony deposits in the Muratdegi region, western Turkey: Mineralium Deposita, v.29, p.361-365.
- Graham, C.M., Viglino, J.A. and Harmon, R.S. 1987. Experimental study of hydrogen-isotope exchange between aluminous chlorite and water and of hydrogen diffusion in chlorite: American Mineralogist, v.72, p.566-579.
- Gregory, R.T. and Taylor, H.P. Jr. 1981. An oxygen isotope profile in a section of Cretaceous oceanic crust, Samail ophiolite, Oman: Evidence for $d^{18}O$ buffering of the oceans by deep (> 5km) seawater-hydrothermal circulation at mid-ocean ridges: Journal of Geophysical Research, v.86, p.2737-2755.
- Hall, D.L., Bodnar, R.J. and Craig, J.R. 1991. Evidence for postentrapment diffusion of hydrogen into peak metamorphic fluid inclusions from the massive sulphide deposits at Ducktown, Tennessee: American Mineralogist, v.76, p.1344-1355.
- Hall, W.E. and Friedman, I. 1963. Composition of fluid inclusions, Cave-in-Rock fluorite district, Illinois and Upper Mississippi Valley zinc-lead district: Economic Geology, v.58, p.886-911.
- Hoebs, J. 1973. Stable isotope geochemistry: Minerals, rocks and inorganic material, Monograph series of theoretical and experimental studies 9, Second edition, Springer, 140p.
- Hoebs, J. 1987. Stable isotope geochemistry: Minerals, rocks and inorganic materials, Monograph series of theoretical and experimental studies 9, Third edition, Springer, 241p.
- Hoebs, J. 1997. Stable isotope geochemistry: Fourth completely revised, updated, and enlarged edition, Springer, 201 p.
- Hollister, L.S. 1981. Information intrinsically available from fluid inclusions, In: Hollister, L.S. and Crawford, M.L., Eds., Fluid inclusions: Applications to petrology: Short Course Handbook, Mineralogical Association of Canada, v.6, p.1-12.
- Hollister, L.S. and Crawford, M.L. 1981. Fluid inclusions: Application to petrology: Short Course Handbook, Mineralogical Association of Canada, v.6, 304p.

- Holt, B.D. and Engelkemeir, A.G. 1970. Thermal decomposition of barium sulfate to sulphur dioxide for mass spectrometric analysis: *Analytical Chemistry*, v.42, p.1451-1453.
- Horita, J. 1988. Hydrogen isotope analysis of natural waters using an H₂-water equilibration method: A special implication to brines: *Chemical Geology (Isotope Geoscience Section)*, v.72, p.89-94.
- Horita, J. and Gat, J.R. 1988. Procedure for the hydrogen isotope analysis of water from concentrated brines: *Chemical Geology (Isotope Geoscience Section)*, v.72, p.85-88.
- James, R.H. and Elderfield, H. 1996. Chemistry of ore-forming fluids and mineral formation rates in an active hydrothermal sulphide deposit on the Mid-Atlantic Ridge: *Geology*, v.24, p.1147-1150.
- Jenkin, G.R.T., Craw, D. and Fallick, A.E. 1994. Stable isotopic and fluid inclusion evidence for meteoric fluid penetration into an active mountain belt: Alpine schist, New Zealand: *Journal of metamorphic Geology*, v.12, p.429-444.
- Kelley, S.P. and Fallick, A.E. 1990. High precision spatially resolved analysis of d³⁴S in sulphides using a laser extraction technique: *Geochimica et Cosmochimica Acta*, v.54, p.883-888.
- Kelly, W.C. and Rye, R.D. 1979. Geologic, fluid inclusion, and stable isotope studies of the tin-tungsten deposits of Panasqueira, Portugal: *Economic Geology*, v.74, p.1721-1822.
- Kerr, R.A. 1984. Continental drilling heading deeper: *Science*, v.224, p.1418-1420.
- Kerr, R.A. 1993. Looking - deeply - into the Earth's crust in Europe: *Science*, v.261, p.295-297.
- Kerrick, R. 1987. The stable isotope geochemistry of Au-Ag vein deposits in metamorphic rocks, *In:* Kyser, T.K., ed., *Stable isotope geochemistry of low temperature fluids: Short Course Handbook*, Mineralogical Association of Canada, v.13, p.287-336.
- Kieffer, S.W. 1982. Thermodynamics and lattice vibrations of minerals: 5. Applications to phase equilibria, isotopic fractionation, and high-pressure thermodynamic properties: *Review in Geophysics and Space Physics*, v.20, p.827-849.
- Kyser, T.K. 1987a. Stable isotope geochemistry of low temperature processes: *Short Course handbook*, Mineralogical Association of Canada, v.13, 452p.
- Kyser, T.K. 1987b. Equilibrium fractionation factors for stable isotopes, *In:* Kyser, T.K., Ed., *Stable isotope geochemistry of low temperature processes: Short Course handbook*, Mineralogical Association of Canada, v.13, p.1-84.

- Landis, G.P. and Rye, R.O. 1974. Geologic, fluid inclusion, and stable isotope studies of the Pasto Bueno tungsten-base metal ore deposit, northern Peru: Economic Geology, v.69, p.1025-1059.
- Lawrence, J.R. and Gieskes, J.M. 1981. Constraints on water transport and alteration in the oceanic crust from the isotopic composition of pore water: Journal of Geophysical Research, v.86, p.7924-7934.
- Long, A., Eastoe, Ch.J., Kaufmann, R.S., Martin, J.G., Wirt, L. and Finley, J.B. 1993. High-precision measurement of chlorine stable isotope ratios: *Geochimica et Cosmochimica Acta*, v.57, p.2907-2912.
- Lorin, J.C. 1992. Oxygen isotope analysis on the Caméca ims-300: Chemical Geology (Isotope Geoscience Section), v.101, p.193-195.
- Magaritz, M., Whitford, D.J. and James, D.E. 1978. Oxygen isotopes and the origin of high- $^{87}\text{Sr}/^{86}\text{Sr}$ andesites: *Earth and Planetary Science Letters*, v.40, p.220-230.
- McKinney, C.R., McCrea, J.M., Epstein, S. and Urey, H.C. 1950. Improvements in mass spectrometers for the measurement of small differences in isotope abundance ratios: *Reviews of Scientific Instruments*, v.21, p.724.
- Michard-Vitrac, A., Albarede, F., Dupuis, C. and Taylor, H.P. Jr. 1980. The genesis of Variscan (Hercynian) plutonic rocks: Inferences from Sr, Pb, and O studies on the Maladeta Igneous Complex, Central Pyrenees (Spain): Contributions to Mineralogy and Petrology, v.72, p.57-72.
- Misra, K.C. and Lu, C. 1992. Hydrothermal calcites from the Mississippi Valley-type Elmwood-Gordonsville zinc deposits, Central Tennessee, U.S.A: Fluid inclusion and stable isotope data: European Journal of Mineralogy, v.4, p.977-988.
- Nesbitt, B.E. 1996. Applications of oxygen and hydrogen isotopes to exploration for hydrothermal mineralization: Society of Economic Geologists, Newsletter 27, p.1-13.
- Nevle, R.J., Brandriss, M.E., Bird, D.K., McWilliams, M.O. and O'Neil, J.R. 1994. Tertiary plutons monitor climate change in East Greenland: *Geology*, v.22, p.775-778.
- Nielsen, H. 1979. Sulphur isotopes, *In:* Jäger, E. and Hunziger, J.C., ed., Lectures in isotope geology: Springer, p.283-312.
- Nier, A.O. 1947. A mass spectrometer for isotope and gas analysis.: *Reviews of Scientific Instruments*, v.18, p.398-411.
- Nier, A.O., Ney, E.P. and Inghram, M.G. 1947. A null method for the comparison of two ion currents ia a mass spectrometer: *Reviews of Scientific Instruments*, v.18, p.294.

- O'Neil, J.R. and Clayton, R.N. 1964. Oxygen isotope geothermometry, *In:* Craig, H., Miller, S.L. and Wasserburg, G.J., eds., Isotopic and cosmic chemistry. Dedicated to H.C. Urey on his seventieth birthday: North Holland Publishing Co., p.157-168.
- O'Neil, J. R. 1986. Theoretical and experimental aspects of isotopic fractionation, *In:* Valley, J.W., Taylor, H.P. Jr and O'Neil, J.R., eds., Stable isotopes in high temperature geological processes: Reviews in Mineralogy, Mineralogical Society of America, v.16, p.1-40.
- O'Neil, J. R. and Truesdell, A.H. 1991. Oxygen isotope fractionation studies of solute-water interactions, *In:* Taylor, H.P. Jr., O'Neil, J.R. and Kaplan, I.R., eds., Stable isotope geochemistry: A tribute to Samuel Epstein: Geochemical Society, p.17-25.
- Ohmoto, H. 1972. Systematics of sulfur and carbon isotopes in hydrothermal ore deposits: Economic Geology, v.67, p.551-578.
- Ohmoto, H. and Rye, R.O. 1974. Hydrogen and oxygen isotopic compositions of fluid inclusions in the Kuroko deposits, Japan: Economic Geology, v.69, p.947-953.
- Ohmoto, H. 1986. Stable isotope geochemistry of ore deposits, *In:* Valley, J.W., Taylor, H.P. Jr. and O'Neil, J.R., Eds., Stable isotopes in high temperature geological processes: Reviews in Mineralogy, Mineralogical Society of America, v.16, p.491-559.
- Pavlenkova, N.I. 1992. The Kola Superdeep Drillhole and the nature of seismic boundaries: Terra Nova, v.4, p.117-123.
- Pollard, P.J., Andrew, A.S. and Taylor, R.G. 1991. Fluid inclusion and stable isotope evidence for interaction between granites and magmatic hydrothermal fluids during formation of disseminated and pipe-style mineralization at the Zaaiplaats tin mine: Economic Geology, v.86, p.121-141.
- Poty, B., Leroy, J. and Jachimowicz, L. 1976. Un nouvel appareil pour la mesure des températures sous le microscope: l'installation de microthermométrie Chaixmeca: Bullétin Minéralogique, v.99, p.182-186.
- Powell, M.D. and Kyser, T.K. 1991. Analysis of $d^{13}C$ and $d^{18}O$ in calcite, dolomite, rhodochrosite and siderite using a laser extraction system: Chemical Geology (Isotope Geoscience Section), v.94, p.55-66.
- Puchelt, H., Sabels, B.R. and Hoering, T.C. 1971. Preparation of sulphur hexafluoride for isotope geochemical analysis: Geochimica et Cosmochimica Acta, v.35, p.625-628.
- Richet, P., Bottinga, Y. and Javoy, M. 1977. A review of hydrogen, carbon, nitrogen, oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules: Annual Review in Earth Planetary Science, v.5, p.65-110.

- Robinson, B.W. and Ohmoto, H. 1973. Mineralogy, fluid inclusions, and stable isotopes of the Echo Bay U-Ni-Ag-Cu deposits, Northwest Territories, Canada: Economic Geology, v.68, p.635-656.
- Robinson, B.W. and Kusakabe, M. 1975. Quantitative preparation of sulphur dioxide, for $^{34}\text{S}/^{32}\text{S}$ analysis, from sulfides by combustion with Cuprous oxide: Analytical Chemistry, v.47, p.1179-1181.
- Roedder, E., Ingram, B. and Hall, W.E. 1963. Studies of fluid inclusions, III: extraction and quantitative analysis of inclusions in the milligram range: Economic Geology, v.58, p.353-374.
- Roedder, E. 1972. The composition of fluid inclusions: U.S. Geological Survey, Professional Paper 440-JJ, 164p.
- Roedder, E. 1979. Fluid inclusions as samples of ore fluids, *In*: Barnes, H.L., Ed., Geochemistry of hydrothermal ore deposits, Wiley, p.684-737.
- Roedder, E. 1981. Origin of fluid inclusions and changes that occur after trapping, *In*: Hollister, L.S. and Crawford, M.L., ed., Fluid inclusions: Applications to petrology: Short Course Handbook, Mineralogical Association of Canada, v.6, p.101-137.
- Roedder, E. 1984. Fluid inclusions: Reviews in mineralogy, Mineralogical Society of America, v.12.
- Rye, R.O. and Ohmoto, H. 1974. Sulfur and carbon isotopes and ore genesis: A review: Economic Geology, v.69, p.826-842.
- Rye, R.O. and Sawkins, F.J. 1974. Fluid inclusion and stable isotope studies on the Casapalca Ag-Pb-Zn-Cu deposit, central Andes, Peru: Economic Geology, v.69, p.181-205.
- Sangster, D.F. 1983. Sediment-hosted stratiform lead-zinc deposits: Short Course Handbook, Mineralogical Association of Canada, v.8, 309 p.
- Santosh, M. 1992. Role of mantle carbon in Archean gold genesis in South India: Evidence from carbon stable isotopic composition of fluid inclusions: Journal Geological Society of India, v.40, p.127-134.
- Sasaki, A., Arikawa, Y. and Folinsbee, R.E. 1979. Kiba reagent method of sulphur extraction applied to isotopic work: Bulletin Geological Survey of Japan, v.30, p.241-245.
- Schöps, D. and Herzog, P.M. 1990. Sulfide composition and microthermometry of fluid inclusions in the Leg 111 sheeted dike section of Ocean Drilling Program Hole 504B, Costa Rica rift: Journal of Geophysical Research, v.95, p.8405-8418.

- Shanks, W.C. III and Criss, R.E. 1989. New frontiers in stable isotopic research: Laser probes, Ion probes, and small-sample analysis: U.S. Geological Survey, Bulletin 1890, 174p.
- Sharp, Z.D. 1990. A laser-based microanalytical method for the in situ determination of oxygen isotope ratios of silicates and oxides: *Geochimica et Cosmochimica Acta*, v.54, p.1353-1357.
- Sharp, Z.D. 1992. In situ laser microprobe techniques for stable isotope analysis: *Chemical Geology* (Isotope Geoscience Section), v.101, p.3-19.
- Sharp, Z.D. and Cerling, T.E. 1996. A laser GC-IRMS technique for in situ stable isotope analyses of carbonates and phosphates: *Geochimica et Cosmochimica Acta*, v.60, p.2909-2916.
- Sheppard, S.M.F. and Taylor, H.P. Jr. 1974. Hydrogen and oxygen isotopic evidence for the origins of water in the Boulder batholith and the Butte ore deposits, Montana: *Economic Geology*, v.69, p.926-946.
- Sheppard, S.M.F. 1977. The Cornubian batholith, SW England: D/H and $^{18}\text{O}/^{16}\text{O}$ studies of kaolinite and other alteration minerals: *Journal geological Society of London*, v.133, p.573-591.
- Sheppard, S.M.F. 1986. Characterization and isotopic variations in natural waters, *In: Valley, J.W., Taylor, H.P. Jr. and O'Neil, J.R., eds., Stable isotopes in high temperature geological processes: Reviews in mineralogy, Mineralogic Society of America*, v.16, p.165-183.
- Shieh, Y.N. and Taylor, H.P. Jr. 1969. Oxygen and carbon isotope studies of contact metamorphism of carbonate rocks.: *The Journal of Petrology*, v.10, p.307-331.
- Simon, K. and Hoefs, J. 1993. O, H, C isotope study of rocks from the KTB pilot hole: Crustal profile and constraints on fluid evolution: *Contributions to Mineralogy and Petrology*, v.114, p.42-52.
- Smalley, P.C., Stijfhoorn, D.E., Råheim, A., Johansen, H. and Dickson, J.A.D. 1989. The laser microprobe and its application to the study of C and O isotopes in calcite and aragonite: *Sedimentary Geology*, v.65, p.211-221.
- Smalley, P.C., Maile, C.N., Coleman, M.L. and Rouse, J.E. 1992. LASSIE (Laser ablation sampler for stable isotope extraction) applied to carbonate minerals: *Chemical Geology* (Isotope Geoscience Section), v.101, p.43-52.
- Stern, C., de Wit, M.J. and Lawrence, J.R. 1976. Igneous and metamorphic processes associated with the formation of Chilean ophiolites and their implication for ocean floor metamorphism, seismic layering, and magmatism: *Journal of Geophysical Research*, v.81, p.4370-4380.

- Suchchevskaya, T.M., Devirts, A.A., Lagutina, Ye.P. and Kiryukhin, V.A. 1991. Hydrogen-isotope composition of the water in fluid inclusions in quartz and the origin of the Sn mineralization at the Solnechnoye deposit, Khabarovsk Kray: Geochemistry International, v.28, p.120-125.
- Suzuoki, T. and Epstein, S. 1976. Hydrogen isotope fractionation between OH-bearing minerals and water: *Geochimica et Cosmochimica Acta*, v.40, p.1229-1240.
- Taylor, B.E. and O'Neil, J.R. 1977. Stable isotope studies of metasomatic Ca-Fe-Al-Si skarns and associated metamorphic and igneous rocks, Osgood Mountains, Nevada: Contributions to Mineralogy and Petrology, v.63, p.1-49.
- Taylor, B.E. 1987. Stable isotope geochemistry of ore-forming fluids, *In:* Kyser, T.K., Ed., Stable isotope geochemistry of low temperature fluids: Short Course Handbook, Mineralogical Association of Canada, v.13, p.337-445.
- Taylor, H.P. Jr. 1971. Oxygen isotope evidence for large-scale interaction between meteoric ground waters and Tertiary granodiorite intrusions, western Cascade Range, Oregon: *Journal of Geophysical Research*, v.76, p.7855-7874.
- Taylor, H.P. Jr. 1973. O¹⁸/O₁₆ Evidence for meteoric-hydrothermal alteration and ore deposition in the Tonopah, Comstock Lode, and Goldfield Mining Districts, Nevada: *Economic Geology*, v.68, p.747-764.
- Taylor, H.P. Jr. 1974. The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition: *Economic Geology*, v.69, p.843-883.
- Taylor, H.P. Jr. 1977. Water/rock interactions and the origin of H₂O in granitic batholiths: *Journal of the Geological Society of London*, v.133, p.509-558.
- Taylor, H.P. Jr. 1979. Oxygen and hydrogen isotope relationships in hydrothermal mineral deposits, *In:* Barnes, H.L., Ed., *Geochemistry of hydrothermal ore deposits*, Wiley & Sons, p.236-277.
- Taylor, H.P. Jr. and Forester, R.W. 1979. An oxygen and hydrogen isotope study of the Skaergaard intrusion and its country rocks: A description of a 55 M.Y. old fossil hydrothermal system: *The Journal of Petrology*, v.20, p.355-419.
- Taylor, H.P. Jr. 1980. The effects of assimilation of country rocks by magmas on ¹⁸O/¹⁶O and ⁸⁷Sr/⁸⁶Sr systematics in igneous rocks: *Earth and Planetary Science Letters*, v.47, p.243-254.
- Taylor, H.P. Jr. and Sheppard, S.M.F. 1986. Igneous rocks: I. Processes of isotopic fractionation and isotopic systematics, *In:* Valley, J.W., Taylor, H.P. Jr. and O'Neil, J.R., eds., *Stable isotopes in high temperature geological processes: Reviews in Mineralogy*, Mineralogical Society of America, v.16, p.227-271.

- Taylor, H.P. Jr., O'Neil, J.R. and Kaplan, I.R. 1991. Stable isotope geochemistry: A tribute to Samuel Epstein, The Geochemical Society, Special Publication No.3, 504p.
- Turner, D.R. and Bowman, J.R. 1992. Origin and evolution of skarn fluids, Empire zinc skarns, Central Mining District, New Mexico, U.S.A: Applied Geochemistry, v.8, p.9-36.
- Valley, J.W., 1986. Stable isotope geochemistry of metamorphic rocks, *In:* Valley, J.W., Taylor, H.P. Jr. and O'Neil, J.R., Eds., Stable isotopes in high temperature geological processes: Mineralogical Society of America, v.16, p.445-489.
- Valley, J.W., Taylor, H.P. Jr. and O'Neil, J.R. 1986. Stable isotopes in high temperature geological processes: Reviews in Mineralogy, Mineralogical Society of America, v.16, 570p.
- Veizer, J., Holser, W.T. and Wilgus, C.K. 1980. Correlation of $^{13}\text{C}/^{12}\text{C}$ and $^{34}\text{S}/^{32}\text{S}$ secular variations.: *Geochimica et Cosmochimica Acta*, v.44, p.579-587.
- Vennemann, T.W. and Smith, H.S. 1990. The rate and temperature of reaction of ClF₃ with silicate minerals, and their relevance to oxygen isotope analysis: *Chemical Geology* (Isotope Geoscience Section), v.86, p.83-88.
- Wiechert, U. and Hoefs, J. 1995. An excimer laser-based micro analytical preparation technique for in-situ oxygen isotope analysis of silicate and oxide minerals: *Geochimica et Cosmochimica Acta*, v.59, p.4093-4101.
- Yanagisawa, F. and Sakai, H. 1983. Thermal decomposition of barium sulphate - vanadium pentaoxide - silica glass mixtures for preparation of sulfur dioxide in sulfur isotope ratio measurements: *Analytical Chemistry*, v.55, p.985-987.
- Zheng, Y.-F. 1991. Calculation of oxygen isotope fractionation in metal oxides: *Geochimica et Cosmochimica Acta*, v.55, p.2299-2307.
- Zheng, Y.-F. 1993a. Calculation of oxygen isotope fractionation in hydroxyl-bearing silicates: *Earth and Planetary Science Letters*, v.120, p.247-263.
- Zheng, Y.-F. 1993b. Calculation of oxygen isotope fractionation in anhydrous silicate minerals: *Geochimica et Cosmochimica Acta*, v.57, p.1079-1091.

____ oOo ____