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Bruce F. Schaefer
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Isotopes and geochemistry

1.1 Introduction

Economic geology is, at heart, the most fundamental form of applied geochemistry. In essence, the industry professional is focused on understanding where accumulations of geochemical anomalies (i.e. the mineralisation) occur. Whether that be in an exploration setting or a resource evaluation context, all geologists involved in this task are trying to pinpoint where a certain element (or elements) are located. In this task a large number of tools are applied: understanding the relationship of mineralogy to structure, fluid pathways, relative timing and often the association of economic commodities with other, more common, chemical proxies.

In essence, isotopes are simply the most distinctive chemical proxy a geologist can have in the toolkit – they are (trace) elements with labels on them. These labels, when interrogated, allow us to varying degrees to investigate when and how the elements got to where they are today. However, often the information isotopes contain is not utilised effectively – the reasons for this are many, including geological and educational. Often, even the specialist needs to refer back to a source of information or reference when understanding a system they have not used for some time or may not have encountered previously, and the same is certainly true of isotopes. Sometimes perceived complexity can obscure fundamental simple understanding, and the converse can be true as well.

This contribution attempts to make the sometimes arcane world of isotopes more accessible and tractable for those who have had little or no formal background in isotope geochemistry, while maintaining a level of sophistication and detail that allows those more familiar with the issues to maximise the benefits of isotopic data sets. To this end, there is some basic background regarding nomenclature and shorthand that the reader should familiarise themselves with, but at heart it is worth remembering that although we are dealing with isotopes and often ‘nuclear’ processes, the way these are distributed in the earth is often controlled by more familiar *chemical* processes. From this basis, a linking of chemistry with the nucleus allows us to interrogate the geological record and apply that understanding in a huge range of situations in the minerals industry. Thus, the isotopic toolkit primarily contains methods of determining when events took place (geochronology) and fingerprinting where elements have come from (geotracing). However, there are many applications which involve the 'how'; and hence at every level the processes involved in the system of interest are intrinsically embedded within understanding. An upshot of this is that a single tool does not enjoy universal application – just because Re–Os molybdenite geochronology might date sulphide mineralisation in one setting does not mean that all molybdenites globally will date their associated sulphide assemblages. At heart, isotopes are only as good as the geological understanding of the situation in which they are being applied, and therefore the geologist needs to consider all possible interpretations. Hopefully this contribution will aid professionals who are time-poor in achieving a fuller understanding of their particular problem, and in some cases possibly encourage them to try new techniques or ideas for situations that were previously ambiguous.

How to use this book

This book is not intended to be a textbook in the instructional sense, although one could use it as such if one wished. Rather, this book is intended to serve as a reference guide for persons with some appreciation of geochemistry and in all likelihood previous exposure to isotopes. Therefore, the user is encouraged instead to dip into the book at the section of interest, which should generally be 'stand-alone' in terms of concepts and applications. This inevitably results in repetition within the book between sections – for example, the introduction to the radioactive decay schemes in Part I is re-emphasised and elaborated further in Part II; however, it is not necessary to have read the section in Part I on the isotope system of interest in order to follow the arguments in Part II.

I also have not shied away from including relevant equations where appropriate. While the equations may appear daunting to those who are not mathematically inclined, I have generally included only those that require no knowledge of calculus, and hence readers with a basic understanding of algebra should be able to use these with ease. The purpose of this is to allow the reader to actually manipulate and recalculate the data they obtain, and form their own interpretations. I have also attempted to include currently accepted values for decay constants and geochemical reservoirs in order to allow the reader to conduct their own modelling and to act as a ready reference. Again, some of the reservoir values are a matter of preference; however, the ability to choose and (re)calculate model ages etc. may greatly aid the explorationist in targeting

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prospective lithologies. Other equations are included purely by means of explanation – some of the logic chains for the reasoning behind the principles described can be summarised succinctly in the language of mathematics, and the more numerate may prefer to view things from this perspective.

Finally, although not the focus of this book, it is inevitable that stable isotopes form a significant portion of the geochemist's repertoire. Therefore I have included a holistic introduction to nomenclature and processes in Part I which forms a basis for understanding both stable and radiogenic isotopes. From this holistic basis it is hoped that the reader can gain an appreciation of the processes responsible for fractionation in all settings, rather than dealing with radiogenic decay in isolation. Chapter 4 therefore attempts to give a flavour for the nature of stable isotope geochemistry in order to allow the reader to navigate the extensive literature available, but is by no means intended to be comprehensive or exhaustive! However, an integrated approach is necessary for a complete understanding of *any* system, and the burgeoning field of transition metal stable isotope geochemistry offers one of the great growth areas in the geosciences.

1.2 Elements and isotopes

Economic geology deals with chemical processes, usually centred upon the behaviour of a single key chemical element, say Pb, Au or Cu. However, many elements contain isotopes, which are in essence chemically identical with each other, but have a different mass due to their nuclear structure. This difference in nuclear configuration permits two fundamental types of behaviour that geochemists can use – namely *fractionation* of masses (isotopes) of the same element, and *radioactive decay* from one element to another. In order to understand these, we need first to clarify what they are and distinguish between some important terms when describing atomic structure.

1.2.1 Atoms, ions and isotopes

An atom is the smallest component of a chemical element that retains the chemical properties of that element. Atoms contain three fundamental particles: **protons** and **neutrons**, which occur in the nucleus and are hence termed **nucleons**; and **electrons**, which orbit the dense nucleus. Protons and neutrons have approximately the same mass, whereas the electron is ~2000 times lighter than the nucleons. For the purposes of geological nuclear chemistry it is usually regarded as having negligible mass. Protons and neutrons weigh ~1 atomic mass unit (amu). An atom is electrically neutral, since the number of orbiting negatively charged electrons balances the number of positively charged protons in the nucleus. Neutrons have no electrical charge.

The number of protons defines the **atomic number (Z)**, and therefore which element it is. In other words, each element has a unique atomic number (e.g. Cu = 29; Au = 79), which governs the corresponding number of electrons and hence the chemical properties of the element. The **atomic mass number (A)** of an element is the total number of nucleons it contains, i.e. the sum of the protons (Z) and the neutrons (N). Therefore $A = N + Z$.

An **ion** is an electrically charged atom; this charge can occur by loss or gain of electrons. This ability to change charge controls the chemical behaviour of the element, which is governed by ions attempting to become electrically stable. A hydrogen atom (H) can *lose* an electron to become *positively* charged since it has one proton more than it has electrons, and hence becomes a hydrogen ion, H^+. Conversely, a chlorine atom can gain an electron to form a chloride ion, Cl^-. These can combine to form an electrically neutral molecule, HCl; i.e.:

$$H^+ + Cl^- \rightarrow HCl.$$

A **cation** is a positively charged ion (i.e. one which has fewer electrons than protons) and an **anion** is negatively charged (containing an excess of electrons). In the above example, H^+ is the cation and Cl^- the anion. Generally, metals produce cationic species and non-metals anionic; however, there are very significant exceptions to these generalisations (particularly among the non-metals, such as S, As and Te).

A **molecule** is therefore the smallest freely existing part of a substance that retains the chemical properties of that substance. They can be multielemental (most common, e.g. HCl, H_2O), monoelemental (e.g. O_2, N_2) and even monoatomic (rare, e.g. Ar gas, Au metal). In geology, we are primarily dealing with molecular materials which are crystalline (e.g. silicates and sulphides) or less frequently ionic species which are dissolved in fluids (e.g. ligands and dissolved metals).

1.2.2 Isotopes

All atoms of a given element have the same number of protons (i.e. they have the same Z); however, they do not necessarily have the same number of neutrons (i.e. they can have different A). These are said to be **isotopes** of the element. Isotopes have (essentially) identical chemical properties, since these are determined by the number of electrons, which is in turn controlled by the number of protons in the nucleus.

The neutrons are necessary to provide a mechanism by which the nuclear force is able to bind protons together – otherwise the positive electromagnetic repulsion drives protons apart and no elements heavier than H would be able to form. The number of neutrons (N) required to prevent the positively charged protons

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from repelling each other is generally greater than or equal to the number of protons (the only stable exceptions to this in nature are ^{1}H (simply one proton) and ^{3}He (two protons and one neutron).

Hence the atomic structure for an element E can be written in shorthand notation as:

$$^{A}_{Z}E$$

Note that *chemical* formulae, whether expressing the charge on an ion, or the number of atoms in a molecule, always use super- and subscripts on the right-hand side of the elemental symbol. By contrast, *nuclear* and hence isotopic properties, such as atomic number (Z) and atomic mass (A) are always expressed using super- and subscripts on the left-hand side of the elemental symbol.

Thus, **isotopes** of a given element are nucleii which have varying A for a constant Z; i.e. variable numbers of neutrons for a given number of protons. E.g. in nature, hydrogen has three isotopes, ^{1}H, ^{2}H (aka deuterium) and ^{3}H (aka tritium) containing zero, one and two neutrons, respectively. However, they all contain only one proton ($Z = 1$). Thus for a given element (i.e. constant Z) there may be a number of different values of A which result in a stable nucleus. Other configurations, such as tritium, may result in either overly light or excessively heavy nucleii which are unstable, and will ultimately fall apart through nuclear (radioactive) decay.

A perhaps more pertinent example to solid earth geochemistry is illustrated in Figure 1.1. The element Sr ($Z = 38$) comprises four naturally occurring isotopes;

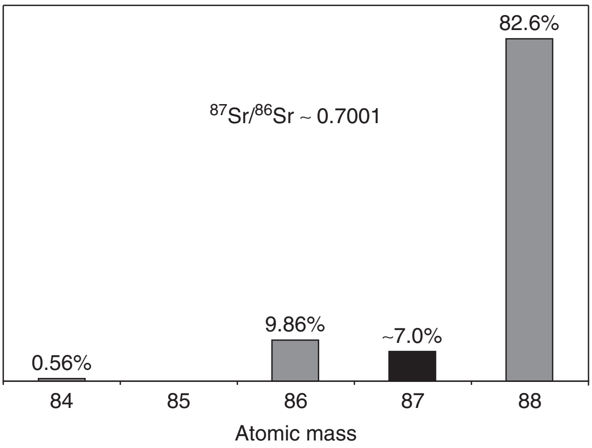

Figure 1.1 An example of an element (Sr) containing isotopes in different relative proportions. Note that ^{87}Sr is continually accumulating due to the decay of ^{87}Rb, and hence the relative proportion of ^{87}Sr with respect to the other isotopes of Sr increases over time.

the most common of these is ^{88}Sr. Significantly, each of these isotopes is stable. Therefore the ratio of ^{86}Sr/^{88}Sr will not be modified by radioactivity. In contrast, ^{87}Sr, despite being stable, is constantly being formed due to the radioactive decay of an isotope of Rb, namely ^{87}Rb. Therefore the relative proportion of ^{87}Sr with respect to ^{86}Sr will change over time. Such changes in the abundances of certain isotopes form the basis of one of the most powerful tools in geochemistry and is at the heart of geochronology. This will be investigated further in Chapter 5, but it is useful to note at this point that the approach of measuring relative ratios of the isotopes, rather than their absolute abundances (i.e. reporting the ^{87}Sr/^{86}Sr ratio rather than the actual number of ^{87}Sr and ^{88}Sr atoms present) is central to both the measurement of isotopes and their interpretation. The reasons for this are both instrumental and mathematical.

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Processes

At this point, with an appreciation of what an isotope actually is with respect to a chemical element and/or an ion, it is useful to investigate the processes that can cause variations in the relative proportions of the isotopes of an element. At heart, this is the key to the isotope geochemistry, as it is the *changes* in isotopic ratios that inform geoscientists of rates and process.

2.1 Fractionation: chemical vs isotopic

In essence, isotope geochemistry is an understanding of fractionation, a term that is used in a range of applications and situations. Fractionation is used in several confusing contexts in geochemistry, and it is important to distinguish between *chemical* fractionation and *isotopic* fractionation.

Although it is often clear from the context, chemical fractionation is the process by which a mixture is separated into smaller quantities of differing compositions. That is, changing the chemical composition through successive operations (e.g. crystallisation, boiling, precipitation), each of which removes one or other of the constituents. Such a process is driven by a gradient, generally thermal or chemical, but it can also be physical. Hence chemical fractionation drives differentiation of magmas (e.g. fractional crystallisation), or can occur during boiling and/or phase separation of hydrothermal fluids. Significantly, however, all chemical fractionation processes generally refer to changing chemical proportions or phases.

A commonly observed example of chemical fractionation in the earth sciences is the presence of the Eu anomaly in magmas crystallising plagioclase (Figure 2.1). Unlike the other rare earth elements (REE), Eu is unique in that it can form Eu^{2+} ions which are small enough to sit happily in the crystal lattice instead of the Ca^{2+} ions which make up the bulk of the crystal. In this case the Eu is said to substitute for Ca, and is extracted from the magma preferentially with respect to the other REE, which are otherwise chemically very similar to Eu. This has the result that the remaining liquid

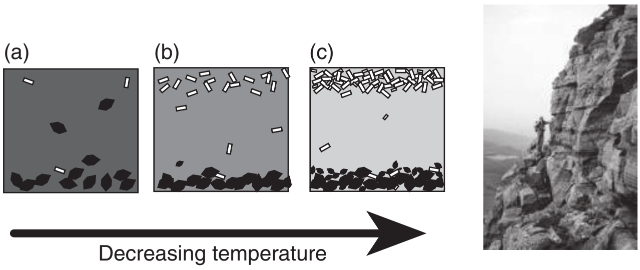

Figure 2.1 A schematic example of chemical fractionation as observed in a hypothetical crystallising magma chamber. A mafic magma may crystallise olivine (a), which is dense and accumulates in the bottom of the chamber. Due to the change in composition of the magma, plagioclase crystallisation is promoted (b), which is less dense and accumulates at the top of the chamber. Crystallisation continues until either the magma has frozen solid or the fractionated liquid in panel (c) is extracted, leaving cumulates of alternating light and dark bands, as observed in the layered ultramafic complex on the Isle of Rum, Scotland.

will not have as much Eu as expected, since it is locked up (fractionated) in the plagioclase. If the magma subsequently separates from the plagioclase and crystallises elsewhere, when we analyse it and observe the presence of the negative Eu anomaly we can infer the role of plagioclase fractionation. Thus chemical fractionation occurs in almost every geological process, and in essence ore deposits are the end product of the most impressive chemical fractionation processes operating in the crust.

2.2 Isotopic fractionation

Chemical fractionation may itself impart an isotopic fractionation between the starting material and the product(s). However, it is useful to think of isotopic fractionation as *any* process which is able to change the *ratio* of two isotopes of the *same chemical element*, and this can occur via four fundamental processes:

(1) equilibrium fractionation
(2) kinetic fractionation
(3) transient kinetic fractionation
(4) mass independent fractionation.

A fifth process, radioactive decay, also changes the isotopic ratios of an element, but the process is distinctly different (i.e. is nuclear, not physicochemical) and is worth considering independently (see Chapter 5). Of these four processes, the first two are of great importance in understanding mineralised systems. The third, transient kinetic fractionation, undoubtedly takes place; however, the geological record does not preserve its effects due to the time scales involved. Mass

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independent fractionation is only now being routinely measured in some isotope systems and is likely to become of greater significance in ore deposit studies in the future.

2.2.1 Equilibrium fractionation

This is the partial separation of isotopes between two or more substances which are in chemical equilibrium: i.e. the forward and backward reaction rates between the reactants are identical. Light isotopes remain in the higher-energy state as the heavier isotopes energetically favour the low-energy state. Most equilibrium fractionations are considered to take place from the reduction in vibrational energy within a molecule when a heavier isotope is substituted for a lighter one.

Significantly, each reactant molecule is identical to a product molecule except for the change in distribution of isotopes. In chemistry such molecules are described as isotopologues.

For example, the equilibrium exchange between quartz and haematite:

$$2\mathrm{Si}^{16}\mathrm{O}_2 + \mathrm{Fe}_3{}^{18}\mathrm{O}_4 \Leftrightarrow 2\mathrm{Si}^{18}\mathrm{O}_2 + \mathrm{Fe}_3{}^{16}\mathrm{O}_4.$$

In this example, the Si–O bond is stronger than the Fe–O and so the reduction in vibrational energy is greater when a heavier O isotope (either ^{17}O or ^{18}O) is substituted for ^{16}O.

Similarly, phase-change reactions, such as evaporation of water or melting of ice, are equilibrium processes (when in a closed system) and are therefore able to fractionate isotopes. The heavy isotopes are invariably concentrated in the denser phase, e.g.:

$$\mathrm{H_2}{}^{16}\mathrm{O}_{(l)} + \mathrm{H_2}{}^{18}\mathrm{O}_{(g)} \Leftrightarrow \mathrm{H_2}{}^{18}\mathrm{O}_{(l)} + \mathrm{H_2}{}^{16}\mathrm{O}_{(g)}$$

and

$$\mathrm{H_2}{}^{16}\mathrm{O}_{(s)} + \mathrm{H_2}{}^{18}\mathrm{O}_{(l)} \Leftrightarrow \mathrm{H_2}{}^{18}\mathrm{O}_{(s)} + \mathrm{H_2}{}^{16}\mathrm{O}_{(l)}.$$

Equilibrium processes are quite common, and can be quite temperature sensitive. Such fractionations form the basis of many of the commonly applied palaeothermometers (O and H isotopes in ice cores, speleothems). The effects are strongest at low temperatures, and in general the isotopes of lighter elements are more susceptible to the effects since the relative difference in mass between the isotopes is greater. For example, ^{2}H is twice as heavy as ^{1}H, and ^{18}O is 12.5 per cent heavier than ^{16}O.

Such behaviour can be described in terms of the **fractionation factor**, α:

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$$\alpha = \frac{({}^{\mathrm{h}}X/{}^{\mathrm{l}}X)_{AX}}{({}^{\mathrm{h}}X/{}^{\mathrm{l}}X)_{BX}}, \qquad \text{(Eq 2.1)}$$

where h and l refer to the heavy and light isotopes of element X in compounds AX and BX. For $\alpha = 1$, the isotopes are distributed evenly between the reactant and product, and hence no isotopic fractionation takes place. $\alpha > 1$ indicates that the heavy isotope is preferentially distributed into substance AX, whereas $\alpha < 1$ indicates that the heavy isotope is concentrated into BX. Using the quartz–haematite example above:

$$\alpha = \frac{({}^{18}\mathrm{O}/{}^{16}\mathrm{O})_{\mathrm{qtz}}}{({}^{18}\mathrm{O}/{}^{16}\mathrm{O})_{\mathrm{hem}}}. \qquad \text{(Eq 2.2)}$$

Note that convention dictates that isotopes are generally expressed in ratios of heavy over light (${}^{\mathrm{h}}X/{}^{\mathrm{l}}X$), so you will often see ${}^{18}O/{}^{16}O$, ${}^{2}H/{}^{1}H$, etc. Exceptions do exist, so it is important to always pay attention to the system in question (see Section 4.1).

Equilibrium fractionation is a type of **mass dependent** fractionation, as the masses of the isotopes involved are controlling or playing a role in their subsequent distribution. Such fractionations are intuitively more readily grasped than **mass independent fractionation** (see Section 2.2.4).

2.2.2 Kinetic fractionation

Kinetic fractionation occurs when the forward and backward reaction rates are not the same, and hence there is a preferred ‘direction’ in the reaction. It is useful to think of kinetic effects as being associated with chemical reactions in which chemical bonds are being broken and new ones being formed. Hence the reaction rates, and therefore relative proportions of isotopes available to be incorporated in the products, can be thought to be a function of the vibrational energy of the bond in question. Since the vibrational energy is itself a consequence of the relative masses of the isotopes at either end, then different isotopes of an element occupying the same chemical bond will react at different rates. Since heavier isotopes will react more slowly than lighter ones, residual reactants will become enriched in heavy isotopes and products enriched in light ones.

Such examples are well illustrated in organic systems, specifically by the relative behaviours of the C–H bond. Substituting a ${}^{1}H$ with ${}^{2}H$ represents a change in mass of 100 per cent, whereas substituting a ${}^{12}C$ with ${}^{13}C$ represents only an 8 per cent mass increase. Significantly, reactions involving a ${}^{12}C$–${}^{1}H$ bond are typically