1 Geochemical Data

1.1 Introduction

This book is about geochemical data and how they can be used to obtain information about geological processes. The major focus of this book is petrological, and the principal themes are the applications of geochemical data to igneous, sedimentary and metamorphic petrology. Minor themes include the application of geochemical data to cosmochemistry and the study of meteorites and to mineral exploration geochemistry. This book does not cover the topics of organic chemistry, hydro-geochemistry, solution chemistry or gas geochemistry and touches only briefly on the subject of environmental geochemistry. For a detailed discussion of these subdisciplines of geochemistry, the reader is referred elsewhere.

Conventionally geochemical data are subdivided into four main categories; these are the major elements, trace elements, radiogenic isotopes and stable isotopes and these four types of geochemical data each form a chapter in this book. Each chapter shows how the particular form of geochemical data can be used and how it provides clues to the processes operating in the suite of rocks in question. Different methods of data presentation are discussed and their relative merits evaluated.

The major elements (Chapter 3) are the elements which predominate in any rock analysis. In silicate rocks they are normally Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and P, and their concentrations are expressed as a weight percent (wt.%) of the oxide (Table 1.1). Major element determinations are usually made only for cations and it is assumed that they are accompanied by an appropriate amount of oxygen. Thus, the sum of the major element oxides will total to about 100% and the analysis total may be used as a rough guide to its reliability. Iron may be determined as FeO and/or Fe₂O₃, but is frequently expressed as ‘total Fe’ and given as Fe₂O₃(tot), Fe₂O₃(t) or Fe₂O₃T. Anions are not routinely determined.

Trace elements (Chapter 4) are defined as those elements which are present at less than the 0.1 wt.% level and their concentrations are expressed in parts per million (ppm) or more rarely in parts per billion (10⁻⁹ = ppb) of the element (Table 1.1). Convention is not always followed, however, and trace element concentrations exceeding the 0.1 wt.% (1000 ppm) level are sometimes cited. The trace elements of importance in geochemistry are shown in Figure 4.1.

Some elements behave as major elements in one group of rocks and as a trace element in another group of rocks. An example is the element K, which is a major constituent of rhyolites, making up more than 4 wt.% of the rock and forming an essential structural part of minerals such as orthoclase and biotite. In some basalts, however, K concentrations are very low and there are no K-bearing phases. In this case K behaves as a trace element.

Volatile species such as H₂O, CO₂ and S can be included in the major element analysis. Water combined within the lattice of silicate minerals and released above 110°C is described as H₂O++. Water present simply as dampness in the rock powder and driven off by heating to 110°C is quoted as H₂O− and is not an important constituent of the rock. Most frequently the total volatile content of the rock is determined by ignition at 1000°C and is expressed as loss on ignition (LOI) as in Table 1.1 (Lechler and Desilets, 1987).

Isotopes are subdivided into radiogenic and stable isotopes. Radiogenic isotopes (Chapter 6) include those isotopes which decay spontaneously due to their natural radioactivity and those which are the daughter products of such a decay scheme. They include the parent-daughter element pairs K-Ar, Rb-Sr, Sm-Nd, Lu-Hf, U-Pb and Re-Os. They are expressed as ratios relative to a non-radiogenic isotope such as ⁸⁷Sr/⁸⁶Sr (Table 1.1) in which ⁸⁶Sr is the radiogenic isotope. Stable isotope studies in geochemistry (Chapter 7) concentrate on the naturally occurring isotopes of light elements such as H, O, C, S and N and a wide range of metallic elements (see Figure 7.29) which may be fractionated on the basis of mass differences between the isotopes of the element. For example, the isotope ¹⁸O is 12.5% heavier than the isotope ¹⁶O and the two are fractionated during the evaporation of water. Stable isotopes contribute significantly to an understanding of fluid and volatile species in geology. They are expressed as...
Geochemical Data

Table 1.1 Geochemical data for peraluminous granites from the North Qilian suture zone, China (after Chen et al., 2014)

<table>
<thead>
<tr>
<th>Sample</th>
<th>09QL-01</th>
<th>09QL-03</th>
<th>11QL-32</th>
<th>11QL-35</th>
<th>09QL-01</th>
<th>09QL-03</th>
<th>11QL-32</th>
<th>11QL-35</th>
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</thead>
<tbody>
<tr>
<td><strong>Major elements (wt.%)</strong></td>
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<td></td>
<td></td>
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<tr>
<td>SiO$_2$</td>
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<td>71.35</td>
<td>69.17</td>
<td>72.57</td>
<td>71.56</td>
<td>72.13</td>
<td>69.92</td>
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<td>0.61</td>
<td>0.37</td>
<td>0.42</td>
<td>0.39</td>
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<td>0.41</td>
</tr>
<tr>
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<td>2.55</td>
<td>4.07</td>
<td>2.46</td>
<td>2.92</td>
<td>2.58</td>
<td>4.11</td>
<td>2.49</td>
</tr>
<tr>
<td>MnO</td>
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<td>0.05</td>
<td>0.06</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>MgO</td>
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<td>1.42</td>
<td>0.78</td>
<td>1.24</td>
<td>0.87</td>
<td>1.44</td>
<td>0.79</td>
</tr>
<tr>
<td>CaO</td>
<td>1.10</td>
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<td>3.31</td>
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<td>1.11</td>
<td>2.03</td>
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<tr>
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<td>1.60</td>
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<td>3.54</td>
<td>2.52</td>
<td>1.62</td>
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<tr>
<td>K$_2$O</td>
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<td>4.72</td>
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<tr>
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<td>0.08</td>
<td>0.12</td>
<td>0.07</td>
<td>0.09</td>
<td>0.08</td>
<td>0.12</td>
<td>0.07</td>
</tr>
<tr>
<td>LOI</td>
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<td>1.08</td>
<td>1.06</td>
<td>1.08</td>
<td>1.03</td>
<td>1.08</td>
<td>1.06</td>
<td>1.08</td>
</tr>
</tbody>
</table>

| **Major elements (wt.%) recalculated dry** |         |         |         |         |         |         |         |         |
| SiO$_2$      | 71.56   | 72.13   | 69.92   | 73.37   | 71.56   | 72.13   | 69.92   | 73.37   |
| TiO$_2$      | 0.38    | 0.32    | 0.62    | 0.37    | 0.42    | 0.39    | 0.78    | 0.41    |
| Fe$_2$O$_3$T | 2.92    | 2.58    | 4.11    | 2.49    | 2.92    | 2.58    | 4.11    | 2.49    |
| MnO          | 0.04    | 0.05    | 0.06    | 0.05    | 0.04    | 0.05    | 0.06    | 0.05    |
| MgO          | 1.24    | 0.87    | 1.44    | 0.79    | 1.24    | 0.87    | 1.44    | 0.79    |
| CaO          | 1.11    | 2.03    | 3.35    | 2.60    | 1.11    | 2.03    | 3.35    | 2.60    |
| Na$_2$O      | 3.54    | 2.52    | 1.62    | 1.68    | 3.54    | 2.52    | 1.62    | 1.68    |
| K$_2$O       | 4.57    | 4.72    | 3.41    | 4.28    | 4.57    | 4.72    | 3.41    | 4.28    |
| P$_2$O$_5$   | 0.09    | 0.08    | 0.12    | 0.07    | 0.09    | 0.08    | 0.12    | 0.07    |

| **Radiogenic isotopes** |         |         |         |         |         |         |         |         |
| $^{87}$Rb/$^{86}$Sr   | 4.5490  | 4.7470  | 2.5920  | 3.0480  | 4.5490  | 4.7470  | 2.5920  | 3.0480  |
| $^{87}$Rb/$^{86}$Sr   | 0.7640  | 0.7780  | 0.7541  | 0.7598  | 0.7640  | 0.7780  | 0.7541  | 0.7598  |
| $^{147}$Sm/$^{144}$Nd | 0.1260  | 0.1230  | 0.1190  | 0.1250  | 0.1260  | 0.1230  | 0.1190  | 0.1250  |
| $^{147}$Sm/$^{144}$Nd | 0.5121  | 0.5120  | 0.5121  | 0.5121  | 0.5121  | 0.5120  | 0.5121  | 0.5121  |

a nd, not determined; data not reported using significant figures.

An example of a typical geochemical dataset is given in Table 1.1 for a suite of peraluminous biotite monzogranites from the Chaidanuo batholith from the North Qilian suture zone in central China from the study by Chen et al. (2014). This dataset shows the major elements with Fe given as Fe$_2$O$_3$T and the volatiles as LOI (Section 3.1.1). The data are also recalculated dry, that is, volatile free. In this study the major elements were determined by inductively coupled plasma optical-emission spectroscopy (ICP-OES). The trace elements reported in Table 1.1 were measured by

ratios relative to a standard using the $\delta$-notation (see Section 7.2.1.1).
inductively coupled plasma mass spectrometry (ICP-MS) and this long list of trace elements shows the range of trace elements readily determined using this method. Where a particular element is not measured it is designated ‘nd’ (not determined) and where it cannot be determined because it is below the limits of detection of the analytical method used it may be reported as ‘bd’. The radiogenic isotopes of Sr and Nd were measured using thermal ionisation mass spectrometry (TIMS).

The major part of this book discusses the four main types of geochemical data outlined above and shows how they can be used to identify and understand geochemical processes. In addition, Chapter 5 shows the way in which trace and major element chemistry is used to determine the tectonic setting of some igneous and sedimentary rocks. Chapter 2 discusses some of the particular statistical problems which arise when analysing geochemical datasets and some recommendations are made about permissible and impermissible methods of data presentation.

In this introductory chapter we consider three topics:

1. The geochemical processes which are likely to be encountered in nature and their geochemical signatures.
2. The interaction between geological fieldwork and the interpretation of geochemical data.
3. The different analytical methods currently used in modern geochemistry.

### 1.2 Geological Processes and Their Geochemical Signatures

A major purpose of this text is to show how geochemical data can be used to identify and interpret geological processes. In this section, therefore, we review the main processes which have taken place during the formation and differentiation of our rocky planet and which have subsequently shaped it into the form that we recognise today.

It is conventional in geochemistry to distinguish between those processes which take place at high temperatures, deep in the Earth, from the low-temperature processes which operate at or near the Earth’s surface. We will follow this pattern here, and so first we review those processes which took place during the formation of the Earth and the subsequent magmatic processes which have led to its differentiation and its reworking during metamorphism. We then discuss those processes which operate at low temperatures at the Earth’s surface and in which there are interactions between rocks and the Earth’s atmosphere, hydrosphere and those living organisms that inhabit them and ultimately lead to the formation of sedimentary rocks. In each case our primary purpose is to seek to identify those geological processes which have a distinctive geochemical signature and which can be recognised through the collection and interpretation of geochemical data. We point the readers to those sections of this book where these processes are described in greater detail.

#### 1.2.1 Processes Which Control the Formation and Differentiation of Planetary Bodies

Any full understanding of our planet must address the question of its origin and its relationship to its planetary neighbours. The answer to this question comes primarily from a knowledge of the overall composition of the Earth, often expressed as the bulk Earth composition. Our principal source of the information on the composition of the Earth comes from the study of meteorites – in particular the most primitive meteorites, chondritic meteorites. Chondritic meteorites are thought to have formed during the condensation of the solar nebula, and so the study of meteorite chemistry takes us into the domain where fields of cosmochemistry and geochemistry overlap (see Section 4.1.1).

After the Big Bang the majority of the chemical elements were formed by the processes of stellar nucleosynthesis during star formation. The distribution of elements in our star – the Sun – as obtained from spectroscopy and the study of meteorites is shown in Figure 1.1 and their relative concentrations provides details about the processes of nucleosynthesis. Chondritic meteorites formed from the condensation of the gas and dust of the solar nebula, and their chemistry and mineralogy provide information about processes in the solar nebula. The cosmochemical processes operating during the condensation of a solar nebula are very different from those of geochemistry for they are largely controlled by the relative volatility of the elements and compounds in the solar nebula (see Table 4.10). In the later stages of condensation
planetary bodies formed by the accretion of dust and rocky fragments and as these early planetary bodies grew they melted and differentiated into a metallic core and silicate mantle.

The chemical study of primitive meteorites illuminates our study of geochemistry in three important ways:

1. Knowing the chemical composition of the materials from which the Earth formed provides a geochemical baseline for measuring the differentiation of the Earth and the fractionation process that take place on the Earth. Typically, trace elements and isotopes are expressed relative to the chondritic composition of the Earth (Sections 4.3.2.2 and 6.2.2) as a measure of the original bulk Earth composition (BE). Alternatively, trace element abundances and isotope ratios may be expressed relative to the Earth’s primordial or primitive mantle (PM) which is the composition of the Earth after the separation of the core and represents the bulk silicate Earth (BSE) (see Sections 3.1.3, 4.4.1.2 and 6.2.2).

2. Some primitive meteorites contain information about processes in the solar nebula and more rarely about even earlier processes. Pre-solar grains of refractory minerals such as diamond and SiC can predate the solar nebula itself and stable isotope studies of elements such as Cr and Mn can provide information about the distribution of nucleosynthetic products in the early solar system (Section 7.4.4.3). Hydrogen isotope ratios are now available for a range of solar system objects and together with measurements made in meteorites are thought to indicate where in the solar system planets and other solar system objects formed (Section 7.3.2.2, Figure 7.7).

3. Meteorites also provide information about the large-scale differentiation of the Earth and the process of core formation. A knowledge of the mantle concentrations of those trace elements which have a high affinity for metallic iron, the highly siderophile elements (Section 4.5), coupled with experimental studies on their metal silicate partition coefficients (Table 4.10), provides information on the process of core formation. In a similar way, it is thought that carbon was sequestered into the Earth’s core, and so the mass balance of carbon isotopes in the Earth’s mantle also contributes to our understanding of this process (Section 7.3.3.2).

1.2.2 Processes Which Control the Chemical Composition of Igneous Rocks

The processes which control the composition of igneous rocks are summarised in Figure 1.2 and are illustrated for basaltic rocks.

1.2.2.1 Processes Which Take Place in the Mantle Source

Basaltic rocks may be extracted by partial melting from a range of mantle source compositions the most primitive of which – the primitive mantle – is the product of the very early differentiation of the Earth. This process involved the separation of the core and maybe formed during the magma-ocean stage of early Earth history. Subsequent partial melting and mixing events have
created the modern upper mantle which is differentiated into domains that are chemically depleted and enriched. Two main processes control the enrichment and depletion of the mantle. These are the extraction, migration and recrystallisation of partial melts, formed at different depths and representing different degrees of partial melting, and the recycling into the mantle of crustal materials through the process of subduction. Modern lavas derived from a source that has escaped later modification and so represents the Earth’s primitive mantle are extremely rare. One example is the 61 Ma picrites from Baffin Island in north-eastern Canada which represent a relatively high melt fraction of deep mantle and have a primitive isotopic signature (McCoy-West et al., 2018).

Characterising the chemical composition of a mantle source region and thereby understanding those processes which take place in the source region is best achieved by measuring its radiogenic isotope composition (Section 6.2) and using selected trace element ratios, sometimes known as canonical trace element ratios, because these ratios are not modified during partial melting and subsequent magma chamber processes (Section 4.6.1.3).

### 1.2.2.2 Partial Melting Processes

Unmodified melts produced by the partial melting of the mantle are known as primary magmas. Their chemical composition is controlled by two main factors. The first controls are those of the chemical composition of the source and its mineralogy. The composition of the source will reflect whether or not it is chemically enriched or depleted, and the mineralogy of the source is a measure of the depth of melting. The second set of controls are the physical conditions of melting, that is, the temperature and depth of melting, the precise mechanism of melting and the degree of partial melting (Section 4.2.2.2). In some instances, the oxygen fugacity of the mantle is also an important control. After the initial melting stage, the primary magma may be modified as it migrates through the mantle through mixing with melts from other sources and through crystallisation and wall-rock reaction processes. The major element, trace element and radiogenic isotope chemistry are all important in unravelling the origins of primary magmas.

### 1.2.2.3 Magma Chamber Processes

Most basaltic rocks are filtered through a magma chamber prior to their emplacement at or near the surface. These magma chambers may be located at the base of the crust or at various levels within the crust. They are fed by what is known as the parental magma, which may or may not be the same as a primary magma. A wide variety of magma chamber processes modify the chemical composition of the parental magma. These include fractional crystallisation, assimilation of the country rock and associated fractional crystallisation, the mixing of magmas from more than one source, the separation of melts through liquid immiscibility or a dynamic mixture of several of these processes (Sections 3.3.4.1, 4.2.2.3 and 6.3.5). Magma chambers are best thought of as dynamic systems into which melt is fed and is differentiated, in which cumulative rocks form and from which melt is erupted. Resolving the chemical effects of these different processes requires the full
range of geochemical tools: major and trace element studies coupled with the measurement of both radiogenic and stable isotope compositions.

1.2.4 Post-solidus Processes
Following the emplacement or eruption of basaltic rocks they may be further chemically modified by the processes of outgassing or by interaction with a fluid such as seawater or groundwater. The outgassing or degassing of the dissolved gases in basaltic melts is the product of pressure release at the Earth’s surface, and the effects are often seen in their stable isotope geochemistry, for this process readily fractionates isotopes on the basis of mass differences (Section 7.3.4.2). Hydrothermal processes operate at a range of temperatures, from several hundred degrees where seawater or groundwater interact with a magma chamber to the much lower temperatures of chemical weathering. Depending upon the temperature, these processes will modify the mineralogy of the parent rock through the development of clay minerals, and both major and trace elements may be mobilised (Sections 3.1.2 and 4.2.2.1). This is seen in igneous plutonic bodies where on emplacement hydrothermal ground-water circulation in the surrounding country rocks is initiated leading to the chemical alteration of the igneous pluton itself and sometimes the formation of ore bodies through the enhanced concentration of elements which have been mobilised. In addition to using major and trace elements, hydrothermal activity can be monitored by the use of radiogenic and stable isotopes, particularly those of strontium, oxygen and hydrogen, to measure the extent of fluid–rock interaction (Sections 6.3.5.2 and 7.3.2.7).

1.2.3 Processes Which Control the Chemical Composition of Metamorphic Rocks

The principal control on the chemical composition of a metamorphic rock is the composition of the protolith, that is, the composition of the rock prior to its metamorphism. Metamorphism is frequently accompanied by deformation, and at high metamorphic grades there may be the mechanical mixing of different protolith compositions through tectonic interleaving, which can give rise to metamorphic rocks of mixed parentage.

Metamorphic recrystallisation is the result of chemical reactions which take place in the solid state by the process of diffusion. These reactions occur during the burial and heating of the protolith and during cooling. They may be isochronal, but most commonly there is a change in chemical composition. This chemical change is related to the mineralogical reactions which take place and the extent to which those elements found in the minerals in the protolith can be accommodated in the new minerals of the metamorphic rock. Most commonly, these mineralogical changes are also controlled by the movement of fluids in the rock. For this reason, the ingress and expulsion of water during metamorphism, chiefly as a consequence of metamorphic hydration and dehydroyation reactions, exerts the major control on element mobility during metamorphism. These processes are controlled by the composition of the fluid phase, most commonly H₂O and CO₂, its temperature and the ratio of the volume of metamorphic fluid to that of the host rock. The extent to which major and trace elements are mobile during metamorphism can sometimes be assessed by reference to the composition of the unmetamorphosed parent rock. Reactions between crustal fluids and metamorphic rocks and the relative volume of the fluids involved can be measured using the stable isotopes of hydrogen and oxygen (Section 7.3.2.7).

At high metamorphic grades, and frequently in the presence of a hydrous fluid, melting may occur. The segregation and removal of a melt phase will differentiate the parental rock into two compositionally distinct components: the melt and the unmelted component, known as the restite. In this case, the precise nature of the chemical change is governed by the melting reaction and the degree of melting (Section 3.4.3).

1.2.4 Low-Temperature Processes in the Earth’s Surficial Environment

Low-temperature processes in the Earth’s surficial environment include the wide array of interactions between the atmosphere, the hydrosphere, and rocks and soils at the Earth’s surface. These interactions are often summarised in diagrams representing geochemical cycles and can be represented by box models which show the mass balance for a particular element between the different Earth reservoirs. Examples of geochemical cycles quantified using stable isotope ratios are given in Chapter 7; see Figure 7.22 for the
elements sulphur, carbon and oxygen, and Figure 7.27 for nitrogen. A cartoon diagram summarising the main surficial processes discussed here is given in Figure 1.3.

1.2.4.1 Atmospheric Processes

A detailed discussion of geochemical processes occurring in the Earth’s atmosphere is beyond the scope of this book. However, there is one aspect of atmospheric geochemistry which is relevant to the petrological processes discussed here, for over geological time the chemical composition of the Earth’s atmosphere has become increasingly oxygenated. This change in the level of oxygen in the atmosphere has a direct bearing on the oxygenation of the oceans and on weathering processes. Thus, those elements which are redox sensitive at the Earth’s surface can play an important role in identifying the different levels of oxygenation in the oceans and other bodies of surface water. Particularly important are the redox sensitive trace elements (Section 4.2.1.3) and the stable isotopes of the transition metals, nitrogen and sulphur (Sections 7.4.4.3 and 7.4.5.3). The process of mass independent fractionation of sulphur isotopes plays a particularly important role in the detecting the earliest oxygenation of the Earth’s atmosphere (Section 7.3.4.4).

1.2.4.2 Weathering Processes

The interaction between the atmosphere and hydrosphere in the terrestrial environment leads to the development of a weathering profile and the formation of soils. This process is often biologically mediated and involves chemical reactions in which silicate minerals are converted into clays. These reactions are governed by the surface temperature and in some circumstances may be used to infer former climatic conditions. The intensity of chemical weathering has been quantified using the chemical index of alteration calculated from major element geochemistry (Section 3.3.1.5) and from the fractionation of the stable isotopes of lithium and silicon (Sections 7.4.1.3 and 7.4.3.2). The temperature of formation of the clay minerals kaolinite and smectite in the weathering environment has been estimated using hydrogen and oxygen isotopes (Section 7.3.2.4).

In the marine environment the interaction between seawater and the rocks of the ocean floor leads to the seafloor weathering of basalts. In some cases the isotopic composition of weathered ocean floor basalts is sufficiently different from that of unaltered basalt that this signature may be used to track the recycling of the altered basalts back into the Earth’s mantle. This is particularly pertinent for Li isotopes (Section 7.4.1.1) and Os isotopes (Section 6.3.3.4).
1.2.4.3 Water Chemistry

The chemical composition of river water is expressed in terms of its dissolved load and its suspended load of particulate matter. Different elements behave in different ways and some may be present in solution; others are adsorbed onto particulate matter. These two components are a consequence of the particular weathering environment, and because of this the chemical composition of rivers from across the globe is very variable. In some weathering environments the fractionation of stable isotopes during the formation of clay minerals is extreme and this geochemical signature can be transferred to river water and in the case of Li isotopes gives it a very distinctive isotopic composition (Section 7.4.1.3). In a similar way the stable isotopes of Mg, Si, Cr and Fe are also highly fractionated in river water relative to silicate rocks (Figures 7.32, 7.33, 7.35 and 7.36).

The chemical composition of seawater is influenced by the input of river water, groundwater, atmospheric dust, hydrothermal fluids, sea-floor weathering and biological activity (Figure 7.3). Ultimately, the elements present in seawater are taken up in to sediments, but the average length of time they remain in the seawater is highly variable. This time interval is known as the residence time. For a given element the length of the residence time is a measure of how well mixed the oceans are for that particular element. This is illustrated for the rare earth elements (REE) in Section 4.3.3.2 and radiogenic isotopes in Section 6.3.2.3. The geochemistry of the oceans is thus not the main focus of this book, although there are two themes which are of petrological interest. These are the interactions between seawater and the rocks of the ocean floor, and the way in which the composition of seawater has changed over time (Figure 6.13). Seawater–rock interactions have been monitored using the stable isotopes of hydrogen and oxygen (Section 7.3.2.7) and these have great relevance to the formation of mineral deposits. The changing composition of seawater can be evaluated in the changing isotopic composition of marine sediments such as those carbonates which are precipitated directly from seawater. The stable isotope ratios of carbon (Section 7.3.3.5) and lithium (Section 7.4.1.3) and the radiogenic isotope ratios of strontium and osmium (Section 6.3.2.3) are particularly sensitive.

1.2.4.4 The Impact of Human Activity on the Earth’s Surface Environment

The impact of anthropogenic activity is increasingly important in environmental geochemistry. Although beyond the scope of this book, two examples are pertinent. Recent work on nitrogen isotopes has shown that it is possible to fingerprint polluting anthropogenic nitrates (Section 7.3.5.3) and in a similar way the remediation of toxic Cr\(^{6+}\) in groundwater can be monitored using the stable isotopes of Cr (Section 7.4.4.3).

1.2.5 Processes Which Control the Chemical Composition of Sedimentary Rocks

1.2.5.1 Provenance

The geochemical make-up of the rocks constitutes the provenance which influences the composition of sediments. In immature sediments there is a direct geochemical link between the major and trace element composition of the sediment and its provenance (Section 5.5). The provenance of fine-grained, clay-rich sediments such as shale can be determined from selected trace elements and isotopes (Sections 4.2.2.4, 5.5.3 and 6.2.3.2). Provenance studies may also be used to determine the original tectonic setting of the basin in which fine-grained sediment formed (Section 5.5).

1.2.5.2 Weathering

Weathering conditions leave their signature in the resultant sediment and, as discussed above, major element and stable isotope studies of sedimentary rocks indicate that former weathering conditions can be recognised in the chemical composition of the sediments. Significant chemical changes may also take place during sediment transport, for some trace elements become concentrated in the clay fraction; others are concentrated in a heavy mineral fraction; while others are diluted in the presence of a quartz-rich fraction. To a large extent these processes are dependent upon the length of time the sediment spends between erosion and deposition.

1.2.5.3 Processes in the Depositional Environment

The chemical changes that occur during the deposition of sediments are governed by the nature of the depositional environment. This in turn is influenced by the subsidence rate and the attendant thermal conditions of the sedimentary basin. The temperature-
dependent fractionation of oxygen isotopes can be used to calculate the geothermal gradient during diagenesis and allows some control on the burial history of the rock (Sections 7.2.5 and 7.3.1.2). In the case of chemical sediments the chemical and biochemical processes controlling the solubility of particular elements coupled with thermal and redox conditions are also important. Post-depositional, fluid-related diagenetic processes are best investigated using stable isotopes. The stable isotopes of oxygen and hydrogen are important tracers of different types of water (Section 7.3.2.3) and the combined application of carbon and oxygen isotopes are important in the study of limestone diagenesis (Section 7.3.3.9).

1.2.6 Biogeochemical Processes

Microbial life is abundant at the surface of the Earth and can leave a geochemical fingerprint in its stable isotope signature. This is because many microbially mediated chemical reactions cause mass fractionation in particular stable isotope systems. For example, the kinetics of the conversion of inorganic carbon into living carbon entails the preferential concentration of the light carbon isotope in the living carbon (Section 7.3.3.6). Isotopic signatures of this kind open up the possibility of identifying specific microbial reactions which may relate to particular metabolic pathways which may be found in both modern environments and in the ancient sedimentary record. Other examples of elements which are essential to life and whose stable isotopes are fractionated by microbial activity are sulphur and nitrogen. In the marine environment sulphur isotopes are fractionated during the reduction of seawater sulphate by anaerobic bacteria (Section 7.3.4.2) and nitrogen isotopes are fractionated during the reduction of nitrate to atmospheric nitrogen through the metabolic processes of denitrification and anammox (Section 7.3.5.2). Magnesium is also an essential element in the biosphere and there is evidence that Mg isotopes are fractionated in plants during photosynthesis (Section 7.4.2.3). Iron isotopes are fractionated during both anaerobic bacterial iron reduction and photosynthetic iron oxidation operating under anaerobic conditions (Section 7.4.5.2).

1.2.6.1 The Search for Early Life on Earth

The preservation of microbially driven stable isotope fractionations in the geological record has been used a means of identifying the presence of life on Earth from the earliest stages of Earth history. One of the first studies was by Schidlowski (1988), who showed that the study of carbon isotopes can be used to trace ancient biological activity through the geological record back as far as 3.7 Ga (Section 7.3.3.7). Subsequent studies used the large negative sulphur isotope values in the sedimentary record as a means of exploring the processes of microbial sulphate reduction in the geological past (Section 7.3.4.6). It has also been suggested that the extreme iron isotope fractionations in Archaean sediments are, in part, the product of microbial activity, although as with other stable isotope systems it is important to establish whether or not similar fractionations could have been produced by abiotic processes (Section 7.4.5.3).

1.3 Geological Controls on Geochemical Data

The most fruitful geochemical investigations are those that test a particular model or hypothesis. This ultimately hinges upon a clear understanding of the geological relationships in the rock suite under investigation. Thus, any successful geochemical investigation must be based upon a proper understanding of the geology of the area. It is not sufficient to carry out a ‘smash and grab raid’, returning to the laboratory with large numbers of samples, if the relationships between the samples are unknown and their relationship to the regional geology is unclear. It is normal to use the geology to interpret the geochemistry. Rarely is the converse true, for at best the results are ambiguous.

In some instances this is self-evident, for example, when samples are collected from a specific stratigraphic sequence or lava pile or from drill core data, and there is a clear advantage in knowing how geochemical changes take place with stratigraphic height and therefore over time. A more complex example would be a metamorphosed migmatite terrain in which several generations of melt have been produced from a number of possible sources. A regional study in which samples are collected on a grid pattern may have a statistically accurate feel and yet will provide limited information on the processes in the migmatite complex. What is required in such a study is the mapping of the relative age relationships between the components present, at the appropriate scale, followed by the careful sampling of each domain. This then allows chemical variations within the melt
and restite components to be investigated and models tested to establish the relationships between them.

A further consideration comes from the different scales on which geochemical data are collected. With the advent of microbeam analytical techniques and the continuation of programmes such as the ocean drilling or continental drilling programmes it is possible to measure geochemical data from the micro to macro scales. For example, the mapping of trace element or isotopic data in a single mineral grain may be used to illuminate processes such as fractionation in an igneous melt, diffusion in a metamorphic rock or changing fluid conditions during sediment diagenesis. This was illustrated in the study of the zonation of iron isotopes in olivines from Kilauea Iki lava lake in Hawai’i by Sio et al. (2013). Equally, the mapping of isotopic variations in ocean floor basalts can be used to identify geographically specific compositional reservoirs in the Earth’s mantle. Hart (1984) mapped the southern hemisphere DUPAL anomaly in this way on the basis of anomalous Sr- and Pb-isotopic compositions. At an intermediate scale, the mapping of the distribution of Pb in stream sediments over a large area of eastern Greece has relevance for both environmental pollution and mineral exploration (see figure 2 in Demetriades, 2014).

A fundamental tenet of this book therefore is that if geochemical data are going to provide information about geological processes, then geochemical investigations must always be carried out in the light of a clear understanding of the geological relationships. This normally means that careful geological fieldwork is a prerequisite to a geochemical investigation. This approach leads naturally to the way in which geochemical data are presented. In the main this is as bivariate (and trivariate) plots in which the variables are the geochemical data. The interpretation of these plots forms the basis for understanding the geological processes operating.

1.3.1 Sample Collection

It is important that any new geochemical investigation has a well-developed sampling strategy. The key parameters are discussed in detail by Ramsay (1997) and for environmental applications by Demetriades (2014). A brief summary is given here.

- Sample size tends to be governed by the grain size of the rock. The overriding principle is that the sample must be representative of the rock. In addition, the portion of the sample used in geochemistry must be fresh and therefore an allowance must be made for any weathered material present which will be removed later. It is also important to retain part of the sample for future research and/or the preparation of a thin section.
- Sampling will normally be done using a hammer. Occasionally, precise sampling or sampling from a difficult surface may be carried out using a coring drill. In either case care must be taken to establish that rock sampling is permitted at the site in question and that sampling is carried out as discretely as possible.
- The number of samples is normally governed by the nature of the problem being solved. Relevant are the geographic extent of the study area and whether or not there are spatial or temporal aspects to the research project. If the research question is very specific a relatively small number (10–20) of well-chosen samples may suffice. Often many more samples than this are required. A further consideration is whether there is the opportunity to return to the field area. If not, then selecting a larger number of samples makes good sense.
- The careful labelling of samples in the field, at the site of collection, is perhaps obvious. A geological description of the site is important, accompanied by photographs and the precise GPS location. This will allow the researcher or their successor to return to the precise sample site if necessary, and such information is often important in the future publication of the results.

1.4 Analytical Methods in Geochemistry

In this section the more widely used analytical methods are reviewed in order to provide a guide for those embarking on geochemical analysis. This text is not principally a book about analytical methods in geochemistry and excellent summaries are given by Gill (1997), Rouessac and Rouessac (2007) and in the second edition of volume 15 of the Treatise on Geochemistry (McDonough, 2014b). First, however, it is necessary to consider the criteria by which a particular analytical technique might be evaluated (Figure 1.4). In this book, in which geochemical data are used to infer geochemical processes, it is the quality of the data which is important. Data quality may be measured in terms of precision, accuracy and detection limits.