

associated country rocks. They postulated that boiling of hydrothermal fluids and separation of a Hg-bearing vapor phase are the most important Hg fractionation processes.

Since Hg takes part in microbial processes, Hg fractionations should occur during methylation processes. Kritee et al. (2007) suggested that Hg isotopes might have the potential for distinguishing between different sources of mercury emissions based on the magnitude of isotope fractionations. Finally, it is important to note that abiological photochemical reduction of  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{Hg}^+$  by sunlight leads to a large mass-independent fractionation of  $^{201}\text{Hg}$  and  $^{199}\text{Hg}$  (Bergquist and Blum 2007).

## 2.20 Thallium

Thallium has two stable isotopes with masses 203 and 205.

$^{204}\text{Tl}$  29.54

$^{205}\text{Tl}$  70.48

Thallium is the heaviest element for which natural variations in isotope composition have been reported (Rehkämper and Halliday 1999). Tl exists in two valence states as  $\text{Tl}^+$  and  $\text{Tl}^{3+}$  and forms in water a variety of complexes. Furthermore it is a highly volatile element which could induce kinetic fractionations during degassing processes. A systematic 2‰ difference between Fe–Mn crusts enriched in  $^{205}\text{Tl}$  and seawater has been observed by Rehkämper et al. (2002), which was interpreted to be due to an fractionation effect during adsorption of Tl onto Fe–Mn particles. In a later study Rehkämper et al. (2004) found that growth layers of Fe–Mn crusts show a systematic change in Tl isotope composition with age, which they explained by time-dependent changes in Tl-isotope composition of seawater. No significant Tl isotope fractionations occur during weathering (Nielsen et al. 2005).

Tl isotope ratios might be also used as a tracer in mantle geochemistry (Nielsen et al. 2006; 2007). Since most geochemical reservoirs except Fe–Mn marine sediments and low temperature seawater altered basalts are more or less invariant in Tl isotope composition, admixing of small amounts of either of these two components into the mantle should induce small Tl isotope fractionations in mantle derived rocks. And indeed, evidence for the presence of Fe–Mn sediments in the mantle underneath Hawaii was presented by Nielsen et al. (2006).

## Chapter 3

# Variations of Stable Isotope Ratios in Nature

### 3.1 Extraterrestrial Materials

Isotope variations found in extraterrestrial materials have been classified according to different processes such as chemical mass fractionation, nuclear reactions, nucleosynthesis, and/or to different sources such as interplanetary dust, solar materials, and comet material. Various geochemical fingerprints point to the reservoir from which the planetary sample was derived and the environment in which the sample has formed. They can be attributed to a variety of processes, ranging from heterogeneities in the early solar nebula to the evolution of a planetary body. For more details the reader is referred to reviews of Thiemens (1988), Clayton (1993, 2004), and McKeegan and Leshin (2001).

Extraterrestrial materials consist of samples from the Moon, Mars, and a variety of smaller bodies such as asteroids and comets. These planetary samples have been used to deduce the evolution of our solar system. A major difference between extraterrestrial and terrestrial materials is the existence of primordial isotopic heterogeneities in the early solar system. These heterogeneities are not observed on the Earth or on the Moon, because they have become obliterated during high-temperature processes over geologic time. In primitive meteorites, however, components that acquired their isotopic compositions through interaction with constituents of the solar nebula have remained unchanged since that time.

Heterogeneities in isotope composition indicate incomplete mixing of distinct presolar materials during formation of the solar system. Such isotope anomalies in light elements have been documented on all scales, from microscopic zoning in meteoritic minerals to bulk asteroids. The most extreme examples, however, have been documented from minute presolar grains extracted from primitive meteorites and measured with the ion microprobe. These grains of silicon carbide, graphite, and diamond show isotope variations that may vary by one or more orders of magnitude. They have acquired their isotope characteristics before the solar system has been formed. The implications of these variations for models of stellar formation have been summarized by Zinner (1998) and Hoppe and Zinner (2000). The abundance

of presolar grains in meteorites is at the level of tens of ppm, thus the bulk isotope composition of meteorites remains more or less unaffected.

Different types of primitive meteoritic materials of the so-called chondritic composition can be distinguished on the basis of their size. The term chondritic is used here to refer to undifferentiated material having approximately solar compositions of all except the most volatile elements. The smallest particles are micron-sized interplanetary dust particles that contribute about  $10^4$  tons per year to the Earth. They can be collected high in the Earth's stratosphere by aircraft at about 20 km altitude. Although these particles are small (typically  $10\mu\text{m}$  in diameter), they have been investigated by ion microprobe measurements (McKeegan 1987; McKeegan et al. 1985, and others).

Deuterium and nitrogen isotope compositions of interplanetary dust materials show enrichments that support an interstellar origin. These isotope enrichments are the results of ionmolecule reactions that are only efficient at very low temperatures (Rietmeijer 1998). D/H ratios of individual dust particles give  $\delta\text{D}$ -values ranging from  $-386$  to  $+2705\text{‰}$ , which thus exceed by far those in terrestrial samples. The hydrogen isotopic composition is heterogeneous on a scale of a few microns demonstrating that the dust is unequilibrated. A carbonaceous phase rather than water appears to be the carrier of the D-enrichment.

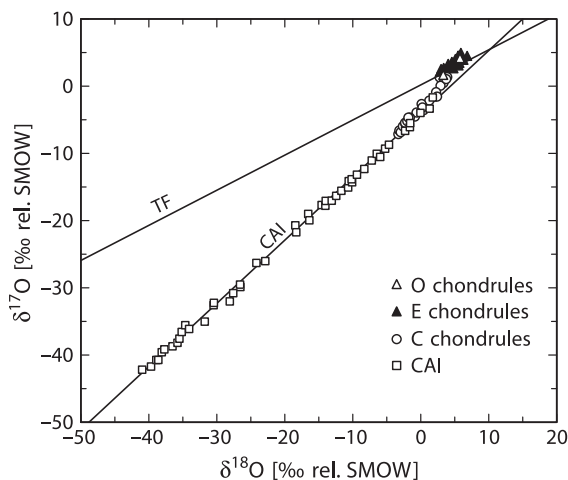
In contrast to D/H and  $^{15}\text{N}/^{14}\text{N}$  ratios, an anomalous carbon isotope composition has not been clearly demonstrated. However, three of the investigated particles exhibit evidence for heterogeneity in their isotopic composition. With respect to oxygen, none of the particles have large  $^{16}\text{O}$  excesses of the type found in refractory oxide and silicate phases from carbonaceous chondrites.

These results suggest that the interplanetary dust particles are among the most primitive samples available for laboratory studies. Isotopically anomalous material constitutes only a small fraction of the investigated particles. Thus, it appears that the isotopic composition of these anomalous particles is not different from those observed in minor components of primitive meteorites.

### 3.1.1 Chondrites

Chondrites are the oldest and most primitive rocks in the solar system. They are hosts for interstellar grains that predate solar system formation. Most chondrites have experienced a complex history, which includes primary formation processes and secondary processes that include thermal metamorphism and aqueous alteration. It is generally very difficult to distinguish between the effects of primary and secondary processes on the basis of isotope composition. Chondrites display a wide diversity of isotopic compositions including large variations in oxygen isotopes.

The first observation, that clearly demonstrated isotopic inhomogeneities in the early solar system, was made by Clayton et al. (1973a). Earlier, it had been thought that all physical and chemical processes must produce mass-dependent O-isotope fractionations yielding a straight line with a slope of 0.52 in a plot of  $^{17}\text{O}/^{16}\text{O}$  vs.



**Fig. 3.1**  $^{17}\text{O}$ - vs  $^{18}\text{O}$ -isotope composition of Ca–Al-rich inclusions (CAI) from various chondrites (Clayton, 1993)

$^{18}\text{O}/^{16}\text{O}$ . This line has been called the “Terrestrial Fractionation Line”. Figure 3.1 shows that O-isotope data from miscellaneous collections of terrestrial and lunar samples fall along the predicted mass-dependent fractionation line. However, selected anhydrous high-temperature minerals in carbonaceous chondrites, notably Allende, do not fall along the chemical fractionation trend, instead define another trend with a slope of 1. Figure 3.1 shows oxygen isotope compositions for four groups of meteoritic samples. The first evidence for oxygen isotope anomalies was found in CaAl-rich refractory inclusions (CAI) in the Allende carbonaceous chondrite, which are composed predominantly of melilite, pyroxene, and spinel.

Bulk meteorites, the Moon and Mars lie within a few percentile above or below the terrestrial fractionation line on a three-oxygen isotope plot (see Fig. 3.1). Therefore, the oxygen isotope composition of the Sun has been assumed to be the same as that of the Earth. This view has changed with the suggestion of Clayton (2002) that the Sun and the initial composition of the solar system are  $^{16}\text{O}$ -rich comparable to the most  $^{16}\text{O}$ -rich composition of CAIs ( $\delta^{17}\text{O} \approx -50$ ;  $\delta^{18}\text{O} \approx -50\text{‰}$ ). According to this model, Solar System rocks had become poor in  $^{16}\text{O}$  due to UV self-shielding of CO, the most abundant oxygen containing molecule in the solar system. Oxygen released by the UV dissociation of CO then form together with other components of the solar system solid minerals with mass-independent oxygen isotope compositions.

Different nebular isotopic reservoirs must have existed, since there are distinct differences in bulk meteoritic O-isotope composition. The carbonaceous chondrites display the widest range in oxygen isotope composition of any meteorite group (Clayton and Mayeda 1999). The evolution of these meteorites can be interpreted as a progression of interactions between dust and gas components in the solar nebula followed by solid/fluid interactions within parent bodies. Young et al. (1999)

have shown that reactions between rock and water inside a carbonaceous chondrite parent body could have produced groups of different carbonaceous chondrite types that explain the diversity in isotope composition.

Yurimoto et al. (2008) have summarized the oxygen isotope composition of the chondrite components (refractory inclusions, chondrules, and matrix) and concluded that O-isotope variations within a chondrite are typically larger than O-isotope variations among bulk chondrites. The question remains as to where, when, and how the isotopic anomalies were originally produced (Thiemens 1988). Even without full understanding of the causes of isotope variations in meteorites, oxygen isotopes are very useful in classifying meteorites and in relating meteorites to their precursor asteroids and planets (Clayton 2004). Oxygen isotope signatures have confirmed that eucrites, diogenites, howardites, and mesosiderites originate from one single parent body probably derived from the asteroid 4 Vesta, as shergottites, nakhlites, and chassignites come from another (Clayton and Mayeda 1996). Main group pallasites represent intermixed core-mantle material from a single disrupted asteroid with no equivalent known (Greenwood et al. 2006).

In addition to oxygen isotopes, the volatile elements H, C, N, and S also show extremely large variations in isotope composition in meteorites. In recent years, most investigations have concentrated on the analyses of individual components with more and more sophisticated analytical techniques.

### 3.1.1.1 Hydrogen

D/H ratios in carbonaceous chondrites may hint on the origin of water on Earth. Robert (2001) suggested that since the contribution of cometary water to terrestrial water should be less than 10%, most of the water on Earth should derive from a meteoritic source.

The D/H ratio of the sun is essentially zero: all the primordial deuterium originally present has been converted into  $^3\text{He}$  during thermonuclear reactions. Analysis of primitive meteorites is the next best approach of estimating the hydrogen isotope composition of the solar system.

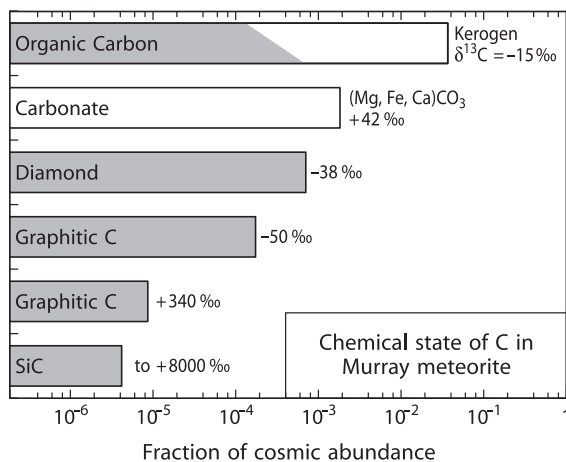
In carbonaceous chondrites, hydrogen is bound in hydrated minerals and in organic matter. Bulk D/H ratios give a relatively homogeneous composition with a mean  $\delta\text{D}$ -value of  $-100\text{‰}$  (Robert et al. 2000). This relatively homogeneous composition masks the very heterogeneous distribution of individual components. Considerable efforts have been undertaken to analyze D/H ratios of the different compounds (Robert et al. 1978; Kolodny et al. 1980; Robert and Epstein 1982; Becker and Epstein 1982; Yang and Epstein 1984; Kerridge 1983; Kerridge et al. 1987; Halbout et al. 1990; Krishnamurthy et al. 1992). Hydrogen in organic matter reveals a  $\delta\text{D}$ -variation from  $-500$  to  $+6,000\text{‰}$  whereas water in silicates gives a variation from  $-400$  to  $+3,700\text{‰}$  (Deloule and Robert 1995; Deloule et al. 1998). Most strikingly, almost the entire range is observed on the scale of single chondrules when traverses are performed (Deloule and Robert 1995).

Two mechanisms have been proposed to account for the deuterium enrichment: (1) for organic molecules, high D/H ratios can be explained by ion molecule reactions that occur in interstellar space and (2) for the phyllosilicates the enrichment can be produced via isotope exchange between water and hydrogen (Robert et al. 2000).

Eiler and Kitchen (2004) have re-evaluated the hydrogen isotope composition of water-rich carbonaceous chondrites by stepped-heating analysis of very small amounts of separated water-rich materials. Their special aim has been to deduce the origin of the water with which the meteorites have reacted. They observed a decrease in  $\delta D$  with increasing extent of aqueous alteration from 0‰ (least altered, most volatile rich) to  $-200‰$  (most altered, least volatile rich).

### 3.1.1.2 Carbon

Besides the bulk carbon isotopic composition, the various carbon phases occurring in carbonaceous chondrites (kerogen, carbonates, graphite, diamond, and silicon carbide) have been individually analyzed. The  $\delta^{13}C$ -values of the total carbon fall into a narrow range, whereas  $\delta^{13}C$ -values for different carbon compounds in single meteorites show extremely different  $^{13}C$ -contents. Figure 3.2 shows one such example, the Murray meteorite after Ming et al. (1989). Of special interest are the minute grains of silicon carbide and graphite in primitive carbonaceous chondrites, which obviously carry the chemical signature of the pre-solar environment (Ott 1993). The SiC grains, present at a level of a few ppm, have a wide range in silicon and carbon isotope composition, with accompanying nitrogen also being isotopically highly variable. The  $^{12}C/^{13}C$  ratio ranges from 2 to 2,500, whereas it is 89 for the bulk Earth. According to Ott (1993), the SiC grains can be regarded as “star dust”, prob-



**Fig. 3.2** Different carbon compounds in primitive meteorites. Species classified as interstellar on the basis of C-isotopes are shaded. Only a minor fraction of organic carbon is interstellar. (after Ming et al. 1989)

ably from carbon stars that existed long before our solar system. Amari et al. (1993) presented ion microprobe data of individual micrometer-sized graphite grains in the Murchison meteorite that also has large deviations from values typical for the solar system. These authors interpreted the isotope variability as indicating at least three different types of stellar sources.

Of special interest is the analysis of meteoritic organic matter, because this may provide information about the origin of prebiotic organic matter in the early solar system. Two hypotheses have dominated the debate over formation mechanisms for the organic matter (1) formation by a Fischer-Tropsch-type process (the synthesis of hydrocarbons from carbon monoxide and hydrogen) promoted by catalytic mineral grains and (2) formation by Miller-Urey-type reactions (the production of organic compounds by radiation or electric discharge) in an atmosphere in contact with an aqueous phase. However, the isotopic variability exhibited by the volatile elements in different phases in carbonaceous chondrites is not readily compatible with abiotic syntheses. Either complex variants of these reactions must be invoked, or totally different types of reactions need to be considered.  $\delta^{13}\text{C}$ -values reported for amino acids in the Murchison meteorite vary between +23 and +44‰ (Epstein et al. 1987). Engel et al. (1990) analyzed individual amino acids in the Murchison meteorite and also confirmed strong  $^{13}\text{C}$  enrichment. Of particular importance is the discovery of a distinct  $\delta^{13}\text{C}$  difference between D- and L-alanine, which suggests that optically active forms of material were present in the early solar system.

### 3.1.1.3 Nitrogen

The nitrogen isotopes  $^{14}\text{N}$  and  $^{15}\text{N}$  are synthesized in two different astrophysical processes:  $^{14}\text{N}$  during hydrostatic hydrogen burning and  $^{15}\text{N}$  during explosive hydrogen and helium burning (Prombo and Clayton 1985). Thus, it can be expected that nitrogen should be isotopically heterogeneous in interstellar matter. What was considered by Kaplan (1975) to be a wide range of  $\delta^{15}\text{N}$ -values in meteorites has continuously expanded over the years (Kung and Clayton 1978; Robert and Epstein 1982; Lewis et al. 1983; Prombo and Clayton 1985; Grady and Pillinger 1990, 1993). In general, chondrites have whole rock nitrogen isotope values of  $0 \pm 50\text{‰}$ . However, some chondrites have  $\delta$ -values up to 850‰ (Grady and Pillinger 1990). Traces of interstellar graphite grains even show larger variations (Amari et al. 1993). The large  $^{15}\text{N}$ -enrichment in bulk meteorites relative to the protosolar gas requires the existence of especially enriched  $^{15}\text{N}$ -compounds and cannot be explained by isotope fractionation processes in planetary environments.

### 3.1.1.4 Sulfur

There are many sulfur components in meteorites which may occur in all possible valence states (−2 to +6). Troilite is the most abundant sulfur compound of iron meteorites and has a relatively constant S-isotope composition (recall

that troilite from the Canyon Diablo iron meteorite is the international sulfur standard, i.e.  $\delta^{34}\text{S}$ -value = 0‰). Carbonaceous chondrites contain sulfur of all valence states: sulfates, sulfides, elemental sulfur, and complex organic sulfur-containing molecules. Monster et al. (1965), Kaplan and Hulston (1966) and Gao and Thiemens (1993a, b) separated the various sulfur components and demonstrated that sulfides are characterized by the highest  $\delta^{34}\text{S}$ -values, whereas sulfates have the lowest  $\delta^{34}\text{S}$ -values, just the opposite from what is generally observed in terrestrial samples. This is strong evidence against any microbiological activity and instead favors a kinetic isotope fractionation in a sulfur-water reaction (Monster et al. 1965). The largest internal isotope fractionation (7‰) is found in the Orgueil carbonaceous chondrite (Gao and Thiemens 1993a). Orgueil and Murchison have internal isotopic variations between different specimens, which may indicate that sulfur isotope heterogeneity existed in meteorite parent bodies. Since sulfur has four stable isotopes, measurements of more than two isotopes may provide some insights on nuclear processes and may help in identifying genetic relationships between meteorites in a similar way to oxygen isotopes. Early measurements by Hulston and Thode (1965) and Kaplan and Hulston (1966), and later ones by Gao and Thiemens (1993a, b), did not indicate any nuclear isotope anomaly. However, small  $^{33}\text{S}$  enrichment was identified for monosulfides in ureilites (Farquhar et al. 2000b).

### ***3.1.2 Evolved Extraterrestrial Materials***

Evolved extraterrestrial materials are generally igneous rocks, which according to their thermal history can be discussed analogously to terrestrial samples. To this category belong planetary bodies, differentiated asteroids, and achondritic meteorites.

#### **3.1.2.1 The Moon**

The Moon is now ubiquitously viewed as the product of a collision between the early Earth and a Mars-size protoplanet. To test whether the impactor has introduced isotopic heterogeneity as a consequence of collision, Wiechert et al. (2001) have searched for small isotope variations by measuring high-precision  $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$  abundances in lunar samples. The three oxygen isotopes, however, provide no evidence of isotopic heterogeneity and suggest that the proto-Earth and the impactor planet formed from an identical mixture of components.

Since the early days of the Apollo missions, it is well known that the oxygen isotope composition of the common lunar igneous minerals is very constant, with very little variation from one sampled locality to another (Onuma et al. 1970; Clayton et al. 1973b). This constancy implies that the lunar interior should have a  $\delta^{18}\text{O}$ -value of about 5.5‰, essentially identical to terrestrial mantle rocks. The fractionations observed among coexisting minerals indicate temperatures of crystallization of about 1,000°C or higher, similar to values observed in terrestrial basalts



(Onuma et al. 1970). By comparison with other terrestrial rocks, the range of observed  $\delta^{18}\text{O}$ -values is very narrow. For instance, terrestrial plagioclase exhibits an O-isotope variation which is at least ten times greater than that for all lunar rocks (Taylor 1968). This difference may be attributed to the much greater role of low-temperature processes in the evolution of the Earth's crust and to the presence of water on the Earth.

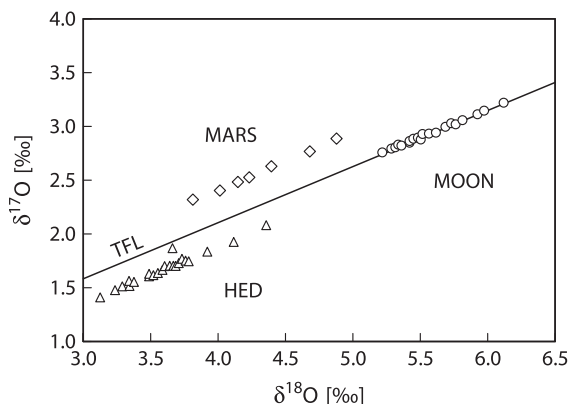
The most notable feature of the sulfur isotope geochemistry of lunar rocks is the uniformity of  $\delta^{34}\text{S}$ -values and their proximity to the Canyon Diablo standard. The range of published  $\delta^{34}\text{S}$ -values is between  $-2$  to  $+2.5\text{‰}$ . However, as noted by Des Marais (1983), the actual range is likely to be considerably narrower than  $4.5\text{‰}$  due to systematic discrepancies either between laboratories or between analytical procedures. The very small variation in sulfur isotope composition supports the idea that the very low oxygen fugacities on the Moon prevent the formation of  $\text{SO}_2$  or sulfates, thus eliminate exchange reactions between oxidized and reduced sulfur species.

As further shown by Des Marais (1983) nitrogen and carbon abundances are extremely low in lunar rocks. Des Marais presented compelling evidence that all lunar rocks are contaminated by complex carbon compounds during sample handling. This carbon, which is released at relatively low combustion temperatures, exhibits low  $\delta^{13}\text{C}$ -values, whereas the carbon liberated at higher temperatures has higher  $^{13}\text{C}/^{12}\text{C}$  ratios. Another complication for the determination of the indigenous isotope ratios of lunar carbon and nitrogen arises from spallation effects, which results from the interaction of cosmic ray particles with the lunar surface. These spallation effects lead to an increase in  $^{13}\text{C}$  and  $^{15}\text{N}$ , the extent depending upon cosmic ray exposure ages of the rocks. Enrichments of the heavy isotopes on the surfaces of the lunar fines are most probably due to the influence of the solar wind. Detailed interpretation of their isotopic variations is difficult due to both the lack of knowledge of the isotopic composition of the solar wind and uncertainties of the mechanisms for trapping. Kerridge (1983) demonstrated that nitrogen trapped in lunar surface rocks consists of at least two components differing in release characteristics during experimental heating and isotopic composition: the low-temperature component is consistent with solar wind nitrogen, whereas the high-temperature component consists of solar energetic particles.

### 3.1.2.2 Mars

In the late 1970s and early 1980s, it was realized that differentiated meteorites referred to as the SNC (Shergottites, Nakhilites, Chassignites) group were samples from Mars (McSween et al. 1979; Bogard and Johnson 1983, besides others). This conclusion is based on young crystallization ages compared to that of other meteorites and compositions of trapped volatiles that match those of the martian atmosphere.

SNC-meteorites have an average  $\delta^{18}\text{O}$ -value of  $4.3\text{‰}$ , which is distinctly lower than the  $5.5\text{‰}$  value for the Earth-Moon system (Clayton and Mayeda 1996; Franchi



**Fig. 3.3** Three oxygen isotope plot of lunar and Martian rocks and HED meteorites supposed to be fragments of asteroid Vesta (after Wiechert et al. 2003)

et al. 1999). Small  $^{18}\text{O}$ -variations among the different SNC-meteorites result primarily from different modal abundances of the major minerals. On a three-isotope plot the  $\delta^{17}\text{O}$  offset between Mars and Earth is  $0.3\text{‰}$  (see Fig. 3.3). In this connection, it is interesting to note that the so-called HED (howardites, eucrites, and diogenites) meteorites, possibly reflecting material from the asteroid Vesta, have an oxygen isotope composition of  $3.3\text{‰}$  (Clayton and Mayeda 1996). The  $\delta^{17}\text{O}$ -offset to the Earth is about  $-0.3\text{‰}$  (Fig. 3.3). These differences in O-isotope composition among the terrestrial planets must reflect differences in the raw material from which the planets were formed.

Volatiles, especially water, on Mars are of special relevance to reveal the geological and geochemical evolution of the planet. The hydrogen isotope composition of the present day Martian atmosphere is enriched by a factor of 5 relative to terrestrial ocean water with a  $\delta\text{D}$ -value of  $+4,000\text{‰}$ . This enrichment is thought to result from preferential loss of H relative to D from the Martian atmosphere over time (Owen et al. 1988). Ion microprobe studies of amphibole, biotite, and apatite in SNC meteorites by Watson et al. (1994) and stepwise heating studies by Leshin et al. (1996) reported large variations in  $\delta\text{D}$ -values. These authors observed that water in the samples originated from two sources: a terrestrial contaminant released largely at low temperatures and an extraterrestrial component at high temperatures showing extreme D-enrichments. Bockrath et al. (2003) observed D-rich water in all minerals analyzed – including nominally anhydrous minerals – but also found low  $\delta\text{D}$ -values, consistent with a more Earth-like composition and concluded no single process can explain the large range in D/H ratios. Instead they suggested that the  $\delta\text{D}$ -values are affected by three reservoirs and mechanisms: a magmatic water component, devolatilization by impact melting and terrestrial contamination.

As is the case for hydrogen, carbon isotope signatures in Martian meteorites present evidence for different carbon reservoirs. Wright et al. (1990) and Romanek et al. (1994) distinguished three carbon compounds: one component released

at temperatures below  $\approx 500^\circ\text{C}$ , mostly derived from terrestrial contamination, a second component, released between  $400$  and  $700^\circ\text{C}$  in heating experiments or by reaction with acid, originates mostly from breakdown of carbonates and gives  $\delta^{13}\text{C}$ -values up to  $+40\text{‰}$  and the third component, released at temperatures above  $700^\circ\text{C}$ , has  $\delta^{13}\text{C}$ -values between  $-20$  and  $-30\text{‰}$  reflecting the isotope composition of magmatic carbon on Mars.

Carbonates in Martian meteorites have been especially well studied due to the hypothesis that they might indicate past life on Mars (McKay et al. 1996). Understanding the conditions of formation of the carbonates is thus crucial to the whole debate. Despite extensive chemical and mineralogical studies, the environment of carbonate formation has remained unclear.  $\delta^{18}\text{O}$ -values of the carbonates are highly variable ranging from about  $5\text{‰}$  to  $25\text{‰}$  depending on different investigators and the carbonate investigated (Romanek et al. 1994; Valley et al. 1997; Leshin et al. 1998). In situ C-isotope analysis by Niles et al. (2005) gave highly zoned  $\delta^{13}\text{C}$ -values from  $\approx +30$  to  $+60\text{‰}$  consistent with a derivation from the Martian atmosphere and suggesting abiotic formation.

McKay et al. (1996) furthermore suggested on the basis of morphology that tiny sulfide grains inside the carbonates may have formed by sulfate-reducing bacteria.  $\delta^{34}\text{S}$ -values of sulfides range from  $2.0$  to  $7.3\text{‰}$  (Greenwood et al. 1997), which is similar to values from terrestrial basalts and probably not the result of bacterial reduction of sulfate.

The isotopic results are therefore not in favor of a microbiological activity on Mars, but the discussion will certainly continue on this exciting topic.

Further evidence about a nonbiogenic origin of Martian carbonates (and even less abundant sulfates) has been presented by Farquhar et al. (1998) and Farquhar and Thiemens (2000). By measuring  $\delta^{17}\text{O}$ - and  $\delta^{18}\text{O}$ -values Farquhar et al. (1998) observed an  $^{17}\text{O}$  anomaly in the carbonates relative to the silicates which they interpreted as being produced by the photochemical decomposition of ozone just as in the Earth's stratosphere. The atmospheric oxygen isotope composition was subsequently transferred to carbonate minerals by  $\text{CO}_2\text{--H}_2\text{O}$  exchange. This finding suggests that carbonates (and sulfates) are derived from atmosphere/regolith interactions on Mars. Similar interactions have also been determined for sulfur isotopes in Martian meteorites (Farquhar et al. 2000a). Photolysis experiments with  $\text{SO}_2$  and  $\text{H}_2\text{S}$  can produce the observed S-isotope compositions and provide a mechanism for abiogenic  $^{34}\text{S}$  fractionations on Mars. Thus, large S isotope fractionations are also not necessarily indicative of biological activity on Mars.

### 3.1.2.3 Venus

The mass spectrometer on the Pioneer mission in 1978 measured the atmospheric composition relative to  $\text{CO}_2$ , the dominant atmospheric constituent. The  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios were observed to be close to the Earth value, whereas the  $^{15}\text{N}/^{14}\text{N}$  ratio is within 20% of that of the Earth (Hoffman et al. 1979). One of the major problems related to the origin and evolution of Venus is that of its "missing

water". There is no liquid water on the surface of Venus today and the water vapor content in the atmosphere is probably not more than 220 ppm (Hoffman et al. 1979). This means that either Venus was formed from a material very poor in water or whatever water that was originally present has disappeared, possibly as the result of escape of hydrogen into space. And indeed Donahue et al. (1982) measured a 100-fold enrichment of deuterium relative to the Earth, which is consistent with such an out-gassing process. The magnitude of this process is, however, difficult to understand.

### 3.2 The Isotopic Composition of the Earth's Upper Mantle

Considerable geochemical and isotopic evidence has accumulated supporting the concept that many parts of the mantle have experienced a complex history of partial melting, melt emplacement, crystallization, recrystallization, deformation, and metasomatism. A result of this complex history is that the mantle is chemically and isotopically heterogeneous.

Heterogeneities in stable isotopes are difficult to detect, because stable isotope ratios are affected by the various partial melting-crystal fractionation processes that are governed by temperature-dependent fractionation factors between residual crystals and partial melt and between cumulate crystals and residual liquid. Unlike radiogenic isotopes, stable isotopes are also fractionated by low temperature surface processes. Therefore, they offer a potentially important means by which recycled crustal material can be distinguished from intra-mantle fractionation processes.

O, H, C, S, and N isotope compositions of mantle-derived rocks are substantially more variable than expected from the small fractionations at high temperatures. The most plausible process that may result in variable isotope ratios in the mantle is the input of subducted oceanic crust, and less frequent of continental crust, into some portions of the mantle. Because different parts of subducted slabs have different isotopic compositions, the released fluids may also differ in the O, H, C, and S isotope composition. In this context, the process of mantle metasomatism is of special significance. Metasomatic fluids rich in  $\text{Fe}^{3+}$ , Ti, K, LREE, P, and other large ion lithophile (LIL) elements tend to react with peridotite mantle and form secondary micas, amphiboles and other accessory minerals. The origin of metasomatic fluids is likely to be either (1) exsolved fluids from an ascending magma or (2) fluids or melts derived from subducted, hydrothermally altered crust and its overlying sediments.

With respect to the volatile behavior during partial melting, it should be noted that volatiles will be enriched in the melt and depleted in the parent material. During ascent of melts, volatiles will be degassed preferentially, and this degassing will be accompanied by isotopic fractionation (see discussion in Sect. 3.4).

Sources of information about the isotopic composition of the upper portion of the lithospheric mantle come from the direct analysis of unaltered ultramafic xenoliths brought rapidly to the surface in explosive volcanic vents. Due to rapid transport, these peridotite nodules are in many cases chemically fresh and considered by most

workers to be the best samples available from the mantle. The other primary source of information is from basalts, which represents partial melts of the mantle. The problem with basalts is that they do not necessarily represent the mantle composition because partial melting processes may have caused an isotopic fractionation relative to the precursor material. Partial melting of peridotites would result in the preferential melting of CaAl-rich minerals leaving behind refractory residues dominated by olivine and orthopyroxene which may differ slightly in the isotopic composition from the original materials. Also, basaltic melts may interact with the crustal lithosphere through which the magmas pass on their way to the Earth's surface. The following section will focus on ultramafic xenoliths, the isotopic characteristics of basalts is discussed in Sect. 3.3.

### 3.2.1 Oxygen

The  $\delta^{18}\text{O}$ -value of the bulk Earth is constrained by the composition of lunar basalts and bulk chondritic meteorites to be close to 6‰. Insight into the detailed oxygen isotope composition of the subcontinental lithospheric mantle has mostly come from the analysis of peridotitic xenoliths entrained in alkali basalts and kimberlites. The first oxygen isotope studies of such ultramafic nodules by Kyser et al. (1981, 1982) created much debate (e.g., Gregory and Taylor 1986; Kyser et al. 1986). The Kyser et al. data showed that clinopyroxene and orthopyroxene had similar and rather constant  $\delta^{18}\text{O}$ -values around 5.5‰, whereas olivine exhibited a much broader variation with  $\delta^{18}\text{O}$ -values extending from 4.5 to 7.2‰. Oxygen isotope fractionations between clinopyroxene and olivine ( $\Delta_{\text{cpx-ol}}$ ) were suggested to vary from  $-1.4$  to  $+1.2$ ‰, implying that these phases are not in isotopic equilibrium at mantle temperatures. Gregory and Taylor (1986) suggested that the fractionations in the peridotite xenoliths analyzed by Kyser et al. (1981, 1982) arose through open-system exchange with fluids having variable oxygen isotope compositions and with olivine exchanging  $^{18}\text{O}$  more rapidly than pyroxene.

It should be recognized, however, that olivine is a very refractory mineral and, as a result, quantitative reaction yields are generally not achieved, when analyzed by conventional fluorination techniques. Matthey et al. (1994) analyzed 76 samples of olivine in spinel-, garnet- and diamond-facies peridotites using laser fluorination techniques and observed an almost invariant O-isotope composition around 5.2‰. Assuming modal proportions of olivine, orthopyroxene, and clinopyroxene of 50:40:10, the calculated bulk mantle  $\delta^{18}\text{O}$ -value would be 5.5‰. Such a mantle source could generate liquids, depending on melting temperatures and degree of partial melting, with O-isotope ratios equivalent to those observed for MORB and many ocean island basalts.

Although the results of Matthey et al. (1994) have been confirmed by Chazot et al. (1997), it should be kept in mind that most of the mantle peridotites that have been analyzed for  $\delta^{18}\text{O}$  originate from the continental lithospheric mantle and not from the mantle as a whole. More recently, there have been several indications that

the O-isotope composition of mantle xenoliths from certain exotic settings can be more variable than indicated by Matthey et al. (1994) and Chazot et al. (1997). Zhang et al. (2000) and Deines and Haggerty (2000) documented complex disequilibrium features among peridotitic minerals and intra-crystalline isotope zonations, which presumably result from metasomatic fluid/rock interactions.

Eclogite xenoliths from diamondiferous kimberlites constitute an important suite of xenoliths because they may represent the deepest samples of the continental lithospheric mantle. Eclogite xenoliths have the most diverse range in  $\delta^{18}\text{O}$ -values between 2.2 and 7.9‰ (McGregor and Manton 1986; Ongley et al. 1987). This large range of  $^{18}\text{O}$ -variation indicates that the oxygen isotope composition of the continental lithosphere varies substantially, at least in any region where eclogite survives and is the most compelling evidence that some nodules represent metamorphic equivalents of hydrothermally altered oceanic crust.

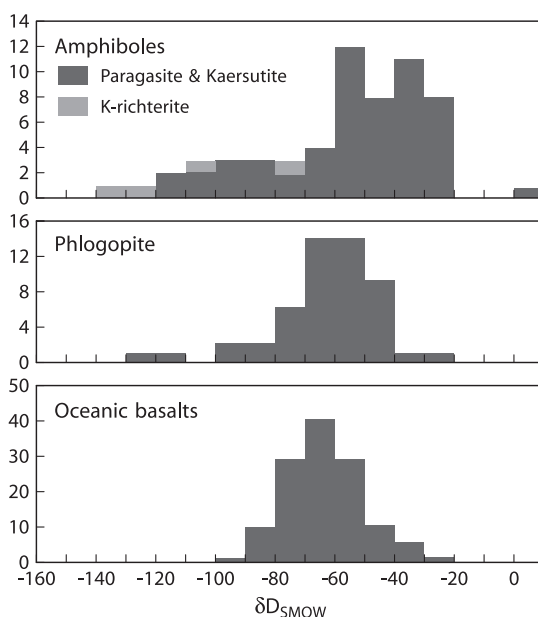
### 3.2.2 Hydrogen

The origin of the water on Earth is a controversial topic with very different schools of thought. One view postulates that water was delivered to Earth from exogeneous sources such as comets and/or meteorites, the other holds that the Earth's water has an indigenous origin (Drake and Richter 2002). Delivery of water from comets and meteorites can be evaluated in the light of their D/H ratios, suggesting that comets and meteorites cannot be major sources of water on Earth. The origin of water on Earth can be best explained by an indigenous source, indicating that the Earth accreted at least in part from hydrous materials, which are not represented by known meteorite classes (Drake and Richter 2002).

In this connection, the concept of "juvenile water" has to be introduced, which has influenced thinking in various fields of igneous petrology and ore genesis. Juvenile water is defined as water that originates from degassing of the mantle and that has never been part of the surficial hydrologic cycle. The analysis of OH-bearing minerals such as micas and amphiboles of deep-seated origin has been considered to be a source of information for juvenile water (e.g. Sheppard and Epstein 1970). Because knowledge about fractionation factors is limited and temperatures of final isotope equilibration between the minerals and water not known, calculations of the H-isotope composition of water in equilibrium with the mantle is rather crude.

Figure 3.4 gives  $\delta\text{D}$ -data on phlogopites and amphiboles, indicating that the hydrogen isotope composition of mantle water should lie in general between  $-80$  and  $-50$ ‰, the range first proposed by Sheppard and Epstein (1970) and subsequently supported by several other authors. Also shown in Fig. 3.4 are analyses for a considerable number of phlogopites and amphiboles which have  $\delta\text{D}$ -values higher than  $-50$ ‰. Such elevated  $\delta\text{D}$ -values may indicate that water from subducted oceanic crust has played a role in the genesis of these minerals. Similar conclusions have been reached as a result of the analysis of water of submarine basalts from the Mariana arc (Poreda 1985) and from estimates of the original  $\delta\text{D}$ -values in boninites from Bonin Island (Dobson and O'Neil 1987).

**Fig. 3.4** Hydrogen isotope variations in mantle-derived materials (modified after Bell and Ihinger, 2000)



Water in the mantle is found in different states: as a fluid especially near subduction zones, as a hydrous phase and as a hydroxyl point defect in nominally anhydrous minerals.  $\delta D$ -values between  $-90$  and  $-110$ ‰ have been obtained by Bell and Ihinger (2000) analyzing nominally anhydrous mantle minerals (garnet, pyroxene) containing trace quantities of OH. Nominally anhydrous minerals from mantle xenoliths are the most D-depleted of all mantle materials with  $\delta D$ -values 50‰ lower than MORB (O'Leary et al. 2005). This difference may either imply that these minerals represent an isotopically distinct mantle reservoir or that the samples analyzed have exchanged hydrogen during or after their ascent from the mantle (meteoric/water interaction?).

Similarly, complex results have been obtained from ion probe measurements of amphiboles on the scale of a few tens of microns with a precision not better than  $\pm 10$ ‰ (Deloule et al. 1991; Harford and Sparks 2001). Samples analyzed included ultramafic xenoliths and megacrysts of various localities, e.g., andesites from Soufriere volcano. Some of the investigated amphiboles show a marked internal crystal heterogeneity, a satisfactory explanation for this has still to be found. Given the rapid diffusion of hydrogen in most minerals, large D/H gradients within individual mantle amphiboles should be homogenized on short time scales under mantle conditions. The existence of heterogeneities imposes significant time constraints on mantle metasomatism and/or on uplift rates of the sampled material.



### 3.2.3 Carbon

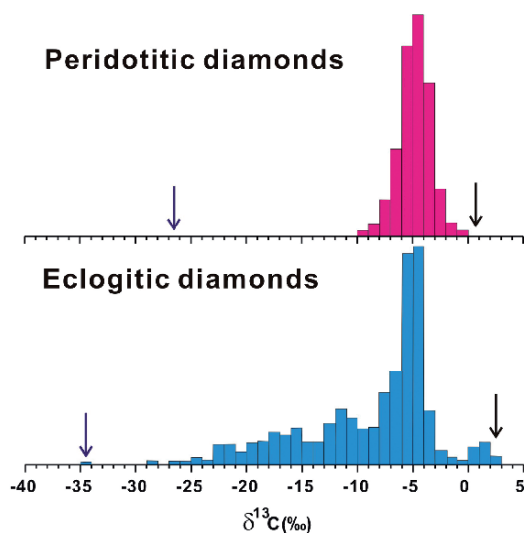
The presence of carbon in the upper mantle has been well documented through several observations: CO<sub>2</sub> is a significant constituent in volcanic gases associated with basaltic eruptions with the dominant flux at mid-ocean ridges. The eruption of carbonatite and kimberlite rocks further testifies to the storage of CO<sub>2</sub> in the upper mantle. Additionally, the presence of diamond and graphite in kimberlites, peridotite, and eclogite xenoliths reflects a wide range of mantle redox conditions, suggesting that carbon is related to a number of different processes in the mantle.

The isotopic composition of mantle carbon varies by more than 30‰ (see Fig. 3.2). To what extent this wide range is a result of mantle fractionation processes, the relict of accretional heterogeneities, or a product of recycling of crustal carbon is still unanswered. In 1953, Craig noted that diamonds exhibited a range of  $\delta^{13}\text{C}$ -values which clustered around  $-5\text{‰}$ . Subsequent investigations which included carbonatites (e.g., Deines 1989) and kimberlites (e.g., Deines and Gold 1973) indicated similar  $\delta^{13}\text{C}$ -values, which led to the concept that mantle carbon is relatively constant in C-isotopic composition, with  $\delta^{13}\text{C}$ -values between  $-7$  and  $-5\text{‰}$ . During the formation of a carbonatite magma, carbon is concentrated in the melt and is almost quantitatively extracted from its source reservoir. Since the carbon content of the mantle is low, the high carbon concentration of carbonatite melts requires extraction over volumes up to 10,000 times higher than the volume of a carbonatite magma (Deines 1989). Thus, the mean  $\delta^{13}\text{C}$ -value of a carbonatite magma should represent the average carbon isotope composition of a relatively large volume of the mantle.

The C-isotope distribution of diamonds is in total contrast to that for carbonatites. As more and more data for diamonds became available (Deines et al. 1984; Galimov 1985b; Cartigny 2005, and others) (at present more than 4,000 C-isotope data; Cartigny 2005), the range of C-isotope variation broadened to more than 40‰. (from  $-38$  to  $+5\text{‰}$  (Galimov 1991; Kirkley et al. 1991; Cartigny 2005). The large  $^{13}\text{C}$  variability is not random but restricted to certain genetic classes: Common “peridotitic diamonds” (diamonds associated with peridotitic xenoliths) have less variable carbon isotope compositions than “eclogitic diamonds”, which span the entire range of  $^{13}\text{C}/^{12}\text{C}$  variations (see Fig. 3.5; Cartigny 2005). Current debate centers on whether the more extreme values are characteristic of the mantle source regions or whether they have resulted from isotope fractionation processes linked to diamond formation.

While some workers have argued that the variations are the result of high-temperature isotope fractionation processes within the mantle (Deines 1980; Galimov 1991), others consider that peridotitic diamonds have formed from primitive carbon, whereas eclogitic diamonds have resulted from recycling of organic carbon (e.g., Kirkley et al. 1991). Recent ion probe measurements by Farquhar et al. (2002) on sulfide inclusions in diamonds from the Orapa kimberlite have yielded anomalous  $\Delta^{33}\text{S}$ -values in 4 out of 26 investigated diamonds. This confirms the conclusion that at least the sulfur in some diamonds derives from the surface. Spatially resolved analyses of individual diamonds by SIMS measurements first described by Harte and Otter (1992) and later by others have been summarized by



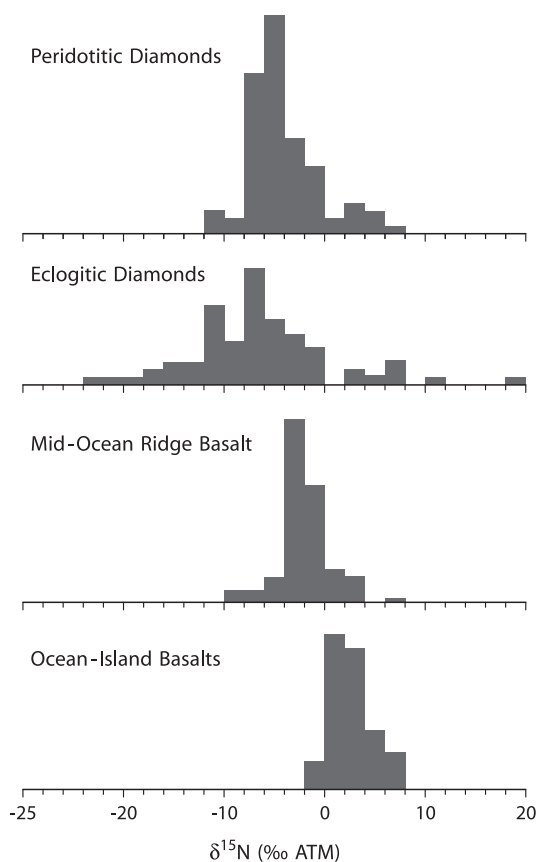


**Fig. 3.5** Carbon isotope variations of diamonds (modified after Cartigny 2005)

Hauri et al. (2002). The latter authors have shown  $\delta^{13}\text{C}$  variations of about 10‰ and more than 20‰ in  $\delta^{15}\text{N}$  which are associated with cathodoluminescence-imaged growth zones. Although the origin of these large variations is still unclear, they point to complex growth histories of diamonds.

### 3.2.4 Nitrogen

Because of the inert nature of nitrogen, it might be expected that the nitrogen isotopic composition of the mantle would be similar to that of the atmosphere. This is, however, not the case. Diamonds provide the most important source of information about mantle nitrogen, because nitrogen is their main trace component. Nitrogen isotopes have been measured in over 700 diamond samples with  $\delta^{15}\text{N}$ -values from +13 to −23‰ (Hauri et al. 2002). Despite this broad distribution, the majority range between −2 and −8‰ (Javoy et al. 1986; Boyd et al. 1992; Boyd and Pillinger 1994; Cartigny et al. 1997, 1998). A similar range in  $\delta^{15}\text{N}$ -values has been obtained by Marty and Humbert (1997) and Marty and Zimmermann (1999) for nitrogen trapped in MORB and OIB glasses (see Fig. 3.6). These negative  $\delta$ -values clearly indicate that the mantle contains nonatmospheric nitrogen. Surprisingly, positive  $\delta$ -values of about +3‰ have been found in deep mantle material sampled by mantle plumes which may suggest that recycling of oceanic crust may account for heavy nitrogen in the deep mantle (Dauphas and Marty 1999).



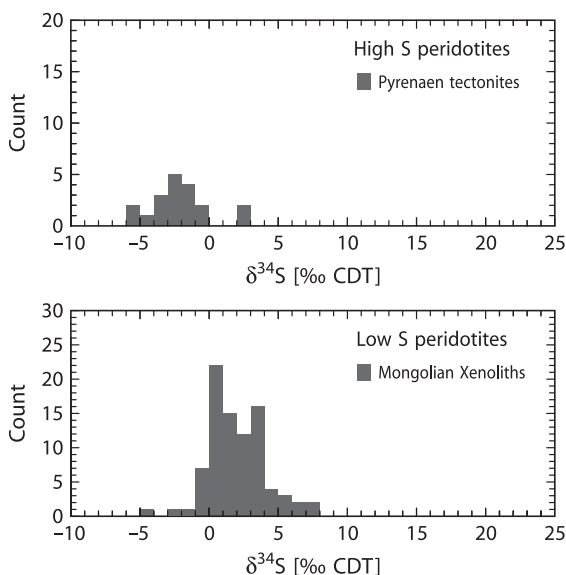
**Fig. 3.6** Nitrogen isotope variations in mantle-derived materials (modified after Marty and Zimmermann, 1999)

### 3.2.5 Sulfur

Sulfur occurs in a variety of forms in the mantle, the major sulfur phase is monosulfide solid solution between Fe, Ni, and Cu. Recent ion microprobe measurements on sulfide inclusions from megacrysts and pyroxenite xenoliths from alkali basalts and kimberlites and in diamonds gave  $\delta^{34}\text{S}$ -values from  $-11$  to  $+14\text{‰}$  (Chaussidon et al. 1987, 1989; Eldridge et al. 1991). Sulfur isotope variations within diamonds exhibit the same characteristics as previously described for carbon: i.e., eclogitic diamonds are much more variable than peridotitic diamonds.

Interesting differences in sulfur isotope compositions are observed when comparing high-S peridotitic tectonites with low-S peridotite xenoliths (Fig. 3.7). Tectonites from the Pyrenees predominantly have negative  $\delta^{34}\text{S}$ -values of around  $-5\text{‰}$ , whereas low-S xenoliths from Mongolia have largely positive  $\delta^{34}\text{S}$ -values of up to  $+7\text{‰}$ . Ionov et al. (1992) determined sulfur contents and isotopic compositions in

**Fig. 3.7** Sulfur isotope compositions of high- and low-S peridotites



some 90 garnet and spinel lherzolites from six regions in southern Siberia and Mongolia for which the range of  $\delta^{34}\text{S}$ -values is from  $-7$  to  $+7$ ‰. Ionov et al. (1992) concluded that low sulfur concentrations ( $<50$  ppm) and largely positive  $\delta^{34}\text{S}$ -values predominate in the lithospheric continental mantle worldwide. S-isotope compositions typical of MORB ( $\delta^{34}\text{S}$ :  $0$ – $1$ ‰) may be produced by melting of moderately depleted lherzolites. Primary melts with positive  $\delta^{34}\text{S}$ -values may be generated from mantle peridotites with larger degrees of depletion and/or from rocks metasomatized by subduction-related fluids.

### 3.2.6 Lithium and Boron

Since lithium and boron isotope fractionations mainly occur during low temperature processes, Li and B isotopes may provide a robust tracer of surface material that is recycled to the mantle (Elliott et al. 2004). Heterogeneous distribution of subducted oceanic and continental crust in the mantle will thus result in variations in Li and B isotope ratios. Furthermore, dehydration processes active in subduction zones appear to be of crucial importance in the control of Li and B isotope composition of different parts of the mantle. For the upper mantle as a whole Jeffcoate et al. (2007) gave an estimated  $\delta^7\text{Li}$ -value of  $3.5$ ‰.

Seitz et al. (2004), Magna et al. (2006) and Jeffcoate et al. (2007) reported significant Li isotope fractionation among mantle minerals. Olivines are about  $1.5$ ‰ lighter than coexisting orthopyroxenes, clinopyroxenes and phlogopites are in contrast highly variable, which might indicate isotope disequilibrium. In situ SIMS

analyses show Li isotope zonations in peridotite minerals. Jeffcoate et al. (2007) report a 40‰ variation in a single orthopyroxene crystal from San Carlos, which is attributed to diffusive fractionation during ascent and cooling.

Since boron concentrations in mantle minerals are exceedingly low, boron isotope analysis of mantle minerals are very restricted. On the basis of a boron budget between mantle and crust, Chaussidon and Marty (1995) concluded that the primitive mantle had a  $\delta^{11}\text{B}$ -value of  $-10 \pm 2\%$ . For MORB Spivack and Edmond (1987) and Chaussidon and Marty (1995) reported a  $\delta^{11}\text{B}$ -value of around  $-4\%$ . Higher and lower  $\delta^{11}\text{B}$ -values observed in some ocean island basalts should be due to crustal assimilation (Tanaka and Nakamura 2005).

### 3.3 Magmatic Rocks

On the basis of their high temperature of formation, it could be expected that magmatic rocks exhibit relatively small differences in isotopic composition. However, as a result of secondary alteration processes and the fact, that magmas can have a crustal and a mantle origin, the variation observed in isotopic composition of magmatic rocks can actually be quite large.

Provided an igneous rock has not been affected by subsolidus isotope exchange or hydrothermal alteration, its isotope composition will be determined by:

1. The isotope composition of the source region in which the magma was generated
2. The temperature of magma generation and crystallization
3. The mineralogical composition of the rock
4. The evolutionary history of the magma including processes of isotope exchange, assimilation of country rocks, magma mixing, etc

In the following sections, which concentrate on  $^{18}\text{O}/^{16}\text{O}$  measurements, some of these points are discussed in more detail (see also Taylor 1968, 1986; Taylor and Sheppard 1986).

#### 3.3.1 Fractional Crystallization

Because fractionation factors between melt and solid are small at magmatic temperatures, fractional crystallization is expected to play only a minor role in influencing the oxygen isotopic composition of magmatic rocks. Matsuhisa (1979), for example, reported that  $\delta^{18}\text{O}$ -values increased by approximately 1‰ from basalt to dacite within a lava sequence from Japan. Muehlenbachs and Byerly (1982) analyzed an extremely differentiated suite of volcanic rocks at the Galapagos spreading center and showed that 90% fractionation only enriched the residual melt by about 1.2‰. On Ascension Island Sheppard and Harris (1985) measured a difference of nearly 1‰ in a volcanic suite ranging from basalt to obsidian. Furthermore,

modeling closed-system crystal fractionation, an  $^{18}\text{O}$ -enrichment of about 0.4‰ per 10 wt% increase in  $\text{SiO}_2$  content can be predicted.

### ***3.3.2 Differences between Volcanic and Plutonic Rocks***

Systematic differences in O-isotope composition are observed between fine-grained, rapidly quenched volcanic rocks and their coarse-grained plutonic equivalents (Taylor 1968; Anderson et al. 1971). Fractionations among minerals in plutonic mafic rocks are on average about twice as great as for the corresponding fractionations observed in equivalent extrusive mafic rocks. This difference may result from retrograde exchange between minerals or post-crystallization exchange reactions of the plutonic rocks with a fluid phase. This interpretation is supported by the fact that basaltic and gabbroic rocks from the lunar surface yield the same “isotopic temperatures” corresponding to their initial temperatures of crystallization. Due to the absence of water on the Moon, no retrograde exchange took place.

### ***3.3.3 Low-Temperature Alteration Processes***

Because of their high glass contents and very fine grain size, volcanic rocks are very susceptible to low-temperature processes such as hydration and weathering, which are characterized by large  $^{18}\text{O}$ -enrichment effects in the altered rocks.

In general, it is probable that Tertiary and older volcanic rocks will exhibit O-isotope compositions that have been modified to higher  $^{18}\text{O}/^{16}\text{O}$  ratios from their primary state to some extent (Taylor 1968; Muehlenbachs and Clayton 1972; Cerling et al. 1985; Harmon et al. 1987). Although there is no way to ascertain the magnitude of these  $^{18}\text{O}$ -enrichments on a sample by sample basis, a crude estimate can be made by determining the water (and carbon dioxide) content and “correcting” to what are considered primary values of the suite of rocks to be analyzed (Taylor et al. 1984; Harmon et al. 1987). The primary water content of a magma is difficult to estimate, however, but it is generally accepted that primary basaltic magmas should not contain more than 1 wt % water. Thus, any water content  $>1\%$  could be of secondary origin and the  $\delta^{18}\text{O}$ -value for such samples should be corrected before such  $^{18}\text{O}$ -measurements are to be used for primary, magmatic interpretations.

### ***3.3.4 Assimilation of Crustal Rocks***

Because the various surface and crustal environments are characterized by different and distinctive isotope compositions, stable isotopes provide a powerful tool for discriminating between the relative role of mantle and crust in magma genesis. This

is especially true when stable isotopes are considered together with radiogenic isotopes, because variations within these independent isotopic systems may arise from unrelated geologic causes. For instance, a mantle melt that has been affected by contamination processes within the upper crust will exhibit increases in  $^{18}\text{O}/^{16}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios that correlate with an increase in  $\text{SiO}_2$  and decrease in Sr content. In contrast, a mantle melt, which evolves only through differentiation unaccompanied by interaction with crustal material, will have an O-isotope composition that mainly reflects that of its source region, independent of variations in chemical composition. In this latter case, correlated stable and radiogenic isotope variations would be an indication of variable crustal contamination of the source region (i.e., crustal material that has been recycled into the mantle via subduction).

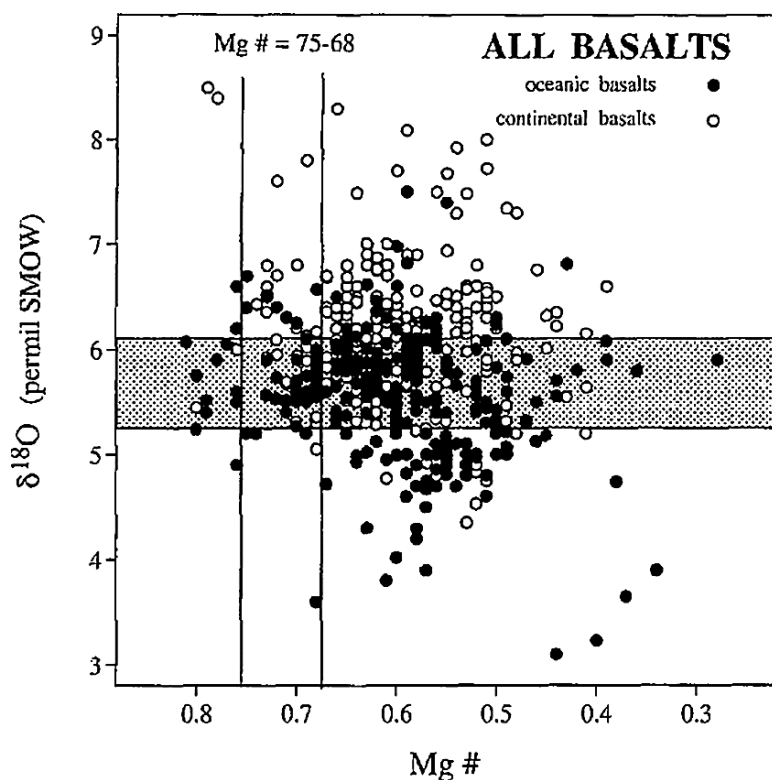
Modeling by Taylor (1980) and James (1981) has demonstrated that it is possible to distinguish between the effects of source contamination as well as crustal contamination. Magma mixing and source contamination are two-component mixing processes which obey two-component hyperbolic mixing relations, whereas crustal contamination is a three-component mixing process, involving the magma, the crustal contaminant, and the cumulates, that results in more complex mixing trajectories on an oxygen–radiogenic isotope plot.

### 3.3.5 Basaltic Rocks from Different Tectonic Settings

Harmon and Hoefs (1995) have assembled a database consisting of 2,855 O-isotope analyses of Neogene volcanic rocks worldwide. They observed a 5‰ variation in the  $\delta^{18}\text{O}$ -values of fresh basalts and glasses, which they have taken as evidence of significant oxygen isotope heterogeneities in the mantle sources of the basalts. This is documented in Fig. 3.8, which plots  $\delta^{18}\text{O}$ -values vs. Mg-numbers (Harmon and Hoefs 1995).

The usage of whole rock data has, however, its ambiguities. Estimates of original magmatic  $\delta^{18}\text{O}$ -values is best achieved through analysis of unaltered phenocrysts within rocks. Laser-based extraction methods on small amounts of separated mineral phases have documented subtle, but resolvable differences among different types of basaltic lavas (Eiler et al. 1996, 2000; Dorendorf et al. 2000; Cooper et al. 2004; Bindeman et al. 2004, 2005, and others).

MORB has a rather uniform O-isotope composition of all basalt types ( $5.5 \pm 0.2\text{‰}$ ) and can be used as a reference against which basalts erupted in other tectonic settings can be compared. By performing high precision laser isotope analyses on MORB glasses from the North Atlantic, Cooper et al. (2004) observed a  $\delta^{18}\text{O}$ -variation range of about 0.5‰, which is larger than originally thought by Harmon and Hoefs (1995).  $^{18}\text{O}$  variations correlate with geochemical parameters of mantle enrichment such as high  $^{87}\text{Sr}/^{86}\text{Sr}$  and low  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios. According to Cooper et al. (2004) the enriched material reflects subducted altered dehydrated oceanic crust.



**Fig. 3.8** Plot of  $\delta^{18}\text{O}$  values vs Mg numbers for oceanic basalts (*filled circles*) and continental basalts (*open circles*). The *shaded field* denotes the  $\pm 2\sigma$  range of a MORB mean value of +5.7‰, the *clear vertical field* denotes the range for primary basaltic partial melts in equilibrium with a peridotitic source (Harmon and Hoefs, 1995)

The largest variability in oxygen isotope composition has been found in subduction related basalts. Bindeman et al. (2005) observed a  $\delta^{18}\text{O}$  range in olivine phenocrysts between 4.9 and 6.8‰. Oxygen isotope variations in arc-related lavas can constrain the contributions of subducted sediments and fluids to the sub-arc mantle assuming the  $\delta^{18}\text{O}$  of the subducted component is known (Eiler et al. 2000; Dorendorf et al. 2000). These authors demonstrated that crustal assimilation or a contribution of oceanic sediments is negligible (<1–2%). Instead, the observed  $^{18}\text{O}$ -enrichment in olivines and clinopyroxenes may result from exchange with high  $^{18}\text{O}$  fluids derived from subducted altered oceanic crust.

Continental basalts tend to be enriched in  $^{18}\text{O}$  relative to oceanic basalts and exhibit considerably more variability in O-isotope composition, a feature attributed to interaction with  $^{18}\text{O}$ -enriched continental crust during magma ascent (Harmon and Hoefs 1995; Baker et al. 2000).

### 3.3.6 Ocean Water/Basaltic Crust Interactions

Information about the O-isotope character of the oceanic crust comes from DSDP/ODP drilling sites and from studies of ophiolite complexes, which presumably represent pieces of ancient oceanic crust. Primary, unaltered oceanic crust has  $\delta^{18}\text{O}$ -values close to MORB ( $\delta^{18}\text{O}$ :5.7‰). Two types of alteration can be distinguished within the oceanic lithosphere: at low temperatures weathering may markedly enrich the groundmass of basalts in  $^{18}\text{O}$ , but does not affect phenocrysts. The extent of this low-temperature alteration correlates with the water content: the higher the water content, the higher the  $\delta^{18}\text{O}$ -values (e.g., Alt et al. 1986). At temperatures in excess of about 300°C hydrothermal circulation beneath the mid-ocean ridges leads to a high-temperature water/rock interaction in which deeper parts of the oceanic crust become depleted in  $^{18}\text{O}$  by 1–2‰. Similar findings have been reported from ophiolite complexes, the most cited example is that of Oman (Gregory and Taylor 1981). Maximum  $^{18}\text{O}$  contents occur in the uppermost part of the pillow lava sequence and decrease through the sheeted dike complex. Below the base of the dike complex down to the Moho,  $\delta^{18}\text{O}$ -values are lower than typical mantle values by about 1–2‰.

Thus, separate levels of the oceanic crust are simultaneously enriched and depleted in  $^{18}\text{O}$  relative to “normal” mantle values because of reaction with sea water at different temperatures. Muehlenbachs and Clayton (1976) and Gregory and Taylor (1981) concluded that the  $^{18}\text{O}$  enrichments are balanced by the  $^{18}\text{O}$  depletions which acts like a buffer for the oxygen isotope composition of ocean water.

Recently, Gao et al. (2006) evaluated the existing database and concluded that apparent differences in mass-weighted  $\delta^{18}\text{O}$ -values exist among profiles through the recent and the fossil oceanic crust depending on differences in spreading rates. Oceanic crust formed under fast spreading ridges usually have depleted or balanced  $\delta^{18}\text{O}$ -values, whereas oceanic crust formed under slow spreading ridges is characterized by enriched  $\delta^{18}\text{O}$ -values. This difference might be due to different depths of sea water penetration in fast and slow spreading ridges.

### 3.3.7 Granitic Rocks

On the basis of  $^{18}\text{O}/^{16}\text{O}$  ratios, Taylor (1977, 1978) subdivided granitic rocks into three groups: (1) normal  $^{18}\text{O}$ -granitic rocks with  $\delta^{18}\text{O}$ -values between 6 and 10‰, (2) high  $^{18}\text{O}$ -granitic rocks with  $\delta^{18}\text{O}$ -values >10‰ and (3) low  $^{18}\text{O}$ -granitic rocks with  $\delta^{18}\text{O}$ -values <6‰. Although this is a somewhat arbitrary grouping, it nevertheless turns out to be a useful geochemical classification.

Many granitic plutonic rocks throughout the world have relatively uniform  $^{18}\text{O}$ -contents with  $\delta^{18}\text{O}$ -values between 6 and 10‰. Granitoids at the low  $^{18}\text{O}$  end of the normal group have been described from oceanic island – arc areas where continental crust is absent (e.g., Chivas et al. 1982). Such plutons are considered to be entirely mantle-derived. Granites at the high end of the normal  $^{18}\text{O}$ -group may have



formed by partial melting of crust that contained both a sedimentary and a magmatic fraction. It is interesting to note that many of the normal  $^{18}\text{O}$ -granites are of Precambrian age and that metasediments of this age quite often have  $\delta^{18}\text{O}$ -values below 10‰ (Longstaffe and Schwarcz 1977).

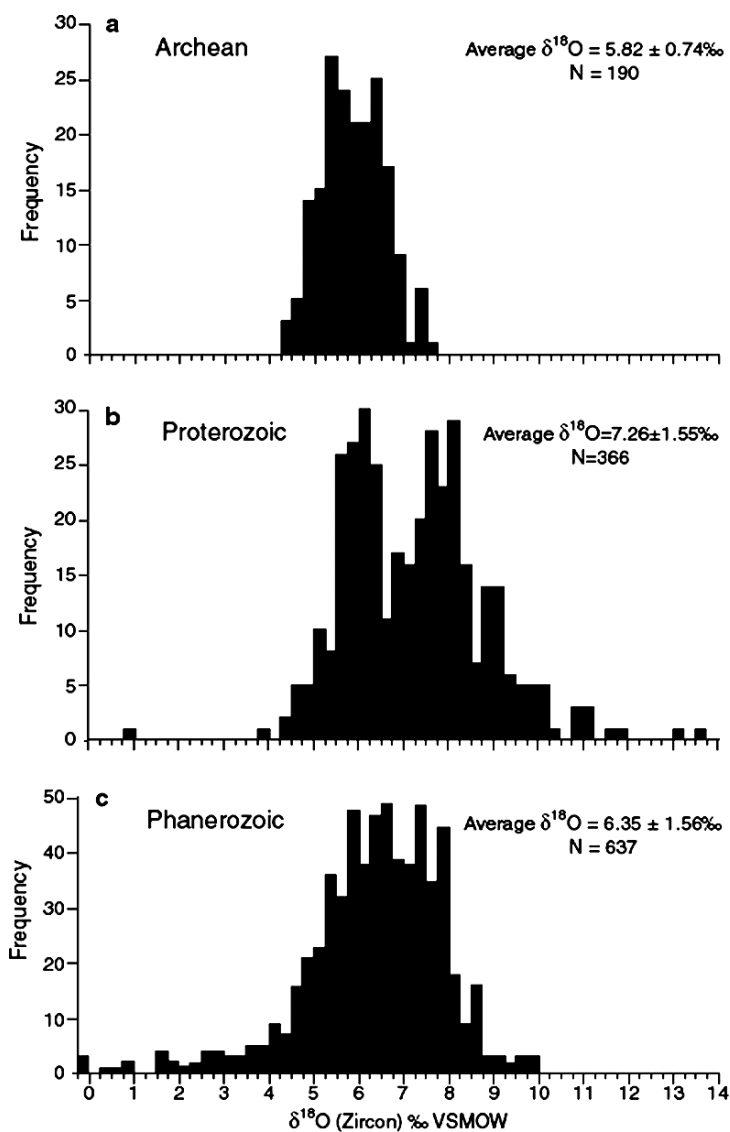
Granitic rocks with  $\delta^{18}\text{O}$ -values higher than 10‰ require derivation from some type of  $^{18}\text{O}$ -enriched sedimentary or metasedimentary protolith. For instance, such high  $\delta^{18}\text{O}$ -values are observed in many Hercynian granites of western Europe (Hoefs and Emmermann 1983), in Damaran granites of Africa (Haack et al. 1982) and in granites from the Himalayas of Central Asia (Blattner et al. 1983). All these granites are easily attributed to anatexis within a heterogeneous crustal source, containing a large metasedimentary component.

Granitic rocks with  $\delta^{18}\text{O}$ -values lower than 6‰ cannot be derived by any known differentiation process from basaltic magmas. Excluding those low  $^{18}\text{O}$  granites which have exchanged with  $^{18}\text{O}$  depleted meteoric–hydrothermal fluids under subsolidus conditions, a few primary low  $^{18}\text{O}$  granitoids have been observed (Taylor 1987). These granites obviously inherited their  $^{18}\text{O}$  depletion while still predominantly liquid, prior to cooling and crystallization. Such low  $^{18}\text{O}$  magmas may be formed by remelting of hydrothermally altered country rocks or by large-scale assimilation of such material in a rift-zone tectonic setting.

### 3.3.7.1 Oxygen Isotopes in Zircon

Recent advances in combining in situ measurements of radiogenic and stable isotopes in zircons allow a better understanding of the petrogenesis of granites and the evolution of the continental crust (Hawkesworth and Kemp 2006). Nonmetamict zircons preserve their  $\delta^{18}\text{O}$ -value from the time of crystallization because of their refractory and robust nature (Valley 2003). Magmas in equilibrium with the mantle crystallize zircon that have a narrow range in  $\delta^{18}\text{O}$ -values of  $5.3 \pm 0.3\text{‰}$ .  $^{18}\text{O}$ -variations toward higher values result if the parental magma incorporates higher  $^{18}\text{O}$  material (supracrustal rocks through melting or assimilation). Zircons with  $\delta^{18}\text{O}$ -values lower than 5.3‰ have been found in A-type granites (Wei et al. 2008) indicating that the zircons originate from low  $^{18}\text{O}$  magmas. O-isotope ratios in zircons thus can be used to discriminate between new mantle derived crust and crust that has been reworked.

Analyses of the oxygen isotope composition of zircons that have been dated may provide a record of growth and maturation of the crust. Valley et al. (2005) have analyzed 1,200 dated zircons representing the whole spectrum of geologic ages. Uniformly low  $\delta^{18}\text{O}$ -values are found in the first half of Earth history, but much more varied values are observed in younger rocks. In contrast to the Archean,  $^{18}\text{O}$ -values during the Proterozoic gradually increase possibly indicating a maturation of the crust (see Fig. 3.9). After 1.5 Ga high  $\delta^{18}\text{O}$ -values above 8‰ reflect gradual changes in the composition of sediments and the rate and style of recycling of surface-derived material into magmas (Valley et al. 2005).



**Fig. 3.9** Histograms of  $\delta^{18}\text{O}$ -values for igneous zircons ((a) Archean, (b) Proterozoic and (c) Phanerozoic) (after Valley et al. 2005)

### 3.4 Volatiles in Magmatic Systems

The isotope composition of magmatic volatiles and related isotope fractionation processes can be deduced by analyses of glasses, volcanic gases, and hot springs. The main process that can cause isotope fractionation of volatile compounds is degassing

and/or change in speciation (e.g.  $\text{SO}_2\text{--H}_2\text{S}$ ). The other process which can alter the isotopic composition of magmatic volatiles is assimilation and contamination. The ultimate origin of volatiles in magmatic systems – whether juvenile in the sense that they originate from primary mantle degassing, or recycled by subduction processes – is difficult to assess, but may be deduced in some cases. Because large differences exist in the isotope compositions of surface rocks relative to the mantle, the analysis of volatiles is important in assessing the extent of volatile transfer from the surface reservoirs to the mantle via subduction. Volatiles from arc related volcanic and hydrothermal systems may indicate an appreciable amount of surface derived materials and provide strong evidence of volatile recycling in subduction zones (Hauri 2002; Snyder et al. 2001; Fischer et al. 2002).

### 3.4.1 Glasses

*Hydrogen.* Water dissolves in silicate melts and glasses in at least two distinct forms: water molecules and hydroxyl groups. Because the proportions of these two species change with total water content, temperature and chemical composition of the melt, the bulk partitioning of hydrogen isotopes between vapor and melt is a complex function of these variables. Dobson et al. (1989) determined the fractionation between water vapor and water dissolved in felsic glasses in the temperature range from 530 to 850°C. Under these conditions, the total dissolved water content of the glasses was below 0.2%, with all water present as hydroxyl groups. The measured hydrogen fractionation factors vary from 1.051 to 1.035 and are greater than those observed for most hydrous mineral – water systems, perhaps reflecting the strong hydrogen bonding of hydroxyl groups in glasses.

Hydrogen isotope and water content data for MORB, OIB, and BAB glasses have been determined by Kyser and O'Neil (1984), Poreda (1985), and Poreda et al. (1986). The range of  $\delta\text{D}$ -values for MORB glasses is from  $-90$  to  $-40\text{‰}$  and is indistinguishable from that reported for phlogopites and amphiboles from kimberlites and peridotites (see Fig. 3.4). Kyser and O'Neil (1984) demonstrated that D/H ratios and water content in fresh submarine basalt glasses can be altered by (1) degassing, (2) addition of sea water at magmatic temperature and (3) low-temperature hydration. Extrapolations to possible unaltered D/H-ratios indicate that primary  $\delta\text{D}$ -values for most basalts are  $-80 \pm 5\text{‰}$ .

The process of degassing has been documented best for rhyolitic magmas where water-rich magmas (about 2%) have a  $\delta\text{D}$ -value of  $-50\text{‰}$ . At very late eruption stages with remaining water contents of around 0.1% the  $\delta\text{D}$ -value is around  $-120\text{‰}$  (Taylor et al. 1983; Taylor 1986). For this process, the decisive parameter is the isotopic fractionation between the vapor and the melt, which can be between 15 and 35‰ (Taylor 1986) and the amount of water lost from the system (Rayleigh fractionation). The degassing process produces an opposite trend to a meteoric water hydrothermal alteration, showing decreasing  $\delta\text{D}$ -values with increasing water content.

*Carbon.* Isotopic fractionation between  $\text{CO}_2$  and dissolved carbon in melts has been estimated by various authors to vary between 2 and 4‰ (as summarized by Holloway and Blank 1994), the vapor being enriched in  $^{13}\text{C}$  relative to the melt. This fractionation can be used to interpret the carbon isotope composition of glasses and  $\text{CO}_2$  in volcanic gases and to estimate the initial carbon concentration of undegassed basaltic melts.

Reported  $\delta^{13}\text{C}$ -values for basaltic glass vary from  $-30$  to about  $-3$ ‰ that represent isotopically distinct carbon extracted at different temperatures by stepwise heating (Pineau et al. 1976; Pineau and Javoy 1983; Des Marais and Moore 1984; Matthey et al. 1984). A “low-temperature” component of carbon is extractable below  $600^\circ\text{C}$ , whereas a “high-temperature” fraction of carbon is liberated above  $600^\circ\text{C}$ . There are two different interpretations regarding the origins of these two different types of carbon. While Pineau et al. (1976) and Pineau and Javoy (1983) consider that the whole range of carbon isotope variation observed to represent primary dissolved carbon, which becomes increasingly  $^{13}\text{C}$  depleted during multistage degassing of  $\text{CO}_2$ , Des Marais and Moore (1984) and Matthey et al. (1984) suggest that the “low-temperature” carbon originates from surface contamination. For MORB glasses, the “high-temperature” carbon has an isotopic composition typical for that of mantle values. Island arc glasses have lower  $\delta^{13}\text{C}$ -values, which might be explained by mixing two different carbon compounds in the source regions: an MORB – like carbon and an organic carbon component from subducted pelagic sediments (Matthey et al. 1984).

*Nitrogen.* The determination of nitrogen isotopes in basaltic glasses is severely complicated by its low concentration, which makes nitrogen sensitive to atmospheric contamination and to addition of surface-derived materials i.e., organic matter. Nitrogen in basaltic glasses has been determined by Exley et al. (1987), Marty and Humbert (1997), and Marty and Zimmermann (1999). The recent studies by Marty and coworkers indicate that nitrogen in MORB and OIB glasses has an average  $\delta^{15}\text{N}$ -value of around  $-4 \pm 1$ ‰ (see Fig. 3.6). The major factors affecting its isotopic composition appear to be magma degassing and assimilation of surface-derived matter.

*Sulfur.* The behavior of sulfur in magmatic systems is particularly complex: sulfur can exist as both sulfate and sulfide species in four different forms: dissolved in the melt, as an immiscible sulfide melt, in a separate gas phase, and in various sulfide and sulfate minerals. MORB glasses and submarine Hawaiian basalts have a very narrow range in sulfur isotope composition, with  $\delta^{34}\text{S}$ -values clustering around zero (Sakai et al. 1982, 1984). In subaerial basalts, the variation of  $\delta^{34}\text{S}$ -values is larger and generally shifted towards positive values. One reason for this larger variation is the loss of a sulfur-bearing phase during magmatic degassing. The effect of this process on the sulfur isotope composition depends on the ratio of sulfate to sulfide in the magma which is directly proportional to the fugacity of oxygen (Sakai et al. 1982). Arc volcanic rocks are particularly enriched in  $^{34}\text{S}$ , with  $\delta^{34}\text{S}$ -values up to  $+20$ ‰ (Ueda and Sakai 1984; Harmon and Hoefs 1986) which is considered to be mainly a product of recycling of marine sulfate during subduction.

### 3.4.2 Volcanic Gases and Hot Springs

The chemical composition of volcanic gases is naturally variable and can be modified significantly during sample collection, storage, and handling. While it is relatively simple to recognize and correct for atmospheric contamination, the effects of natural contamination processes in the near-surface environment are much more difficult to address. Thus, the identification of truly mantle-derived gases except helium remains very problematic. In addition to assimilation/contamination processes, the degassing history can significantly alter the isotopic composition of magmatic volatiles.

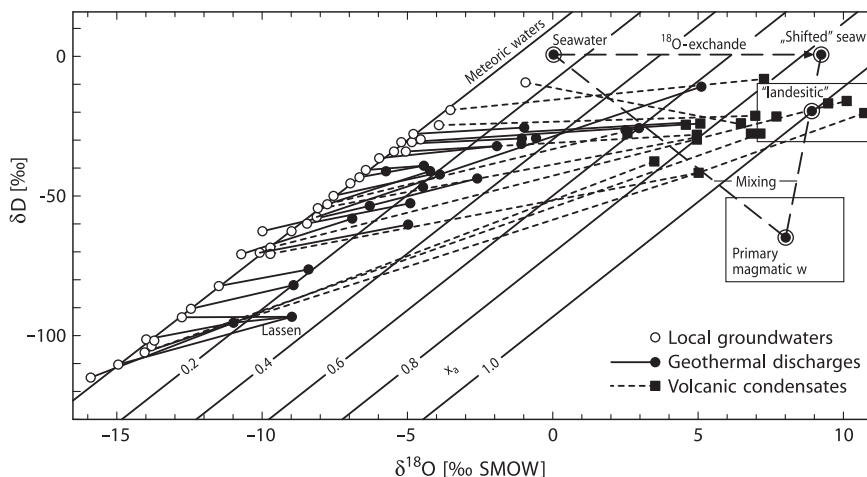
#### 3.4.2.1 Water

A long-standing geochemical problem is the source of water in volcanic eruptions and geothermal systems: how much is derived from the magma itself and how much is recycled meteoric water? One of the principal and unequivocal conclusions drawn from stable isotope studies of fluids in volcanic hydrothermal systems is that most hot spring waters are meteoric waters derived from local precipitation (Craig et al. 1956; Clayton et al. 1968; Clayton and Steiner 1975; Truesdell and Hulston 1980, and others).

Most hot spring waters have deuterium contents similar to those of local precipitation, but are usually enriched in  $^{18}\text{O}$  as a result of isotopic exchange with the country rock at elevated temperatures. The magnitude of the oxygen isotope shift depends on the O-isotope composition of both water and rock, the mineralogy of the rock, temperature, water/rock ratio, and the time of interaction.

There is increasing evidence, however, that a magmatic water component cannot be excluded in some volcanic systems. As more and more data have become available from volcanoes around the world, especially from those at very high latitudes, Giggenbach (1992) demonstrated that “horizontal”  $^{18}\text{O}$  shifts are actually the exception rather than the rule: shifts in oxygen isotope composition are also accompanied by a change in the deuterium content (Fig. 3.10). Giggenbach (1992) argued that all these waters followed similar trends corresponding to mixing of local ground waters with a water having a rather uniform isotopic composition with a  $\delta^{18}\text{O}$ -value of about 10‰ and a  $\delta\text{D}$ -value of about  $-20\text{‰}$ . He postulated the existence of a common magmatic component in andesite volcanoes having a  $\delta\text{D}$  of  $-20\text{‰}$  which is much higher than the generally assumed mantle water composition. The most likely source would be recycled sea water carried to zones of arc magma generation by the subducted slab.

What is sometimes neglected in the interpretation of isotope data in volcanic degassing products are the effects of boiling. Loss of steam from a geothermal fluid can cause isotopic fractionations. Quantitative estimates of the effects of boiling on the isotopic composition of water can be made using known temperature-dependent fractionation coefficients and estimates of the period of contact between the steam and liquid water during the boiling process (Truesdell and Hulston 1980).



**Fig. 3.10** Isotopic composition of thermal waters and associated local groundwaters. Lines connect corresponding thermal waters to local groundwaters (Giggenbach, 1992)

### 3.4.2.2 Carbon

$\text{CO}_2$  is the second most abundant gas species in magmatic systems. In a survey of  $\text{CO}_2$  emanations from tectonically active areas worldwide, Barnes et al. (1978) attributed  $\delta^{13}\text{C}$ -values between  $-8$  and  $-4\text{‰}$  to a mantle source. This is, however, problematic, because average crustal and mantle isotope compositions are more or less identical and surficial processes that can modify the carbon isotope composition are numerous. A more promising approach may be to analyze the  $^{13}\text{C}$ -content of  $\text{CO}_2$  collected directly from magmas at high temperatures.

The volcano where gases have been collected and analyzed for the longest time is Kilauea in Hawaii, the database covering a period from about 1960 to 1985 (Gerlach and Thomas 1986; Gerlach and Taylor 1990). Gerlach and Taylor (1990) consider a  $\delta^{13}\text{C}$ -value of  $-3.4 \pm 0.05\text{‰}$  to be the best estimate of the mean for the total summit gas emission of Kilauea. A two-stage degassing model was developed to explain these values: (1) ascent and pressure equilibration in the summit magma chamber and (2) rapid, near surface decompression of summit-stored magma during ascent and eruption. The study demonstrated that the gas at the summit is a direct representation of the parental magma C-isotope ratio ( $\delta^{13}\text{C}$ :  $-3.4\text{‰}$ ), whereas gases given off during East Rift Zone eruptions have a  $\delta^{13}\text{C}$ -value of  $-7.8\text{‰}$ , corresponding to a magma which had been affected by a degassing in a shallow magmatic system.

It is well documented that carbon dioxide in vesicles of MORB is derived from the upper mantle. In island arcs and subduction-related volcanism major portions of carbon may derive from limestones and organic carbon. Sano and Marty (1995) demonstrated that the  $\text{CO}_2/{}^3\text{He}$  ratio in combination with the  $\delta^{13}\text{C}$ -value can be used to distinguish between sedimentary organic, limestone, and MORB carbon. Using this approach Nishio et al. (1998) and Fischer et al. (1998) concluded

that about two-thirds of the carbon in a subduction zone originates from carbonates, whereas up to one-third is derived from organic carbon. Even larger portions (>80%) of CO<sub>2</sub> derived from marine carbonates have been found by Shaw et al. (2003) in volcanoes from the Central American arc. Carbon derived from a primary mantle source thus only plays a minor role in a subduction environment.

Besides CO<sub>2</sub>, methane has been reported in high-temperature hydrothermal vent fluids (Welhan 1988; Ishibashi et al. 1995). The origin of this methane is somewhat unclear, even in systems which are associated with <sup>3</sup>He anomalies. Whereas a non-biogenic magmatic origin of methane has been assumed for the East Pacific Rise (Welhan 1988), a thermogenic origin has been proposed for the Okinawa trough (Ishibashi et al. 1995).

In recent years there is a growing evidence that methane can be produced abiogenic during a Fischer-Tropsch type synthesis (reduction of CO or CO<sub>2</sub> by H<sub>2</sub> in the presence of a catalyst) (Sherwood-Lollar et al. 2006; McCollom and Seewald 2006 and others). Hydrocarbons (C<sub>1</sub>–C<sub>4</sub>) synthesized under abiogenic hydrothermal conditions are significantly depleted in <sup>13</sup>C relative to their CO<sub>2</sub> source. The magnitude of <sup>13</sup>C depletion may be similar to C-isotope fractionations during biological processes making it impossible to distinguish between biogenic and abiogenic sources of reduced carbon. This finding has important implications for the discussion of the Earth earliest biosphere. Sherwood-Lollar et al. (2002) observed a trend of decreasing <sup>13</sup>C contents with increasing carbon numbers C<sub>1</sub>–C<sub>4</sub> just opposite to gases derived from biologic sources. Experiments by Fu et al. (2007), however, could not confirm the trend observed by Sherwood-Lollar et al. (2002).

### 3.4.2.3 Nitrogen

Nitrogen in particular is a potential tracer of volatile recycling between the surface and the mantle, because of the large differences in N-isotope composition of MORB ( $\delta^{15}\text{N}$ : –5‰), the atmosphere 0‰ and sediments (6–7‰). As demonstrated by Zimmer et al. (2004), Clor et al. (2005) and Elkins et al. (2006), nitrogen isotopes are very well suited for determining the fate of organic matter in subduction zones. These authors have demonstrated variable contributions of organic matter-derived nitrogen along arcs in Costa Rica, Nicaragua, and Indonesia. For instance, Elkins et al. (2006) estimated that sediment contributions to volcanic and geothermal gases in the Nicaraguan volcanic front are around 70%.

### 3.4.2.4 Sulfur

Elucidation of the origin of sulfur in volcanic systems is complicated by the fact that next to SO<sub>2</sub>, significant amounts of H<sub>2</sub>S, sulfate and elemental sulfur can also be present. The bulk sulfur isotope composition must be calculated using mass balance constraints. The principal sulfur gas in equilibrium with basaltic melts at low pressure and high temperature is SO<sub>2</sub>. With decreasing temperature and/or increasing

water fugacity,  $\text{H}_2\text{S}$  becomes more stable.  $\delta^{34}\text{S}$ -values of  $\text{SO}_2$  sampled at very high temperatures provide the best estimate of the  $^{34}\text{S}$ -content of magmas (Taylor 1986). Sakai et al. (1982) reported  $\delta^{34}\text{S}$ -values of 0.7 to 1‰ in the solfataric gases of Kilauea which can be compared well with the  $\delta^{34}\text{S}$ -values of 0.9 to 2.6‰ for Mount Etna gases, measured by Allard (1983).  $\text{SO}_2$  from volcanoes of andesitic and dacitic composition is more enriched in  $^{34}\text{S}$ . This is especially pronounced in arc volcanoes from Indonesia, where Poorter et al. (1991) measured a  $\delta^{34}\text{S}$ -value of 5‰ for the bulk sulfur. Subducted oceanic crust may provide the  $^{34}\text{S}$  enriched sulfur to arc volcanoes.

In summary, stable isotope analysis (H, C, S) of volcanic gases and hot springs allow for estimates of the isotopic composition of the mantle source. However, it must be kept in mind that numerous possibilities for contamination, assimilation, and gas phase isotopic fractionation, especially in the surficial environment, make such deductions problematic at best. In cases where it may be possible to “see through” these secondary effects, small differences in H, C, N, and S isotope compositions of volcanic gases and hot springs might be characteristic of different geotectonic settings.

### ***3.4.3 Isotope Thermometers in Geothermal Systems***

Although there are many isotope exchange processes occurring within a geothermal fluid, many of which have the potential to provide thermometric information, only a few have generally been applied, because of suitable exchange rates for achieving isotope equilibrium (Hulston 1977; Truesdell and Hulston 1980; Giggenbach 1992). Temperatures are determined on the basis of calculated fractionation factors of Richet et al. (1977). Differences among geothermometers in the C–O–H–S system are generally ascribed to differences in exchange rates in the decreasing order  $\text{CO}_2\text{--H}_2\text{O}$  (oxygen) >  $\text{H}_2\text{O--H}_2$  (hydrogen) >  $\text{SO}_2\text{--H}_2\text{S}$  (sulfur) >  $\text{CO}_2\text{--CH}_4$  (carbon). Especially pronounced are the differences for the  $\text{CO}_2\text{--CH}_4$  thermometer which are often higher than the actual measured temperatures. Recent investigations on Nisyros volcano, Greece, however, suggest that chemical and isotopic equilibrium between  $\text{CO}_2$  and  $\text{CH}_4$  may occur down to temperatures as low as 320°C (Fiebig et al. 2004).

## **3.5 Ore Deposits and Hydrothermal Systems**

Stable isotopes have become an integral part of ore deposits studies. The determination of light isotopes of H, C, O, and S can provide information about the diverse origins of ore fluids, about temperatures of mineralization and about physico-chemical conditions of mineral deposition. In contrast to early views, which assumed that almost all metal deposits owed their genesis to magmas, stable isotope investigations



have convincingly demonstrated that ore formation has taken place in the Earth's near-surface environment by recycling processes of fluids, metals, sulfur, and carbon. Reviews of the application of stable isotopes to the genesis of ore deposits have been given by Ohmoto (1986), Taylor (1987) and Taylor (1997).

In as much as water is the dominant constituent of ore-forming fluids, knowledge of its origin is fundamental to any theory of ore genesis. There are two ways for determining  $\delta D$ - and  $\delta^{18}O$ -values of ore fluids:

1. By direct measurement of fluid inclusions contained within hydrothermal minerals
2. By analysis of hydroxyl-bearing minerals and calculation of the isotopic composition of fluids from known temperature-dependent mineral-water fractionations, assuming that minerals were precipitated from solutions under conditions of isotope equilibrium.

A. There are two different methods through which fluids and gases may be extracted from rocks: (1) thermal decrepitation by heating in vacuum and (2) crushing and grinding in vacuum. Serious analytical difficulties may be associated with both techniques. The major disadvantage of the thermal decrepitation technique is that, although the amount of gas liberated is higher than by crushing, compounds present in the inclusions may exchange isotopically with each other and with the host mineral at the high temperatures necessary for decrepitation. Crushing in vacuum largely avoids isotope exchange processes. However, during crushing large new surfaces are created which easily adsorb some of the liberated gases and that, in turn, might be associated with fractionation effects. Both techniques preclude separating the different generations of inclusions in a sample and, therefore, the results obtained represent an average isotopic composition of all generations of inclusions.

Numerous studies have used the  $\delta D$ -value of the extracted water to deduce the origin of the hydrothermal fluid. However, without knowledge of the internal distribution of hydrogen in quartz, such a deduction can be misleading (Simon 2001). Hydrogen in quartz mainly occurs in two reservoirs: (1) in trapped fluid inclusions and (2) in small clusters of structurally bound molecular water. Because of hydrogen isotope fractionation between the hydrothermal fluid and the structurally bound water, the total hydrogen extracted from quartz does not necessarily reflect the original hydrogen isotope composition. This finding may explain why  $\delta D$ -values from fluid inclusions often tend to be lower than  $\delta D$ -values from associated minerals (Simon 2001).

B. Oxygen-bearing minerals crystallize during all stages of mineralization, whereas the occurrence of hydrogen-bearing minerals is restricted in most ore deposits. Examples of hydroxyl-bearing minerals include biotite and amphibole at high temperatures (in porphyry copper deposits), chlorite and sericite at temperatures around 300°C, and kaolinite at around 200°C.

The mineral alunite, and its iron equivalent jarosite, is a special case. Alunite ( $KAl_2(SO_4)_2(OH)_2$ ) contains four sites where elements containing stable isotopes are found and both the sulfate and hydroxyl anionic groups may provide information on fluid source and condition of formation.

Alunite forms under highly acidic oxidizing conditions and is characterized by the assemblage alunite + kaolinite + quartz  $\pm$  pyrite. Stable isotope data of alunite in combination with associated sulfides and kaolinite permit recognition of environments and temperatures of formation (Rye et al. 1992).

The indirect method of deducing the isotope composition of ore fluids is more frequently used, because it is technically easier. Uncertainties arise from several sources: uncertainty in the temperature of deposition, and uncertainty in the equations for isotope fractionation factors. Another source of error is an imprecise knowledge of the effects of fluid chemistry ("salt effect") on mineral-water fractionation factors.

Several studies (e.g., Berndt et al. 1996; Driesner and Seward 2000; Horita et al. 1995; Shmulovich et al. 1999) have demonstrated that the approach of using mineral – pure water fractionation factors to deduce the origin of the water is incorrect. Isotope fractionations involving aqueous solutions depend not only on temperature and fluid composition, but also on the presence or absence of phase separation ("boiling"). Phase separation is an important process causing potentially isotope fractionation. Hydrogen isotope studies (Berndt et al. 1996; Shmulovich et al. 1999) indicate that high temperature phase separation produces D-enrichment in the vapor and D-depletion in the conjugate fluid. If the fractionation effect inherent in a boiling fluid system is disregarded, one may easily misinterpret the isotope composition of hydrothermal minerals, since boiling may mask the source of the parent fluids. In addition, for hydrogen isotope fractionations, pressure may have some control on mineral-water fractionations (Driesner 1997; Horita et al. 1999).

### 3.5.1 *Origin of Ore Fluids*

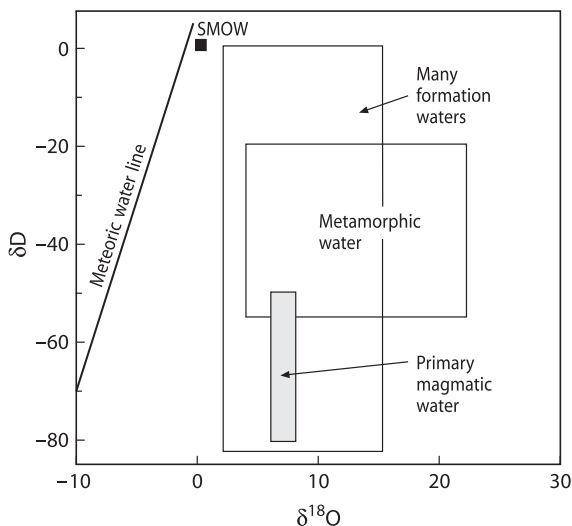
Ore fluids may be generated in a variety of ways. The principal types include (1) sea water, (2) meteoric waters and (3) juvenile water, all of which have a strictly defined isotopic composition. All other possible types of ore fluids such as formation, metamorphic, and magmatic waters can be considered recycled derivatives or mixtures from one or more of the three reference waters (see Fig. 3.11).

#### 1. Sea water

The isotopic composition of present day ocean water is more or less constant with  $\delta$ -values close to 0‰. The isotopic composition of ancient ocean water is less well constrained, but still should not be removed from 0 by more than 1 or 2‰. Many volcanogenic massive sulfide deposits are formed in submarine environments from heated oceanic waters. This concept gains support from the recently observed hydrothermal systems at ocean ridges, where measured isotopic compositions of fluids are only slightly modified relative to 0‰.  $\delta^{18}\text{O}$  and  $\delta\text{D}$ -values of vent fluids are best understood in terms of sea water interaction with the ocean crust (Shanks 2001).

Bowers and Taylor (1985) have modeled the isotopic composition of an evolving sea water hydrothermal system. At low temperatures, the  $\delta^{18}\text{O}$ -value of the fluid decreases relative to ocean water because the alteration products in the oceanic crust are  $^{18}\text{O}$ -rich. At around 250°C, the solution returns to its initial sea water isotopic

**Fig. 3.11** Plot of  $\delta D$  vs  $\delta^{18}O$  of waters of different origins



composition. Further reaction with basalt at  $350^{\circ}\text{C}$  increases the  $\delta^{18}\text{O}$ -value of modified sea water to  $\sim 2\text{‰}$ . The  $\delta D$ -value of the solution increases slightly at all temperatures because mineral-water fractionations are generally less than 0. At  $350^{\circ}\text{C}$ , the  $\delta D$ -value of the solution is  $2.5\text{‰}$ . The best-documented example for the role of ocean water during ore deposition is for the Kuroko-type deposits (Ohmoto et al. 1983).

## 2. Meteoric waters

Heated meteoric waters are a major constituent of ore-forming fluids in many ore deposits and may become dominant during the latest stages of ore deposition. The latter has been documented for many porphyry skarn-type deposits. The isotopic variations observed for several Tertiary North American deposits vary systematic with latitude and, hence, palaeo-meteoric water composition (Sheppard et al. 1971). The ore-forming fluid has commonly been shifted in O-isotope composition from its meteoric  $\delta^{18}\text{O}$ -value to higher  $^{18}\text{O}$  contents through water-rock interaction. Meteoric waters may become dominant in epithermal gold deposits and other vein and replacement deposits.

## 3. Juvenile water

The concept of juvenile water has influenced early discussions about ore genesis tremendously. The terms “juvenile water” and “magmatic water” have been used synonymously sometimes, but they are not exactly the same. Juvenile water originates from degassing of the mantle and has never existed as surface water. Magmatic water is a non-genetic term and simply means a water that has equilibrated with a magma.

It is difficult to prove that juvenile water has ever been sampled. One way to search for juvenile water is by analyzing hydroxyl-bearing minerals of mantle origin (Sheppard and Epstein 1970). The estimated isotopic composition of juvenile water from such an approach is  $\delta D: -60 \pm 20\text{‰}$  and  $\delta^{18}\text{O}: +6 \pm 1\text{‰}$  (Ohmoto 1986).

### 3.5.1.1 Magmatic Water

Despite the close association of intrusions with many ore deposits, there is still debate about the extent to which magmas contribute water and metals to ore-forming fluids. Many early studies of the stable isotope composition of hydrothermal minerals indicated a dominance of meteoric water (Taylor 1974), more recent studies show that magmatic fluids are commonly present, but that their isotopic compositions may be masked or erased during later events such as the influx of meteoric waters (Rye 1993; Hedenquist and Lowenstern 1994).

The  $\delta D$ -value of magmatic water changes progressively during degassing, resulting in a positive correlation between  $\delta D$  and the residual water content of an igneous body. Thus, late-formed hydroxyl-bearing minerals represent the isotopic composition of a degassed melt rather than that of the initial magmatic water. The  $\delta D$ -values of most of the water exsolved from many felsic melts are in the range of  $-60$  to  $-30\text{‰}$ , whereas the associated magmatic rocks may be significantly depleted in D.

The calculated range of isotopic composition for magmatic waters is commonly between 6 and 10‰ for  $\delta^{18}O$ -values and  $-50$  and  $-80\text{‰}$  for  $\delta D$ -values. Magmatic fluids may change their isotopic composition during cooling through isotope exchange with country rocks and mixing with fluids entrained within the country rocks. Thus, the participation of a magmatic water component during an ore-forming process is generally not easily detected.

### 3.5.1.2 Metamorphic Water

Metamorphic water is defined as water associated with metamorphic rocks during metamorphism. Thus, it is a descriptive, non-genetic term and may include waters of different ultimate origins. In a narrower sense, metamorphic water refers to the fluids generated by dehydration of minerals during metamorphism. The isotopic composition of metamorphic water may be highly variable, depending on the respective rock types and their history of fluid/rock interaction. A wide range of  $\delta^{18}O$ -values ( $5$ – $25\text{‰}$ ) and  $\delta D$ -values ( $-70$  to  $-20\text{‰}$ ) is generally attributed to metamorphic waters (Taylor 1974).

### 3.5.1.3 Formation Waters

The changes in the D- and  $^{18}O$ -contents of pore fluids depend on the origin of initial fluid (ocean water, meteoric water), temperature and the lithology of rocks with which the fluids are or have been associated. Generally, formation waters with the lowest temperature and salinity have the lowest  $\delta D$ - and  $\delta^{18}O$ -values, approaching those of meteoric waters. Brines of the highest salinities are generally more restricted in isotopic composition. It is still an unanswered question though whether meteoric water was the only source of water to these brines. The final isotope

composition of brines can be produced by reactions between meteoric water and sediments, or result from mixtures of fossil ocean water trapped in the sediments and meteoric water.

### ***3.5.2 Wall-Rock Alteration***

Information about the origin and genesis of ore deposits can also be obtained by analyzing the alteration products in wall-rocks. Hydrogen and oxygen isotope zonation in wall-rocks around hydrothermal systems can be used to define the size and the conduit zones of a hydrothermal system. The fossil conduit is a zone of large water fluxes, generally causing a strong alteration in the rocks and lowering the  $\delta^{18}\text{O}$ -values. Thus, fossil hydrothermal conduits can be outlined by following the zones of  $^{18}\text{O}$ -depletion. Oxygen isotope data are especially valuable in rock types that do not show diagnostic alteration mineral assemblages as well as those in which the assemblages have been obliterated by subsequent metamorphism (e.g., Beatty and Taylor 1982; Green et al. 1983). Criss et al. (1985, 1991) found excellent spatial correlations between low  $\delta^{18}\text{O}$ -values and economic mineralization in siliceous rocks. Similar zonation around ore deposits in carbonate rocks has also been observed (e.g., Vazquez et al. 1998). Thus, zones having anomalously low  $^{18}\text{O}$ -contents may be a useful guide for exploration of hydrothermal ore deposits.

### ***3.5.3 Fossil Hydrothermal Systems***

Mainly through the work of Taylor and coworkers, it has become well established that many epizonal igneous intrusions have interacted with meteoric groundwaters on a very large scale. The interaction and transport of large amounts of meteoric water through hot igneous rocks produces a depletion in  $^{18}\text{O}$  in the igneous rocks by up to 10–15‰ and a corresponding shift in the  $^{18}\text{O}$  content of the water. About 60 of such systems have been observed to date (Criss and Taylor 1986). They exhibit great variations in size from relatively small intrusions ( $<100\text{km}^2$ ) to large plutonic complexes ( $>1,000\text{km}^2$ ). Amongst the best documented examples are the Skaergaard intrusion in Greenland, the Tertiary intrusions of the Scottish Hebrides, and the Tertiary epizonal intrusions of the northwestern United States and southern British Columbia, where 5% of the land surface has been altered by meteoric hydrothermal water (Criss et al. 1991).

The best-studied example of a hydrothermal system associated with a gabbro is the Skaergaard intrusion (Taylor and Forester 1979; Norton and Taylor 1979). The latter authors carried out a computer simulation of the Skaergaard hydrothermal system and found a good match between calculated and measured  $\delta^{18}\text{O}$ -values. They further demonstrated that most of the subsolidus hydrothermal exchange took place at very high temperatures (400–800°C), which is compatible with the general

absence of hydrous alteration products in the mineral assemblages and with the presence of clinopyroxene.

In granitic hydrothermal systems, temperatures of alteration are significantly lower because of differences in the intrusion temperatures. The most conspicuous petrographic changes are chloritization of mafic minerals, particularly of biotite, and a major increase in the turbidity of feldspars. Large nonequilibrium quartz – feldspar oxygen isotope fractionations are typical. Steep linear trajectories on plots of  $\delta^{18}\text{O}_{(\text{feldspar})}$  vs.  $\delta^{18}\text{O}_{(\text{quartz})}$  are a characteristic feature of these hydrothermally altered rocks (see Fig. 2.17 (Chap. 2)). The trajectories result from the fact that feldspar exchanges  $^{18}\text{O}$  with hydrothermal fluids much faster than coexisting quartz and from the fact that the fluids entering the rock system have  $\delta^{18}\text{O}$ -values which are out of equilibrium with the mineral assemblage. The process seldom goes to completion, so the final mineral assemblage is in isotope disequilibrium, which is the most obvious fingerprint of the hydrothermal event.

Taylor (1988) distinguished three types of fossil hydrothermal systems on the basis of varying water/rock ratios, temperatures, and the length of time that fluid/rock interaction proceeds:

*Type I.* Epizonal systems with a wide variation in whole rock  $^{18}\text{O}$ -contents and extreme oxygen isotope disequilibrium among coexisting minerals. These systems typically have temperatures between 200 and 600°C and life-times  $< 10^6$  y.

*Type II.* Deeper-seated and/ or longer-lived systems, also with a wide spectrum of whole rock  $^{18}\text{O}/^{16}\text{O}$  ratios, but with equilibrated  $^{18}\text{O}/^{16}\text{O}$  ratios among coexisting minerals. Temperatures are between 400 and 700°C and life-times  $> 10^6$  y.

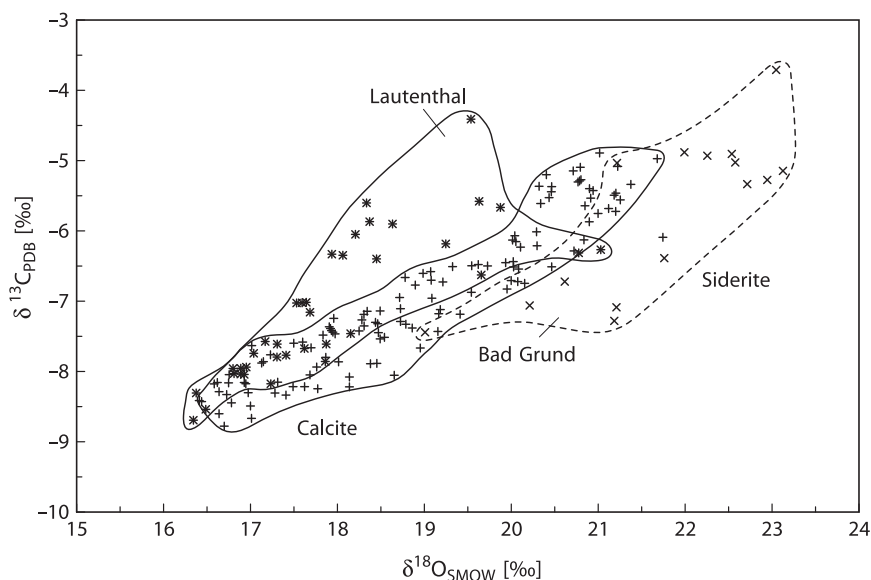
*Type III.* Equilibrated systems with a relatively uniform oxygen isotope composition in all lithologies. These systems require a large water/rock ratio, temperatures between 500 and 800°C, and life times around  $5 \times 10^6$  y.

These types are not mutually exclusive, Type III systems for example may have been subjected to Type I or Type II conditions at an earlier stage of their hydrothermal history.

### 3.5.4 Hydrothermal Carbonates

The measured  $\delta^{13}\text{C}$ - and  $\delta^{18}\text{O}$ -values of carbonates can be used to estimate the carbon and oxygen isotope composition of the fluid in the same way as has been discussed before for oxygen and hydrogen. The isotopic composition of carbon and oxygen in any carbonate precipitated in isotopic equilibrium with a fluid depends on the isotopic composition of carbon and oxygen in the fluid, the temperature of formation, and the relative proportions of dissolved carbon species ( $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and/or  $\text{CO}_3^{2-}$ ). To determine carbonate speciation, pH and temperature must be known; however, in most geologic fluids with temperatures above about 100°C, the content of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  is negligible compared to  $\text{CO}_2$  and  $\text{H}_2\text{CO}_3$ .

Experimental investigations have shown that the solubility of carbonate increases with decreasing temperature. Thus, carbonate cannot be precipitated from



**Fig. 3.12** C- and O-isotope compositions of calcites and siderites from the Bad Grund and Lautenthal deposits, Harz, Germany (after Zheng and Hoefs, 1993)

a hydrothermal fluid due to simple cooling in a closed system. Instead, an open system is required in which processes such as  $\text{CO}_2$  degassing, fluid–rock interaction or fluid mixing can cause the precipitation of carbonate. These processes result in correlation trends in  $\delta^{13}\text{C}$  vs.  $\delta^{18}\text{O}$  space for hydrothermal carbonates as often observed in nature and theoretically modeled by Zheng and Hoefs (1993).

Figure 3.12 presents  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ -values of hydrothermal carbonates from the Pb–Zn deposits of Bad Grund and Lautenthal, Germany. The positive correlation between  $^{13}\text{C}/^{12}\text{C}$ - and  $^{18}\text{O}/^{16}\text{O}$ -ratios can be explained either by calcite precipitation due to the mixing of two fluids with different NaCl concentrations or by calcite precipitation from a  $\text{H}_2\text{CO}_3$ -dominant fluid due to a temperature effect coupled with either  $\text{CO}_2$  degassing or with fluid–rock interaction.

### 3.5.5 Sulfur Isotope Composition of Ore Deposits

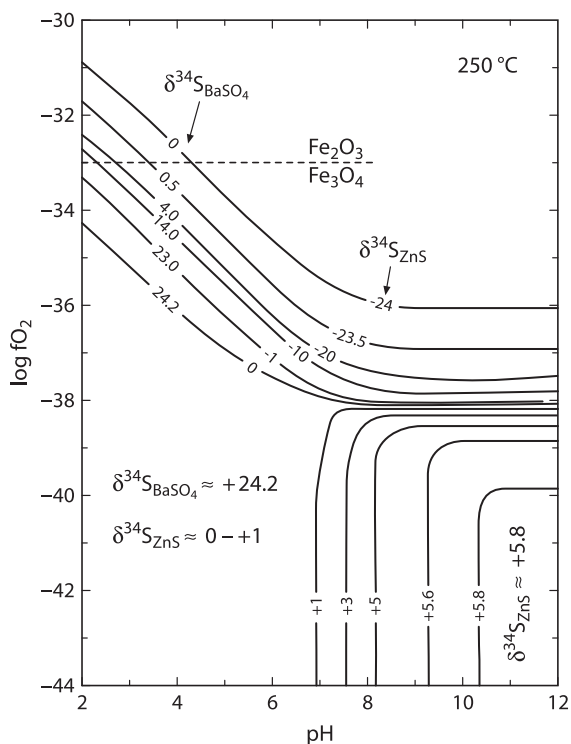
A huge amount of literature exists about the sulfur isotope composition in hydrothermal ore deposits. Some of this information has been discussed in earlier editions and, therefore, is not repeated here. Out of the numerous papers on the subject, the reader is referred to comprehensive reviews by Rye and Ohmoto (1974), Ohmoto and Rye (1979), Ohmoto (1986), Taylor (1987) and Ohmoto and Goldhaber (1997). The basic principles to be followed in the interpretation of  $\delta^{34}\text{S}$ -values in sulfidic ores were elucidated by Sakai (1968), and subsequently, were extended by Ohmoto (1972).

The isotopic composition of a hydrothermal sulfide is determined by a number of factors such as (1) isotopic composition of the hydrothermal fluid from which the mineral is deposited, (2) temperature of deposition, (3) chemical composition of the dissolved element species including pH and  $fO_2$  at the time of mineralization, and (4) relative amount of the mineral deposited from the fluid. The first parameter is characteristic of the source of sulfur, the three others relate to the conditions of deposition.

### 3.5.5.1 The Importance of $fO_2$ and pH

First, consider the effect of pH-increase due to the reaction of an acidic fluid with a carbonate-bearing host rocks. At pH = 5, practically all of the dissolved sulfur is undissociated  $H_2S$ , whereas at pH = 9 the dissolved sulfide is almost entirely dissociated. Since  $H_2S$  concentrates  $^{34}S$  relative to dissolved sulfide ion, an increase in pH leads directly to an increase in the  $\delta^{34}S$  of precipitated sulfides.

An increase in oxygen fugacities has a much stronger effect on the  $\delta^{34}S$ -values than a pH change, because of the large isotope fractionation between sulfate and sulfide. Figure 3.13 shows an example of the effect of pH and  $fO_2$  variation on the



**Fig. 3.13** Influence of  $fO_2$  and pH on the sulfur isotope composition of sphalerite and barite at 250 °C and  $\delta^{34}S_{SS} = 0$  (modified after Ohmoto, 1972)



sulfur isotope compositions of sphalerite and barite in a closed system at 250°C with  $\delta^{34}\text{S}_{\Sigma\text{S}} = 0\text{‰}$ . The curves are  $\delta^{34}\text{S}$  contours, which indicate the sulfur isotope compositions of the minerals in equilibrium with the solution. Sphalerite  $\delta^{34}\text{S}$ -values can range from  $-24$  to  $+5.8\text{‰}$  and those for barite from about  $0$  to  $24.2\text{‰}$  within geologically reasonable limits of pH and  $f\text{O}_2$ . In the low  $f\text{O}_2$  and pH region, sulfide  $^{34}\text{S}$  contents can be similar to  $\delta^{34}\text{S}_{\Sigma\text{S}}$  and can be rather insensitive to pH and  $f\text{O}_2$  changes. In the region of high  $f\text{O}_2$  values where the proportion of sulfate species becomes significant, mineral  $\delta^{34}\text{S}$ -values can be greatly different from  $\delta^{34}\text{S}_{\Sigma\text{S}}$  and small changes in pH or  $f\text{O}_2$  may result in large changes in the sulfur isotope composition of either sulfide or sulfate. Such a change must, however, be balanced by a significant change in the ratio of sulfate to sulfide.

In summary, interpretation of the distribution of  $\delta^{34}\text{S}$ -values relies on information about the source of sulfur and on a knowledge of the mineral parageneses that constrain the ambient temperature, EH and pH. If the oxidation state of the fluid is below the sulfate/ $\text{H}_2\text{S}$  boundary, then the  $^{34}\text{S}/^{32}\text{S}$  ratios of sulfides will be insensitive to redox shifts.

In the following section different classes of ore deposits are discussed.

### 3.5.5.2 Magmatic Ore Deposits

Magmatic deposits are characterized by sulfides which precipitate from mafic silicate melts rather than hydrothermal fluids. They can be divided into S-poor (deposits of platinum group elements) and S-rich magmatic sulfide systems (Ni–Cu deposits) (Ripley and Li 2003). Typical examples are the deposits of Duluth, Stillwater, Bushveld, Sudbury, and Noril'sk. In many of these deposits, relatively large deviations in  $\delta^{34}\text{S}$ -values from the presumed mantle melt value near zero are observed, which may indicate magma contamination by interactions with country rocks. The large spread in  $\delta^{34}\text{S}$  is generally attributed to assimilation of sulfur from the wall rocks, provided that the sulfur isotope composition of the country rocks is significantly different from the magma.

### 3.5.5.3 Magmatic Hydrothermal Deposits

This group of deposits is closely associated in space and time with magmatic intrusions that were emplaced at relatively shallow depths. They have been developed in hydrothermal systems driven by the cooling of magma (e.g., porphyry-type deposits and skarns). From  $\delta\text{D}$ - and  $\delta^{18}\text{O}$ -measurements, it has been concluded that porphyry copper deposits show the clearest affinity of a magmatic water imprint (Taylor 1974) with variable involvement of meteoric water generally at late stages of ore formation.

The majority of  $\delta^{34}\text{S}$ -values of sulfides fall between  $-3$  and  $1\text{‰}$  and of sulfates between  $8$  and  $15\text{‰}$  (Field and Gustafson 1976; Shelton and Rye 1982; Rye 2005). Sulfate–sulfide isotope data suggest a general approach to isotope equilibrium.

Calculated sulfate–sulfide temperatures, for conditions of complete isotope equilibrium, are typically between 450 and 600°C and agree well with temperatures estimated from other methods. Thus, the sulfur isotope data and temperatures support the magmatic origin of the sulfur in porphyry deposits.

#### 3.5.5.4 Epithermal Deposits

Epithermal ore deposits are hydrothermal deposits that form at shallow crustal levels. A wide spectrum of ore deposits of a different nature occurs in this category. Typical temperatures of mineralization range from 150 to 350°C with variable salinities. Individual deposits often reveal that more than one type of fluid was involved in the formation of a single ore deposit. One of the fluids involved often appears to be of meteoric origin. In many deposits different fluids were alternatively discharged into the vein system and promoted the precipitation of a specific suite of minerals, such as one fluid precipitating sulfides and another precipitating carbonates (Ohmoto 1986).

Compared to porphyry copper deposits  $\delta^{34}\text{S}$ -values in epithermal deposits are more variable due to lower temperatures of formation and significant amounts of both sulfide and sulfate in the hydrothermal fluid.

#### 3.5.5.5 Recent and Fossil Sulfide Deposits at Mid-Ocean Ridges

Numerous sulfide deposits have been discovered in the sea floor along the East Pacific Rise, Juan de Fuca Ridge, Explorer Ridge, and Mid-Atlantic Ridge (Shanks 2001). These deposits are formed from hydrothermal solutions which result from the interaction of circulating hot sea water with oceanic crust. Sulfides are derived mainly from two sources: (1) leaching from igneous and sedimentary wall rocks and (2) thermochemical sulfate reduction due to interaction with ferrous silicates and oxides or with organic matter.

The role of sulfur in these vents is complex and often obscured by its multiple redox states and by uncertainties in the degree of equilibration. Studies by Styr et al. (1981), Arnold and Sheppard (1981), Skirrow and Coleman (1982), Kerridge et al. (1983), Zierenberg et al. (1984), and others have shown that the sulfur in these deposits is enriched in  $^{34}\text{S}$  relative to a mantle source (typical  $\delta^{34}\text{S}$  ranges are between 1 and 5‰), implying small additions of sulfide derived from sea water.

Vent sulfides at sediment covered hydrothermal systems may carry, in addition, signatures of sulfides derived from bacterial reduction.  $\delta^{34}\text{S}$ -values alone may be unable to distinguish between the different sulfur sources. High precision measurements of  $\delta^{33}\text{S}$ ,  $\delta^{34}\text{S}$ , and  $\delta^{36}\text{S}$  allow, however, the distinction of biological isotope fractionation from abiological fractionation (Ono et al. 2007; Rouxel et al. 2008). Biogenic sulfides are characterized by relatively high  $\Delta^{33}\text{S}$ -values compared to hydrothermal sulfides. Sulfides from the East Pacific Rise and the Mid-Atlantic Ridge,

analyzed by Ono et al. (2007), gave low  $\Delta^{33}\text{S}$ -values compared to biogenic sulfides suggesting no contribution of biogenic sulfides. In altered oceanic basalts at ODP Site 801, however, Rouxel et al. (2008) provided evidence for secondary biogenic pyrite. These authors estimated that at least 17% of pyrite sulfur was derived from bacterial reduction.

For ancient seafloor sulfide deposits an alternative model has been discussed by Ohmoto et al. (1983), in which  $\text{H}_2\text{S}$  and sulfides are buffered by precipitated anhydrite and where  $\delta^{34}\text{S}$ -values reflect temperature dependent equilibrium fractionations between  $\text{SO}_4$  and  $\text{H}_2\text{S}$ .

To the category of ancient hydrothermal seafloor ore deposits belong volcanic associated massive sulfide deposits. They are characterized by massive Cu–Pb–Zn–Fe sulfide ores associated with submarine volcanic rocks. They appear to have been formed near the seafloor by submarine hot springs at temperatures of 150–350°C. Massive sulfide deposits have  $\delta^{34}\text{S}$ -values typically between zero and the  $\delta$ -value of contemporaneous oceanic sulfate, whereas the sulfate has  $\delta$ -values similar to or higher than contemporaneous sea water. According to Ohmoto et al. (1983) the ore-forming fluid is evolved sea water fixed as disseminated anhydrite and then reduced by ferrous iron and organic carbon in the rocks.

Another group belonging to this category of ore deposits is sedimentary-exhalative (sedex) massive sulfide deposits. Just as volcanic massive sulfide deposits, this group has formed on the seafloor or in unconsolidated marine sediments. Its members differ from volcanogenic massive deposits in that the dominant host-rock lithologies are marine shales and carbonates, the associated igneous activity is minor or negligible, and water depths seem to be considerably less than the >2,000 m proposed for most volcanogenic deposits. The total range of sulfide  $\delta^{34}\text{S}$ -values is much larger than the range observed in volcanogenic massive sulfide deposits.

Sulfides are fine-grained and texturally complex containing multiple generations of minerals. Two different origins of sulfur can be envisaged: biogenic and hydrothermal. Mineral separation methods cannot insure that mineral separates contain only one type of sulfur. Therefore, conventional techniques cannot answer questions such as: is most of the sulfur produced by bacterial reduction of sea water or is it inorganically acquired and hydrothermally introduced together with the metals? In situ ion microprobe techniques allow isotope analysis on a scale as small as 20  $\mu\text{m}$ . Studies by Eldridge et al. (1988, 1993) have revealed extremely large variations on distances of millimeters with gross disequilibrium between base metal sulfides and overgrown pyrites. Thus, the mean  $\delta^{34}\text{S}$ -values of these deposits are not particularly diagnostic of its origin, but additional measurements of  $\Delta^{33}\text{S}$  might be able to distinguish between different sulfur sources.

### 3.5.5.6 Mississippi Valley Type Deposits

The Mississippi Valley Type (MVT) deposits are epigenetic Zn–Pb deposits which mainly occur in carbonates from continental settings (Ohmoto 1986).

Characteristics often ascribed to MVT deposits include temperatures generally  $<200^{\circ}\text{C}$  and deposition from externally derived fluids, possibly basinal brines. Sulfur isotope values from MVT deposits suggest two major sulfide reservoirs, one between  $-5$  and  $+15\text{‰}$  and one greater than  $+20\text{‰}$  (Seal 2006). Both sulfide reservoirs can be related, however, to a common sea water sulfate source that has undergone different sulfur fractionation processes. Reduction of sulfate occurs either bacterially or by abiotic thermochemical reduction. High  $\delta^{34}\text{S}$ -values should reflect minimal fractionations associated with thermochemical reduction of sea water sulfate (Jones et al. 1996).

### 3.5.5.7 Biogenic Deposits

The discrimination between bacterial sulfate and thermal sulfate reduction in ore deposits on the basis of  $\delta^{34}\text{S}$ -values is rather complex. The best criterion to distinguish between both types is the internal spread of  $\delta$ -values. If individual sulfide grains at a distance of only a few millimeters exhibit large and nonsystematic differences in  $\delta^{34}\text{S}$ -values, then it seems reasonable to assume an origin involving bacterial sulfate reduction. Irregular variations in  $^{34}\text{S}$ -contents are attributed to bacteria growing in reducing microenvironments around individual particles of organic matter. In contrast, thermal sulfate reduction requires higher temperatures supplied by external fluids, which is not consistent with the closed system environment of bacterial reduction.

Two types of deposits, where the internal S-isotope variations fit the expected scheme of bacterial reduction, but where the biogenic nature was already known from other geological observations, are the “sandstone-type” uranium mineralization in the Colorado Plateau (Warren 1972) and the Kupferschiefer in Central Europe (Marowsky 1969), although thermal sulfate reduction may have occurred at the base of the Kupferschiefer (Bechtel et al. 2001).

### 3.5.5.8 Metamorphosed Deposits

It is generally assumed that metamorphism reduces the isotopic variations in a sulfide ore deposit. Recrystallization, liberation of sulfur from fluid and vapor phases, such as the breakdown of pyrite into pyrrhotite and sulfur, and diffusion at elevated temperatures should tend to reduce initial isotopic heterogeneities.

Studies of regionally metamorphosed sulfide deposits (Seccombe et al. 1985; Skauli et al. 1992) indicate, however, little evidence of homogenisation on the deposit scale. Significant changes may take place in certain restricted parts of the deposit as a result of special local conditions, controlled by factors such as fluid flow regimes and tectonics. Thus, a very limited degree of homogenisation takes place during metamorphism (Cook and Hoefs 1997). The extent of this is obscured by primary distribution and zonation patterns.

### 3.5.6 Metal Isotopes

One of the most important questions in the genesis of ore deposits is the origin of the metals. Recent analytical developments have provided a new tool for the analysis of metal isotopes (Fe, Cu, Zn, Mo). Since the bulk silicate earth (crust + mantle) shows a uniform mean isotope composition of the metals, different metal reservoirs with distinct isotopic compositions are not easily recognizable. Thus, investigations by Markl et al. (2006a, b) on Cu and Fe ores have indicated that tracing of ore sources is ambiguous.

Magmatic processes do not appear to produce significant Cu and Fe isotope variations. Markl et al. (2006a, b) demonstrated that primary ores from high temperature hydrothermal ores from the Schwarzwald mining district show a restricted range despite the fact that the analyzed ores came from a large area and formed during different mineralization events.

A range of more than 5‰ in  $\delta^{65}\text{Cu}$  has been interpreted by Markl et al. (2006a) as being due to redox processes among dissolved Cu-species and to fractionations during precipitation of Cu minerals. A 2.5‰ variation of iron minerals in  $\delta^{56}\text{Fe}$  has been explained by mixing models either through mixing with oxygen-rich surface waters resulting in  $^{56}\text{Fe}$ -depleted hematite or through mixing with  $\text{CO}_2$ -rich fluids leading to precipitation of isotopically depleted siderite (Markl et al. 2006b). Thus, an important new research field is the identification of low-temperature alteration processes in hydrothermal ore deposits, where biogenic and abiogenic redox processes potentially lead to significant isotope fractionations as already has been demonstrated in Sects. 2.13, 2.14, and 2.18, for Fe, Cu and Mo isotopes.

## 3.6 Hydrosphere

First, some definitions concerning water of different origin are given. The term *meteoric* applies to water that has been part of the meteorological cycle, and participated in processes such as evaporation, condensation, and precipitation. All continental surface waters, such as rivers, lakes, and glaciers, fall into this general category. Because meteoric water may seep into the underlying rock strata, it will also be found at various depths within the lithosphere dominating all types of continental ground waters. The *ocean*, although it continuously receives the continental run-off of meteoric waters as well as rain, is not regarded as being meteoric in nature. *Connate* water is water, which has been trapped in sediments at the time of burial. *Formation* water is present in sedimentary rocks and may be a useful nongenetic term for waters of unknown origin and age within these rocks.

### 3.6.1 Meteoric Water: General Considerations

When water evaporates from the surface of the ocean, the water vapor is enriched in H and  $^{16}\text{O}$  because  $\text{H}_2^{16}\text{O}$  has a higher vapor pressure than  $\text{HDO}$  and  $\text{H}_2^{18}\text{O}$  (see Table 1.1 in Chap. 1). Under equilibrium conditions at  $25^\circ\text{C}$ , the fractionation factors for evaporating water are 1.0092 for  $^{18}\text{O}$  and 1.074 for D (Craig and Gordon 1965). However, under natural conditions, the actual isotopic composition of water is more negative than the predicted equilibrium values due to kinetic effects (Craig and Gordon 1965). Vapor leaving the surface of the ocean cools as it rises and rain forms when the dew point is reached. During removal of rain from a moist air mass, the residual vapor is continuously depleted in the heavy isotopes, because the rain leaving the system is enriched in  $^{18}\text{O}$  and D. If the air mass moves poleward and becomes cooler, additional rain formed will contain less  $^{18}\text{O}$  than the initial rain. This relationship is schematically shown in Fig. 3.14. The isotope composition of mean world-wide precipitation is estimated to be  $\delta\text{D} = -22$  and  $\delta^{18}\text{O} = -4\text{‰}$  (Craig and Gordon 1965).

The theoretical approaches to explain isotope variations in meteoric waters evolved from the “isolated air mass” models, which are based on Rayleigh condensation, with immediate removal of precipitation and with a part of the condensate being kept in the cloud during the rain-out process. Isotope studies of individual rain events have revealed that successive portions of single events may vary drastically (Rindsberger et al. 1990). Quite often the pattern is “V-shaped”, a sharp decrease of  $\delta$ -values is usually observed at the beginning of a storm with a minimum somewhere in the middle of the event. The most depleted isotope values usually correspond to the period of most intense rain with little evaporation experienced by individual rain drops. It has also been observed that convective clouds produce precipitation with higher  $\delta$ -values than stratiform clouds. Thus, the isotope composition of precipitation from a given rain event depends on meteorological history of the air mass in which the precipitation is produced and the type of cloud through

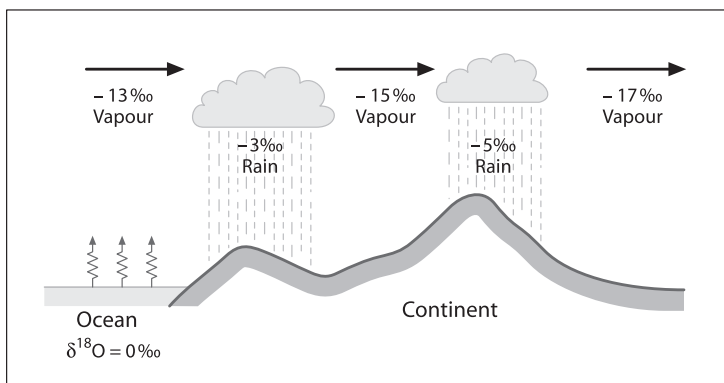
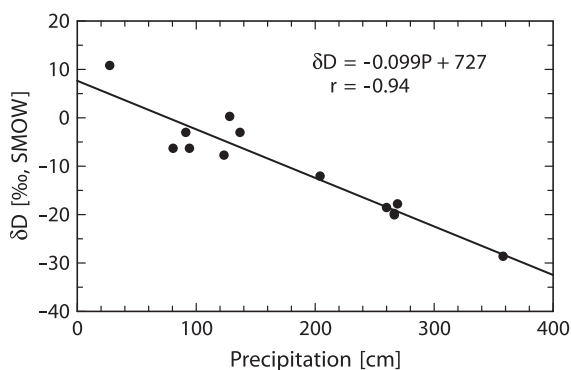


Fig. 3.14 Schematic O-isotope fractionation of water in the atmosphere (after Siegenthaler 1979)

which it falls. Liquid precipitation (rain) and solid precipitation (snow, hail) may differ in their isotope composition in so far as rain drops may undergo evaporation and isotope exchange with atmospheric vapor on their descent to the surface. By analyzing hailstones, discrete meteorological events can be studied because hailstones keep a record on the internal structure of a cloud. Jouzel et al. (1975) concluded that hailstones grow during a succession of upward and downward movements in a cloud.

The International Atomic Energy Agency (IAEA) has conducted a world-wide survey of the isotope composition of monthly precipitation for more than 35 years. The global distribution of D and  $^{18}\text{O}$  in rain has been monitored since 1961 through a network of stations (Yurtsever 1975). From this extensive database it can be deduced how geographic and meteorological factors (rainout, temperature, humidity) influence the isotopic composition of precipitation.

The first detailed evaluation of the equilibrium and nonequilibrium factors that determine the isotopic composition of precipitation was published by Dansgaard (1964). He demonstrated that the observed geographic distribution in isotope composition is related to a number of environmental parameters that characterize a given sampling site, such as latitude, altitude, distance to the coast, amount of precipitation, and surface air temperature. Out of these, two factors are of special significance: temperature and the amount of precipitation. The best temperature correlation is observed in continental regions nearer to the poles, whereas the correlation with amount of rainfall is most pronounced in tropical regions as shown in Fig. 3.15. The apparent link between local surface air temperature and the isotope composition of precipitation is of special interest mainly because of the potential importance of stable isotopes as palaeoclimatic indicators. The amount effect is ascribed to gradual saturation of air below the cloud, which diminishes any shift to higher  $\delta^{18}\text{O}$ -values caused by evaporation during precipitation (Fricke and O'Neil 1999).



**Fig. 3.15** Average  $\delta\text{D}$  values of the annual precipitation from oceanic islands as a function of the average amount of annual rainfall. The island stations are distant from continents, within  $30^\circ$  of the equator and at elevations less than 120 m (after Lawrence and White, 1991)

A compilation of studies throughout the world's mountain belts has revealed a consistent and linear relationship between change in the isotopic composition of precipitation and change in elevation (Poage and Chamberlain 2001). The isotopic composition of precipitation decreases linearly with increasing elevation by about 0.28‰/100 m in most regions of the world except in the Himalayas and at elevations above 5,000 m.

### 3.6.1.1 $\delta D$ - $\delta^{18}O$ Relationship

In all processes concerning evaporation and condensation, hydrogen isotopes are fractionated in proportion to oxygen isotopes, because a corresponding difference in vapor pressures exists between  $H_2O$  and  $HDO$  in one case and  $H_2^{16}O$  and  $H_2^{18}O$ , in the other. Therefore, hydrogen and oxygen isotope distributions are correlated in meteoric waters. Craig (1961a) first defined the following relationship:

$$\delta D = 8 \delta^{18}O + 10$$

which is generally known as the “Global Meteoric Water Line”.

Later, Dansgaard (1964) introduced the concept of “deuterium excess”,  $d$  defined as  $d = \delta D - 8 \delta^{18}O$ . Neither the numerical coefficient, 8, nor the deuterium excess,  $d$ , are really constant, both depend on local climatic processes. The long-term arithmetic mean for all analyzed stations of the IAEA network (Rozanski et al. 1993) is:

$$\delta D = (8.17 \pm 0.06) \delta^{18}O + (10.35 \pm 0.65) \text{‰}, r^2 = 0.99, n = 206.$$

Relatively large deviations from the general equation are evident when monthly data for individual stations are considered (Table 3.1). In an extreme situation, represented by the St. Helena station, a very poor correlation between  $\delta D$  and  $\delta^{18}O$  exists. At this station, it appears that all precipitation comes from nearby sources and represents the first stage of the rain-out process. Thus, the generally weaker correlations for the marine stations (Table 3.1) may reflect varying contributions of air masses with different source characteristics and a low degree of rain-out.

The imprint of local conditions can also be seen at other coastal and continental stations. The examples in Table 3.1 demonstrate that varying influences of different sources of vapor with different isotope characteristics, different air mass trajectories, or evaporation and isotope exchange processes below the cloud base, may often lead to much more complex relationships at the local level between  $\delta D$  and  $\delta^{18}O$  than suggested for the regional or continental scale by the global “Meteoric Water Line” equation.

Knowledge about the isotopic variations in precipitation is increased when single rain events are analyzed from local stations. Especially under mid-latitude weather conditions, such short-term variations arise from varying contributions of tropical, polar, marine, and continental air masses.



**Table 3.1** Variations in the numerical constant and the deuterium excess for selected stations of the IAEA global network (Rozanski et al. 1993)

Station	Numerical constant	Deuterium excess	r <sup>2</sup>
Continental and coastal stations			
Vienna	7.07	−1.38	0.961
Ottawa	7.44	+5.01	0.973
Addis Ababa	6.95	+11.51	0.918
Bet Dagan, Israel	5.48	+6.87	0.695
Izobamba (Ecuador)	8.01	+10.09	0.984
Tokyo	6.87	+4.70	0.835
Marine Stations			
Weathership E (N.Atlantic)	5.96	+2.99	0.738
Weathership V (N.Pacific)	5.51	−1.10	0.737
St.Helena (S.Atlantic)	2.80	+6.61	0.158
Diego Garcia Isl. (Indian Oc.)	6.93	+4.66	0.880
Midway Isl. (N.Pacific)	6.80	+6.15	0.840
Truk Isl. (N.Pacific)	7.07	+5.05	0.940

### 3.6.1.2 $\delta^{17}\text{O}$ – $\delta^{18}\text{O}$ Relationships

It has been common belief for many years that the  $^{17}\text{O}$  abundance in meteoric waters carries no additional information to that of  $^{18}\text{O}$ . Although mass-independent fractionations are not known to occur in water,  $\text{H}_2^{17}\text{O}$  is a useful tracer within the hydrologic cycle (Angert et al. 2004; Luz and Barkan 2007). Improvements in analytical techniques allow to measure  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  with a precision of a few 0.01‰ which permits calculation of  $\Delta^{17}\text{O}$  with similar precision and the tracing of very small  $\delta^{17}\text{O}$  variations.

As is well known the isotopic composition of water is controlled by two mass-dependent processes (1) the equilibrium fractionation that is caused by the different vapor pressures of  $\text{H}_2^{17}\text{O}$  and  $\text{H}_2^{18}\text{O}$  and (2) the kinetic fractionation that is caused by the different diffusivities of  $\text{H}_2^{17}\text{O}$  and  $\text{H}_2^{18}\text{O}$  during transport in air. Angert et al. (2004) have demonstrated that for kinetic water transport in air, the slope in a  $\delta^{17}\text{O}$ – $\delta^{18}\text{O}$  diagram is 0.511, whereas it is 0.526 for equilibrium effects. Similar values have been given by Luz and Barkan (2007).  $\Delta^{17}\text{O}$  is thus a unique tracer, which is, in contrast to the deuterium excess, temperature-independent and which may give additional information on humidity relations.

### 3.6.1.3 Ancient Meteoric Waters

Assuming that the H- and O-isotope compositions and temperatures of ancient ocean waters are comparable to present day values, the isotopic composition of ancient meteoric waters may have been governed by relations similar to those existing presently. However, given the local complexities, the application of this relation-

ship back through time should be treated with caution. To date, however, there is no compelling evidence that the overall systematics of ancient meteoric waters were very different from the present meteoric water relationship (Sheppard 1986). If the isotope composition of ocean water has changed with time, but global circulation patterns were like today, the “meteoric water line” at a specific time would be parallel to the modern meteoric water line, that is the slope would remain at a value of 8, but the intercept would be different.

The systematic behavior of stable isotopes in precipitation as a function of altitude can be used to provide estimates of paleoaltitude. In this approach the isotopic composition of paleoprecipitation is estimated from the analysis of in situ formed authigenic minerals (Chamberlain and Poage 2000; Blisnink and Stern 2005, and others). These authors have demonstrated that the effect of topography on the isotopic composition of precipitation is most straightforward in temperate mid-latitude regions, in topographically and in climatically simple settings.

### 3.6.2 Ice Cores

The isotopic composition of snow and ice deposited in the Polar Regions and at high elevations in mountains depend primarily on temperature. Snow deposited during the summer has less negative  $\delta^{18}\text{O}$ - and  $\delta\text{D}$ -values than snow deposited during the winter. A good example of the seasonal dependence has been given by Deutsch et al. (1966) on an Austrian glacier, where the mean  $\delta\text{D}$ -difference between winter and summer snow was observed to be  $-14\text{‰}$ . This seasonal cycle has been used to determine the annual stratigraphy of glaciers and to provide short-term climatic records. However, alteration of the snow and ice by seasonal melt water can result in changes of the isotopic composition of the ice, thus biasing the historical climate record. Systematic isotope studies also have been used to study the flow patterns of glaciers. Profiles through a glacier should exhibit lower isotope ratios at depth than nearer the surface, because deep ice may have originated from locations upstream of the ice-core site, where temperatures should be colder.

In the last decades, several ice cores over 1,000 m depth have been recovered from Greenland and Antarctica. In these cores, seasonal variations are generally observed only for the uppermost portions. After a certain depth, which depends on accumulation rates, seasonal variations disappear completely and isotopic changes reflect long-term climatic variations. No matter how thin a sample one cuts from the ice core, its isotope composition will represent a mean value of several years of snow deposition.

The most recent ice cores – investigated in great detail by large groups of researchers – are the Vostok core from East Antarctica (Lorius et al. 1985; Jouzel et al. 1987) and the GRIP and GISP 2 cores from Greenland (Dansgaard et al. 1993; Grootes et al. 1993). In the Vostok core, the low accumulation rate of snow in Antarctica results in very thin annual layers, which means that climate changes of a century or less are difficult to resolve. The newer Greenland ice cores GRIP and