Geol. 656 Isotope Geochemistry

lecture 32 Spring 2003

HYDROTHERMAL ACTIVITY, METAMORPHISM, AND ORE DEPOSITS I

STABLE ISOTOPES IN HYDROTHERMAL SYSTEMS

Ridge Crest Hydrothermal Activity and Metamorphism of the Oceanic Crust

Early studies of "greenstones" dredged from mid-ocean ridges and fracture zones revealed they were depleted in ^{18}O relative to fresh basalts. Partitioning between of oxygen isotopes between various minerals, such as carbonates, epidote, quartz and chlorite, in these greenstones suggested they had equilibrated at about 300° C (Muehlenbachs and Clayton, 1972). This was the first, but certainly not the only, evidence that the oceanic crust underwent hydrothermal metamorphism at depth. Other clues included highly variable heat flow at ridges and an imbalance in the Mg fluxes in the ocean. Nevertheless, the importance of hydrothermal processes was not generally recognized until the discovery of low temperature (~20° C) vents on the Galapagos Spreading Center in 1976 and high temperature (350° C) "black smokers" on the East Pacific Rise in 1979. Various pieces of the puzzle then began to fall rapidly into place and it was soon clear that hydrothermal activity was a very widespread and important phenomenon. Most of the oceanic crust is affected to some degree by this process, which also plays an important role in controlling the composition of seawater.

Hydrothermal metamorphism occurs because seawater readily penetrates the highly fractured and therefore permeable oceanic crust. A series of chemical reactions occurs as the seawater is heated, transforming it into the reduced, acidic, and metal-rich fluid. Eventually the fluid rises and escapes, forming the dramatic black smokers. There is still some debate about why hydrothermal fluid vent at relatively uniform temperatures of about 350° C*. The commonly held view is that this results from the density and viscosity minimum that occurs close to this temperature at pressures of 200-400 bars. Cathles, however, dissents and believes the venting temperature reflects temperature-dependent permeability. Above these temperatures, he argues, rock is so impermeable that fluid cannot penetrate further and hence rises.

Of the reactions that occur in the process, only one, namely oxygen isotope exchange, concerns us here. Seawater entering the oceanic crust has a $\delta^{18}O$ of 0, fresh igneous rock has a $\delta^{18}O$ of +5.7. As seawater is heated, it will exchange O with the surrounding rock until equilibrium is reached. At temperatures in the range of 300-400° C and for the mineral assemblage typical of greenschist facies basalt, the net water-rock fractionation is small†, 1 or 2‰. Thus isotopic exchange results in a decrease in the $\delta^{18}O$ of the rock and an increase in the $\delta^{18}O$ of the water. Surprisingly, there have only been a few oxygen isotope measurements of vent fluids, which indicate $\delta^{18}O$ of about +2.

At the same time hydrothermal metamorphism occurs deep in the crust, low-temperature weathering proceeds at the surface. This also involves isotopic exchange. However, for the temperatures (~2° C) and minerals produced by these reactions (smectites, zeolites, etc.), fractionations are quite large (something like 20‰). The result of these reactions is to increase the $\delta^{18}O$ of the shallow oceanic crust and decrease the $\delta^{18}O$ of seawater. Thus the effects of low temperature and high temperature reactions are opposing.

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* While this is typical, temperatures of 400° C or so have also been found. Most low-temperature vents waters, such as those on the GSC appear to be mixtures of 350° C hydrothermal fluid and ambient seawater, with mixing occuring at shallow depth beneath the seafloor.

† While the mineral-water fractionation factors for quartz and carbonate are in the range of +4 to +6 at these temperatures, the fractionation factor for anorthite and chlorite are close to zero, and that for magnetite is negative.

Muehlenbachs and Clayton (1976) suggested that these opposing reactions actually buffered the isotopic composition of seawater at a $\delta^{18}O$ of ~0. According to them, the net of low and high temperature fractionations was about +6, just the observed difference between the oceanic crust and the oceans. Thus, the oceanic crust ends up with an average $\delta^{18}O$ value about the same as it started with, and the net effect on seawater must be close to zero also. Could this be coincidental? One should always be suspicious of apparent coincidences in science, and they were.

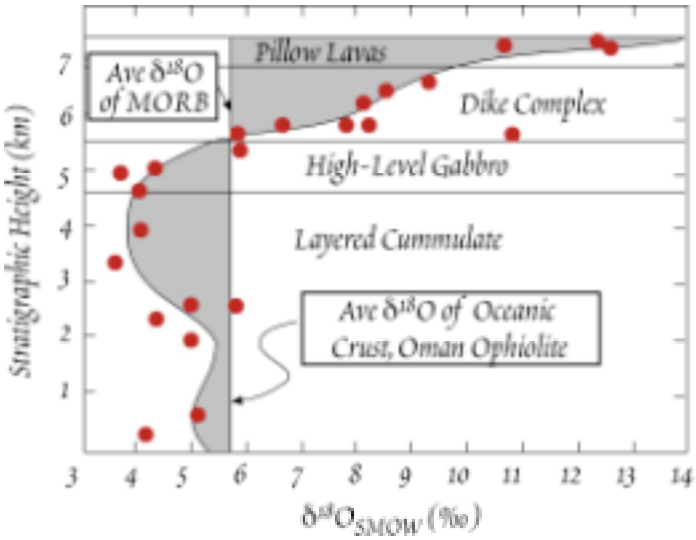


Figure 32.1. $\delta^{18}O$ of the Samail Ophiolite in Oman as a function of stratigraphic height. After Gregrory and Taylor (1981).

Let's think about this a little. Let's assume the net fractionation is 6, but suppose the $\delta^{18}O$ of the ocean was –10 rather than 0. What would happen? Assuming an infinite amount of oceanic crust available and a simple batch reaction with a finite amount of water, the net of high and low temperature basalt-seawater reactions would leave the water with $\delta^{18}O$ of –10 + 6 = –4. Each time a piece of oceanic crust is allowed to equilibrate with seawater, the $\delta^{18}O$ of the ocean will increase a bit. If the process is repeated enough, the $\delta^{18}O$ of the ocean will eventually reach a value of 6 – 6 = 0. Actually, what is required of seawater–oceanic crust interaction to maintain the $\delta^{18}O$ of the ocean at 0‰ is a net increase in isotopic composition of seawater by perhaps 1–2‰. This is because low-temperature continental weathering has the net effect of decreasing the $\delta^{18}O$ of the hydrosphere. This is what Muehlenbachs and Clayton proposed.

The "half-time" for this process, has been estimated to be about 46 Ma. The half-time is defined as the time required for the disequilibrium to decrease by half. For example, if the equilibrium value of the ocean is 0 ‰ and the actual value is -2 ‰, the $\delta^{18}O$ of the ocean should increase to –1 ‰ in 46 Ma. It would then require another 46 Ma to bring the oceans to a $\delta^{18}O$ of –0.5‰, etc.

This hypothesis was essentially confirmed by the first thorough oxygen isotope study of an ophiolite by Gregory and Taylor (1981). Their results for the Samail Ophiolite in Oman are shown in Figure 32.1. As expected, they found the upper part of the crust had higher $\delta^{18}O$ than fresh MORB and while the lower part of the section had $\delta^{18}O$ lower than MORB. Their estimate for the $\delta^{18}O$ of the entire section was +5.8, which is essentially identical to fresh MORB. Ocean Drilling Project (ODP) results show much the same pattern as the Samail ophiolite, though no complete section of the oceanic crust has yet been drilled. ODP results do show that hydrothermal alteration is not uniform. In Hole 504B, the deepest hole yet drilled, the transition to the hydrothermally altered zone was found to be quite sharp.

Although hydrothermal fluids with temperatures substantially above 400° C have not been found, there is abundance evidence that water-rock reactions occur at temperatures up to 700° C.

METEORIC GEOTHERMAL SYSTEMS

Hydrothermal systems occur not only in the ocean, but just about everywhere that magma is intruded into the crust. In the 1950's a debate raged about the rate at which the ocean and atmosphere were created by degassing of the Earth's interior. W. W. Rubey assumed that water in hydrothermal systems such as Yellowstone was magmatic and argued that the ocean and atmosphere were created quite gradually through magmatic degassing. Rubey turned out to be wrong. One of the first of many important contributions of stable isotope geochemistry to understanding hydrothermal systems was

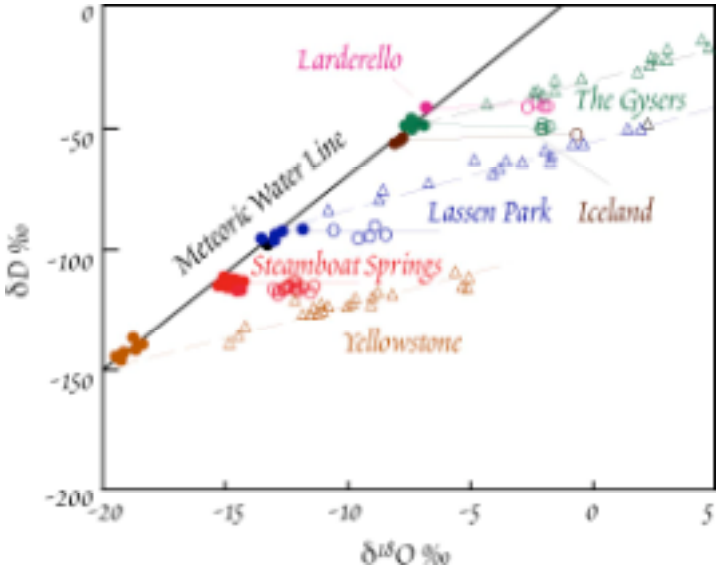


Figure 32.2. δD and $\delta^{18}O$ in meteoric hydrothermal systems. Closed circles show the composition of meteoric water in the vicinity of Yellowstone, Steamboat Springs (Colorado), Mt. Lassen (California), Iceland, Larderello (Italy), and The Geysers (California), and open circles show the isotopic composition of chloride-type geothermal waters at those locations. Open triangles show the location of acidic, sulfide-rich geothermal waters at those locations. Solid lines connect the meteoric and chloride waters, dashed lines connect the meteoric and acidic waters. The "Meteoric Water Line" shows the correlation between δD and $\delta^{18}O$ observed in precipitation (Figure 29.6).

the demonstration by Craig (1963) that water in these systems was meteoric, not magmatic. The argument is based upon the data shown in Figure 32.2. For each geothermal system, the δD of the "chloride" type geothermal waters is the same as the local precipitation and groundwater, but the $\delta^{18}O$ is shifted to higher values. The shift in $\delta^{18}O$ results from "high" temperature (~300°C) reaction of the local meteoric water with hot rock. However, because concentration of hydrogen in rocks is nearly 0 (more precisely because ratio of the mass of hydrogen in the water to mass of hydrogen in the reacting rocks is extremely high), there is essentially no change in the hydrogen isotopic composition of the water. If the water involved in these systems was magmatic, it would not have the same isotopic composition as local meteoric water (though it is possible that these systems contain a few percent magmatic water).

Acidic, sulfide-rich water from these systems does have δD that is different from local meteoric water. This shift occurs when hydrogen isotopes are fractionated during boiling of geothermal waters. The steam produced is enriched in sulfide, accounting for their acidic character. The water than condenses from this steam the mixes with meteoric water to produce the mixing lines observed.

Water-Rock Reaction: Theory

Very often in geology it is difficult to observe the details of processes occurring today and our understanding of many of Earth processes comes from observing the effects these processes have had in the past, i.e., the record they have left in the rocks. So it is with hydrothermal systems. In present systems, we very often can observe only the water venting, we cannot observe the reactions with rocks or the pattern of circulation. However, these, as well as temperatures involved and water-rock ratios, can be inferred from the imprint left by ancient hydrothermal systems.

Estimating temperatures at which ancient hydrothermal systems operated is a fairly straightforward application of isotope geothermometry, which we have already discussed. If we can measure the oxygen (or carbon or sulfur) isotopic composition of any two phases that were in equilibrium, and if we know the fractionation factor as a function of temperature for those phases, we can estimate the temperature of equilibration. We will focus now on water-rock ratios, which may also be estimated using stable isotope ratios.

For a closed hydrothermal system, we can write two fundamental equations. The first simply describes equilibrium between water and rock:

$$\Delta = \delta^{f}_{w} - \delta^{f}_{r} \qquad 32.1$$

where we use the subscript *w* to indicate water, and *r* to indicate rock. The superscript *f* indicates the final value. So 32.1 just says that the difference between the final isotopic composition of water and rock is equal to the fractionation factor (we implicitly assume equilibrium). The second equation is just a statement of mass balance for a closed system: the amount of isotope present before reaction must be the same as after reaction:

$$c_w W \delta^i_w + c_r R \delta^i_r = c_w W \delta^f_w + c_r R \delta^f_r \qquad 32.2$$

where *c* indicates concentration (we assume concentrations do not change, which is valid for oxygen, but perhaps not valid for other elements), *W* indicates the mass of water involved, *R* the mass of rock involved and the superscript *f* denotes the final isotope ratio.

Substituting equation 32.1 and rearranging, we derive the following equation:

$$\frac{W}{R} = \frac{\delta^f_r - \delta^i_r}{\delta^i_w - \delta^f_r - \Delta} \frac{c_r}{c_w} \qquad 32.3$$

The term on the left is the ratio of water to rock in the reaction. Notice that the r.h.s. does not include the final isotopic composition of the water, information that we would generally not have. The initial oxygen isotope composition of the water can be estimated in various ways. For example, we can determine the hydrogen isotopic composition (of rocks) and from that determine the oxygen isotope composition using the $\delta D - \delta^{18}O$ meteoric water line. The initial $\delta^{18}O$ can generally be inferred from unaltered samples, and the final isotopic composition of the rock can be measured. The fractionation factor can be estimated if we know the temperature and the phases in the rock. For oxygen, the ratio of concentration in the rock to water will be close to 0.5 in all cases.

Equation 32.3 is for a closed system, i.e., a batch reaction where we equilibrate W grams of water with R grams of rock. That is not very geologically realistic. In fact, a completely open system, where water makes one pass through hot rock, would be more realistic. In this case, we might suppose that a small parcel of water, *dW*, passes through the system and induces and incremental change in the isotopic composition of the rock. In this case, we can write:

$$R c_r d\delta_r = \left(\delta^i_w - \left[\Delta + \delta_r\right]\right) c_w dW \qquad 32.4$$

This equation states that the mass of isotope exchanged by the rock is equal to the mass of isotope exchanged by the water (we have substituted $\Delta + \delta_r$ for δ^f_w). Rearranging and integrating, we have:

$$\frac{W}{R} = \ln\left[\frac{\delta^f_r - \delta^i_r}{\delta_r - \Delta^f_r + \delta^i_w - \Delta}\right] + 1\left[\frac{c_r}{c_w}\right] \qquad 32.5$$

Thus it is possible to deduce the water rock ratio for an open system as well as a closed one.

Using this kind of approach, Gregory and Taylor (1981) estimated water/rock ratios of ≤ 0.3 for the gabbros of the Oman ophiolite. It should be emphasized, however, that this can be done with other isotope systems as well. For example, McCulloch et al. (1981) used Sr isotope ratios to estimate water/rock ratios varying from 0.5 to 40 for different parts of the Oman ophiolite.

The Skaergaard Intrusion

A classic example of a meteoric hydrothermal system is the Early Tertiary Skaergaard intrusion in East Greenland. The Skaergaard has been studied for 50 years or more as a classic mafic layered intrusion. Perhaps ironically, the initial motivation for study of the Skaergaard was determination of primary oxygen and hydrogen isotopic compositions of igneous rocks. The results, however, showed that the oxygen isotope composition of the Skaergaard has been pervasively altered by hydrothermal fluid flow. This was the first step in another important contribution of stable isotope geochemistry, namely the demonstration that most igneous intrusions have reacted extensively with water subsequent to crystallization. Figure 32.3 shows a map of the Skaergaard with contours of $\delta^{18}O$ superimposed on it. Figure 32.4 shows a restored cross section of the intrusion with contours of $\delta^{18}O$. There are several interesting features. First, it is clear that circulation of water was strongly controlled by permeability. The impermeable basement gneiss experienced little exchange, as did the part of the in-

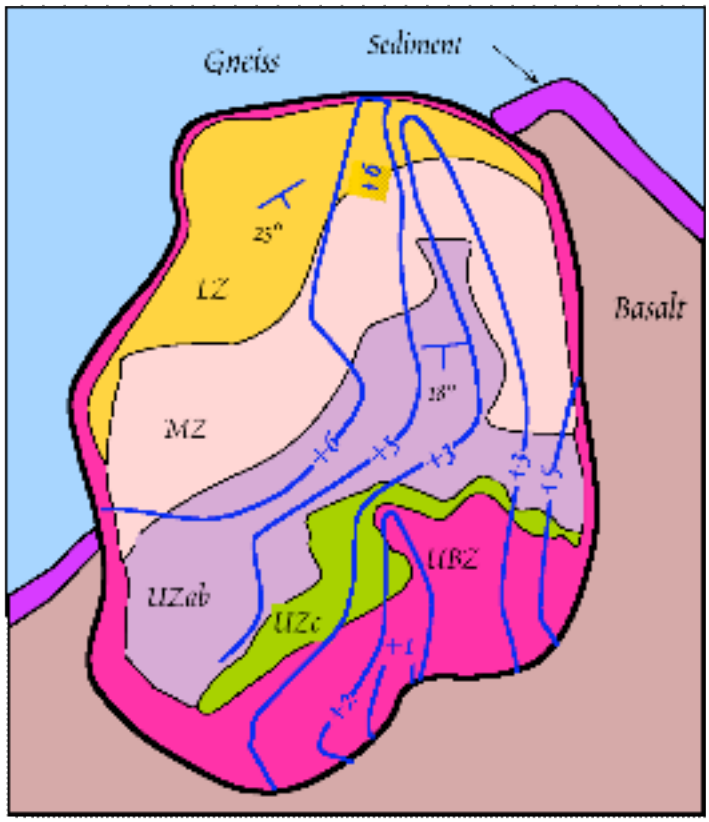


Figure 32.3. Oxygen isotope variations in the Skaergaard Intrusion. LZ, MZ, and UZ refer to the 'lower zone, 'middle zone' and 'upper zone' of the intrusion, which dips 20-25° to the southeast. UBZ refer to the 'upper border group'. The $\delta^{18}O$ = +6 contour corresponds more or less to the trace of the gneiss-basalt contact through the intrusion (SW to NE). The gneiss is essentially impermeable, while the basalt is highly fractured. Thus most water flow was above this contact, and the gabbro below it retained its original 'mantle' isotopic signature (+6). After Taylor (1974).

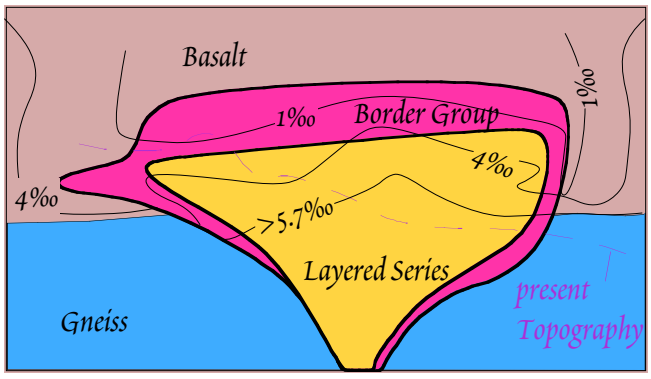


Figure 32.4. Restored cross-section of the Skaergaard intrusion with contours of $\delta^{18}O$.

trusion beneath the contact of the gneiss with the overlying basalt. The basalt is quite permeable and allowed water to flow freely through it and into the intrusion. Figures 32.3 and 32.4 define zones of low $\delta^{18}O$ which is the region of hydrothermal upwelling. Water was apparently drawn into the sides of the intrusion and then rose above. This is just the sort of pattern observed with finite element models of fluid flow through the intrusion.

Calculated water-rock ratios for the Skaergaard were 0.88 in the basalt, 0.52 in the upper part of the intrusion and 0.003 for the gneiss, demonstrating the importance of the basalt in conduction the water into the intrusion and the inhibiting effect of the gneiss. Models of the cooling history of the intrusion suggest that each cm^3 of rock was exposed to between 10^5 and 5×10^6 cm^3 of water over the 500,000 year cooling history of the intrusion. This would seem to conflict with the water/rock ratios estimated from oxygen isotopes. The difference is a consequence of each cc of water flowing through many cc's of rock, but not necessarily reacting with it. Once water had flowed through enough grams of rock to come to isotopic equilibrium, it would not react further with the rock through which it subsequently flowed (assuming constant temperature and mineralogy). Thus it is important to distinguish between W/R ratios calculated from isotopes, which reveal only the mass (or molar) ratio of water and rock in the net reaction, to flow models. Nevertheless, the flow models demonstrate that each gram of rock in such a system is exposed to an enormous amount of water. Figure 32.5 is a cartoon illustrating the hydrothermal system deduced from the oxygen isotope study.

Oxygen Isotopes and Mineral Exploration

Oxygen isotope studies can be a valuable tool in mineral exploration. Mineralization is very often (though not exclusively) associated with the region of greatest water flux,

such as areas of upward moving hot water above intrusions. Such areas are likely to have the lowest values of $\delta^{18}O$. To understand this, let's solve equ. 32.5, the final value of $\delta^{18}O$:

$$\delta_r^f = \left(\delta_r^i - \Delta_w^i + \Delta\right) e^{\frac{W c_w}{R c_r}} + \delta_w^i - \Delta \qquad 32.6$$

If we assume a uniform initial isotopic composition of the rocks and the water, then all the terms on the r.h.s. are constants except W/R and Δ, which is a function of temperature. Thus the final values of $\delta^{18}O$, i.e., the values we measure in an area such as the Skaergaard, are functions of the temperature of equilibration, and an exponential function of the W/R ratio. Figure 32.6 shows $\delta^{18}O_r^f$ plotted as a function of W/R and Δ, where $\delta^{18}O_r^i$ is assumed to be +6 and $\delta^{18}O_w^i$ is assumed to be -13.

Figure 32.7 shows another example of the $\delta^{18}O$ imprint of an ancient hydrothermal system: the Bohemia mining district in Lane County, Oregon, where Tertiary volcanic rocks of the Western Cascades have been intruded by a series of dioritic plutons. Approximately $1,000,000 worth of gold was removed from the region between 1870 and 1940. $\delta^{18}O$ contours form a bull's eye pattern, and the region of low $\delta^{18}O$ corresponds roughly with the area of prophylitic (i.e., greenstone) alteration. Notice that this region is broader than the contact metamorphic aereole. The primary area of mineralization occurs within the $\delta^{18}O < 0$ contour. In this area relatively large volumes of gold-bearing hydrothermal solution, cooled, perhaps to mixing with ground water, and precipitated gold. This is an excellent example of the value of oxygen isotope studies to mineral exploration. Similar bull's eye patterns are found around many other hydrothermal ore deposits.

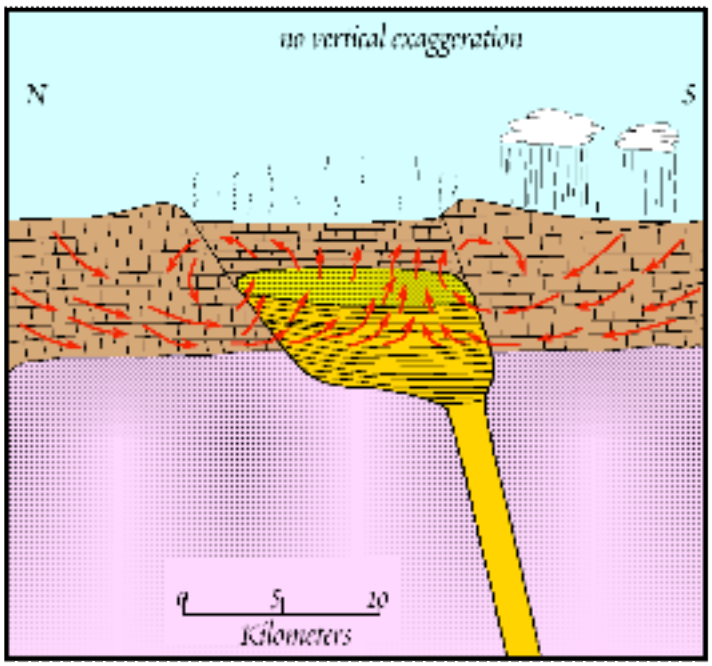


Figure 32.5. Cartoon illustrating the hydrothermal system in the Skaergaard intrusion. After Taylor (1968).

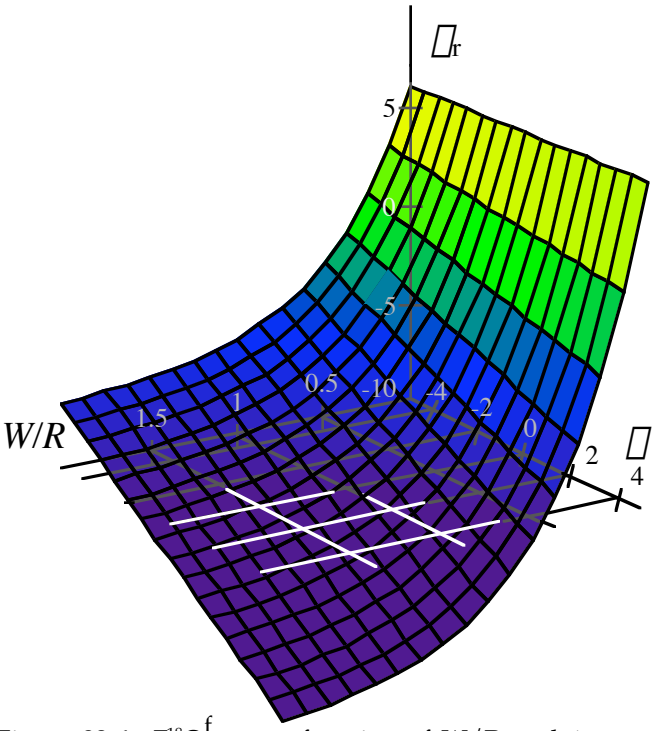


Figure 32.6. $\delta^{18}O_r^f$ as a function of W/R and Δ computed from equation 32.6.

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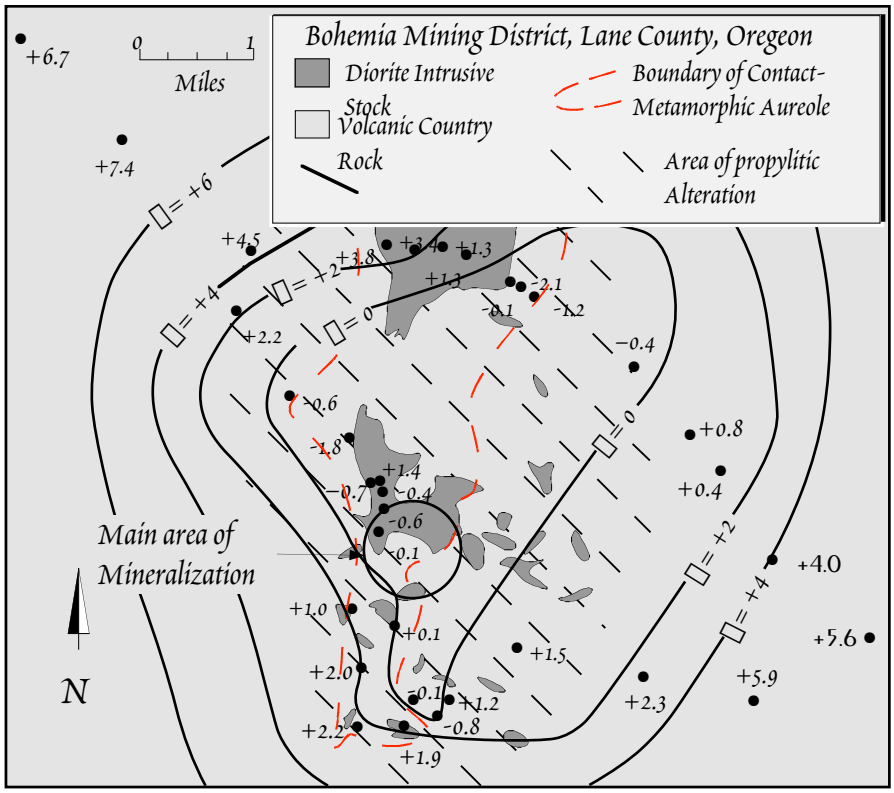


Figure 32.7. $\delta^{18}O$ variations in the Bohemia miing district, Oregon. Note the bull's eye pattern of the $\delta^{18}O$ contours. After Taylor, 1968.

Sulfur Isotopes and Ores

Introduction

A substantial fraction of all economically valuable metal ores are sulfides. These have formed in a great variety of environments and under a great variety of conditions. Sulfur isotope studies have been very valuable in sorting out the genesis of these deposits. Of the various stable isotope systems we will consider in this course, sulfur isotopes are undoubtedly the most complex. This complexity arises in part because of there are four common valence states in which sulfur can occur in the Earth, +6 (e.g., $BaSO_4$), +4 (e.g., SO_2), 0 (e.g., S), –1 (e.g., FeS_2) and –2 (H_2S). Significant equilibrium isotopic fractionations occur between each of these valence states. Each of these valence states forms a variety of compounds, and fractionations can occur between these as well. Finally, sulfur is important in biological processes and fractionations in biologically mediated oxidations and reductions are often different from fractionations in the abiological equivalents.

There are two major reservoirs of sulfur on the Earth that have uniform sulfur isotopic compositions: the mantle, which has $\delta^{34}S$ of ~0 and in which sulfur is primarily present in reduced form, and seawater, which has $\delta^{34}S$ of +20 and in which sulfur is present as SO_4^{2-}. Sulfur in sedimentary, metamorphic, and igneous rocks of the continental crust may have $\delta^{34}S$ that is both greater and smaller than these values (Figure 32.8). All of these can be sources of sulfide in ores, and further fractionation may occur during transport and deposition of sulfides. Thus the sulfur isotope geochemistry of sulfide ores is remarkably complex.

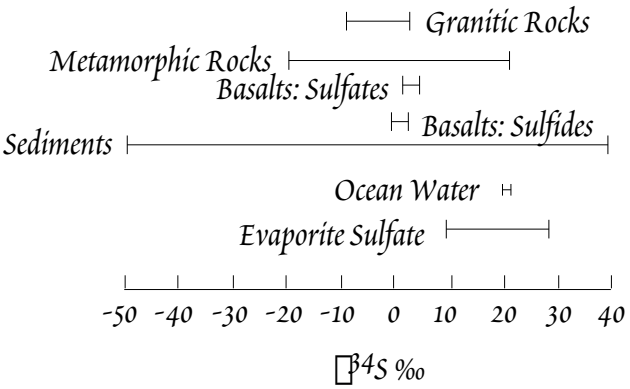


Figure 32.8. $\delta^{34}S_{CDT}$ in various geologic materials (after Hoefs, 1987).

Sulfur Isotope Fractionations in Magmatic Processes

Sulfur is present in peridotites as trace sulfides, and that is presumably its primary form in the mantle. At temperatures above about 400 °C, H_2S and SO_2 are the stable forms of sulfur in fluids and melts. In basaltic melts, sulfur occurs predominantly as dissociated H_2S: HS^-. It is un-

likely that significant fractionation occurs between these forms during melting. Indeed, as we have seen, the mean $\delta^{34}S$ in basalts (~+0.1) is close to the value in meteorites, which is presumably also the mantle value. The solubility of H_2S in basalt appears to be only slightly less than that of water, so that under moderate pressure, essentially all sulfur will remain dissolved in basaltic liquids. The solubility of H_2S in silicate melts is related to the Fe content, decreasing with decreasing Fe.

As basalts rise into the crust, cool, and crystallize, several processes can affect the oxidation state and solubility of sulfur and the produce isotopic fractionations. First, the decreasing pressure results in some of the sulfide partitioning into the gas (or fluid) phase. In addition, H_2 can be lost from the melt through diffusion. This increases the f_{O_2} of the melt, and as result, some of the sulfide will be oxidized to SO_2, which is very much less soluble in silicate melts than H_2S. Decreasing Fe content as a consequence of fractional crystallization will also decrease the solubility of S in the melt, increasing its concentration in a coexisting fluid or gas phase. Isotope fractionation will occur between the three species (dissolved HS^-, H_2S, SO_2). The isotopic composition of the fluid (gas) will differ from that of the melt, and can be computed as:

$$\delta^{34}S_{fluid} = \delta^{34}S_{melt} \; \Delta_{HS^-} + \Delta_{SO_2} \left[\frac{R}{R+1} \right] \qquad 32.7$$

where Δ_{HS} is the fractionation factor between HS^- and H_2S, Δ_{SO_2} is the fractionation factor between H_2S and SO_2. R is the molar ratio SO_2/H_2S and is given by:

$$R = \frac{X_{SO_2}}{X_{H_2S}} = \frac{K \gamma_{H_2S} f_{O_2}^{3/2}}{P_f \gamma_{H_2O} X_{H_2O} \gamma_{SO_2}} \qquad 32.8$$

where γ is the activity coefficient, P_f is the fluid pressure (generally equal to total pressure), f_{O_2} is oxygen fugacity, and K is the equilibrium constant for the reaction:

$$H_2S_{(g)} + \frac{3}{2} O_2 \rightleftarrows H_2O_{(g)} + SO_{2(g)} \qquad 32.9$$

Figure 32.9 shows the sulfur isotope fractionation between fluid and melt calculated from equations 32.7 and 32.8 as a function of function of temperature and f_{O_2} for P_{H_2O} = 1 kB. At the temperatures and f_{O_2} of most basalts, sulfur will be present primarily as H_2S in the fluid (gas phase) and SH^- in the melt. The fractionation between these species is small (~ 0.6 ‰), so the isotopic composition of fluid phase will not be very different that of the melt. For rhyolites and dacites, a significant fraction of the sulfur can be present as SO_2, so that greater fractionation between melt and fluid is possible.

An interesting feature of the above equations is that the fractionation between fluid and melt depends on the water pressure. Figure 32.9 is valid only for P_{H_2O} = 1 kB. A decrease in P_f or X_{H_2O} (the mole fraction of water in the fluid) will shift the SO_2/H_2S equal concentration boundary and the $\delta^{34}S$ contours to lower f_{O_2}. Conversely, an increase the in the water content will shift to boundary toward higher f_{O_2}.

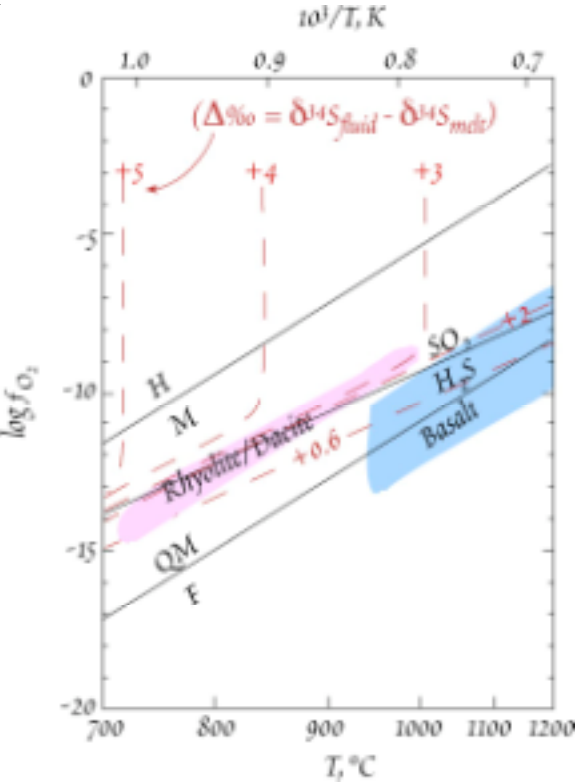


Figure 32.9. Fractionation of sulfur isotopes between fluid and melt (shown by dashed curves) as a function of oxygen fugacity and temperature for P_{H_2O} = 1 kB. Solid lines show equal concentration boundaries for quartz + magnetite ⇄ fayalite (QM-F), $H_2S \rightleftarrows SO_2$, and Magnetite ⇄ Hematite (M-H). After Ohmoto and Rye (1979).

Both the eruptions of El Chichón in 1983 and Pinatubo in 1991 release substantial amounts of SO_2. The SO_2–rich nature of these eruptions is thought to result from mixing of a mafic, S-bearing magma with a more oxidized dacitic magma, which resulted in oxidation of the sulfur, and consequent increase of SO_2 in the fluid phase. There are a number of other processes that affect the solubility and oxidation state of sulfur in the melt, and hence isotopic fractionation. Wall rock reactions could lead to either oxidation or reduction of sulfur, crystallization of sulfides or sulfates could cause relatively small fractionations and additionally affect the SO_2/H_2S ratio of the fluid. Depending on the exact evolutionary path taken by the magma and fluid, $\delta^{34}S$ of H_2S may be up to –13‰ lower than that of the original magma. Thus variations in the isotopic composition of sulfur are possible even in a mantle-derived magma whose initial $\delta^{34}S$ was that of the mantle (~ 0‰). Variability of sulfur isotopic compositions do, however, give some indication of the f_{O2} history of a magma. Constant $\delta^{34}S$ of magmatic sulfides suggests f_{O2} remained below the SO_2/H_2S boundary; variability in isotopic composition suggests a higher f_{O2}.

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