HIGH TEMPERATURE APPLICATIONS II: OXYGEN ISOTOPES AS AN INDICATOR OF ASSIMILATION

INTRODUCTION

We noted earlier that the equilibrium constant of isotope exchange reactions, K, was proportional to the inverse square temperature and that isotopic fractionation at high temperature will be limited. In magmatic systems, another factor limiting the fractionation of stable isotopes is the limited variety of bonds that O is likely to form. Silicate liquids have short-range structure. Most of the oxygen is not present as free ions, but is bound to silicon atoms to form silica tetrahedra in the melt, which will be linked to varying degrees depending on the composition of the melt. The silica tetrahedra, and the Si–O bonds in the melt, are essentially identical to those in silicate minerals. Thus we would expect the fractionation of oxygen isotopes between silicate liquids (magmas) and silicate minerals crystallizing from those liquids to be rather limited. We would expect somewhat greater fractionation when non-silicates such as magnetite (Fe_3O_4) crystallize. In general, crystallization of quartz will lead to a depletion of ^{18}O in the melt, crystallization of silicates such as olivine, pyroxene, hornblende, and biotite will lead to slight enrichment of the melt in ^{18}O, and crystallization of oxides such as magnetite and ilmenite will lead to a more pronounced enrichment of the melt in ^{18}O (however, oxides such as magnetite are generally only present at the level of a few percent in igneous rocks, which obviously limits their effect). Crystallization of feldspars can lead to either enrichment or depletion of ^{18}O, depending on the temperature and the composition of the feldspar and the melt. Because quartz generally only crystallizes very late, the effect of fractional crystallization on a magma is generally to increase $\delta^{18}O$ slightly, generally not more than a few per mil. As we have seen, the range of $\delta^{18}O_{SMOW}$ in the fresh, young basalts and other mantle materials is about +4.5 to +7. Because this range is narrow, and the range of crustal materials is much greater, O isotope ratios are a sensitive indicator of crustal assimilation. Isotope ratios outside this range suggest, but do not necessarily prove, the magmas have assimilated crust (or that post-eruptional isotopic exchange has occurred).

OXYGEN ISOTOPE CHANGES DURING CRYSTALLIZATION

The variation in O isotope composition produced by crystallization of a magma will depend on the manner in which crystallization proceeds. The simplest, and most unlikely, case is *equilibrium* crystallization. In this situation, the crystallizing minerals remain in isotopic equilibrium with the melt until crystallization is complete. At any stage during crystallization, the isotopic composition of a mineral and the melt will be related by the fractionation factor, α. Upon complete crystallization, the rock will have precisely the same isotopic composition as the melt initially had. At any time during the crystallization, the isotope ratio in the remaining melt will be related to the original isotope ratio as:

$$\frac{R_l}{R_o} = \frac{1}{f + \alpha(1-f)}; \quad \alpha \equiv \frac{R_s}{R_l} \qquad 30.1$$

where R_l is the ratio in the liquid, R_s is the isotope ratio of the solid, R_0 is the isotope ratio of the original magma, f is the fraction of melt remaining. This equation is readily derived from mass balance, the definition of α, and the assumption that the O concentration in the magma is equal to that in the crystals; an assumption valid to about 10%. Since we generally do not work with absolute ratios of stable isotopes, it is more convenient to express 30.1, in terms of δ:

$$\delta = \delta_{melt} - \delta_0 \approx \left[\frac{1}{f + \alpha(1-f)} - 1\right] * 1000 \qquad 30.2$$

where δ_{melt} is the value of the magma after a fraction f-1 has crystallized and δ_o is the value of the original magma. For silicates, α is not likely to be much less than 0.998 (i.e., $\Delta = \delta^{18}O_{melt} - \delta^{18}O_{xtals} \geq 2$). For α = 0.999, even after 99% crystallization, the isotope ratio in the remaining melt will change by only 1 per mil.

Fractional crystallization is a process analogous to Rayleigh distillation. Indeed, it is governed by the same equation (27.12), which we can rewrite as:

$$\delta = 1000(\delta^{f-1} - 1) \qquad 30.3$$

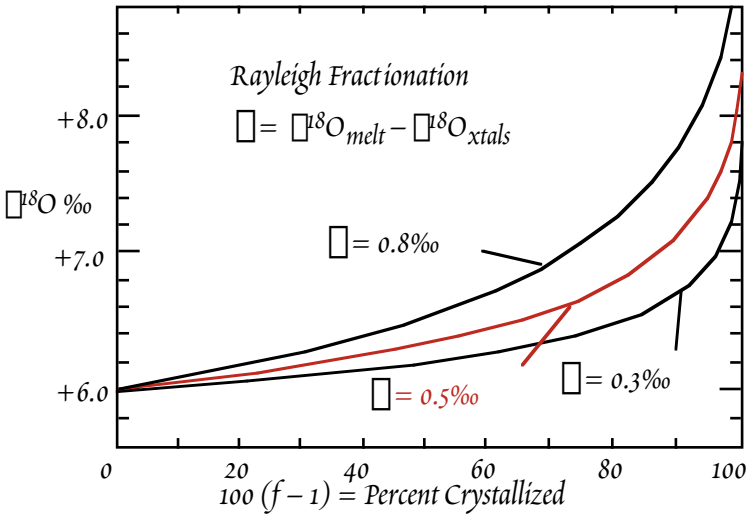


Figure 30.1. Plot of $\delta^{18}O$ versus fraction of magma solidified during Rayleigh fractionation, assuming the original $\delta^{18}O$ of the magma was +6. After Taylor and Sheppard (1986).

The key to the operation of either of these processes is that the product of the reaction (vapor in the case of distillation, crystals in the case of crystallization) is only instantaneously in equilibrium with the original phase. Once it is produced, it is removed from further opportunity to attain equilibrium with original phase. This process is more efficient at producing isotopic variations in igneous rocks, but its effect remains limited because α is generally not greatly different from 1. Figure 30.1 shows calculated change in the isotopic composition of melt undergoing fractional crystallization for various values of Δ ($\approx 1000(\alpha-1)$). In reality, Δ will change during crystallization because of (1) changes in temperature (2) changes in the minerals crystallizing, and (3) changes in the liquid composition. The changes will generally mean that the effective Δ will increase as crystallization proceeds. We would expect the greatest isotopic fractionation in melts crystallizing non-silicates such as magnetite and melts crystallizing at low temperature, such as rhyolites, and the least fractionation for melts crystallizing at highest temperature, such as basalts.

Figure 30.2 shows observed $\delta^{18}O$ as a function of temperature in two suites: one from a propagating rift on the Galapagos Spreading Center, the other from the island of Ascension. There is a net change in $\delta^{18}O$ between the most and least differentiated rocks in the Galapagos of about 1.3‰; the change in the Ascension suite is only about 0.5‰. These, and other suites, indicate the effective Δ is generally small, on the order of 0.1 to 0.3‰.

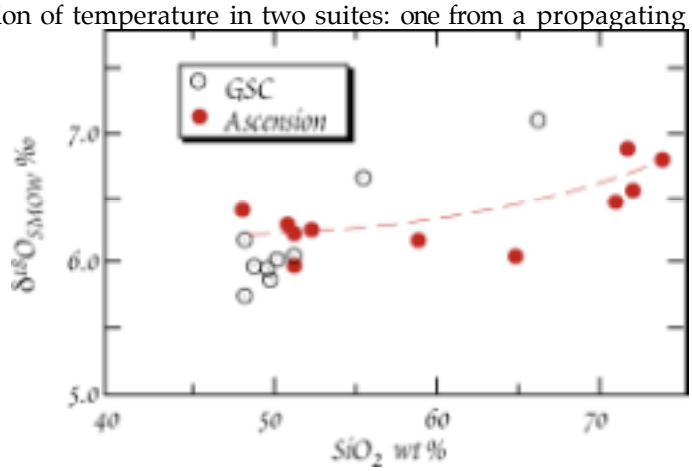


Figure 30.2. $\delta^{18}O$ as a function of SiO_2 in a tholeiitic suite from the Galapagos Spreading Center (GSC) (Muehlenbachs and Byerly, 1982) and an alkaline suite from Ascension Island (Sheppard and Harris, 1985). Dashed line shows model calculation for the Ascension suite.

We can generalize the temperature dependence of stable isotopes by saying that at low temperature (ambient temperatures at the surface of the Earth up to the temperature of hydrothermal systems, 300-400° C), stable isotope ratios are changed by chemical processes. The amount of change can be used as an indication the nature of the process involved, and, under equilibrium conditions, of the temperature at which the process occurred. At high tem-

peratures (temperatures of the interior of the Earth or magmatic temperatures), stable isotope ratios are no longer affected by chemical processes and can be used as tracers much as radiogenic isotope ratios are.

These generalizations lead to a final axiom: *igneous rocks whose oxygen isotopic compositions show significant variations from the primordial value (~6) must either have been affected by low temperature processes, or must contain a component that was at one time at the surface of the earth* (Taylor and Sheppard, 1986).

Rocks that have equilibrated with water at the surface of the Earth, e.g., sediments, tend to have $\delta^{18}O$ values significantly higher than +6 (generally greater than +10). Waters on the surface of the Earth typically have $\delta^{18}O$ significantly lower than +6 (0 for seawater, generally lower for meteoric, or fresh, waters). Interestingly, the δD values of sedimentary rocks and mantle-derived igneous rocks are rather similar (- 50 to -85). This may be coincidental since the δD of sediments are controlled by fractionation between minerals and water, whereas δD of igneous rocks reflects the isotopic composition of mantle hydrogen (mantle water). One the other hand, it is possible that it is not coincidental. Plate tectonics results in the return of water-being rocks from the surface of the Earth to the mantle (i.e., via subduction). It may well be that after 4.5 billion years, the subduction process essentially controls the isotopic composition of H in the upper mantle.

COMBINED FRACTIONAL CRYSTALLIZATION AND ASSIMILATION

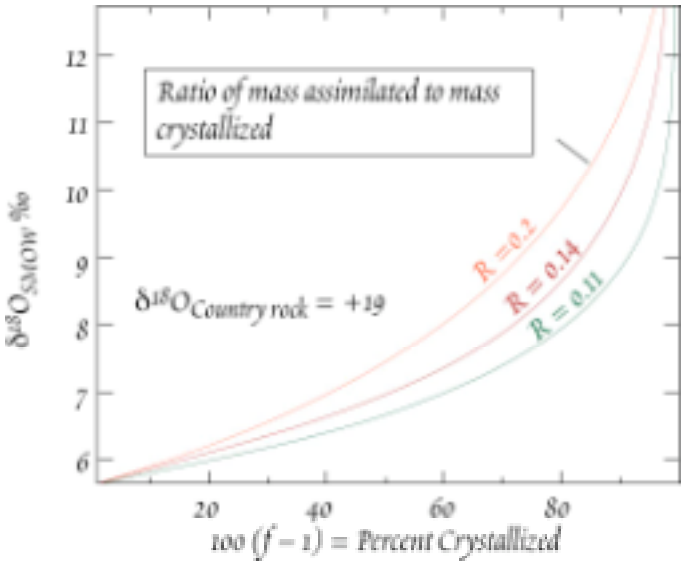


Figure 30.3. Variation in $\delta^{18}O$ of a magma undergoing AFC vs. amount crystallized. Initial $\delta^{18}O$ of the magma is +5.7. After Taylor (1980).

Because oxygen isotope ratios of mantle-derived magmas are reasonably uniform and generally different from rocks that have equilibrated with water at the surface of the Earth, oxygen isotopes are a useful tool in identifying and studying the assimilation of country rock by intruding magma. We might think of this process as simple mixing between two components: magma and country rock. In reality, it is always at least a three-component problem, involving country rock, magma, and minerals crystallizing from the magma. Magmas are essentially never superheated; hence the heat required to melt and assimilate surrounding rock can only come from the latent heat of crystallization of the magma. Approximately 1000 J/g would be required to heat rock from 150° C to 1150°C and another 300 J/g would be required to melt it. If the latent heat of crystallization is 400 J/g, crystallization of 3.25 g of magma would be required to assimilate 1 g of country rock. Since some heat will be lost by simple conduction to the surface, we can conclude that the amount of crystallization will inevitably be greater than the amount of assimilation (the limiting case where mass crystallized equals mass assimilated could occur only at very deep layers of the crust where the rock is at its melting point to begin with). The change in isotopic composition of a melt undergoing the combined process of assimilation and fractional crystallization (AFC) is given by:

$$\delta_m - \delta_0 = \left[\frac{\Delta}{R+1}\right]\left[\delta_a - \delta_0\right] + \frac{\Delta}{R}\left\{1 - f^{R/(R-1)}\right\} \qquad 30.4$$

where R is the mass ratio of material assimilated to material crystallized, Δ is the difference in isotope ratio between the magma and the crystals, f is the fraction of liquid remaining, δ_m is the $\delta^{18}O$ of

the magma, δ_o is the initial $\delta^{18}O$ of the magma, and δ_a is the $\delta^{18}O$ of the material being assimilated. The assumption is made that the concentration of oxygen is the same in the crystals, magma and assimilant, which is a reasonable assumption. This equation breaks down at R = 1, but as discussed above, this is unlikely: R will always be less than 1. Figure 30.3 shows the variation of $\delta^{18}O$ of a magma with an initial $\delta^{18}O = 5.7$ as crystallization and assimilation proceed.

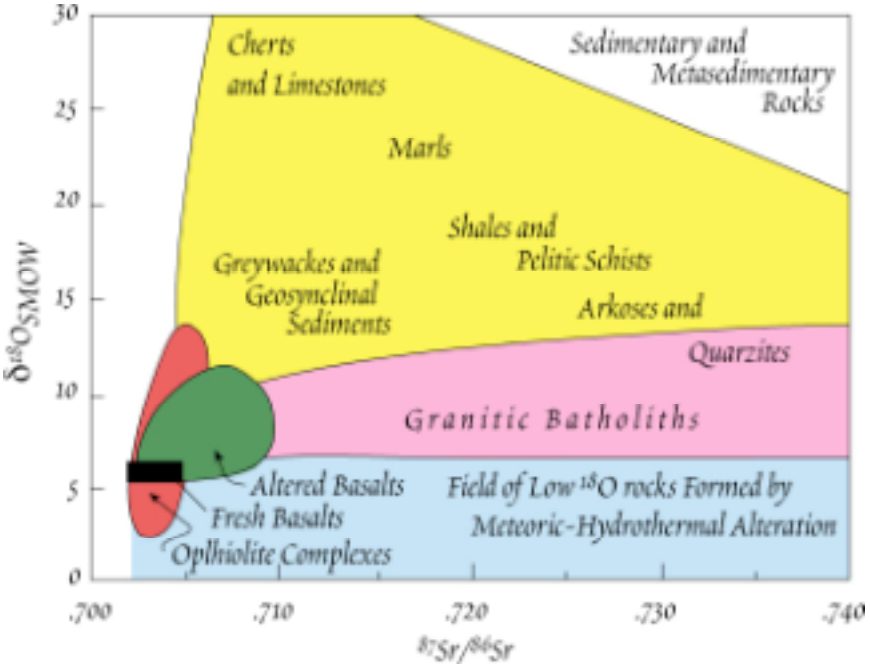


Figure 30.4. $\delta^{18}O$ vs. $^{87}Sr/^{86}Sr$ showing range of isotopic composition in various terrestrial rocks. After Taylor and Sheppard (1986).

COMBINING RADIOGENIC AND STABLE ISOTOPES

A more powerful tool for the study of assimilation processes can result if O isotopes are combined with a radiogenic isotope ratio such as $^{87}Sr/^{86}Sr$. There are several reasons for this. First, radiogenic isotopes and stable isotopes each have their own advantages. In the case of basaltic magmas, radiogenic elements, particularly Nd and Pb, often have lower concentrations in the magma than in the assimilant. This means a small amount of assimilant will have a large effect on the radiogenic isotope ratios. On the other hand, oxygen will be present in the magma and assimilant at nearly the same concentration, making calculation of the mass assimilated fairly straight-forward. Also, it is easier to uniquely characterize the assimilant using both radiogenic and stable isotope ratios, as suggested in Figure 30.4.

The equation governing a radiogenic isotope ratio in a magma during AFC is more complex because we cannot assume the concentration of the element is the same in all the components. The general equation describing the variation of the concentration of an element in a magma during AFC is:

$$\frac{C_m}{C_m^0} = f^{-z} + \left(\frac{R}{R-1}\right)\left(\frac{C_a}{zC_m^0}\right)(1-f^{-z}) \qquad 30.5$$

where C_m is the concentration of the element in the magma, and C^o is the original concentration in the magma, Δ is the solid/liquid partition coefficient, f is the fraction of liquid remaining, R is the ratio of mass assimilated to mass crystallized as above, and z is defined as:

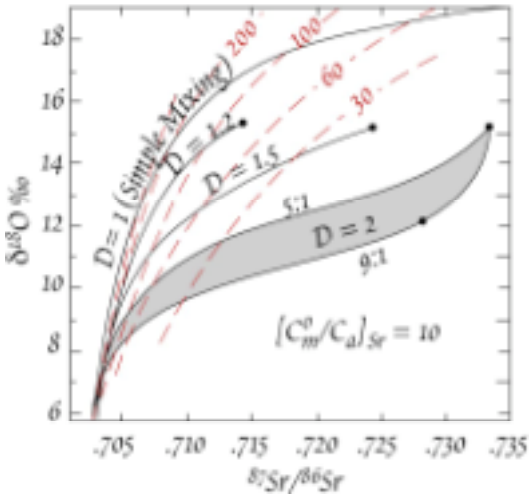


Figure 30.5. Variation of $\delta^{18}O$ with $^{87}Sr/^{86}Sr$ during AFC for a magma with an initial $\delta^{18}O = 5.7$ and $^{87}Sr/^{86}Sr = 0.703$, and an assimilant with $^{87}Sr/^{86}Sr = 0.735$ and $\delta^{18}O = +19$. All curves are for R = 0.2 (5:1), except for one with $\Delta = 2$ for which R = 0.11 (labeled 9:1). dashed red lines are calculated Sr concentrations (ppm) assuming an initial concentration of Sr in the magma of 500 ppm. Where $\Delta = 1$, the problem simplifies to one of simple mixing. From Taylor (1980).

$$z = \frac{R + \Delta - 1}{R - 1} \qquad z = \frac{R + \Delta - 1}{R - 1} \qquad 30.6$$

The isotopic composition of the magma is the given by (DePaolo, 1981):

$$\delta_m = \frac{\left(\frac{R}{R-1}\right)\left(\frac{C_a}{z}\right)(1 - f^{-z})\delta_a + C_m^0 f^{-z}\delta_m^0}{\left(\frac{R}{R-1}\right)\left(\frac{C_a}{z}\right)(1 - f^{-z}) + C_m^0 f^{-z}} \qquad 30.7$$

where δ is the isotope ratio with subscripts *m*, *a* and 0 denoting the magma, the assimilant, and the original magma respectively and the other parameters are defined as in equation 30.5. Figure 30.5 shows calculated AFC curves on a plot of $\delta^{18}O$ vs. $^{87}Sr/^{86}Sr$. Note that except in the case where $z = 1$, where the problem simplifies to one of simple mixing, the mixing lines end at $f = 0.01$ (99% crystallized).

Figure 30.6 shows an actual case, the Adamello Massif in Italy. Actual analyses are plotted as dots with the concentrations of Sr in the sample shown adjacent to the dot. AFC lines are computed assuming the original magma had $\delta^{18}O = 5.6$, $^{87}Sr/^{86}Sr = 0.704$, and 750 ppm Sr, and the country rocks have $^{87}Sr/^{86}Sr = 0.736$, $\delta^{18}O = +13.6$, and 150 ppm Sr. Dashed lines are contours of *calculated* Sr concentrations in the magma. There is reasonably good agreement between the calculated model and the actual data, if we assume the bulk partition coefficient varied a bit (which would certainly be the case).

REFERENCES AND SUGGESTIONS FOR FURTHER READING

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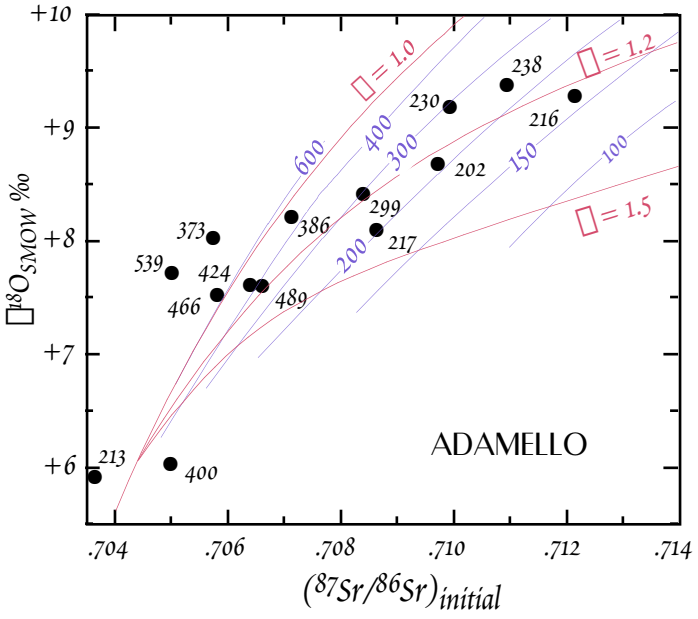


Figure 30.6. Variation of $\delta^{18}O$ with $^{87}Sr/^{86}Sr$ in the Adamello Massif in Italy compared with model AFC process using equation 25.4- 25.6. After Taylor and Sheppard (1986).