Analysis of Oxygen and Sulfur Isotope Ratios in Oxide and Sulfide Minerals by Spot Heating with a Carbon Dioxide Laser in a Fluorine Atmosphere

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Introduction

Several of the geochemically interesting light elements (hydrogen, carbon, nitrogen, oxygen, and sulfur) consist of mixtures of stable isotopes whose abundance can be readily measured with high precision by mass spectrometry. These isotopes with their mass numbers and element symbols are ^{1}H, ^{2}H, ^{12}C, ^{13}C, ^{14}N, ^{15}N, ^{16}O, ^{17}O, ^{18}O, ^{32}S, ^{33}S, ^{34}S, and ^{36}S. The ratios of the stable isotopes of these elements are not quite constant in nature because of differences in the thermodynamic and kinetic properties of isotopically substituted molecules. The equilibrium constant for the exchange of oxygen between calcite ($CaCO_3$) and water, for example, differs by as much as 4% when the common ^{16}O is replaced by the heavier ^{18}O. The change in equilibrium is temperature dependent and forms the basis of the oxygen isotope paleotemperature method that has been valuable in deducing ancient climatic variations. Similarly, there are differences in the rates of chemical processes for isotopically substituted molecules. Atmospheric $^{12}CO_2$ is fixed 1–3% faster than $^{13}CO_2$ during photosynthesis by plants, the extent of isotope fractionation depending on the biochemical mechanism of CO_2 fixation dominant in particular plant species. Herbivores acquire characteristic $^{13}C/^{12}C$ ratios based on the carbon isotopic configuration of the plants they eat. Such effects have been used to determine the diet of fossil organisms.

Stable isotope geochemistry has proven valuable in tracing water flow to great depths in Earth's crust. (Note that access to samples of deeply buried rocks is gained by drilling, by uplift along earthquake faults, or by ejection of rock fragments during volcanic eruptions.) Rain water circulates to depths of at least 5 km, indelibly changing the $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios of granites and ore deposits.[1] Studies in our laboratory[2] show that water penetrated ostensibly impermeable rocks to depths of at least 10 km. We found fossil bachiopods (clam-like bivalves) where $\delta^{18}O$ values had been lowered 10‰ and whose shells had been replaced concomitantly by wollastonite ($CaSiO_3$) during burial to depths of 10 km and heating to 600 °C. The transformation of the fossils was accomplished by flowing water at least quadruple the volume of the fossils themselves.

Until recently, the spatial resolution in performing isotopic analysis of solids has been coarse: limited to the millimeter scale by existing methods of sample preparation. Samples could be obtained by drilling powders from mineral surfaces with a diamond-tipped drill, but the drill holes were a millimeter or more in diameter and spaced several millimeters apart. Such spatial resolution cannot accurately characterize microscopic mineral structures where concentric growth zones tens of micrometers in thickness record unique information on evolving environmental conditions. The inadequacy of conventional resolution in isotopic studies became especially frustrating inasmuch as micrometer-sized chemical zonation structures in minerals had been studied for decades with the *in-situ* microanalytical capability of electron-beam microprobes and microscopes. The likelihood of the existence of similar isotope-zonation structures was undoubted, but the features could not be measured. Recent development of microanalytical, *in-situ* techniques for isotopic analysis has increased the potential impact of stable isotope geochemistry, making possible definitive investigations of the reaction mechanisms whereby water, minerals, and rocks interact in Earth's crust and mantle.

A number of methods for *in-situ* isotopic analysis of minerals have now been established including secondary ion mass spectrometry[3] and laser methods using CO_2,[4] Nd:YAG[5], or Ar-ion lasers.[6] In the following Account, we describe methods and results of isotopic analysis using a CO_2 laser to spot heat minerals immersed in F_2 gas.

Method

Isotope ratio analysis is made by comparison of standard and unknown working gases in a gas source,

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Table 1. Interlaboratory Comparisons and Precision of Sulfur Isotope Analyses

		$\delta^{34}S_{CDT}$ (‰)	
sample[a]	laboratory[b]	conventional	CO_2 laser
CDT	GL	−0.08 (±0.1)[c]	0.00 (±0.11)[8]
	GSC		0.09 (±0.17)[8]
			0.19 (±0.04)[8]
			0.37 (±0.05)[8]
	UCSD	0.41 (0.04)[8]	
NBS-123	various	16.4−17.8[9]	
	GL		17.9 (±0.2)
CdS	GL	33.57	33.86 (±0.11)
	USGS	34.04	

[a] Samples: CDT = Cañon Diablo Troilite; NBS-123 = sphalerite, National Institute of Standards and Technology; CdS = cadmium sulfide. [b] Laboratories: GL = Geophysical Laboratory; GSC = Geological Survey of Canada (B. E. Taylor and G. Beaudoin); UCSD = University of San Diego (M. H. Thiemens); USGS = U.S. Geological Survey (W. C. Shanks). [c] The number in parentheses is 1 standard deviation of replicate analyses of three or more aliquots of sample.

dual inlet, multicollector, single focusing, magnetic sector mass spectrometer.[7] The working gases used in mass spectrometry are O_2 for $^{18}O/^{16}O$ and SF_6 for $^{34}S/^{32}S$. Isotope enrichments are reported in relation to reference standards in δ notation (parts per thousand):

$$\delta^{18}O_{SMOW} = \left[\frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{SMOW}}{(^{18}O/^{16}O)_{SMOW}}\right] \times 1000$$

where the standard for oxygen isotope analysis is "standard mean ocean water" (SMOW). δ values for sulfur isotope ratios are defined similarly and reported relative to "Cañon Diablo Troilite" (CDT), from a meteorite.

Data on accuracy and precision of analyses for $\delta^{34}S$, $\delta^{18}O$, and $\delta^{17}O$ are given in Tables 1 and 2. The data inadvertently highlight a recurring problem with interlaboratory standards: the more closely they are studied, the more likely it is that they will be found to be inhomogeneous. It has been concluded,[8] for example, that the sulfur isotope standard, Cañon Diablo Troilite, is inhomogeneous in $\delta^{34}S$.

The goal of the method is to obtain spatially resolved, isotope ratio analyses of mineral microstructures. It is achieved by spot heating a mineral with a focused CO_2 laser beam in an F_2 atmosphere. The heeated mineral spot reacts quickly with F_2, releasing O_2 from silicate or oxide minerals, or producing SF_6 quantitatively from sulfide minerals. The unheated material surrounding the spot remains unreacted.

The apparatus shown in Figures 1 and 2 is satisfactory for spot analyses of $^{18}O/^{16}O$ in silicate and oxide minerals and for *in-situ* analysis of $^{34}S/^{32}S$ in sulfide minerals. Provision is made for choosing either BrF_5 or purified F_2[10] as fluorinating agent to permit optimization for specific minerals. The use of F_2 is preferred because it reacts with most minerals more rapidly than BrF_5. Samples are loaded through a quick-release flange into the reaction chamber, evacuated, and briefly treated with 30 Torr of F_2 (unheated) to eliminate absorbed H_2O and to estimate room-temperature "blank". Waste F_2 is disposed of by reaction with KBr heated to 100 °C. Fresh F_2 is expanded to 30−50 Torr in the reaction chamber. A 25-W, sealed, rf-excited CO_2 laser is focused on the sample with a target He−Ne laser and fired in 1-s pulses until sufficient working gas has been accumulated for mass spectrometry (1−3 μmol). Optimum laser operating conditions must be established by experiment on a mineral-by-mineral basis. It is generally desirable to use the minimum irradiance necessary to initiate fluorination because violent sputtering has been observed to result in isotope fractionation between minerals and working gases.

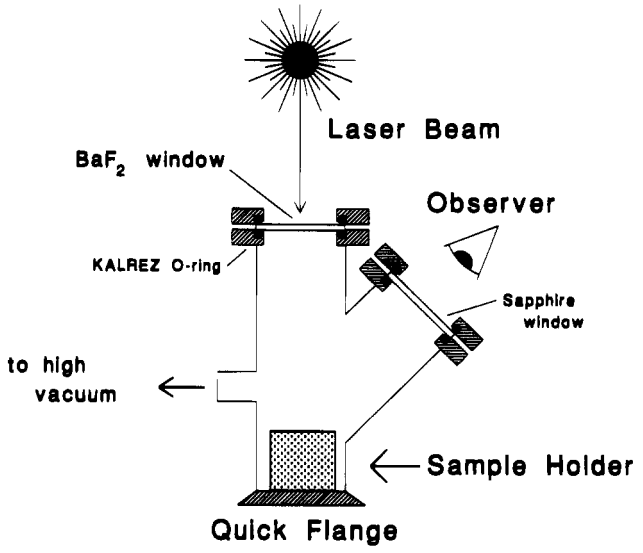

Figure 1. Reaction chamber[4] for laser fluorination of silicate, oxide, and sulfide minerals.

The procedure outlined above is applicable for the analysis of silicate, oxide, and sulfide minerals. Once the sample gases O_2 or SF_6 have been generated, however, they follow different pathways through the apparatus. Oxygen from silicate and oxide minerals is separated from F_2 by passage through heated KBr. The transfer of O_2 is accelerated by an in-line, single-stage, Hg-diffusion pump which also serves to scavenge residual F_2. It is conventional to convert O_2 to CO_2 with an electrically-heated graphite rod owing to the ease with which a condensable gas may be transferred to the mass spectrometer inlet by freezing in liquid nitrogen. The conversion of O_2 to CO_2 is not satisfactory for small samples, however, because of isotopic fractionation between CO_2 and small amounts of incompletely combusted CO.[11] We transfer O_2 directly to the mass spectrometer without fractionation by cryogenic absorption onto 5A molecular sieves.[12]

The procedure for the sample gas SF_6 produced from sulfide minerals differs from that described above for oxygen. Throughout the duration of laser heating, the

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Table 2. Interlaboratory Comparisons and Precision of Oxygen Isotope Analyses

		$\delta^{18}O_{SMOW}$ (‰)		$\delta^{17}O_{SMOW}$ (‰)	
sample	laboratory[b]	conventional	CO_2 laser	conventional	CO_2 laser
NBS-28	GL		9.30 (±0.2)		4.84 (±0.08)
	UW	9.45 (±0.2)	9.46 (±0.19)		
NCSU					
	GL	11.58 (±0.14)	11.16 (±0.14)		5.84 (±0.36)
	NCSU	11.66 (±0.28)			
spinel	GL		22.08 (±0.10)		11.71 (±0.18)
	UC	22.29		11.56	

[a] Sample: NBS-28 = African glass sand, National Institute of Standards and Technology; NCSU = pegmatite quartz, North Carolina State University; spinel = Burmese spinel, U.S. National Museum No. NMNH R12013-2. [b] Laboratories: GL = Geophysical Laboratory; UW = University of Wisconsin (Elsenheimer and Valley, 1993); UC = University of Chicago (R. N. Clayton and T. K. Mayeda, personal communication); NCSU = North Carolina State University (W. Showers, personal communication).

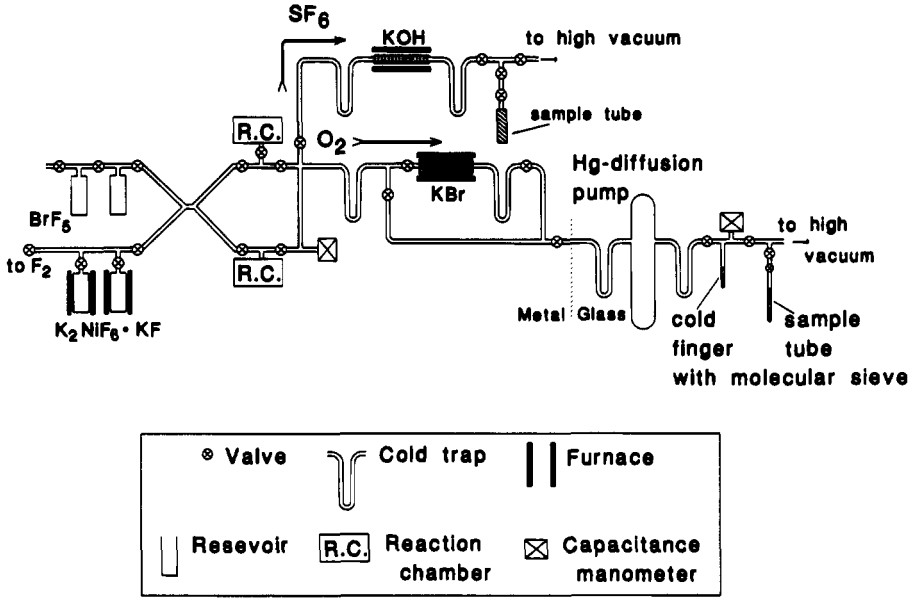

Figure 2. Vacuum line for laser heating minerals in F_2 or BrF_5 vapor.[13,14] $K_2NiF_6 \cdot KF$ is used to purify F_2.

reaction chamber is open to a liquid nitrogen cold trap (Figure 2). By this means, SF_6 is removed from the reaction site as soon as it forms, promoting rapid completion of the fluorination reaction. Waste F_2 is eliminated by reaction with heated KBr. The SF_6 is expanded over moist KOH pellets heated to 100 °C to remove residual halogens. Additional purification is achieved by preparative gas chromatography using a column of Chromosorb 106 to eliminate impurities such as fluorocarbons (fragment $^{12}C_3F_5^+$ interferes with $^{36}SF_5^+$), CO_2, SiF_4, C_2F_5Br, SO_2F_2, and SOF_2.[13]

Pitfalls

Precautions must be taken to guard against unwanted isotope fractionation effects. The most commonly encountered sources of fractionation have been (1) oxygen isotope fractionation in the walls of laser craters; (2) sulfur isotope fractional owing to the formation of SO_2F_2 and SOF_2 during laser fluorination of disseminated sulfide minerals in a silicate matrix; and (3) sulfur isotope separation in SF_6 when irradiated with a CO_2 laser.

(1) During analysis of $^{18}O/^{16}O$ in silicate minerals it is observed that the total volume of oxygen obtained by laser heating and fluorination consists of a component derived quantitatively from the laser crater, itself, and an additional amount from the walls of the crater.[14,15] Contamination from wall oxygen can be reduced proportionately through defocusing the laser beam and enlarging the crater, but spatial resolution suffers. Maps of element concentration in craters in garnet (e.g., $(Fe,Mg,Ca,Mn)_3Al_2Si_3O_{12}$) show that residual oxygen remains in crater walls, thus accounting for observed isotope fractionation (Figure 3). The oxygen-deficient annulus consists of a matrix of glass enclosing micron-size, dendritic crystallites of fluorides and oxides. In terms of bulk chemistry, relative to garnet, crater walls are deficient in oxygen, enriched in fluorine, and inhomogeneous in Fe, Mg, Mn, Ca, and Al. Silicon is absent from crater walls due to the volatility of SiF_4.

(2) Analysis for $^{34}S/^{32}S$ in 30-μm pyrite grains (FeS_2) disseminated in a silicate matrix gave fractionated results because of side reactions producing SO_2F_2 and SOF_2 as well as the desired SF_6.[16] The laser beam diameter is larger than that of the pyrite grains; consequently matrix silicates were heated as well as sulfides. These fractionations were not observed during the analysis of massive sulfides free from silicate minerals. A technique for fluorinating the undesired side products is needed, but until is has been achieved,

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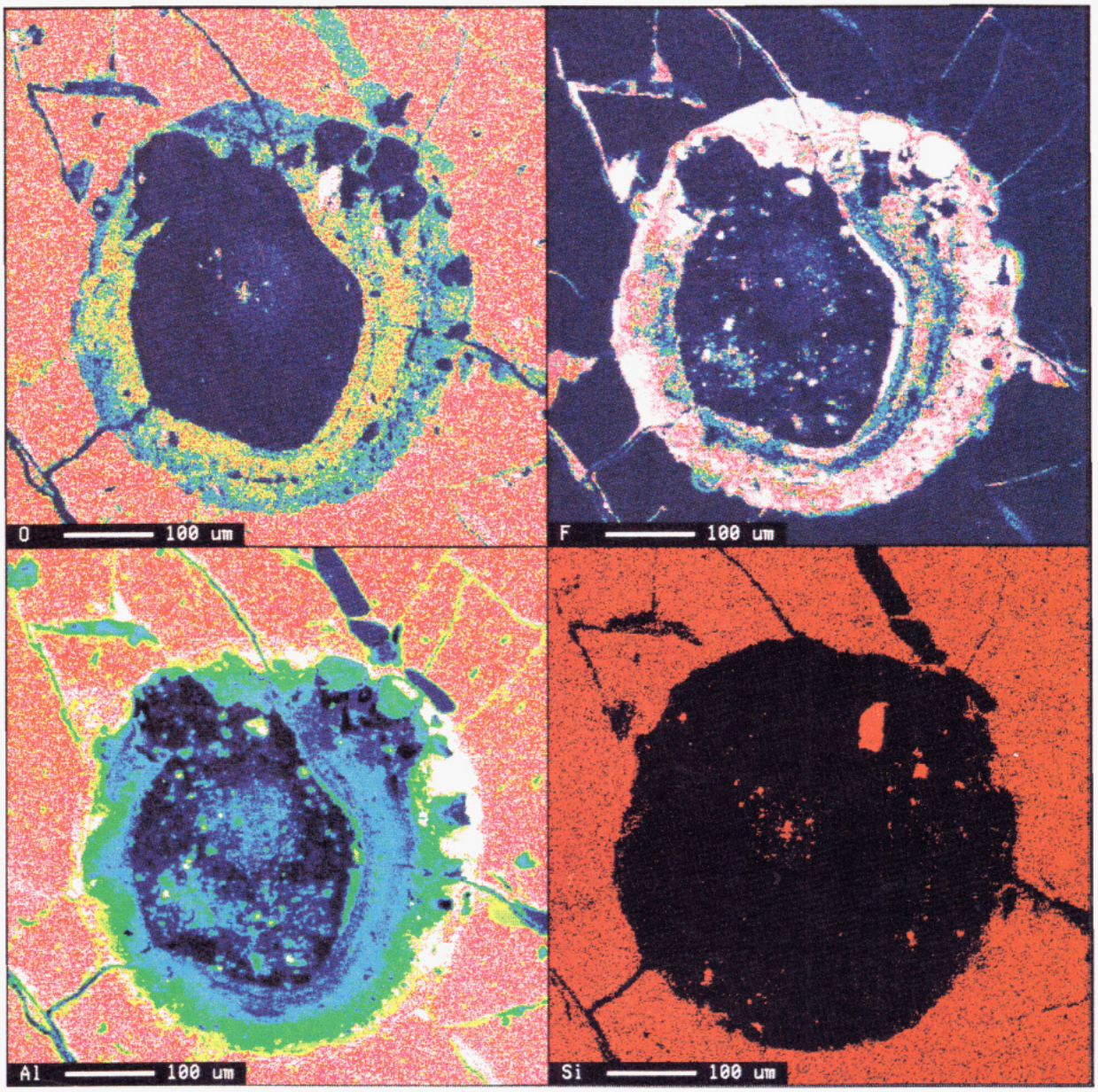

Figure 3. Elemental concentration maps of polished section of garnet with laser crater. Elemental analyses obtained with JEOL JXA-8900 electron microprobe operating with 15-kV electron beam focused to a 1-μm spot size. Sample was translated beneath beam to develop image. In false color images, black is zero concentration and delimits crater hole and cracks in specimen. Note 100-μm scale bars on maps. (A, upper left) Oxygen: red = stoichiometric O in garnet; blue-yellow = oxygen-deficient crater wall. (B, upper right) Fluorine: white-red = fluorides in crater wall. (C, lower left) Aluminum: red = stoichiometric Al in garnet; green-blue = AlF_3 in crater wall. (D, lower right) Silicon: red = stoichiometric Si in garnet. Element maps courtesy of E. D. Young.

it is advisable to avoid analyzing samples containing a fine-grained mixture of silicate and sulfide minerals.

(3) Laser isotope separation occurs when SF_6 is irradiated with the P(16) line of the 10.6-μm band of a tunable, powerful TEA (transverse excitation atmospheric pressure) CO_2 laser. Virtually all of the $^{32}SF_6$ molecules disappear from natural abundance mixtures after 2×10^3 laser pulses because of selective, irreversible disassociation.[17] Isotope separation was not observed in our analyses because of the use of a liquid nitrogen cold trap to remove SF_6 from the laser beam path (Figure 2). The occurrence of isotope separation has been found, however, when the reaction chamber is not exposed to a liquid N_2 cold trap during lasing.[18] Isotope fractionation by CO_2 laser probably explains aberrant results obtained when BrF_5 was used as fluorinating agent.[13] Liquid nitrogen cannot be used during laser fluorination with BrF_5 because the reagent condenses.

Current Analytical Capability

The CO_2-laser microprobe has proven itself superior to conventional methods for the analysis of $^{18}O/^{16}O$ and $^{17}O/^{16}O$ in chips and powders of silicate and oxide minerals. The advantages of the microprobe are small sample size (0.5−1.0 mg), speed, and the power to heat to incandescence and melting even the most refractory

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minerals. There is no fractionation because the powdered sample is quantitatively fluorinated. The applicability of the CO_2-laser microprobe to *in-situ* analysis is limited by crater wall fractionation, a problem that can be overcome but at the cost of spatial resolution. A viable alternative to achieve comparable spatial resolution is to saw or pluck mineral fragments for analysis from a polished thin section.[19]

The CO_2-laser microprobe has also shown itself superior in analyzing $^{34}S/^{32}S$ and $^{33}S/^{32}S$ in sulfide minerals. Its advantages are small sample size, speed, and relatively high spatial resolution, *in-situ* analysis. The melting and recrystallization observed in crater walls of silicates has not been observed in most sulfide minerals tested. Galena (PbS), sphalerite (ZnS), and pyrite (FeS_2) remain stoichiometric within 3 μm of laser craters. Chalcopyrite ($CuFeS_2$) is the only mineral found that shows crater wall effects; it forms a rim of bornite (Cu_3FeS_3) 100 μm thick.[13]

Ongoing Developments

There are a number of improvements in technique currently under development. It is crucial to obtain better spatial resolution. The CO_2 laser, because of its long, 10.6-μm nominal wavelength, cannot be focused to a smaller spot size than approximately 100 μm, with a typical beam delivery system. An ultraviolet (UV) laser has a shorter wavelength than a CO_2 laser, and its beam can be focused to a smaller spot size. Wiechert and Hoefs[20] have reported successful $\delta^{18}O$ analysis of olivine [$(Fe,Mg)_2SiO_4$] with a Kr–F excimer laser in a F_2 atmosphere. Feasibility tests[21] of UV-laser fluorination in our laboratory show that garnets remain stoichiometric within a few microns of UV-laser craters, in strong contrast to the 100+-μm-thick damaged rims made by CO_2 lasers (Figure 3). Current research is fueled by the expectation that development of a UV-laser microprobe will eliminate the crater wall fractionation of $^{18}O/^{16}O$ characteristic of CO_2 and Nd:YAG lasers. Substantial improvements in the spatial resolution of *in-situ* analysis for oxygen isotopes in silicate and oxide minerals are likely.

Application of laser fluorination methods to the analysis of isotope ratios in new minerals is in an active state of development. Minerals such as garnet and olivine, difficult to fluorinate in externally-heated vessels, are now analyzed routinely because they may be heated to white-hot incandescence with a CO_2 laser without adverse effects on reaction chambers whose walls remain at room temperature.[4,11,15] The oxygen isotopic composition of biogenic apatite [$Ca_5(PO_4)_{2.7}$-$(CO_3)_{0.3}(OH,F)$] is of importance to biogeochemists and paleoclimatologists but is difficult to measure with conventional methods. Recent results suggest that laser fluorination may offer improvements in accuracy.[22]

Results

The laser fluorination methods described above have been applied in our laboratory to two distinct depth zones of water–rock interaction in Earth's crust. In the first of these studies, metalliferous veins from depths of 1–2 km are being analyzed for sulfur isotope ratios. The objective of the work is to trace the origin of waters and dissolved sulfur species that circulated through fractures in volcanic rocks and filled cracks with pyrite and calcite ($CaCO_3$). The study is part of an integrated, collaborative investigation of core samples recovered through the U.S. Continental Scientific Drilling Program at Creede, CO, led by P. M. Bethke. Isotopic analysis of 3–5-mm-thick veins show variations of from −16‰ to 67‰ in $\delta^{34}S$ from a single vein. These values are extraordinary in that they represent a major fraction of the total range in natural variation of $^{34}S/^{32}S$ yet analysis spots are separated by only a few millimeters. Conventional analysis of the veins would have obtained a misleading average isotope ratio of bulk sulfur with no indication of possible heterogeneity. Such large isotopic effects are caused by isotope partitioning during bacterial or thermochemical reduction of SO_4^{2-} in solution leading to precipitation of insoluble pyrite.[23]

The second study concerns garnet-bearing schists from southern Vermont that have been metamorphosed (e.g., recrystallized) at 550–650 °C and 6–8 kbar. Concentric, annular zones of $^{18}O/^{16}O$ enrichment in garnets have been discovered in a number of samples.[14,24] The magnitude of oxygen isotope zoning ranges from enrichments as small as 1.5‰ to as large as 3‰. The spatial pattern of zonation in the garnets correlates with chemical zoning in Fe,Mg,Mn, and Ca and with other textural features such as overgrowths of chlorite [$(Fe,Mg)_9Al_6Si_5O_{20}(OH)_{16}$]. The significance of these discoveries is 2-fold: (1) The concentric zonation and its similarity in spatial distribution to chemical zoning prove that the isotopic values were acquired during garnet growth under conditions of deep burial. (2) The isotopic zoning reflects a change in the rock's bulk $^{18}O/^{16}O$ ratio, a change that could have been accomplished only by isotopic exchange with infiltrating water of different $\delta^{18}O$. The interesting conclusion is that water is able to circulate through "impermeable" rocks to depths of 15–20 km.

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