Reports

Meteoric Water in Magmas

Abstract. *Oxygen isotope analyses of sanidine phenocrysts from rhyolitic sequences in Nevada, Colorado, and the Yellowstone Plateau volcanic field show that* $\delta^{18}O$ *decreased in these magmas as a function of time. This decrease in* $\delta^{18}O$ *may have been caused by isotopic exchange between the magma and groundwater low in* ^{18}O*. For the Yellowstone Plateau rhyolites, 7000 cubic kilometers of magma could decrease in* $\delta^{18}O$ *by 2 per mil in 600,000 years by reacting with water equivalent to 3 millimeters of precipitation per year, which is only 0.3 percent of the present annual precipitation in this region. The possibility of reaction between large magmatic bodies and meteoric water at liquidus temperatures has major implications in the possible differentiation history of the magma and in the generation of ore deposits.*

During the last 10 years, there has been increasing realization that meteoric water is an important agent in igneous processes. The evidence for this is based on the fact that meteoric water usually has a deuterium and ^{18}O content that serves to identify it in deep-seated environments (*1*). In all these examples, meteoric water was thought to have been part of a circulating convective cell set up by the proximity of a large heat source—usually a large intrusive magma body—and most of the evidence concerns postconsolidation effects that took place during cooling of the magma. Direct interaction between meteoric water and magmas has also been inferred (*2*), but the new data presented here are the first evidence for such interactions at liquidus temperatures during long periods of time—as much as half a million years. Analyses of feldspar phenocrysts from naturally quenched glassy parts of ash-flow tuffs and lavas from Nevada, Colorado, and the region including Yellowstone National Park demonstrate progressive decreases in ^{18}O content with time, which we interpret as reflecting interactions with meteoric waters.

The sanidine crystals were separated from glass by conventional means. The ^{18}O was determined by: (i) reaction with BrF_5 to liberate oxygen; (ii) reaction of the oxygen with hot graphite to give CO_2; and (iii) mass spectrometric analysis of the CO_2 for the $^{18}O/^{16}O$ ratio (*3*). The results are reported as $\delta^{18}O$ per mil relative to standard mean ocean water (SMOW) and are considered precise to ± 0.1 per mil (2 standard deviations). For interlaboratory comparison, we determined a δ value of +9.75 per mil for the NBS-28 quartz reference standard.

The first group of analyses is of mineral separates from four ash-flow sheets and related lava flows from the Timber Mountain–Oasis Valley caldera complex, southwestern Nevada (*4*). Each of the ash-flow sheets is compositionally zoned, with basal rhyolitic tuff grading upward into quartz latite. This zonation is thought to represent samples of a differentiated magma body in which a rhyolitic upper part overlaid quartz latite. The upper rhyolitic material was first erupted, followed by the quartz latite. The volumes of the individual sheets are very large—as much as 2000 km^3—and they represent the quenched upper parts of batholithic magma chambers.

The oldest compositionally zoned sheet, the Topopah Spring Member of the Paintbrush Tuff, was erupted from the Oasis Valley caldera area about 13.1 million years ago, causing a large caldera to form (*4*). The area then remained relatively quiescent for about half a million years, during which time the magma body again differentiated to develop a rhyolitic top overlying lower magma of quartz latitic composition. The most significant subsequent ash-flow eruption of the Paintbrush Tuff resulted in the emplacement of the Tiva Canyon Member, with associated further caldera collapse (*4*). A similar sequence about 1.5 million years later resulted in the eruption of first the Rainier Mesa Member and then the Ammonia Tanks Member of the Timber Mountain Tuff, with associated collapse of the Timber Mountain caldera.

Table 1 gives the $\delta^{18}O$ values of sanidines from glassy samples of the four units. The data show that for the Paintbrush sequence the minerals from the later-erupted Tiva Canyon Member are, on the average, depleted in $\delta^{18}O$ by about 1 per mil compared to the earlier Topopah Spring Member. For the Timber Mountain sequence, the younger Ammonia Tanks Member is also depleted, by approximately 2 per mil, compared to the earlier-erupted Rainier Mesa Member. These differences in $\delta^{18}O$ between earlier- and later-erupted units hold true for other mineral phases analyzed, including plagioclase, quartz, biotite, augite, and magnetite (*5*), which indicates to us that these differences reflect variations in magmatic environment and cannot be explained by surface cooling effects. We also recognize no major difference in $\delta^{18}O$ values of phenocrysts that might result from variable rates of cooling—for example, material from porous glassy pumice blocks from the quenched base or top of an ash-flow sheet compared to that from densely welded glassy pumice lenses from the more slowly cooled interior of a sheet.

We interpret these changes in $\delta^{18}O$ in terms of interaction of meteoric water, which had an original $\delta^{18}O$ of −10 to −15 per mil, with the molten magma, which had a $\delta^{18}O$ of +7 to +9 per mil. This interaction would tend to lower the ^{18}O of the magma. The longer the magma interacts with meteoric water before eruption, the greater the lowering in ^{18}O, all other factors (amounts of magma and rate of water interaction) being constant. Because these bodies of magma were large—the Paintbrush Tuff (Topopah Spring and Tiva Canyon Members) has an estimated initial volume of 1300 km^3 and the Timber Mountain Tuff (Rainier

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Mesa and Ammonia Tanks) has a volume of about 3200 km^3 (*4*)—the amounts of interacting meteoric water would also have been sizable, several hundred cubic kilometers, assuming complete exchange. The amount of water required would have been proportionally greater to the extent that exchange was incomplete and that the magma involved was more voluminous than the erupted portion.

Variations in $\delta^{18}O$ can be brought about by other mechanisms, but none seem adequate to explain the data. Quartz and feldspar crystals formed from the molten magma may tend to be enriched in ^{18}O by a small amount, but the ferromagnesian phases—biotite, augite, and particularly iron oxide—will have a lower $\delta^{18}O$ than the melt. Any variations caused by the formation of phenocrysts will be small, and enrichment due to crystallization of quartz and feldspar will tend to be offset by depletion due to crystallization of the ferromagnesian phases. Phenocryst settling, which presumably was significant in differentiation of the Paintbrush and Timber Mountain magmas (*4, 6*), could not have augmented this crystallization effect significantly, because the ^{18}O variations are as great in the little-fractionated quartz latites as in the highly differentiated rhyolites.

In the Yellowstone Plateau volcanic field investigations by Christiansen and Blank (*7*) have resulted in the recognition of three major ash-flow sheets related to formation of large calderas. The oldest ash-flow sheet, the Huckleberry Ridge Tuff, has been dated by J.D.O. at 2 million years. The next oldest, the Mesa Falls Tuff, has been dated at 1.2 million years, and the most recent, the Lava Creek Tuff, at 0.6 million years. These tuffs were also derived from large magma chambers; the material that erupted, beginning with the Huckleberry Ridge Tuff and ending with the most recent flows, has a volume of about 7000 km^3.

Table 2 shows the $\delta^{18}O$ values of sanidine from the Yellowstone region, together with the K-Ar ages of the samples. Figure 1 is a plot of the ages of the samples against $\delta^{18}O$. Sanidines from the first ash-flow sheet, the Huckleberry Ridge Tuff, have an average $\delta^{18}O$ of about +6 per mil. Sanidines in the next ash-flow sheet, the Mesa Falls Tuff, which was erupted 0.8 million years later, have a $\delta^{18}O$ of about +4 per mil, corresponding to a change of 2 per mil. The last major

Table 1. Values of $\delta^{18}O$ for sanidine phenocrysts from Nevada ash-flow sheets.

Unit, rock type, and sample number	$\delta^{18}O$ (per mil)
Timber Mountain Tuff	
Second eruptive unit (Ammonia Tanks Member)	
Quartz latite pumice (67L-209-14)	+5.5
Quartz latite pumice (67L-209-5)	+4.8
Quartz latite vitrophyre (67L-211-1)	+4.9
Rhyolite pumice (67L-209-10)	+4.8
Rhyolite pumice (67L-209-11)	+5.0
Rhyolite vitrophyre (67L-210)	+4.8
Mean	+5.0
First eruptive unit (Rainier Mesa Member)	
Quartz latite pumice (67L-205-B1)	+6.6
Quartz latite pumice (67L-205-B2)	+7.1
Quartz latite vitrophyre (67L-206-C)	+7.3
Rhyolite vitrophyre (67L-206-B)	+7.7
Mean	+7.2
Paintbrush Tuff	
Second eruptive unit (Tiva Canyon Member)	
Quartz latite vitrophyre (67FB-2A)	+6.4*
Transitional vitrophyre (67L-212-A)	+6.6
Rhyolite vitrophyre (67L-214)	+6.4
Mean	+6.5
First eruptive unit (Topopah Spring Member)	
Rhyolite pumice (67L-201-B-1)	+7.4
Rhyolite pumice (67L-201-B-5)	+6.9
Rhyolite vitrophyre (67L-204-C-2)	+7.7
Quartz latite pumice (67L-203-B)	+7.4
Quartz latite vitrophyre (67L-204-D)	+6.9
Mean	+7.3

* Determined on plagioclase.

Table 2. Values of $\delta^{18}O$ for sanidine phenocrysts from ash-flow tuffs and lavas of Yellowstone Plateau volcanic field.

Unit and sample number	K-Ar age (million years)	$\delta^{18}O$ (per mil)
Huckleberry Ridge Tuff*	2.0	
68-0-46		+5.8
OCB-66-01		+5.5
OCB-66-02		+6.3
OCB-66-03		+6.1
Mesa Falls Tuff*	1.2	
8YC-460A		+4.0
OCB-66-04		+4.1
Mount Jackson Rhyolite		
OYC-601	1.14	+3.8
OCB-66-11	0.81	+4.9
OCB-66-10	0.59	+5.7
Lava Creek Tuff*	0.6	
Y5-516		+5.6
68-0-45		+4.2
68-0-48		+4.6
68-0-49		+4.8
Plateau Rhyolite (postcaldera lavas)		
Upper Basin Member 8YC-441	0.26	+2.8
Obsidian Creek Member OYC-608	0.31	+6.4
Mallard Lake Member 69-0-18	0.15	+3.7
Central Plateau Member		
OCB-66-13	0.16	+3.5
72-0-75	0.12	+4.3
69-0-19	0.16	+3.1
72-0-73	0.10	+4.1
OCB-66-14A	0.15	+3.5
72-0-76	0.14	+3.7
OCB-66-12	0.16	+3.8
YG-72-7	0.16	+3.8
YG-70-15	0.15	+2.9
YM-405A	0.09	+3.9
YG-72-5	0.11	+4.0
OCB-66-09	0.12	+3.3
YG-68-4	0.07	+3.1
YG-70-13	0.07	+3.7
69-0-17	0.16	+2.6

* Yellowstone Group (the major ash-flow sheets). The samples from these tuffs are of the ages indicated.

ash-flow sheet, the Lava Creek Tuff, which erupted 0.6 million years after the Mesa Falls, has sanidine compositions of about +5 per mil. Lava flows of the Mount Jackson Rhyolite, erupted intermittently between these two latter ash-flow sheets, bridge the isotopic transition. The eruption about 0.3 to 0.5 million years later than the Lava Creek have $\delta^{18}O$ values of +2.6 to +4.3 per mil. This sequence of changes in isotopic composition is more complex than for the southern Nevada rocks, but the Yellowstone data are especially interesting because of the narrow time constraints on development of the isotopic variations.

The complexity of the sequential changes and the sizable range of values for individual tuff units, such as the Lava Creek, make interpretation of the Yellowstone data problematic compared with the interpretation of the sample trends for the Nevada rocks. Based in part on analogy with the Nevada trends, our interpretation of the Yellowstone $\delta^{18}O$ age pattern is as follows: The first ash-flow eruption of the Huckleberry Ridge Tuff was from a very large magma body that probably had reacted only moderately with meteoric water. After the eruption, the magma chamber remained relatively quiescent for about 800,000 years. During this time groundwater interacted with the magma—some of the water remaining in the magma, some moving out into the surrounding rocks. By the time the Mesa Falls Tuff was erupted (about 1.2 million years ago), the magma was about 2 per mil lighter than during the Huckleberry Ridge eruption. After eruption of the Mesa Falls Tuff, the $\delta^{18}O$ of the magma increased, as indicated by sanidines from lavas of the Mount Jackson Rhyolite. We interpret this reversal in ^{18}O composition as reflecting the influx of a large volume of new magma from deeper levels. Additional interaction with meteoric water may have occurred during the relatively quiescent 600,000 years between the Mesa Falls and Lava Creek eruptions. However, much new magma appears to have been added to the principal storage chambers, and the dilution by meteoric water was correspondingly small. After the eruption of the Lava Creek Tuff, the remaining magma, plus any new magma that was introduced, continued to react with meteoric water, changing the $\delta^{18}O$ by another 2 per mil to final values of +2.2 to +4.3 per mil, which are the values for extrusives erupted 250,000 to 70,000 years ago.

How much water is necessary to produce these ^{18}O changes in such large amounts of magma? A simple calculation shows that 3 mm of precipitation annually, which is about 0.3 percent of the present annual precipitation on the Yellowstone Plateau, acting for about 600,000 years over the area of the caldera, would be sufficient to alter the $\delta^{18}O$ by the observed amount. In making this calculation we have assumed an initial magma composition of +7.5 per mil, a meteoric water composition of −17 per mil, and a change of 2 per mil in the magma in 600,000 years. The water is assumed to have entered the magma, exchanged ^{18}O completely with well-mixed magma, and then left the system. If the water mixes and exchanges incompletely before leaving, or if the volume of the magma is larger than the erupted part, more water is necessary. The amount of water quoted above is then a lower limit.

Oxygen isotope data on Oligocene ash-flow tuffs and lavas of the San Juan volcanic field in southwestern Colorado (*8*) show relations that are generally compatible with the interpretations presented here for the Nevada and Yellowstone National Park rocks. Feldspar phenocrysts from successive ash-flow sheets derived from the central San Juan Mountains caldera cluster become progressively lighter in ^{18}O with time, but lava flows that predate and postdate the ash-flow eruptions are relatively constant in isotopic composition (*5*). These lavas, which are mostly andesitic to quartz latitic in composition—distinctly more mafic than the associated ash-flow sheets—are thought to represent eruption from relatively deep undifferentiated levels of the magma reservoir, below the level of interaction with meteoric water.

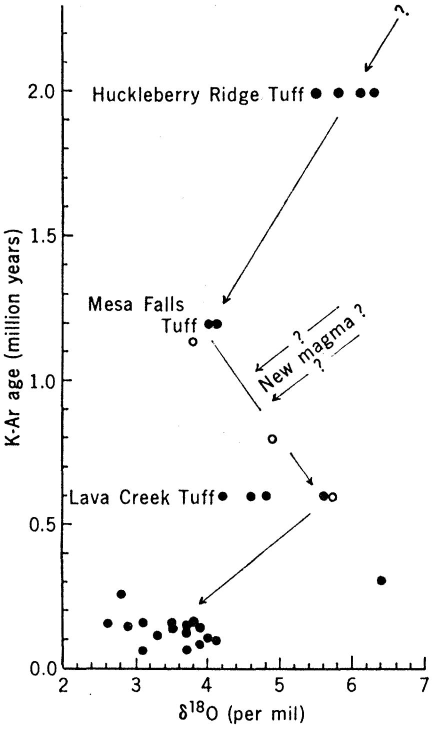

Fig. 1. Relations between oxygen isotope composition and age of sanidine phenocrysts from ash-flow tuffs and lavas of Yellowstone National Park area. Arrows indicate the inferred evolution of oxygen isotope composition with time (see text). The anomalous sample (Obsidian Creek Member) is the only sample of Plateau Rhyolite from outside (5 to 6 km) the Yellowstone caldera. (Solid circles) Yellowstone Group and Plateau Rhyolite, (open circles) Mount Jackson Rhyolite.

The existence of volcanic rocks having low ^{18}O contents was reported previously (*1*, *9*). The significance of our results is the demonstration of ^{18}O depletion with time in individual magma series and the conclusion that the change in ^{18}O contents of the phenocrysts represents variations in ^{18}O that occurred in the magma at liquidus conditions.

Few data are available elsewhere that bear on our hypothesis of the significance of meteoric water in magmas. Stuckless and O'Neil (*10*) failed to find evidence of interaction between meteoric waters and the magmas that produce volcanic rocks of the Superstition-Superior area, Arizona. Higgins (*11*) has concluded that the development of a lake in the Newberry caldera, Oregon, acted to change the differentiation trend of the underlying magma. He attributes this effect to differences in the oxygen fugacity in the magma related to the presence of large volumes of water in the caldera lake. Although lakes often fill calderas after collapse, a lake probably need not be present above a magma chamber in order for meteoric water to reach the magma. The oxygen isotope changes that we have documented all occurred in magma chambers that underlay large calderas, but all that seems necessary for such changes is that groundwater have access to the magma in sufficient quantity. In the large magma bodies in the Yellowstone National Park area, the equivalent of only 3 mm of water per year over the plan area of the assumed magma chamber can account for the observed changes in $\delta^{18}O$.

Perhaps more significant than the

presence or absence of a caldera lake is the arrival of the magma body at a crustal level sufficiently shallow to interact with meteoric water. An important factor is the amount of time spent by the magma at shallow crustal levels. Taylor (*1*) has observed that isotopic interactions are most commonly around the margins of intrusions into flat-lying volcanic terranes, but the main control may be merely the shallow crustal positions of the volcanics. This postulated interaction of magmatic bodies of batholithic dimensions with meteoric water, all at liquidus temperatures, has other implications. The water entering the magma may modify the original minor element composition, and this possibility should be considered in studies of strontium and lead in igneous rocks, as well as rocks surrounding large intrusions. The volatiles leaving the magma may carry metal ions that may be the source of ore deposits associated with igneous intrusions. The amount of water available for ore transport by this process is far greater than that available by the simple outgassing of a statically crystallizing magma (even if it is saturated with volatiles).

The course of magmatic differentiation can also be affected by the availability of meteoric water. The accumulation of abundant volatiles in the upper parts of a shallow magma chamber should lower the solidus temperature and the viscosity of the magma in this region, resulting in the establishment of strong physical gradients in this part of the magma. Gradients of this type must have been present in the differentiated magma chamber sources of the Paintbrush and Timber Mountain Tuffs in order to permit the observed variation in phenocryst content, which increases downward in the magma chambers. Finally, convective circulation of water far in excess of that cognate to the magma may have permitted significant differentiation by some volatile transfer process, a differentiation mechanism that has been considered possibly significant (*12*), although the precise nature of such a process is difficult to evaluate.

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Nuclear Magnetic Resonance Studies and Water "Ordering" in the Crystalline Lens

Abstract. *Nuclear magnetic resonance studies of the relaxation times of the water in the crystalline lens show that, as in all interfacial systems, these parameters are markedly reduced from their values in pure water, that* T_2 *is less than* T_1*, and that both depend on water content. Determination of diffusion coefficients and studies on physiologically inert lenses indicate that reduced relaxation times do not provide direct evidence for ordering of the bulk of the cell water.*

Numerous studies of the water of living cells by proton magnetic resonance techniques have appeared in the literature (*1–5*). All of these studies show that both the longitudinal or spin-lattice relaxation time (T_1) and the transverse or spin-spin relaxation time (T_2) are reduced in living cells compared to their values in pure water. Two types of mechanism have been proposed to account for these findings: (i) ordering of the major portion of the cell water (*1*), and (ii) a two-phase rapid exchange mechanism in which only a small fraction of the cell water is ordered (*2, 5*); rapid exchange between this ordered fraction and the bulk water would give rise to an observed relaxation time intermediate between those of the two phases. In an attempt to differentiate between these alternatives, we made measurements of proton relaxation phenomena in the crystalline lens of the eye. Our results give a useful perspective on the entire problem.

We employed pulsed nuclear magnetic resonance (NMR) techniques to examine the relaxation times of the water protons in living frog and rabbit lens in vitro, in various states of hydration and after treatment designed to destroy the physiological integrity of the lens. The diffusion coefficient of the water molecules in rabbit lens was also determined.

For the major portion of the studies on frog lens we used an NMR spectrometer with a 12-inch (~0.3-m) Varian magnet with flux density 7 kgauss at a frequency of 30.3 Mhz. Time T_1 was determined by using a null method of Carr and Purcell (*6*), and T_2 by using a Carr-Purcell sequence [method B, with pulse train 90°-180°-180° . . . (*6*)]. A few studies of T_2 on frog lens were performed with a Praxis model PR102 with a small permanent magnet and a frequency of 10 Mhz, by using repeated 90°-180° pulse sequences [method A (*6*)]. The term T_2 is usually reserved for the relaxation time of a purely exponential process. Because transverse relaxation is a multicomponent rather than a simple exponential process in the lens (see below), the time for the height of the signal following the 180° pulse to decay to $1/e$ of the height of the 90° pulse will be designated T_2^*. Since the T_2^* data obtained with the Praxis and the Varian were entirely compatible, they have been pooled.

Studies of rabbit lens were performed with a spin echo apparatus in conjunction with a 12-inch Varian V-4007 research magnet (*7*) at 25.0 Mhz. Time T_1 was determined by using a 180°-90° pulse sequence at varying pulse intervals (*8*), and T_2^* was determined by using method A, measuring the voltage with a "boxcar" integrator (*9*), and averaging the results of six repetitions at each pulse interval. This