Formation of low-$\delta^{18}$O rhyolites after caldera collapse at Yellowstone, Wyoming, USA

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ABSTRACT
We present a new model for the genesis of low-$\delta^{18}$O rhyolites of the Yellowstone caldera based on analyses of zircons and individual quartz phenocrysts. Low-$\delta^{18}$O rhyolites were erupted soon after the massive caldera-forming Lava Creek Tuff eruption (602 ka, ~1000 km$^3$) and contain xenocrysts of quartz and zircon inherited from precaldera rhyolites. These zircons are isotopically zoned and out of equilibrium with their host low-$\delta^{18}$O melts and quartz. Diffusion modeling predicts that magmatic disequilibria of oxygen isotopes persists for as much as tens of thousands of years following nearly total remelting of the hydrothermally altered igneous roots of the depressed caldron, in which the alteration-resistant quartz and zircon initially retained their $\delta^{18}$O values. These results link melting to caldera collapse, rule out rapid or catastrophic magma–meteoric water interaction, and indicate wholesale melting rather than assimilation or partial melting.

Keywords: Yellowstone, zircon, oxygen isotopes, caldera, low $\delta^{18}$O.

INTRODUCTION
Meteoric water plays an important role in the genesis of ore deposits, explosive volcanism, and hydrothermal activity. Low values of $\delta^{18}$O unambiguously provide evidence of this process. Although the alteration of rocks by meteoric water is well understood, the incorporation of meteoric water into magma remains controversial. Studies of low-$\delta^{18}$O volcanic and shallow plutonic magmas in which tens of percent of their total oxygen must have been ultimately derived from meteoric or surface water provide important insight into mechanisms of fluid-magma interaction (Friedman et al., 1974; Muehlenbachs et al., 1974; Criss and Taylor, 1986; Taylor, 1987). The genesis of low-$\delta^{18}$O magmas has been variously proposed to require: (1) direct, sometimes catastrophic meteoric water addition into magma (Friedman et al., 1974; Hildreth et al., 1984); (2) more gradual, multistage assimilation of hydrothermally altered rocks (Taylor and Sheppard, 1986; Balsley and Gregory, 1998); or (3) partial melting of the walls of the magma chamber (Bacon et al., 1989).

Classic examples of low-$\delta^{18}$O lavas are found in the Yellowstone Plateau volcanic field, Wyoming, USA, where abrupt $^{18}$O depletions (accompanied by changes in Sr and Pb isotopes) in magmas occurred after caldera-forming eruptions at 2.0 and 0.6 Ma. The most dramatic drop in $\delta^{18}$O values (by ~5.5‰) of quartz phenocrysts occurred after the last caldera-forming eruption, which deposited the Lava Creek Tuff and formed the Yellowstone caldera (Hildreth et al., 1984, 1991). The $>40$ km$^3$ of postcaldera, low-$\delta^{18}$O lavas with $\delta^{18}$O quartz (Qz) <3‰ appear exclusively within the Yellowstone caldera. It is remarkable that their whole-rock major and trace element composition is similar to that of isotopically normal high-silica rhyolites of precaldera lavas or lavas erupted simultaneously outside the caldera.

We report analyses of more than 200 individual quartz phenocrysts and zircon separates from the Lava Creek Tuff and younger intra-caldera lavas (602–70 ka). The ability to analyze samples smaller than an individual quartz phenocryst allows us to measure the phenocryst-scale (<1 mm) variability, which was not possible in earlier studies.

SAMPLE PREPARATION AND ANALYTICAL TECHNIQUE
Individual phenocrysts of quartz and sanidine, and obsidian spheres, were handpicked from hand specimens or from crushed rock. Quartz was purified in fluoroboric acid to dissolve feldspar and glass. Special attention was paid to glass inclusions and phenocryst morphology to assure that all analyzed phenocrysts are primary and not the result of precipitation from a secondary hydrothermal fluid. Zircons were separated from 20 kg samples of rock using standard techniques of density and magnetic separations. The extracted 50–250 mg of zircons were purified from admixed minerals and glass by cold HF.

The University of Wisconsin CO$_2$-laser mass-spectrometer system (Valley et al., 1995) allows precise analysis of 1–2 mg samples with the average reproducibility of better than ±0.10‰ (1 standard deviation, s.d.). Quartz was analyzed by the rapid heating technique (Spicuzza et al., 1998a). For analyses of more reactive sanidine and obsidian, we used an airlock sample chamber (Spicuzza et al., 1998b). We measured four to seven aliquots of UWG-2 garnet standard on each day of analysis. Nine analyses of NBS-28 quartz yielded an average value of 9.55‰. Air abrasion of zircon fractions was done in a corundum mortar and normally took from 1 to 5 days. Selected ion microprobe analyses were performed on 20-µm-diameter spots, 3 µm into prismatic crystal growth faces of zircon using a Cameca ims-4f at the University of Edinburgh, Scotland, with a Cs$^+$ primary beam and energy filtering (Valley et al., 1998).

ZONING AND VARIABILITY OF $\delta^{18}$O IN INDIVIDUAL QUARTZ PHENOCRYSTES AND ZIRCONES
Values of $\delta^{18}$O in individual obsidian spheres (Table 1) within several lava flows were measured and are homogeneous ($\delta^{18}$O = ±0.3‰). These values are similar to those reported by Hildreth et al. (1984), demonstrating a remarkable homogeneity of $\delta^{18}$O in magmas parental to low-$\delta^{18}$O lavas. In contrast, all low-$\delta^{18}$O rhyolites erupted immediately after the Lava Creek Tuff are distinctly variable in the $\delta^{18}$O values of individual quartz phenocrysts (Fig. 1). Variations of 1.0‰–1.5‰ are common among quartz phenocrysts from a single hand specimen, and variation is in excess of 2‰ for the Canyon flow and the South Biscuit Basin flow. The highest values of $\delta^{18}$O among quartz phenocrysts in the South Biscuit Basin flow and the Canyon flow approach +6‰.

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similar to normal-δ¹⁸O quartz in precaldera rocks and in Lava Creek Tuff. Despite similar whole-rock chemical compositions, low-δ¹⁸O lavas contain fewer quartz phenocrysts. The external morphology and internal structure of quartz (as shown by cathodoluminescence imaging) reveal resorption and solution reprecipitation.

Another characteristic feature of low-δ¹⁸O lavas is oxygen isotope disequilibrium between quartz and zircon (Zrc). Values of Δ(Qz-Zrc) between individual quartz phenocrysts and bulk separates of zircon are as much as a few per mil smaller than the equilibrium fractionation of 2‰ for magmatic temperatures (Fig. 1). Most precaldera, extracaldera, and intracaldera rhyolites erupted more than 150 k.y. after the Lava Creek Tuff do not show such disequilibrium and have Δ(Qz-Zrc) ~2‰.

Differences of as much as 0.7‰ in δ¹⁸O exist between the smallest (<53 µm diameter) and largest (>149 µm) zircons from low-δ¹⁸O lava flows erupted after the Lava Creek Tuff. These differences suggest that smaller zircons grew later in a magma of changing δ¹⁸O, or that zircons have exchanged oxygen as a function of surface area/mass. To test these hypotheses, larger zircons (>105 µm, or >149 µm) were air abraded, and the residual cores were analyzed for δ¹⁸O. Cores of zircons from low-δ¹⁸O rocks have δ¹⁸O values that are as much as 2.5‰ higher than those of the smallest zircons (Fig. 1; Table 1). The highest δ¹⁸O values in abraded cores range from 1.8‰ to 3.7‰, approaching the δ¹⁸O of zircons in precaldera rhyolites (+4‰) and suggesting that large zircons are inherited from the precaldera magma or country rock.

Successful air abrading were made of abundant zircons in the Middle Biscuit Basin flow to monitor δ¹⁸O after each step of rim removal (Fig. 2). Optical measurements and weight loss were used to determine the decrease in the average radius of zircons that became ellipsoidal to nearly spherical. Values of δ¹⁸O are plotted as a function of average radii of residual zircons. The resulting profile shows a steep gradient of ~1‰ per 2–3 µm at grain boundaries while Δ(core-rim) approaches 5‰.

It is important to note that the bulk analyses of the smallest zircons (<53 µm) yielded δ¹⁸O values more than 1‰ higher than either the calculated rim composition based on zircon abrasion, the ion microprobe analyses of zircon rims, or zircon in equilibrium with their host obsidian. This finding suggests that even the smallest grains of zircon are isotopically zoned and contain higher δ¹⁸O cores. Such zoning would suggest that much of the total mass of zircons was inherited and that diffusive exchange with low-δ¹⁸O magma was an important process, affecting a larger mass percentage of smaller crystals because of their larger surface area/mass.

It is remarkable that all studied zircons from low-δ¹⁸O rhyolites younger than the Lava Creek Tuff show evidence of δ¹⁸O zoning, whereas all abraded zircon fractions from precaldera and extracaldera rhyolite rocks are homogeneous. The Scaup Lake flow and other voluminous rhyolites erupted after an ~200 k.y. quiescence in eruptive activity inside the caldera show no significant heterogeneity in quartz phenocrysts, no isotopic zoning in zircon, and no Δ(Qz-Zrc) disequilibria (Fig. 1).

Two processes operated to reequilibrate zircon, quartz, and magma: (1) diffusive oxygen exchange, and (2) solution reprecipitation on inherited cores and new overgrowth in equilibrium with the melt. Oxygen diffusion coefficients in zircon in Yellowstone water-bearing magmas are on the order of 10⁻¹²–10⁻¹⁸ cm²/s (water-saturated experiments at 750–850 °C, Watson and Cherniak, 1997), making it possible to equilibrate a typical 50-µm-radius zircon grain after a few tens of thousands of years (Fig. 2). Sluggish rates of zircon growth and dissolution in magmas (10⁻¹⁵–10⁻¹⁷ cm²/s, at the same temperatures and rate of cooling or heating of 0.01 °C/yr, Watson, 1996) suggest that it may take at least tens of thousands of years to form a 50-µm-thick zircon overgrowth. U-Th disequilibrium and U-Pb dating of zircon cores show that zircon may reside for ~200 k.y. in similar rhyolitic systems (e.g., Reid et al., 1997; Brown and Fletcher, 1999). Several lines of evidence support zircon recycling as the main mechanism of Zr mass balance: relatively short time scales of volcanic melting-crystallization phenomena, similar compositions of most Yellowstone rhyolites (low-δ¹⁸O or normal) including relatively constant Zr concentrations (Hildreth et al., 1991, 1984), and thus similar zircon saturation temperatures.

**OXYGEN ISOTOPE REEQUILIBRATION**

Diffusive exchange of oxygen isotopes in quartz and zircon was modeled using equation 6.18 of Crank (1975) for diffusion in a normal δ¹⁸O sphere surrounded by an infinite reservoir of low-δ¹⁸O magma. Calculations were made at 750 and 850 °C, the latter consistent with Fe-Ti oxide temperature estimates for Yellowstone’s high-silica rhyolites (Hildreth et al., 1984) and with our zircon saturation-temperature estimates. Measured zircon zoning profiles (Fig. 2) are between pro-
files calculated for 500 and 5000 yr at 850 °C. Figure 3 shows the measured δ¹⁸O ranges of zircon and quartz phenocrysts and the calculated exchange curves at 850 °C. Crystals of observed sizes were chosen and the δ¹⁸O values of both the core and the bulk crystal were computed. The water-saturated diffusion coefficients of Watson and Cherniak (1997) were used for zircons. We also consider the case in which new overgrowth of a rim in equilibrium with the melt occurs simultaneously with isotopic exchange by diffusion. For quartz, the diffusion coefficients of Farver and Yund (1991), Elphick et al. (1986), Gilette and Yund (1984), and Dennis (1984) all yield similar results for water-saturated oxygen diffusion at 850 °C. A decrease in temperature to 750 °C increases the time of equilibration (~10 times) without changing the relative position of the curves (owing to the similar activation energy for oxygen diffusion in quartz and zircon).

The curves of δ¹⁸O equilibration between cores of quartz, cores of zircon, and melt show that maximum disequilibrium and core-rim heterogeneity would occur 500–5000 yr after normal δ¹⁸O crystals became immersed in low-δ¹⁸O melt. During this transition, the predicted Δ(Qz–Zrc) shows wide variations similar to our measurements in low-δ¹⁸O lavas (Fig. 1 and Fig. 3, bottom). Although the natural quartz crystals are larger, the zircons need 100 times longer to reequilibrate with the magma by diffusion. As a result, intervals with the maximum difference of δ¹⁸O between cores of large crystals of quartz and zircons are offset in time. For example, variability of δ¹⁸O in quartz in the South Biscuit Basin flow and the Canyon flow (Table 1) indicates a shorter time of immersion in magma before eruption (~500 yr at 850 °C) because the quartz had not achieved homogeneity, whereas the zircons are already zoned. In contrast, quartz phenocrysts in the Middle Biscuit Basin flow and the Dunraven Road flow show only limited remaining heterogeneity, whereas zircons are highly zoned. This result suggests that Middle Biscuit Basin magma existed long enough to reequilibrate quartz, but not long enough to reequilibrate zircon. Therefore, the observed heterogeneities in quartz and zircon also indicate that their residence in low-δ¹⁸O magma was on the order of 10²–10³ yr at 850 °C or 10³–10⁴ yr at 750 °C.

**ORIGIN OF LOW-δ¹⁸O MAGMAS**

Given the slow rates of oxygen diffusion, high closure temperatures, and slow crystal growth of zircon (Watson and Cherniak, 1997; Watson, 1996), the newly discovered isotope heterogeneity both in zircon and quartz (Figs. 1 and 2) rules out a rapid (100 yr) or catastrophic (a few hours to days) process such as phreatic meteoric water-magma interaction at the time of eruption or posterosive oxygen exchange or overgrowth. The exchange calculations herein also restrict the maximum period over which such heterogeneity might be preserved.

Assimilation or partial melting of wall rocks as a mechanism of genesis of tens of cubic kilometers of magmas with δ¹⁸O values of ~0‰ would require mixing nearly equal proportions of Lava Creek-type (+6‰) magma and unusually low-δ¹⁸O magma or rock (~5‰ to ~15‰) (e.g., Hildreth et al., 1984, 1991). Such low-δ¹⁸O rocks (or low-δ¹⁸O xenocrysts) have not been found at Yellowstone despite detailed searching. Furthermore, it would be difficult to achieve the observed bulk textural, chemical, and isotopic homogeneity of low-δ¹⁸O lavas by mixing of two viscous rhyolites, given the time considerations already discussed.

The critical observation for understanding of the genesis of the low-δ¹⁸O Yellowstone magmas is the δ¹⁸O zonation and variation, which indicates that most of the mass of zircon (even the smallest crystals) in low-δ¹⁸O magmas was inherited from a higher δ¹⁸O source, similar to normal precaldera rocks. Dispersal of old zircons in a new magma could occur by near total fusion of source rocks containing these zircons. A similar argument applies to quartz. Lower abundance, smaller sizes, and resorbed morphology of quartz in low-δ¹⁸O as opposed to normal lavas is consistent with a relict or xenocrystic origin. The source rock may have achieved low-δ¹⁸O values of ~0‰ or lower through hydrothermal alteration of volcanic glass, matrix, and feldspars, but quartz and zircon phenocrysts are alteration resistant (Valley et al., 1994; Criss and Taylor, 1986). Any initial δ¹⁸O variations in melt anneal several orders of magnitude faster (even by diffusion) than variations in quartz and zircon (Zhang et al., 1991).

Caldera collapse created conditions favorable to remelting of the hydrothermally altered roots of the cauldron and thus for the genesis of low-δ¹⁸O magmas (Fig. 4). The estimated vertical drop due to caldera subsidence following eruption of the Lava Creek Tuff was at least ~500 m (Hildreth et al., 1984), and large blocks may have been brought down nearer the magma chamber. Following the views of Smith (1979) and Smith and Christiansen (1980) that most magma remains in the batholith-scale magma chambers beneath the Yellowstone caldera, caldera subsidence would have juxtaposed the hydrothermally altered and water-rich intracaldera roots of the down-dropped block with significantly hotter underlying magma. Most ¹⁸O-depleted source rocks were originally located closer to the
magma chamber, because the intensity of hydrothermal alteration increases toward the heat source. They thus melted first, giving rise to most low-$\delta^{18}$O magmas (Fig. 4) that erupted independently around two resurgent domes of the Yellowstone caldera as much as 45 km apart. Each lava resulted from the nearly total melting of hydrothermally altered, low-$\delta^{18}$O precursor rocks. The earlier alteration lowered $\delta^{18}$O in the matrix of the precursor rock, but normal $\delta^{18}$O phenocrysts of zircon and some quartz survived both the hydrothermal alteration and subsequent residence in low-$\delta^{18}$O melt before it erupted and formed glassy lava. The time interval between melting and eruption was on the order of hundreds to thousands of years at 850 °C.

Isotopic recovery toward less $\delta^{18}$O-depleted magmas is seen in progressively younger intra-caldera lavas (Fig. 1) and could result from progressive remelting of less $\delta^{18}$O-depleted rocks of the caldera block, and mixing with the less $\delta^{18}$O-depleted magma from the interior of the magma reservoir (Hildreth et al., 1984, 1991).

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