Melt inclusions in olivine: Reliable witnesses to Earth's interior?

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Our knowledge of the composition and chemical state of the interior of Earth is largely based on a combination of geochemical measurements of samples from depth, geophysical observations, and experimental studies of phase equilibrium and material behavior. While plate tectonic processes do bring deep subsurface rocks to Earth's surface, such as in ophiolites, these are significantly altered during ascent, and extraction of appropriate chemical and volatile information is unlikely to be highly robust. By far, the most reliable measures of chemical conditions in Earth's interior come from samples brought to the surface with minimal opportunity for resetting the key chemical markers (e.g., ferric-ferrous iron ratios, volatile contents). The most common of these samples are xenolithic materials transported in basaltic or kimberlitic magmas and cooled rapidly. A critical question for such samples involves the extent to which they have been reset in terms of the signature of the source region during entrainment and ascent to the surface. Such signatures may be retained in the individual xenolith mineral grains or within inclusions trapped in the interior of these minerals. In this issue of *Geology*, Gaetani et al. (2012, p. 915) provide the results of an experimental study that give fresh insight into the effectiveness of melt inclusions within xenolithic olivine grains in retaining the water content and oxygen fugacity (f_{O_2}) at the time of entrapment.
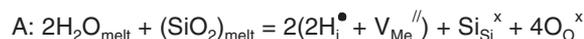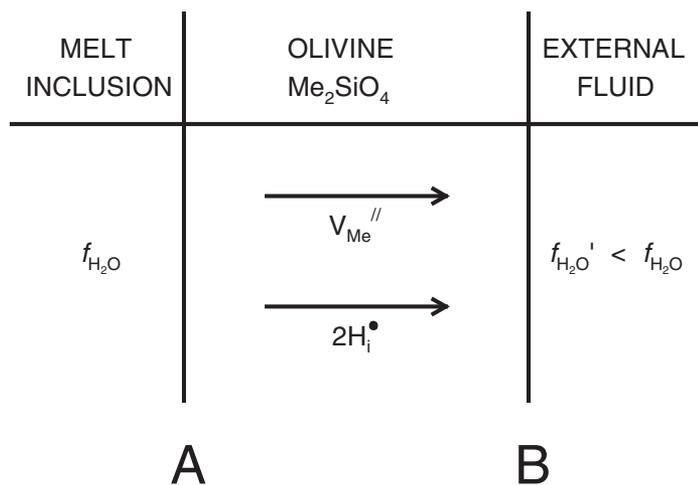
Hydroxyl signatures in minerals contained in xenoliths have been studied in order to constrain the water contents of the mantle source region (Demouchy et al., 2006; Peslier and Luhr, 2006; Li et al., 2008; Peslier et al. 2008). All xenolithic minerals appear to exchange hydrogen species with the entraining melt phase to some extent during transport, no matter how fast they are brought to the surface. However, the measurement of core-rim variation in hydrogen content in xenolithic mineral grains, coupled with experimental measurements of hydrogen diffusion, shows promise for extracting information on source conditions. Hydrogen diffusion in minerals often occurs through the movement of protons, locally charge-compensated by the cooperative diffusion of a negatively charged defect, such as a metal vacancy (an unoccupied divalent cation site, normally occupied by magnesium or iron). Alternatively, hydrogen diffusion may also occur through counter-diffusion of protons with another positively charged defect, such as a polaron. A polaron is the mobile excess charge (an electron hole) on ferric iron in a regular divalent cation site. In olivine, diopside, and enstatite, a process of proton-polaron exchange has been demonstrated, which is rate limited by the diffusivity of the protons (e.g., Mackwell and Kohlstedt, 1990; Ingrin and Skogby, 2000; Stalder and Skogby, 2003; Stalder and Behrens, 2006). In this mechanism, proton loss is coupled to an increase in the ferric-ferrous iron ratio of the mineral. A second proton transport mechanism, in which protons move cooperatively with metal vacancies, has been characterized in olivine (e.g., Kohlstedt and Mackwell, 1998; Demouchy and Mackwell, 2006). In this case, the rate of diffusion is slower and is limited by the diffusivity of the vacancies, which are orders of magnitude more mobile than magnesium or iron ions. Although the total amount of hydrogen that can be transported by the proton-polaron mechanism in mantle minerals is limited by the amount of ferric iron that can be tolerated in the mineral (maximum ferric/total iron ratios in olivine rarely exceed 1%), significantly higher numbers of protons can be transported cooperatively with metal vacancies (Demouchy and Mackwell, 2006), so that millimeter-sized olivine grains can fully dehydrate in a matter of hours at 1000 °C. Both mechanisms of hydrogen diffusion in mantle minerals allow relatively rapid resetting of internal hydrogen contents, raising concerns about the utility of mineral water contents in xenoliths in constraining source-region water concentrations.

Interrogation of material trapped in mineral "bottles" offers an alternative technique to determine conditions deep in the Earth. Studies of inclusions in diamonds have indicated sources in the mantle transition zone, and even the lower mantle (e.g., Walter et al., 2011, and references therein). Inclusions trapped in other minerals can also provide important information about the crust and mantle. Fluid inclusions are frequently used to constrain the composition, temperature, and pressure of the mineralizing environment. Melt inclusions in xenolithic olivine have been used to infer pressure, temperature, and melt composition at various stages in the evolution of magmatic systems. They have also been used to determine pre-eruptive water contents of degassed magmas. Such melt inclusions generally have far higher volatile concentrations than the host olivine. Assessment of the rate of loss of volatiles from trapped inclusions requires an understanding of the flux of volatiles through the surrounding mineral, which reflects not only the diffusivity of the volatile species in the mineral but also its solubility. Total loss rates will remain small if the solubility of the volatile in the mineral is very low, even when it diffuses relatively rapidly. For this reason, melt inclusions are much more likely to retain the water content in the source region than the mineral grains themselves.

A number of recent studies have suggested that water loss/gain in melt inclusions is strictly limited, based on the presumption that loss of protons from the melt phase would cause an increase in the ferric to ferrous iron ratio in the inclusion due to release of oxygen when protons move into the olivine. It was argued (e.g., Sobolev and Danyushevsky, 1994; Danyushevsky et al., 2002) that such loss/gain of water would be limited to less than 1 wt% by how much ferrous/ferric iron was available in the melt inclusion to support the reactions. Gaetani et al. (2012), however, report a new experimental study that clearly demonstrates that oxidation of the melt is not required for diffusive loss of hydrogen through the surrounding olivine. In their two sets of experiments at 1250 °C, they showed that significant loss from or gain of water by melt inclusions was not correlated with a major change in the ferric-ferrous iron ratio in the melt, that rapid equilibration occurred in f_{O_2} between the external environment and the melt inclusions, and that sulfur and oxygen are largely immobile on the time scales of the experiments. Based on these results, they conclude that at the melt-olivine interface, water in the melt can form/consume defects in the olivine involving protons associated with metal (octahedral cation) vacancies, with no change in the oxidation state of iron, as shown Figure 1. In the process, the inclusion melt phase becomes more silica-rich (water loss) or silica-poor (water gain). It should also be noted that the loss/gain of water in the inclusion is limited by the flux of defects involving protons associated with metal vacancies through the olivine, which is dependent on both the diffusivity and solubility of the defects under the conditions of the experiments. Thus, the experimental results of Gaetani et al. are fully consistent with the previous measurements of hydrogen transport in olivine (e.g., Kohlstedt and Mackwell, 1998; Demouchy and Mackwell, 2006).

The interpretation provided by Gaetani et al. of their experiments appears to satisfy their observations, in that they see significant changes in volatile content of the melt inclusions but little evidence of associated changes in ferric-ferrous ratios for iron. Their model however, as illustrated in Figure 1, does suggest that as the water content of the inclusions

A: $2H_2O_{melt} + (SiO_2)_{melt} = 2(2H_i^{\bullet} + V_{Me}^{//}) + Si_{Si}^{x} + 4O_O^{x}$

B: $2(2H_i^{\bullet} + V_{Me}^{//}) + Si_{Si}^{x} + 4O_O^{x} = 2H_2O_{melt} + (SiO_2)_{melt}$

or:

$2(2H_i^{\bullet} + V_{Me}^{//}) + 2Me_{Me}^{x} + 2Si_{Si}^{x} + 8O_O^{x} = 2H_2O_{gas} + 2MeSiO_3$

Figure 1. Schematic of the kinetics of hydrogen loss from an inclusion through the olivine host to the external fluid when the external water fugacity (f_{H_2O}) is lower than the inclusion water fugacity, such as during dehydration experiments. If the external f_{H_2O} is higher than in the inclusions, the arrows would be reversed. The chemical equations, which use the Kröger-Vink notation (Kröger and Vink, 1956), show the reactions at interface A between melt and olivine, and interface B for the cases where the external fluid is either melt or gas. In this notation, chemical species are shown with their associated site (subscript) and net charge relative to the perfect olivine lattice (superscript, with • [dot] as a charge of +1; / [slash] as −1; × as neutral). For example, an interstitial proton is shown as $H_i^{\bullet}$, a metal vacancy as $V_{Me}^{//}$, and silicon in its regular site as Si_{Si}^{x}. Me symbolizes a metal (octahedral cation), which is generally magnesium or iron.

during the evolution of magmas. Further, the expansion of melt inclusion studies to include other major xenolithic minerals with different defect kinetics will likely result in major new insight into magma genesis, chemical stratification, and rheological behavior in Earth's interior.

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Printed in USA

drops, the silica content is expected to also decrease. Parallel to this, for experiments in a gas medium, one would expect to find an enstatite rim on the outside of the olivine samples after dehydration. If such manifestations of changes in silica activity are not observed, then the model may need to be revisited. This model also suggests that changes in water content of the inclusion due to interactions with the external environment will result in a gradient in silica activity across the olivine, which may act to suppress further changes in the water content of the inclusion. However, the observation of rapid equilibration of the f_{O_2} in the melt inclusions to that in the external environment suggests that silicon and/or oxygen defects may also diffuse across the olivine host on the time scales of the experiments (e.g., Mackwell et al., 1988). Such mobility would potentially allow equilibration of both the f_{O_2} and silica activity. Accommodation of such effects in the model by Gaetani et al. could further improve our understanding of the effectiveness of olivine melt "bottles" as reliable witnesses to conditions