

Water and other volatiles in the Hawaiian plume: A SIMS study of melt inclusions

E. H. Hauri

DTM, Carnegie Institution of Washington, Washington, DC
20015, USA

The importance of water in many mantle processes cannot be overestimated. Water has a substantial influence on lowering the melting temperature of the mantle (Kushiro, 1972), and even small amounts of water in olivine (50 ppm) can lower the viscosity of this mineral by almost three orders of magnitude (Hirth and Kohlstedt, 1996). Because of the significant role of water in modulating viscous mantle flow as well as depth and extent of mantle melting, it is imperative to understand the distribution of water in the Earth's interior, the origin of water in various mantle reservoirs, and the cycling of water between these reservoirs. Hawaii is especially important in studies of mantle water, due to the presence of several distinct mantle components identified from geochemical studies of shield-stage basalts. One of these components is recognized to have a substantial 'primordial' volatile signature (Loihi seamount), while another exhibits many isotopic and geochemical features expected from subducted and recycled crustal material (Koolau volcano). As a result, studies of Hawaiian lavas provide a means of accessing two potentially distinct sources of water in the Earth's interior, and may permit a search for water which has survived passage through a palaeo-subduction zone.

Using methods developed for microanalysis of the volatiles H₂O, CO₂, S, F and Cl by ion microprobe, we have addressed the origin of water in the sub-Hawaiian mantle by examining the geochemistry of small inclusions of melt trapped within olivine phenocrysts from a number of Hawaiian volcanoes (Loihi, Kilauea, Mauna Loa, Koolau). In addition, we have recently developed the capacity to measure by ion probe the D/H ratios of magmatic water contained within these melt inclusions, thereby providing an important isotopic tracer for various processes (both deep and shallow) involving water. All analyses are made with a primary beam of Cs⁺ ions (1–10 nA) and collection of negative secondary ions. Detection limits are 20–30 ppm H₂O, 5 ppm CO₂, and <5 ppm for S, F and Cl. Reproducibility of D/H ratios in glasses with 1% to 0.2% H₂O ranges

from 21 to 51 (1 σ) in a 20–40 μ m spot. Analysis times are 5 minutes for volatile concentrations and 45 minutes for D/H ratios.

Shallow-level effects

Many processes involving H₂O must be understood before examining variations in mantle sources, all of which may alter the H₂O and D/H signature of mantle melts. These processes include (1) formation of shrinkage bubbles and post-entrapment crystallization of inclusions within host olivines, (2) diffusive loss of H and D from slowly-cooled inclusions, (3) degassing of melts in shallow magma chambers, (4) assimilation of hydrated crustal material, and (5) varying degrees of partial melting in the mantle source. All of these effects can be observed in Hawaiian melt inclusions, and can best be recognized and distinguished by measuring all volatiles on the same inclusions with concurrent measurements of isotopic data for these same volatiles.

Nearly all Hawaiian melt inclusions are partially crystallized (ol+cpx^oopx); analysis of heterogeneous inclusions is complicated by varying proportions of crystal and glass under the ion beam. In addition, many inclusions contain a shrinkage bubble, and the volatiles within these bubbles must be reequilibrated with the melt under conditions similar to those present during entrapment. All the Hawaiian inclusions have been reheated to 1275°C at QFM for 10 minutes in a 1-atm. gas mixing furnace in order to homogenize the inclusions. This procedure is sufficient to produce totally glassy inclusions in all Hawaiian olivines. Following reheating, the inclusions are polished and measured by electron probe for their major element composition, correcting the compositions to equilibrium with the host olivine.

Since hydrogen moves through olivine as protons, the diffusivity of hydrogen is exceedingly rapid, and can result in losses of H and D over hour-long time scales, with consequent large positive shifts in melt inclusion D/H ratios. Reheating experiments longer

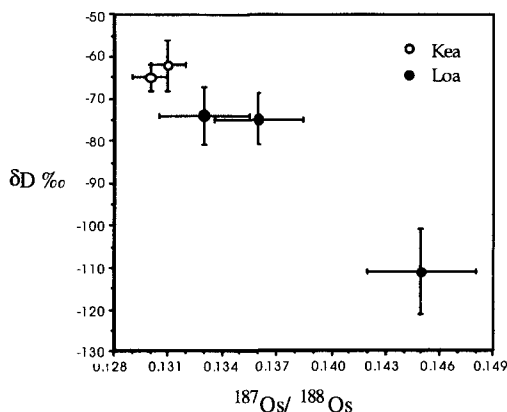


FIG. 1. Averages of hydrogen isotope (from melt inclusions and submarine glasses) and Os isotope (from whole rocks) data for Hawaiian shield-stage basalts.

than 30 minutes demonstrate this effect clearly in the laboratory. In nature, this effect is important when the host olivines come from subaerial lava flows which have extensively degassed and cooled slowly. Melt inclusions from one Mauna Loa flow show water contents of 0.07–0.1 wt.% and D/H ratios of up to +30‰ due to this process.

Low-pressure H_2O degassing trends are also observed in some melt inclusions from Koolau. The key observations which identify these trends are positive relationships between H_2O and D/H ratios, which are consistent with known vapour-melt partitioning of hydrogen isotopes during open-system degassing. Degassing of H_2O from Koolau inclusions results in δD values as low as -160‰ . Loihi inclusions show a rough positive correlation between H_2O and CO_2 contents which may be related to mixing of degassed and undegassed magmas. Variations in D/H ratios are minor ($<5\text{--}10\text{‰}$) in the inclusions with the highest water contents.

Several Loihi melt inclusions show clear correlations between Cl contents and D/H ratios indicative of mixing with seawater-derived brines in the magma chamber. Most Loihi melt inclusions have δD of -80‰ , but others with high Cl contents range down to -100‰ . The extreme end-member of this group is an irregular basanitic Loihi inclusion with 1.35% Cl;

this inclusion has a 'normal' H_2O content (0.60 wt.%) but δD of -118‰ . This δD value may represent that of the brine present in the Loihi magmatic system, and would be consistent with an origin as a residual fluid from boiling of seawater. Several 'outlier' inclusions from Koolau, with somewhat elevated Cl contents, may have also suffered similar contamination.

Water in the Hawaiian mantle

When these processes are taken into account, Hawaiian melt inclusions and deeply erupted submarine glasses (Garcia *et al.*, 1989; Dixon *et al.*, 1997) show correlations among major elements, H_2O -S-Cl-F contents, D/H ratios, and isotope ratios of the host lavas, all of which may be related to variations between distinct mantle sources. D/H ratios range from -70‰ at Loihi to -120‰ at Koolau, when considering inclusions with the highest H_2O and CO_2 contents. Though $\text{H}_2\text{O}/\text{K}_2\text{O}$ ratios are highest at Loihi and lowest at Koolau, estimation of $[\text{H}_2\text{O}]$ in the mantle sources is complicated by poor constraints on their relative K contents and on the absolute degree of melting of the eclogite-bearing Koolau source.

This study indicates that the recycled slab component in Koolau lavas contains low $[\text{H}_2\text{O}]$, low [Cl] and low D/H ratios, consistent with extensive dehydration during ancient subduction. In order to preserve the observed Hawaiian H isotope heterogeneity against rapid H diffusion and homogenization in the mantle, the Koolau slab component must be very thick (order 10–20 km) or be relatively young (< 1 Ga) or both.

References

- Kushiro, I. (1972) *J. Petrol.*, **13**, 311–34.
- Hirth, G. and Kohlstedt, D.L. (1996) *Earth. Planet. Sci. Lett.*, **144**, 93–108.
- Garcia, M.O., Muenow, D.W., Aggrey, K.E. and O'Neil, J.R. (1989) *J. Geophys. Res.*, **94**, 10,525–38.
- Dixon, J.E., Clague, D.A., Wallace, P. and Poreda, R. (1997) *J. Petrol.*, **38**, 911–39.