Oxygen fugacity of hotspot xenoliths: A window into the Earth's mantle



Smithsonian National Museum of Natural History

Introduction

Mantle xenoliths—chunks of the Earth's interior carried to the surface by volcanic eruptions—provide a rare glimpse into the chemistry of the deep Earth (Fig. 1). Of particular interest is the oxygen fugacity (fO2; the effective 'partial pressure' of oxygen) of these xenoliths' mantle sources. The availability of oxygen has a powerful influence over the types of rocks that form on our planet, and has important implications for planetary evolution and



Fig. 1. A spinel-lherzolite mantle xenolith.

current global-scale geologic processes. Previous studies have focused on the fO_2 of mantle beneath mid-ocean ridges and subduction zones; however, intraplate volcanic islands, or "hotspots," have been under-represented. With xenolith analyses from the Pacific ocean islands of Savai'i, Tahiti, and Tubuai (Fig. 2), we present the first fo₂ values for the mantle beneath these localities.



Methods

We determined the fO_2 recorded by xenoliths by measuring the ratio of Fe³⁺ to total iron in the mineral spinel. With increasing oxidation, iron is converted from Fe²⁺ to Fe³⁺ by the equilibrium reaction:

> $6Fe_2SiO_4 + O_2 \iff 3Fe_2Si_2O_6 + 2Fe_3O_4$ (magnetite in spl) (favalite in ol) (ferrosilite in opx)

Using electron microprobe analysis, and standards measured by Mössbauer spectroscopy for calibration (Wood and Virgo, 1989), we determined $Fe^{3+}/\Sigma Fe$ ratios in spinel (spl) and Fe^{2+} concentrations in olivine (ol) and orthopyroxene (opx) to calculate fO_2 with the Wood et al. (1990) oxybarometer.

Fig. 3. Example of a plane-polarized transmitted light image (left) of a xenolith thin section (TAH 9-2). Samples must contain the three minerals of interest (labeled) in order for us to determine f_{O_2} by the above equilibrium. Backscatter electron (BSE) image of the same sample (right).



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Peridotite xenoliths recorded fo₂ ranges of -1.4 to 0.9 (Savai'i), 0.6 to 0.7 (Tahiti), and -1.0 to 0.2 (Tubuai) log units relative to the quartz-fayalite-magnetite (QFM) buffer (Fig. 9). These values are within the range of oxygen fugacities for peridotites from other tectonic settings: more oxidized than those from ridges but more reduced than those from subduction zones. Within some samples we observe two trends: TiO₂ increasing with fO_2 , and a link between fO_2 and spinel habit, such that fine, "wispy" spinel records higher apparent fO_2 than large blocky grains.

In sample TBA 4-14, fo_2 and TiO₂ concentration increase systematically with proximity to the xenolith edge (and host basalt; Figs. 4, 5). High TiO₂ is a common indicator of melt-rock interaction. The TAH samples are uniformly high in TiO_2 (Fig. 5) and show melt refertilization textures throughout.



In samples TBA 1-1, SAV 1-3, and SAV 1-5, we observe two distinct populations in f_{O_2} : lower f_{O_2} in larger grains, and higher fo₂ in fine, "wispy" intergrowth textures (Fig. 7). There is preliminary evidence in SAV 1-5 that the larger grains may have rims of a composition similar to the intergrowth (Fig. 6).

Fig. 6. X-ray line scan showing an increase in Al_2O_3 and decrease in FeO from rim ('0 μm') to core of the blocky spinel labeled 'X' in Fig. 7. Note that FeO represents total Fe and may include both Fe³⁺ (interchangeable in spinel structure with AI^{3+}) and Fe^{2+} .







Fig. 4. BSE image of TBA 4-14, with apparent f_{O_2} labeled next to each spinel grain analyzed. **Fig. 5.** TiO_2 vs. apparent fO_2 per grain in each sample. Different symbols represent individual spinel grains. In TBA 4-14, red indicates qualitative proximity to xenolith edge.



Fig. 7. BSE image of SAV 1-5, with apparent fO_2 labeled for each spinel grain analyzed (circled in red). Fig. 8. Apparent fO₂ vs. Cr# for each grain. Note in SAV 1-5 the extreme two-log-unit difference between the blocky spinels and wispy intergrowth (Fig. 7).

In Global Context

Fig. 9. *f*O₂ of these samples plotted against Cr#, with global data from arc peridotites and ridge peridotites. Also shown are new data from Ko'olau volcano, Hawai'i (Davis, unpub). Arc peridotites display a correlation between fO_2 and Cr# (Parkinson and Pearce, 1998); however, we do not observe this relationship in ocean islands.

We observe an intriguing dichotomy in apparent fO_2 between spinels of different habit within a single sample. In these samples, there is no indication that melt has interacted with the rock. We hypothesize that an increase in temperature induced by lithosphereplume interaction has resulted in major element diffusion and an apparent shift in fO_2 . We suggest that these xenoliths erupted before the interiors of large spinels could diffusively reequilibrate.

An outstanding mystery in the fO_2 realm is that ridge peridotites are an order of magnitude more reduced than lavas erupted at ridges. If basalts derive from peridotite, this does not make sense: partial melting is an equilibrium process, so the two should record the same fO_2 . Some authors have explained the difference by inferring that melting must be an oxidizing process, but no one has proposed a mechanism or rationale. We propose an alternate explanation: ridge peridotite did have the same fO_2 as the basalt at the temperature and pressure at which partial melting occurred, but between melting and being exposed at the surface, the 'freezing' of upwelling asthenosphere into lithosphere caused it to reach a new (more reduced) fO_2 (Fig. 9).



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References: Parkinson and Pearce, Journal of Petrology, 1998; Wood et al., Science, 1990; Bryndzia and Wood, American Journal of Science, 1990.



Discussion

Conclusions

 On average, ocean island peridotites are more oxidized than abyssal peridotites, but more reduced than arc peridotites.

• We observe no correlation between Cr# and fO_2 at ocean islands.

• Upwelling melts are more oxidized than the lithosphere through which they rise—but this does not necessitate oxidation as a property of melting. Rather, it suggests that the process of freezing asthenosphere into lithosphere—a separate process from partial melting—reduces the fO_2 of the entire parcel of mantle.

Acknowledgements & References

