P dependence of V coordination in glasses and V oxybarometry

PAOLA ARDIA* AND MARC M. HIRSCHMANN

Dept. Geology and Geophysics, University of Minnesota, Minneapolis (*correspondence: pardia@umn.edu)

The variable oxidation state (ox. st.) of V in natural silicate melts (V^{2+}, V^{3+}, V^{4+}, and V^{5+}) and associated changes in geochemical behavior are powerful probes of the ox. st. of planetary basalts and their mantle source regions. Measures of V ox. st. include direct measurement by XANES or indirect inference by the comparative behavior of V and Sc. V becomes less compatible with increasing oxygen fugacity (f_{O2}) as more oxidized V inos have smaller ionic radii, lower coordination states and symmetry, resulting in higher V/Sc ratios in basalts. These changes also produce systematic shifts in XANES spectra of quenched glasses, which allowed Sutton *et al.* (2005) to produce a calibration of f_{O2} in quenched silicate glasses by V XANES, taking advantage of the increase in magnitude of the XANES pre-edge peak with increasing V ox. st., using glasses synthesized at 1 bar.

We used XANES to investigate the V pre-edge and K-edge features of hydrous haplobasaltic glasses quenched from 1.5, 3, 5, & 8 GPa and 1400°C with f_{O2} fixed at the Ni-NiO (NNO) buffer using double capsules. Additional experiments at 1.5 GPa were performed at the Fe-FeO (IW) and Ru-RuO_2 buffers. XANES spectra were collected at the V K-edge using the bending-magnet at sector 13 at APS, using steps of 2s fot the Pre-edge, 0.25s for the XANES region and 2s for the EXAFS regions. Four to six spectra were collected and averaged for each sample, and analyzed as described by Sutton *et al.* (2005).

With increasing fO_2 at 1.5 GPa, pre-edge centroid position and intensity and the K-edge position increase, consistent with increasing V ox. st.. Also, glasses quenched from 1.5 to 8 GPa at NNO show similar K-edge positions suggesting little influence of pressure on V ox. st.. Critically, the position and especially the intensity of the pre-edge peak diminishes significantly with increasing pressure at NNO. Compared to the pre-edge peak height expected at NNO at 1 atm, the intensity at 1.5 GPa is 58% as great and at 3 GPa it is 20% as great, more similar to that found at IW at 1 atm. At 5 and 8 GPa, the peak is near the limit of detection. Our preliminary interpretation is that the coordination of V^{4+} and V^{5+} in silicate melts increase with pressure at conditions similar to those typical of basalt generation in planetary mantles. If such coordination changes also influence partitioning of V betweeen minerals and melts, the relationship between mantle oxidation state and V/Sc systematics in basalts may be affected.

Gallium and germanium abundances in MORB and OIB: Evidence for pyroxenitic source components?

RICARDO AREVALO JR.* AND WILLIAM F. MCDONOUGH

Department of Geology, University of Maryland, College Park, MD 20740, USA
(*correspondence: rarevalojr@gmail.com)

The prevalence of pyroxenitic lithologies in the source regions of mid-ocean ridge basalts (MORB) and intraplate ocean island basalts (OIB) remains unresolved. Partial melting of mantle pyroxenites can produce melts that are either saturated or undersaturated in silica, depending on the phase proportions of the pyroxenite; these melts are commonly associated with excess alumina relative to typical alkalic OIB. Gallium (Ga) and germanium (Ge) approximate the geochemical behavior of Al and Si, respectively, and thus may serve as sensitive tracers of pyroxenitic source components. Unfortunately, Ga and particularly Ge data are scarce in the literature. A new *in situ* LA-ICP-MS investigation into the Ga and Ge chemistry of a global suite of MORB shows that the geochemical behavior of Ge is positively correlated with that of Mn, Fe, Zn, and Ga, and negatively correlated with Ni (all $r^2 > 0.75$), suggestive of Ga and Ge compatibility in a spinel phase during MORB genesis. Additionally, our initial results reveal elevated Ga/Ge ratios in Hawaiian tholeiitic basalts relative to MORB, potentially reflecting the role of garnet/spinel and/or contribution of pyroxentic lithologies during Hawaiian source melting.

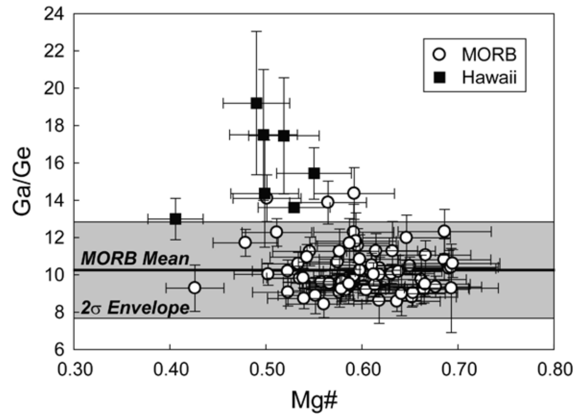

Figure 1: Ga/Ge ratios in global MORB compared to those observed in Hawaiian volcanics, including in-house measurements of Kilauea basalts plus Lanai data from Stoll *et al.* [1].

[1] Stoll *et al.* (2008) *Geostd. Geoanal. Res.* **32**, 5–26.