Apparent oxygen fugacity structure beneath O’ahu, Hawai’i

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Oxygen fugacity is a key parameter controlling the geophysical and geochemical behavior of the Earth’s mantle. However, the fO_2 of the oceanic mantle associated with plume volcanism is less well understood. Here we present the first ^{57}Fe Mössbauer determinations and $Fe^{3+}/\sum Fe$ ratios in lherzolitic spinels and pyroxenitic garnet-clinopyroxene pairs from xenoliths of the sub-oceanic mantle beneath Hawai’i (Pali, Kaau & Salt Lake Crater (SLC) vents, Koolau shield).

$Fe^{3+}/\sum Fe$ ratios in peridotitic spinels range from 0.038 to 0.394, indicating relatively oxidized conditions (+0.3 to +1.0 $\Delta \log fO_2$ (FMQ), except one sample at -2.9). These values overlap the oxidation range of arc peridotites and are 1 to 2 log units more oxidized than what is expected for residues of MORB melting. The SLC peridotite isotope and trace element data have been interpreted as the product of recent metasomatism of the oceanic lithosphere (*in situ* or recylced) by rejuvenated volcanism stage melts [1, 2]. The oxidized nature of the SLC peridotites appears consistent with such a metasomatic process, and indicates that the metasomatizing agent (melt/fluid) imparts an increase in the apparent fO_2 of spinel peridotites. $Fe^{3+}/\sum Fe$ of the pyroxenitic garnets range from 0.061 to 0.074 and coexisting clinopyroxenes from 0.279 to 0.340, indicating relatively reduced fO_2 (-2.9 to -3.8 $\Delta \log fO_2$ (FMQ) at 4GPa) conditions; significantly more reduced than the Hawaiian peridotites, abyssal peridotites and estimates for MORB and Hawaiian volcanism. Experimental data suggest that with increasing pressure Fe^{3+}-mineral components become increasingly more stable resulting in lower oxygen fugacity [3]. Therefore, SLC garnet clinopyroxenites are consistent with a high pressure origin (>4GPa) i.e. within the asthenosphere and the upwelling Hawaiian plume.

[1] Bizimis *et al.* (2003) *EPSL* **217**, 43–58. [2] Bizimis *et al.* (2007) *EPSL* **257**, 259–273. [3] Stagno *et al.* (2009) *EOS* **90**, V11D-1986.

Tracing Mg transfer from rock to the oceans: Insights from Mg isotope ratios in the rivers of the Mackenzie Basin

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Magnesium is one of the major constituants of the rock forming minerals. It is a soluble element, and one of the most concentrated cations in many river waters. This transfer from rock to river, and ultimately to seawater constitutes one of the major biogeochemical cycles in terms of mass transfer. However, isolating the sources of Mg and the processes that release mineral bound Mg to solute Mg are surprisingly underconstrained, but are critical for a complete understanding of global biogeochemical cycles. River water elemental or isotopic ratios are generally controlled by mixtures of end-members with differing compositions. The compositions of such end-members are either inherited from heterogeneity in the orginal lithological sources (e.g. carbonate, silicate) or from process-related fractionation of elemental or isotopic ratios during weathering. The rivers of the Mackenzie Basin are very concentrated in solute Mg (up to 1000 micromolar), and the Mackenzie is estimated to be the 11th largest river in terms of Mg flux to the oceans. Well-characterised samples (isotope ratios of Sr, Os, B, Li, U-series, O, S are already published on the same samples) combined with the high Mg concentrations make this basin ideal for understanding what controls the weathering input of Mg to the oceans at a continental scale. The $^{26}Mg/^{24}Mg$ ratio (expressed as $\delta^{26}Mg$, and analysed by Neptune MC-ICP-MS) shows in excess of one per mil variability. Although in the first order, riverine $\delta^{26}Mg$ values vary with the major geological units drained (North American Cordillera, the Rockies, the Interior Platform, and the Canadian Shield) there appears to be no co-variation between proxies for carbonate or silicate derived Mg (such as strontium isotope ratios or sodium/calcium ratios) despite a four per mil difference in $\delta^{26}Mg$ values between carbonate and silicate rocks of the Mackenzie Basin. Rather, Mg isotope ratios show coherent trends with elemental ratios that suggest that Mg isotopes are more likely controlled by process-related fractionation, even at the continental scale of the Mackenzie Basin. Such a result challenges our current understanding of solute Mg at spatial scales from the critical zone to the continental scale rivers. Possible interpretations and implications will be discussed.