Redox Evolution of the Mantle from 3.5 Ga to the Present

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The oxygen fugacity (fO_2) of the mantle is an important intensive variable controlling the behavior of redox-sensitive elements during magmatic processes. Previous studies have disagreed on whether mantle fO_2 has changed since 3.5 Ga [1-3]. Here, we use vanadium partitioning data between olivine and silicate melt for 15 Archean and post-Archaen komatiite and picrite systems to address this controversy. Representative whole rock samples from each system were analyzed for V and other trace metal concentrations using the solution SA-ICP-MS technique. Trace metal concentrations plotted against MgO contents closely followed olivine control lines and were thus shown to be immobile during secondary processes. These data were used to calculate trace metal concentrations in the emplaced lavas for each of the 15 komatiite and picrite systems. The LA-ICP-MS technique was used to determine the V contents of liquidus olivine in equilibrium with their respective emplaced lavas. The partition coefficients for V between olivine and melt were then used with the empirical equation from [3] to determine fO_2 of each system relative to the FMQ buffer with a precision of 0.4 log units or better. The combined dataset yielded a resolvable trend of increasing mantle oxygen fugacity of ~1.6 log units ΔFMQ over the past 3.5 Ga. Three different mechanisms that could have been responsible for oxidizing the mantle are considered: recyling of oxidized oceanic crust into the mantle, venting oxygen from the outer core into the lower mantle, and homogenization of primordial magma ocean redox heterogenities within the mantle. Our modeling shows that oceanic crust recycling is unlikely to fully account for the observed trend. Inner core crystallization could have triggered venting of oxygen into the lower mantle, but it likely began much later than 3.5 Ga [4]. Gradual homogenization of early-formed post-magma ocean oxidized domains [5] is considered here to be the most plausible mechanism to account for the observed trend. However, additional geochemical and geophysical constraints are needed to further determine the viability of each of these models.

[1] Li and Lee (2004) *EPSL* 228. [2] Aulbach and Stagno (2016) *Geology* 44. [3] Nicklas *et al.* (2018) *GCA* 222. [4] Labrosse *et al.* (2001) *EPSL* 190. [5] Nicklas *et al.* (2016) *AGU Fall Meeting Abstract* V11D-03.