The oxidation state of Archaen komatiites revisited

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Oxygen fugacity (fO_2) is an important intensive variable in magmatic systems that controls such fundamental processes of terrestrial evolution as core segregation, mantle differentiation, and oxygenation of the atmosphere. Previous studies argued that, at the current level of resolution (0.5 to 1.0 ΔNNO log units), the mantle has been at a near-constant oxidation state since the completion of core segregation [1,2]. Here, we revisit this hypothesis using the V partitioning between olivine and komatiite liquid as an oxybarometer [1] by obtaining high-precision V abundance data for six well preserved Archaen differentiated komatiite lava flows ranging in age from 3.55 to 2.41 Ga.

Whole-rock samples collected across each lava flow were analyzed for transition metal abundances using the standard addition solution ICP-MS technique; liquidus olivines in equilibrium with the komatiite lavas were analyzed using laser ablation ICP-MS. Our level of external reproducibility for V concentrations is 5% ($2\sigma_{SD}$) for solution ICP-MS, based on analysis of standard reference materials and replicate sample aliquots. For all six systems, the V data, when plotted against indices of magmatic differentiation, define regression lines consistent with olivine control for V over the entire range of magma compositions. Linear regression analysis was used to determine V abundances of the komatiite lavas for each system, using known MgO contents. Calculated partition coefficients for V between olivine and the respective komatiite magma compositions were used to determine the oxygen fugacity of each komatiite system [1] with a precision of between 0.12 and 0.05 ΔNNO log units ($2\sigma_{SE}$).

The calculated oxygen fugacities of the komatiite systems show a resolvable increase (>0.5 ΔNNO log units) over time, approaching that of modern mantle. One exception is the 3.55 Ga Schapenburg komatiite, which plots 0.5 log units above the trend, likely reflecting primordial mantle heterogeneity. Our new high-resolution data indicate that the mantle source regions of Archean komatiites were becoming increasingly more oxidized leading up to the Great Oxidation Event (GOE). This is likely the result of a decrease in deep Earth buffering capacity, as the oxygen produced by photosynthetic cyanobacteria accumulated in the ocean and was recycled into the mantle for >200 Ma prior to the GOE.

[1] Canil (1997) *Nature* **389**. [2] Li *et al*. (2004) *EPSL* **228**.