

Global variations in redox at oceanic ridges inferred from V/Sc ratios

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Variations in the redox state of the Earth's mantle are controlled by equilibria between transition metals (principally Fe) and volatile species (C and S). Vanadium exhibits oxidation states from +2 to +5 in the mantle, and behaves more compatibly at lower oxygen fugacity, while Sc exhibits a +3 redox state. The V/Sc ratio in MORB was employed as a redox indicator and shown to vary between 5-10 [1]. We have developed a series of refinements of the V/Sc ratio involving better corrections for the effects of fractional crystallization. We used a suite of 450 MORB glasses analyzed by a precise LA-ICP-MS technique at FSU, and a suite of 942 MORB glasses analyzed by DCP or ICP-MS from the literature. There is an inverse correlation between Mg# and V/Sc due to cpx crystallization in MORB, with results from different labs showing no resolvable interlab biases. Correction of the fractional crystallization effect in MORB to Mg#70 results in an average $(V/Sc)_{70} = 5.4 \pm 0.7$ (1σ), only slightly higher than the PM value of 5.

Both V and Sc are weakly incompatible so that their abundances are not affected by melt depletion in DMM vs. PM. The $(V/Sc)_{70}$ ratio of MORBs correlate with indices of partial melting like the $(Gd/Yb)_{CI}$ ratio. The MORB data set was divided by lab and by locality into E-MORB, N-MORB and D-MORB using the K_2O/TiO_2 ratio. Even at this finer scale no inter-lab biases were detected, so samples were further averaged by locality alone. The average $(V/Sc)_{70}$ ratio for ridge sections of E-MORB, N-MORB and D-MORB form resolved trends vs. $(Gd/Yb)_{CI}$, representing 37 localities world-wide in all ocean basins. This result is qualitatively in agreement with redox variations recently recognized between E-MORB and N-MORB using Fe-XANES [2]. This result implies that globally, MORB sources show redox variations with E-MORB being more reduced than D-MORB, which is attributable to the role of carbon in MORB sources. This study finds that the redox-controlling form of C is apparently incompatible and is enriched in E-MORB, presumably by the same processes that generated incompatible element enrichments and radiogenic isotope characteristics [2].

[1] C.-T. A. Lee et al. (2005), *J. Petrol.* **46**, 2313-2336. [2] E. Cottrell and K. A. Kelley (2013) *Science* **340**, 1314-1317.