Redox heterogeneity in MORB as a function of mantle source

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Mantle oxygen fugacity (fO_2) has a first-order effect on the geochemical evolution of Earth's mantle and is predicted to influence several geophysical observables [1], yet systematic variations in mantle oxidation state at mid-ocean ridges have not previously been reported. We use XANES spectroscopy to provide $Fe^{3+}/\Sigma Fe$ ratios of submarine mantle-derived basalts from mid-ocean ridges (MORB) as a proxy for fO_2 [2]. $Fe^{3+}/\Sigma Fe$ ratios of MORB, far from plumes, decrease with indices of mantle enrichment such as $^{87/86}Sr$ and $^{208/204}Pb$ (n=22). In primitive glasses (MgO>8.5wt.%, n=19), $Fe^{3+}/\Sigma Fe$ ratios decrease strongly with increasing trace element enrichment, such as the Ba/La ratio. The strong inverse relationship between upper mantle fO_2 and enrichment recorded by MORB glasses globally contrasts with the positive relationship hinted at by abyssal peridotite oxybarometry, and with the prediction of a positive correlation born of the expectation that Fe^{3+} can be treated as more incompatible than Fe^{2+} during mantle melting.

These data unequivocally link upper mantle oxidation state to mantle source enrichment. Further, because the data require ancient fractionation of radiogenic parent-daughter pairs, the factors that lead to variation in mantle oxidation state must be preserved on plate tectonic time scales.

Reduced lavas share isotopic and trace element signatures with low-degree carbonatitic and/or kimberlitic melts of peridotite. These include EM-1 isotopic flavor, Hf depletion relative to Nd, and strong enrichment of highly incompatible elements. Because upper mantle carbon may act to simultaneously reduce iron [3] and generate melts that share geochemical traits with our reduced samples, we propose that variations in mantle carbon lead to magmas that are reduced and enriched. Estimates of mantle carbon concentration from Siqueiros and 'popping rock' support this interpretation, though other processes that might link enrichment to reduction, such as ancient subduction of reducing sediments or mobilization of reduced fluids at depth, cannot be ruled out.

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Volcanic degassing of the Gunbarrel large igneous province and its environmental repercussions

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It has long been known that large volcanic eruptions have the capacity to influence the global environment (McCormick *et al.*, 1995; Payne *et al.*, 2008; Self *et al.*, 2008). Five principal mechanisms exist through which volcanic activity can perturb the environment: 1) cooling due to loading of atmospheric sulfate (McCormick *et al.*, 1995); 2) warming due to loading of atmospheric CO_2; 3) ocean acidification through elevated levels of oceanic CO_2 (Fraile-Nuez *et al.*, 2012; Hall-Spencer *et al.*, 2008); 4) ocean anoxia caused by an enhanced weathering flux of reduced volcanic material to the oceans (Sinton and Duncan, 1997); 5) ocean anoxia caused by an increased delivery of bio-limiting nutrients to the oceans (Frogner *et al.* 2001, Sinton & Duncan 1997).

Due to their size and duration, Large Igneous Provinces (LIP) have often been implicated in global environmental catastrophes, such as mass extinctions (e.g.. Wignall, 2005; Wignall, 2001). However, this simple relationship between eruptive size and environmental impact is complicated by the fact that unlike typical volcanic eruptions, which occur over short time intervals (i.e. days), the eruption of LIP occurs over a few million years.

The compilation of marine carbonate isotope ratios ($d^{13}C$) for the Neoproterozoic suggests a major perturbation to the global carbon cycle at ~780 Ma, coinciding with the eruption of the Gunbarrel LIP. We have use $d^{34}S$ and [S] from volcanic rocks associated with this LIP along with trace element geochemistry of coeval marine carbonates to assess what impact, if any, the Gunbarrel LIP may have had on the surface environment during the Neoproterozoic.

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