

Carbon-rich melts in the deep mantle

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The noble gas and radiogenic isotope geochemistry of global carbonatites ($n > 527$ [1]) likely represent concentrations of asthenospheric mantle carbon and provide an indirect measure of deep carbon flux through time. If as geochemists propose [2], their sources are deeper than sub-lithospheric mantle, then carbonatites cannot be derived directly by oxidation of typical diamond reservoirs sampled by kimberlites. Recent surveys of nominally carbon-free mantle silicate minerals point to the increased significance of discrete carbon phases as deep mantle carbon reservoirs. In other words, deep carbon is unlikely to be stored in the same way as water; there is no deep carbon equivalent to oceans of nominally anhydrous silicates (NAH's). Therefore, new data for the stabilities of deep mantle carbonate minerals is particularly important, since different structured Mg- and Ca-carbonate minerals are predicted to be stable through the deep mantle and in a Ca-carbonate phase may perhaps be stable at pressures of ~ 136 GPa at the core mantle boundary (CMB [3]). The physical properties of carbonate melts have only been measured at modest pressures (< 5.5 GPa), and are characterized by extraordinarily low viscosities compared to silicate melts [4], but there is, so far, insufficient data to derive a full equation of state for higher-P carbonate melts > 6 GPa in the deeper mantle. However, first order estimates can be derived from calculated carbonate mineral data in the lower mantle, and compared with recent physical data for silicate melts under different geotherms applicable to Earth's history, including magma oceans (Stixrude pers comm). Deep carbonate melts may be extremely important agents for selective transfer of components, and they may supercede the role of metasomatic fluids widely recognised in relatively shallow mantle diamond. Simple dynamic constraints will be used to illustrate where deep carbonate melts are expected, and how these may be expected to compare or contrast with their shallow pressure counterparts (carbonatites).

[1] Woolley & Kjaergaard (2009) *J. Pet* [2] Bell & Simonetti (2010) *Min & Pet* **98**, 77–89 [3] Oganov *et al.* (2008) *EPSL* **273**, 38–47 [4] Dobson *et al.* (1996) *EPSL* **143**, 207–215 [5] Stoppa *et al.* (2009) *CEJGeoscience* **1**, 131–151.

Biogeochemistry of Mn oxidation in Lake Matano, Indonesia

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Most studies of Mn cycling to date have focused on sediments and stratified, euxinic basins. In these sediments and basins, Mn biogeochemistry has been linked to the cycling of C, Fe, S, and trace metals through both redox and sorption reactions. Lake Matano is an iron-rich, sulfur-poor, persistently stratified lake. Steep gradients in O_2 , NH_4^+ , Mn (II), Fe (II), and CH_4 exist within its 120 m deep chemocline. Our studies to date reveal that Mn is the only major redox active species with gradients that are not governed solely by physical transport [1], illustrating the rapid kinetics of Mn biogeochemical reactions. Among these reactions is Mn oxidation, which is known to proceed primarily via microbial catalysis. Using incubations and reaction transport modeling, we have constrained the rates of microbial Mn oxidation in Lake Matano's chemocline. Within error, these two independent methods give the same rate of $0.1 \mu\text{mol l}^{-1} \text{d}^{-1}$, and suggest that authigenic Mn (III/IV) may provide substantial oxidizing power to the deep waters. To examine the physiology of Mn oxidation, we have isolated microbes from the chemocline. Preliminary evidence indicates that these isolates generate soluble Mn (III) during oxidation. Only recently detected in nature [2], the role of soluble-Mn (III) in biogeochemical cycling remains enigmatic. Soluble Mn (III) can be a potent oxidant, and if produced in Lake Matano, it may bridge electron transport between the oxic surface waters and the reduced waters of the deep basin.

[1] Katsev *et al.* (2010) *L&O* **55**, 763–776. [2] Trouwborst *et al.* (2006) *Science* **313**, 1955–1957.