

Trace element partitioning between carbonate globules and silicate glass in volcanic carbonatites

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The origin of globular-shaped carbonate in silicate glass in carbonatites is subject to much debate. Whether such 'globules' represent immiscible carbonatite melts or rounded calcite crystals has important implications for calcio-carbonatite genesis. Here we present major and trace element analyses of carbonate and silicate glass from volcanic carbonatites in the Calatrava Volcanic Province (CVP), Spain and the Auvergne, France, as well as new experiments reproducing the CVP textures.

Compelling textural evidence for liquid immiscibility includes curved menisci against silicate melt, and budding of globules (suggestive of coalescence) [1]. However, experiments have shown that similar globules can form as solid carbonate crystals in equilibrium with silicate melt [2]. Experimentally produced immiscible carbonate melts also do not reproduce the stoichiometric calcite and dolomite compositions observed in the natural volcanic carbonatites.

One way to resolve whether the globules formed as melts or solids in natural and experimental samples is to investigate the way elements are distributed between the two phases. LA-ICP-MS has been employed for *in-situ* trace element analysis of both carbonate and glass. Partitioning into a crystalline phase is controlled by the characteristics of the lattice site where the element resides, subject to strictly defined constraints related to the element size (ionic radius) and the charge. Classic Onuma parabolae are observed, suggesting a crystal control over the partitioning in some volcanic carbonatites, with calcite globules representing crystalline carbonate crystallised from carbonate-rich silicate melt. Experimentally we have reproduced these pure calcite 'globules', as well as more complex immiscible alkali-bearing carbonate melts. We report on the partitioning characteristics for both and draw comparisons with the natural samples in order to elucidate their origin as solids or melts.

[1] Bailey *et al.* (2005) *Min Mag* **69**, 907-915 [2] Brooker & Kjarsgaard (2011) *J. Pet* **52**, 1281-1305

Iron supply and cycling on the Oregon-California shelf: Comparisons with the Gulf of Mexico hypoxic zone

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The riverine supply of fine-grained sediment to coastal regions along the Northeast Pacific margin generates a patchy "depositional" setting with sediments containing varying amounts of sands and muds. The mid-shelf adjacent to the Umpqua River, features a mud-rich sediment patch that is relatively rich in operationally defined reactive iron. Reactive iron concentrations here covary with the distribution of organic material, suggesting that there may be a coupling between their delivery and burial.

Downcore profiles of dissolved iron from a number of locations along the Oregon margin shows that sediments can range from being relatively enriched to depleted in dissolved iron concentrations. Although this pattern may point to a connection between the diagenesis of continentally derived sediment and the iron supply to coastal waters from the sediments, other factors such as rates of fluid advection, bottom water dissolved oxygen contents, and the availability of fresh organic material likely influence net iron transport across the sediment-bottom water boundary. In an effort to separate some of the factors that might influence dissolved iron input to the overlying water column, we compare iron benthic fluxes along the Oregon and California margin with fluxes from the "hypoxic" shelf region in the Gulf of Mexico. Our results do not suggest significantly greater benthic iron fluxes within the Gulf of Mexico compared to the Oregon and California margins.