

Submicrometer exsolution lamellae in volcanic pyroxenes as indicators of magma residence times

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Pyroxene geothermometry is a well-established tool for the determination of thermal conditions of magmatic systems. Such applications are based largely on the presence of solvus relations within the pyroxene group that govern shifts in equilibrium composition as a function of temperature. These same solvus constraints can result in the subsolidus formation of exsolution lamellae in pyroxene. Many natural examples exist in plutonic pyroxenes. Since coarsening of these lamellae is largely a diffusion-moderated process [1], examination of their size and spacing can potentially be exploited to obtain timescales or cooling histories of magmatic systems, provided that empirical calibrations of controlling parameters (e.g. activation energies) are available. Volcanic systems present a unique challenge for this application because the pyroxene lamellae that they contain are typically nm-scale, owing to rapid cooling, and are also highly localized. Here we report the results of a chemical and crystallographic study of three suites of rhyodacitic samples. To locate, image, and analyze multiple exsolution lamellae of tens to hundreds of nm in size within clinopyroxene phenocrysts, we used a combined approach consisting of initial characterization by SEM/EPMA/EBSD, targeted FIB sampling, and detailed imaging and analysis by TEM/ATEM/SAED/EELS. Coupling these results with laboratory-calibrated models of lamellae formation and various end-member thermal cooling models of magma reservoirs [2] allows us to propose that these rhyodacites, erupted decades apart, originated from a common long-lived (several thousands of years) and relatively large (tens of km³) magma reservoir. The study of exsolution lamellae in volcanic pyroxenes should prove useful to constrain the thermal histories and sizes of magma bodies below active volcanoes, but analytical obstacles abound. One significant challenge is to obtain quantitative TEM-based chemical analysis (EDS and EELS) with sufficient precision for geothermometry.

[1] Weinbruch *et al* (2003) *GCA* **67**, 5071-5082. [2] Costa *et al* (2008) *RiMG* **69**, 545-594.

Molybdenum and uranium isotope dynamics in a Paleozoic epicontinental black shale

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Reconstructing the history of global ocean anoxia during the Neoproterozoic and the Paleozoic is challenging since plate tectonic activity has destroyed the majority of the deep ocean floor from those time periods. In recent years, Mo and U isotopes have been used as a proxy to track global O₂ levels. However, these studies generally have to rely on the sedimentary record of shallow epicontinental seas. Here we present Mo and U isotope variations of a Paleozoic black shale (Hushpuckney Shale) from three different cores from across the same depositional basin to test whether global marine redox conditions can be determined reliably from a single section within an epicontinental settings.

We find that, based on Mo and U enrichment factors (EF) and nitrogen isotopes, three different intervals within the black shale can be distinguished. These intervals are characterized by strong spatial and temporal geochemical gradients that indicate that the basin experienced non uniform environmental conditions along the black shale horizon. These gradients are reflected in systematic offsets of U isotopes across the basin by up to 0.5‰. Furthermore, during the transition to the most reducing conditions (based on several geochemical proxies), the U isotopes attain their heaviest values while Mo isotopes attain their lightest values. This indicates that local redox conditions can lead to anomalous isotopic signatures as current understanding of these isotope systems suggests that both Mo and U should track each other during that transition. These results suggest that chemical gradients across an epicontinental basin can lead to local redox conditions that have a strong effect on the Mo and isotopic signatures. This spatial heterogeneity potentially challenges our ability to accurately reconstruct the accumulation of O₂ on Earth from only one section from such settings.