

X-ray Spectromicroscopy: Illuminating the biogeochemical cycles of elements in the marine environment

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The geochemical cycling of elements on Earth's surface is intrinsically linked to biological processes. These links include biologically-mediated formation/solution of minerals, sorption/desorption onto surfaces modified by organic matter, and biological activity. All such processes begin at the nanoscale. Therefore the ability to examine biologically generated or modified sediments, soils and other particulates at nanoscales provides a fundamental view into the cycling of elements. Unexpected insights are often generated using instruments capable of examining the nanoscale composition, speciation, redox state and co-association of elements within particulates. For example, in the marine environment, one can consider the generation and sequestration of carbon by phytoplankton as being limited by the availability of necessary nutrients, such as phosphorus (P) and iron (Fe). X-ray spectromicroscopy of P within planktonic organisms, sinking particulates, and underlying sediments has revealed a wide array of P types, including organic P compounds, polyphosphates, apatites and other P-containing minerals. Further examination of the associations of P, Fe and other elements also shows a variety of nutrient removal mechanisms. The results begin to show how P is sequestered in the environment, first through the preservation and burial of poorly organized but relatively pure biogenic polyphosphates and calcium phosphates, then through transformation into more ordered, and substituted mineral phases. Overall the picture of P chemistry at sub-micron scales reveals a complex system interacting both with biologically produced particulate P and terrestrially- or aeolian-derived P mineral phases.

Mesozoic MORB

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Formation of the oceanic crust at mid-ocean ridge spreading centres and its subsequent evolution has an important influence on sea-level, the carbon cycle and seawater chemistry over timescales of 10-100 Ma. Previous geochemical studies of ancient MORB (e.g. [1, 2, 3]) reported chemical differences between Mesozoic and young mid-ocean ridge basalt (MORB) that were interpreted as the result of a 50-60°C higher upper mantle temperature [1, 2]. Higher mantle temperature on average would cause shallower depth of mid-ocean ridges, rising sea-levels and global warming by increased CO₂ emission.

We present new major and trace element data, measured using electron microprobe and LA-ICPMS techniques, for more than 360 glasses from 30 DSDP-ODP-IODP drill sites. The age of the oceanic crust at these sites ranges from 6 Ma up to 160-170 Ma, and all sites were drilled into normal oceanic crust far from hotspots. We have analysed exclusively fresh volcanic glasses, since whole-rock samples may be compromised by alteration and accumulation of phenocrysts.

We find that there are small but significant differences between fractionation corrected major element compositions of old (drilled) and zero-age (dredged) samples, e.g. for Na₇₂, Fe₇₂, Ca₇₂, and Al₇₂. We can exclude any analytical bias, alteration effects or uncertainties in fractionation correction for these differences. For both, Pacific and Atlantic, there is no clear systematic change in fractionation corrected major element composition of drilled MORB with time, as would be expected for a change in mantle temperature [1]. Some of these differences between zero-age and drilled MORB samples could arise if the oceanic crust is compositionally layered. MORB drilled from off-axis represent younger flows erupted further from the ridge axis. In contrast, most samples in the zero-age MORB dataset were dredged from the ridge axis, which eventually make up the lowermost section of the oceanic crust [4].

Lavas erupted off-axis may sample different parts of the melting region and/or undergo different fractional crystallisation histories to lavas erupted at the ridge axis. This effect could mean that average MORB compositions calculated using only samples dredged from the ridge axis are not completely representative of the extrusive section of the oceanic crust.

[1] Humler et al. (1999) *Earth Planet. Sci. Lett.* **173**, 7-23. [2] Fisk and Kelley (2002) *Earth Planet. Sci. Lett.* **202**, 741-752. [3] Janney and Castillo (2001) *Earth Planet. Sci. Lett.* **192**, 291-302. [4] Hooft et al. (1996) *Earth Planet. Sci. Lett.* **142**, 289-309.