Understanding trace metal sorption by marine minerals to validate and calibrate geochemical palaeoproxies

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In many cases marine sediments provide the ultimate sink for a wide variety of trace metals in the marine environment, including those that might be used as geochemical palaeoproxies. Within the sediments, specific mineral phases including ferromanganese (hydr)oxides and carbonates, through adsorption and incorporation reactions, provide important hosts for trace metals. Marine sediments, and in particular ferromanganese (hydr)oxides and carbonates, are therefore used as sedimentary archives, storing a wealth of trace metal chemical information that can be used to reflect on past environmental conditions at the time of deposition. In order to fully exploit these abundant sedimentary repositories, we must understand the processes that control the initial drawdown of trace metals from seawater into the host mineral phases – do sedimentary archives directly reflect seawater chemistry or do the processes of drawdown superimpose a secondary chemical signature? – and we must understand subsequent diagenetic alteration of the primary mineral hosts in order to evaluate the robustness of sedimentary archives over time – do these repositories still reflect original seawater chemistry and thus the contemporaneous environmental conditions? We use a combination of advanced, high resolution analytical techniques, including X-ray absorption spectroscopy and microscopy, and laboratory sorption and isotope fractionation experiments, to investigate the controls on the sequestration and preservation of trace metal signals in marine sediments. We will highlight the power of these microanalytical approaches to help validate and calibrate emerging trace metal palaeoproxies including Cr isotopes archived in ferromanganese crusts and carbonates, and Mo concentrations recorded in iron- and organic-rich sediments.