Sorption models for complex materials – modeling approaches and data requirements

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Surface complexation models (SCMs) can be applied to complex geologic materials such as sediments and soils using various approaches, which are generally variants on either the component additivity (CA) or generalised composite (GC) models [1]. The CA approach involves modeling the sorption of a trace metal (or radionuclide) by additively combining sorption models for the individual mineral components of a soil. The GC approach is more generic, but is often parameterised using bulk properties such as the specific surface area (SSA) or ion exchange capacity.

These approaches are demonstated using data for cobalt adsorption on complex materials from Australian field sites. The GC modeling estimated the number of sorbing sites from the measured BET surface area (assuming a site density of 2.31 sites/nm^2 [2,3]). A simplified CA model that conceptualised the surface sites as having equivalent sorption properties to amorphous Fe oxide was also moderately successful in explaining the pH dependence of the Co sorption data sets. This example demonstrates the basic utility and predictive capability of these modeling approaches. However, as with literature examples of SCMs for complex materials, it does not fully test the underlying assumptions. These outcomes raise questions about the uniqueness and general applicability of these modeling approaches [3].

A principal requirement to further develop the CA modeling approach is adequate models for trace metal sorption on component mineral phases of complex environmental sorbents and conclusive demonstration of their role in each sample. Similarly, the GC approach requires experimental measurement of sorption data on a range of complex samples of differing mineralogy and SSA under various conditions. Given that it is relatively straightforward to experimentally study sorption and measure SSA, it might be expected that numerous sets of trace-metal sorption data for complex samples having a range of properties would be available. However, while individual studies typically report sorption data across a range of chemical conditions (pH, ionic strength, etc), the experiments often involve only a single solid sample (or limited number of samples). Consequently, a significant constraint on obtaining the required data for establishing relationships between sorption and SSA (or other soil properties) is that few literature data sets report sorption as a function of SSA (or mineralogy) for a number of different solid phases. Thus, there is an urgent need for more experimental sorption work with a range of sorbent samples.

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[2] Dzombak and Morel (1990) *Surface complexation modeling – hydrous ferric oxide*. John Wiley and Sons, New York, 393pp.
[3] Payne *et al.* (2009). *Applied Radiation and Isotopes*. **67**, 1269-1276.

Deciphering the Cenozoic Tl isotope record of marine ferromanganese crusts – new evidence from adsorption experiments

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Thallium stable isotopes, recorded in authigenic marine ferromanganese crusts, may provide new constraints on past changes in environmental conditions, the Earth's carbon cycle, and their impact on global climate.[1-3] Specifically, the Cenozoic Tl isotope curve shows a pronounced evolution of Tl isotope composition around the Palaeocene-Eocene boundary, from ~ 6 ε^{205}Tl at 55 Myr to ~ 12 ε^{205}Tl at 45 Myr (where ε^{205}Tl is the deviation of the ^{205}Tl/^{203}Tl ratio of a sample from the NIST SRM 997 Tl isotope standard in parts per 10000).[2] After this pronounced shift, the Tl isotope composition of crusts appears to have changed little over the last 40 Myr, with a globally uniform, modern signature of ~ 13 ε^{205}Tl. Despite the compelling appearance, the record provided by Tl isotopes (and other heavy-metal stable isotope systems) is not straightforward because the temporal shift in isotope composition may reflect either variability in the ε^{205}Tl value of seawater, or changes in the conditions that govern incorporation of the element into the structure of the ferromanganese minerals. Furthermore, modern crusts are ~ 19 ε^{205}Tl (or ~ 2 ‰) heavier than the contemporaneous seawater, and combined with their globally uniform signature this implies there is an equilibrium stable isotope fractionation between Tl in seawater and the Tl incorporated into crust minerals.

To improve our understanding of the Tl isotope record preserved in crusts it is important to develop a detailed characterisation of how Tl is sequestered by ferromanganese minerals, and a quantitative and mechanistic understanding of any stable isotope fractionation that occurs during this process. Here we present the results of novel experimental work that combines molecular-level, X-ray absorption spectroscopy with stable isotope analyses of Tl sorbed to ferromanganese minerals, as a function of time, temperature, pH and ferromanganese mineralogy. Based on the experiments, we have constrained the mechanistic basis for Tl enrichment and stable isotope fraction in ferromanganese crusts, and we will discuss the effect of the experimental parameters on the fractionation factor between simulated seawater and solid minerals.

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