Redox oscillations in a freshwater analogue of marine pelagic sediments: Lake Superior

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Much attention has been given recently to the dynamics of redox boundaries in environments ranging from coastal sediments to flood planes to abyssal Arctic sediments [1]. We report on a multi-year investigation of transient diagenetic phenomena in a freshwater system. Deep (160-318 m) sediments in Lake Superior have sedimentation rates (0.01-0.04 cm y^{-1}) similar to those in marine hemipelagic and pelagic sediments and are similar to such sediments in terms of oxygen uptake, carbon degradation rates, carbon mineralization efficiency, and surface bioturbation rates. The reactivity of deposited organic carbon decreases with age according to a power law similar to the one established for marine environments. In Lake Superior, oxygen penetration into sediments ranges from 3.5 to >12 cm. Seasonal variations of only ~20% in bottom water oxygen concentrations cause it to vary by several cm, more than previously acknowledged. Using measurements and diagenetic modeling, we analyze the causes of these variations and their effects on sediment diagenesis and fluxes. On decadal time scales, our results show that multiple Mn- and Fe-rich (up to 10 wt %) layers in Lake Superior sediments are diagenetically mobile even where organic carbon is only weakly reactive ($k \approx 0.005$ y^{-1}). We draw parallels with the metal-rich layers that are found in deep Arctic sediments where they are often used as indicators of paleo-redox conditions [2] and discuss the diagenetic mobility of such layers on time scales up to 100 ky.

[1] Katsev et al. (2006) *Limnol. Oceanogr*. **51**, 1581-1593.
[2] März et al. (2011) *Geochim. Cosmochim. Acta* **75**, 7668-7687.

Impact of Ternary Surface Complexes on Metal Ion Adsorption

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Introduction

The fate and transport of metal ions released into the environment rely heavily upon their interactions with the mineral–water interface. Surface complexation models (SCMs) such as the Charge Distribution Multi-Site Complexation (CD-MUSIC) model are capable of describing and predicting adsorption processes over a range of environmental conditions in well-controlled systems with few competing or co-adsorbing species. In recent years, research objectives have focused on applying these models to more complex systems containing multiple adsorbing species and mixed mineral assemblages.

Results

In this research, surface charge, isotherm, and pH adsorption edge data taken from several published studies were modeled using CD-MUSIC to examine how different adsorbents (goethite and gibbsite) and complexing ligands (e.g. carbonate, chloride, selenite, and sulfate) influence metal ion adsorption and surface speciation (e.g. Figure 1). Mineral's surface site density was estimated, when possible, using a new approach that incorporates the proton reactive site density [1], along with maximum oxyanion adsorption data and pertinent crystallographic information regarding the adsorbent of interest. The impact of ternary complexes was ligand and adsorbent dependent.

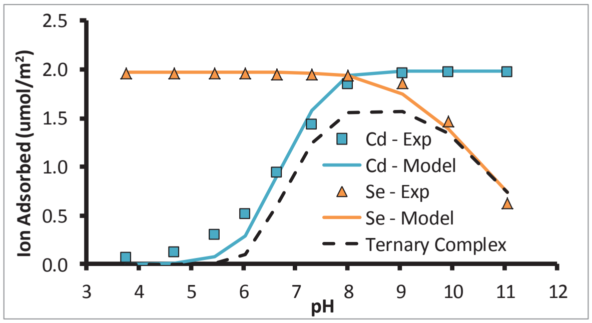

Figure 1: Adsorption and CD-MUSIC model for Cd^{2+} and SeO_3^{2-} bi-solute adsorption to goethtite. Model predictions of the $CdSeO_3$ ternary complex are represented by the dashed line.

Conclusion

This investigation reveals the pivotal role that ternary surface complexes can play in adsorption processes, and further illustrates the necessity of accurately depicting surface and aqueous complexes in SCM predictions.

[1] Salazar-Camacho and Villalobos (2010) *Geochim. Cosmochim. Acta* **74**, 2257-2280.