

## **YREE scavenging in seawater: A physical chemist's perspective**

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Ever since the first reliable measurements for seawater were published in the early 1980s, it has been known that YREE vertical profiles resemble those of the major plant nutrients, particularly silicate, showing concentrations that gradually increase with depth. This is generally believed to reflect scavenging in the upper ocean onto mostly biogenic particles and subsequent release when these sink and are bacterially remineralized. In 1990, Byrne and Kim devised a simplistic yet surprisingly successful model that describes YREE scavenging as a competition between complexation with dissolved ligands and with functional groups on the particle surface. A wealth of new field and laboratory data, due in equal parts to the emergence of ICP-MS and to the international GEOTRACES program, has enabled a revision of that model, obviating some of its dubitable assumptions.

My presentation will review experiments conducted over the past 20 years, at the University of South Florida and at UMCES, to determine the stability of YREE complexes with dissolved organic and inorganic ligands, as well as the extent of YREE sorption on model organic and inorganic surfaces as a function of pH, ionic strength, and temperature, all in non-coordinating media. Comparisons with older literature illustrate how employing a variety of techniques, including cation-exchange, solubility, potentiometric titration, ligand competition, rapid-scan spectrophotometry, and ion-selective electrodes, has improved thermodynamic data for YREE complexation with carbonate, hydroxide, fluoride, chloride, sulfate, and a few small organic acids. In addition, we have developed detailed surface complexation models for YREE sorption on hydrous ferric oxide (HFO), hydrous manganese oxide (HMO), HFO/HMO mixtures, and macroalgal tissue.

Using the latest data with an inversion of the Byrne and Kim model yields some interesting insights into the identity and properties of the marine particles primarily responsible for YREE scavenging in the shallow and deep ocean. These results demonstrate the benefits of a chemical approach to modeling metal scavenging in the open ocean. On the other hand, the limitations of a purely equilibrium model must be recognized, as scavenging clearly has an important dynamic component that it does not capture. Some attention will thus be given to complementary mechanisms like co-precipitation with phosphate, one of the most analytically challenging and therefore least well studied inorganic YREE ligands.