A molecular approach towards understanding the biogenic formation of CeO_2 and its interactions with biomolecules

JAVIERA CERVINI-SILVA[1], BENJAMIN GILBERT[2], SIRINE FAKRA[2] AND JILLIAN BANFIELD[1]

[1]Department of Earth and Planetary Science, University of California, Berkeley (javiera@eps.berkeley.edu)
[2]Lawrence Berkeley National Laboratory

Cerium is the most abundant lanthanide and generally the only one to undergo redox reactions at the Earth's surface. The oxidation state influences the environmental chemistry and toxicology of Ce because it alters the mechanisms of interaction between Ce and biomolecules. For instance, as opposed to Ce(III) or other lanthanide ions, Ce(IV) has shown a remarkable efficiency to hydrolyze DNA. The selectivity of Ce as Ce(IV) relates to the specific coordination of water molecules and their orientation. Ce(IV) may also bind selectivity to biomolecules such as RNA-type substrates, or monocleotides such as AMP, to instigate conformational changes or cleavage of complexes, which affect metabolic pathways pivotal to growth and survival. On the other hand, biogenic ligands can promote the oxidation of Ce(III) to small sized-CeO_2 and are subsequently degraded by this product to CO_2 and humic material. Here, we study molecular interactions between CeO_2 and biomolecules (e.g., catechol) using carbon and cerium, XRD, and IR spectroscopy. Results show a progressive increase in catechol transformation (as % carbon) with decreasing CeO_2 particle diameter ($13 < d < 84$ Å), which substantiates an intimate relation between CeO_2 unit cell expansion and reactivity towards organics susceptible to undergo redox transformations. As shown by C and Ce spectroscopy, organic polymers that form because of catechol oxidation are distributed next to the mineral surface and its occurrence is coupled to Ce reduction-oxidation.