



A Molecular Approach towards Understanding the Biogenic Formation of CeO₂ and its Interactions with Biomolecules

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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 selectively to biomolecules such as RNA-type substrates, or mononucleotides 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-CeO₂ and are subsequently degraded by this product to CO₂ and humic material. Here, we study molecular interactions between CeO₂ 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 CeO₂ particle diameter ($13 < d < 84 \text{ \AA}$), which substantiates an intimate relation between CeO₂ 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.