Difference of Cesium and Selenium Adsorptions between Biogenic and Synthetic Ferrihydrite

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Adsorption chemistry on ferrihydrite is one of the important topics because of its considerable impacts on trace element geochemistry in the surface environment. Although synthetic ferrihydrite has been used as an adsorbent for laboratory studies, there is a growing recognition that biogenic Fe(III) oxyhydroxides (BIOS) are common in natural environment. The aim of our study is to reveal the adsorption characteristics of BIOS different from synthetic ferrihydrite. We compare cesium (Cs) and selenium (Se(IV), Se(VI)) adsorptions between BIOS and synthetic ferrihydrite based on molecular scale mechanisms.

Our batch adsorption experiments revealed significant difference in Cs and Se adsorptions between BIOS and synthetic ferrihydrite. Compared to synthetic ferrihydrite, BIOS showed enhanced adsorption for positively-charged Cs whereas decreased adsorption for negatively-charged Se(IV) and Se(VI). Zeta potential measurement showed that BIOS was negatively charged over a wide pH range, which is in contrast to positively charged synthetic ferrihydrite. Thus, different adsorption of Cs and Se on BIOS from synthetic ferrihydrite can roughly be explained by the electrostatic effect caused by the impurities such as silicic acid and/or organic matters in BIOS. On the other hand, adsorption of Se(VI) on BIOS was more strongly inhibited compared to that of Se(IV). The Se K-edge EXAFS revealed that Se(VI) mainly forms an outer-sphere complex whereas Se(IV) forms an inner-sphere complex on both BIOS and synthetic ferrihydrite. Therefore, we consider that inner-sphere Se(IV) complex is less influenced by the surface charge of BIOS beecause of their stronger affirnity via formation of chemical bonding to BIOS, which is contrasting to outer-sphere Se(VI) complex.