Cadmium isotope fractionation during complexation with environmentally relevant surfaces

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Isotope tracing of metals in the environment becomes challenging as it is crucial to identify and quantify isotope fractionation during separate biogeochemical processes. The resulting isotope data are influenced by many processes occurring within reactive environmental compartments (soils and sediments), such as sorption, precipitation, redox changes, interactions with plants and microorganisms, etc. Cadmium isotopes are also known to fractionate during complexation with various environmentally relevant surfaces and ligands. In general, lighter Cd isotopes are preferably adsorbed to Mn and Fe (oxyhydr)oxides and humic acid [1,2,3]. At high ionic strengths, Cd isotope fractionation on organic matter mainly depends on its complexation with carboxylic sites. Outer-sphere complexation occurs at equilibrium together with inner-sphere complexation as well as with the change of the first Cd coordination and its hydration complexes in solution. At low ionic strengths, nonspecific Cd binding induced by electrostatic attractions plays a dominant role and promotes Cd isotope fractionation during complexation [3]. It is also important to note that concentration equilibrium usually differs from isotope fractionation equilibrium and metal coordination chemistry in solution is crucial to decipher the resulting metal isotopic fractionation. Consistent presentation of adsorption/complexation data coupled with robust solid state analysis (EXAFS) are also needed to interpret well the results. This presentation aims at summarizing data on Cd isotope fractionation after complexation with various environmental surfaces, describe the involved mechanisms, and identify potential drawbacks of this approach.

[1] Komárek, Ratié, Vaňková, Šípková & Chrastný (2022) *Critical Reviews in Environmental Science and Technology* 52, 3573-3603.

[2] Yan, Zhu, Li, Peacock, Ma, Wen, Liu, Zhou, Zhu & Yin (2021) *Environmental Science & Technology* 55, 11601-11611.

[3] Ratié, Chrastný, Guinoiseau, Marsac, Vaňková & Komárek (2021) *Environmental Science & Technology* 55, 7430-7444.