

# Mass dependent fractionation of geochemical twins by coordination change

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The element pairs Y-Ho, Zr-Hf, and Nb-Ta are called geochemical twins because they do not fractionate from each other in most geochemical contexts due to their identical cation charge (3+, 4+, and 5+, respectively) and similar ionic radius between the members of each pair. They can fractionate considerably under certain particular conditions, especially during fluid-mineral or melt-mineral interaction, which makes observable Y/Ho, Zr/Hf, and Nb/Ta fractionation useful probes for such conditions. While a range of *conditions associated* with geochemical twin fractionation are known, the *underlying mechanisms* are still poorly understood. If we consider the differences in effective charge and radius within each pair negligible, the only possible root causes for these mechanisms to act upon are the non binding electrons and the large mass difference (86%, 96%, and 95%, respectively).

We investigated complexation of Zr<sup>4+</sup> and Hf<sup>4+</sup> in fluoride-rich (1.0 mol/kg HF) aqueous solutions at 40 MPa and 100 - 400 °C, using synchrotron X-ray absorption spectroscopy (X-ray absorption near edge structure, XANES and extended X-ray absorption fine structure, EXAFS) combined with classical and *ab initio* molecular dynamics simulations. Below 200 °C, octahedral [MF<sub>2</sub>(OH)<sub>2</sub>·2H<sub>2</sub>O]<sup>0</sup> complexes dominate strongly. Above, tetrahedral [MF<sub>2</sub>(OH)<sub>2</sub>]<sup>0</sup> complexation starts to increase through loss of H<sub>2</sub>O from the first coordination shell. The ratio of the different complexes is different for Zr and Hf between 200 and 300 °C. This coincides with typical formation temperatures for hydrothermal vein fluorite, which is known to exhibit some of the most prominent deviations of Zr/Hf ratios from the chondritic value, suggesting that coordination change by loss of electrically neutral solvent molecules (H<sub>2</sub>O) may be an effective Zr/Hf fractionation mechanism. Similar effects are known for isotope fractionation in aqueous systems, indicating that the mass difference between Zr and Hf is likely more relevant than the electronic differences here. We discuss several different geochemical twin fractionation mechanisms and their potential implications for the use of these element pairs as geological process indicators.