

# Mixed oxidation state of uranium in geological samples: insight from HERFD X-ray absorption spectroscopy at U M<sub>4</sub> edge

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The mixed oxidation state of uranium is well described for the U-O system [1]. In geochemistry, our knowledge of the oxidation state of uranium present as a trace component in rocks and host minerals remains very limited. Whereas the oxidation/reduction of uranium is expected to be common in different geological contexts, the quantification of U(IV), U(V) and U(VI) in rocks and host minerals remains challenging. The recently developed synchrotron-based technique of high-energy resolution fluorescence detection (HERFD) X-ray absorption spectroscopy at U M<sub>4</sub> edge (3728 eV) opens new perspectives for fingerprinting the oxidation state of uranium at low U concentration (down to ppm level) [1]. The principles of HERFD are based on the selection of emitted fluorescence with an X-ray emission spectrometer equipped with crystal analyzers [2]. The maximum of M<sub>4</sub> HERFD-XANES spectra is shifted by energy with oxidation state. The chemical shift between various oxidation states U(IV)–U(V)–U(VI) is not linear, i.e. the shift between U(IV) and U(V) (1.5eV) is much greater than the one between U(V) and U(VI) (0.5 eV) (Figure 1). The coordination geometry may impact the energy shift only by 0.1 – 0.2 eV. Thus, the principal component analysis of HERFD-XAS spectra at the U M<sub>4</sub> edge is straightforward for accurate quantification of different oxidation states even if the pure structural end-members are not known. Our measurements of natural samples (black shales, volcanic glasses) and model systems (U-O system under high T) clearly show the presence of mixed oxidation states of U, i.e. U(IV)+U(V), U(V)+U(VI), U(IV)+U(VI) and U(IV)+U(V)+U(VI). Studying the oxidation state of U will improve our understanding of uranium geochemistry and the geochemical model of U reactivity and mobility in the environment.

[1] Kvashnina, K. et al. (2022) Chem. Commun. 58, 327 – 342.

[2] Scheinost, A. C. et al (2020) J. Synchrotron Rad. 28, 333 – 349.

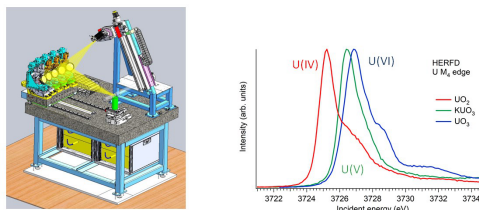


Figure 1. (Left) Schematic drawing of the five-crystal X-ray emission spectrometer at ROBL beamline at ESRF. (Right) Uranium M<sub>4</sub> HERFD data of UO<sub>2</sub>, KUO<sub>3</sub> and UO<sub>3</sub> with U(IV), U(V) and U(VI) oxidation states, respectively.