

## Linking the oxidation state of U incorporated in Fe (oxyhydr)oxides to environmental parameters

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There is growing evidence from laboratory experiments that incommensurate metals such as U(VI, V) and Tc(IV) can be incorporated into iron (oxyhydr)oxides either during coprecipitation under hydrothermal conditions or redox-induced transformation of ferrihydrite to more stable forms such as goethite. The redox-induced incorporation pathway occurs even at room temperature. Further, the oxidation state of incorporated U responds to the solution Eh and thus is not isolated from the environment. However, in order to write a reaction between an incorporated metal and solution species one needs to know the oxidation state of the metal, and local charge compensation schemes (CCS). For example, incorporated U(VI) substituting for Fe(III) may be associated with deprotonation of hydroxyl groups and/or Fe(III) vacancy formation. More reduced U(V) or U(IV) may also require localized excess electron density. The method of choice for determining the local bonding environment of such metals has been EXAFS with XANES and XPS constraining oxidation states. XPS has proven most useful for determining oxidation states of U because satellite structures yield robust signatures for U(IV), U(V) and U(VI) whereas the U L<sub>III</sub> edge position, commonly used in geochemistry, is not sufficient to resolve U(V). Information on U oxidation states is contained in the shape of the L<sub>III</sub> white line, but care must be taken to determine the bonding environment which can have a strong effect (e.g., uranyl and uranate display very different white line shapes). EXAFS does encode information on oxidation states and CCS via the local coordination environment. However, a lack of standards for trace U in oxides leads to underconstrained fits and loss of potential information.

Here, *ab initio* MD simulations were used to constrain the interpretation of U-L<sub>III</sub> EXAFS of U incorporated in goethite. Best fits using dynamical structure models indicate the predominance of U(V) in uranate octahedral coordination with deprotonation and excess electrons providing local CCS. Further, a variety of structures are accessible at RT; thus, only considering the most stable structure can be misleading.