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Niobium speciation in minerals revealed by $L_{2,3}$-edges XANES spectroscopy

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Abstract

The systematic mineralogy of niobium (Nb) is complex, with more than one hundred species dominated by multicomponent oxides of similar chemistry. The determination of Nb speciation in solids (i.e., the distribution between the phases and the crystal-chemical environment of Nb) is thus a challenge in geological contexts. Here, we present the first Nb $L_{2,3}$-edges X-ray absorption near-edge structure (XANES) measurements on various Nb minerals and synthetic oxides with geological relevance. The interpretation of Nb $L_{2,3}$-edges XANES spectra in the light of crystal-field theory shows the sensitivity of spectra to local site symmetry and electronic environment around Nb atoms. Crystal-field multiplet simulations give estimates of the 10Dq crystal-field parameter values for Nb^{5+}, which range from 2.8 to 3.9 eV depending on Nb coordination and Nb–O distances. Rather than a 10Dq vs. R^{-5} relationship (where R represents the average Nb–O bond distance) expected in a point-charge model, we find a R^{-3} dependence with the crystal-field splitting for reference materials with octahedrally coordinated Nb. Complementary ligand-field multiplet simulations provide evidence of charge transfer between Nb and O. The contribution of the ionic and covalent characters to the Nb–O bonds is equivalent, unlike more ionic 3d metal–O bonds. This systematic characterization of the $L_{2,3}$-edges XANES spectral properties of Nb provides information on the mechanisms by which Nb^{5+} substitutes for Fe^{3+}, Ti^{4+}, or Ce^{4+} in oxides common in geological contexts. Whereas the substitution of Nb^{5+} for Ce^{4+} does not modify the local structure of the cation site in cerianite, the substitution of Nb^{5+} for Ti^{4+} in rutile and anatase results in an increase of the cation-ligand distance and a decrease in the symmetry of the cation site. Conversely, the substitution of Nb^{5+} for Fe^{3+} in hematite and goethite results in a smaller cation site distortion. Our study demonstrates the usefulness of $L_{2,3}$-edges XANES spectroscopy to determine Nb speciation in minerals to understand the processes of enrichment of this critical metal.

Keywords: Niobium, XANES, multiplet, 10Dq, local structure, speciation