

The valence states of Nb and Ta in magmatic-hydrothermal systems: Insights from combined SXAS and XPS analyses of titanite and ilmenite in two Chinese anorogenic suites

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ABSTRACT

Niobium and tantalum are the so-called “geochemical twins,” sharing similar properties and having long been used to constrain magmatic sources and trace geological and planetary processes. Significant fractionations of Nb and Ta have recently been documented in diverse magmatic-hydrothermal and metamorphic systems, but their origin remains unclear. Nb and Ta are preferentially incorporated in Ti-rich minerals such as ilmenite, rutile, and titanite. In this study, representative samples of Nb-rich titanite and ilmenite exhibiting large Nb/Ta variations (5 to 65) from two anorogenic alkaline suites in the Fangcheng and Ziyang regions of China and associated hydrothermal alteration have been investigated by Raman spectroscopy, synchrotron X-ray adsorption spectroscopy (SXAS) and X-ray photoelectron spectroscopy (XPS). The Raman spectra of Nb-rich titanite and ilmenite show only minor degrees of metamictization. The Nb *K*-edge SXAS spectra of Nb-rich ilmenite with Nb/Ta > 30 are similar to those of Nb₂O₅, indicating a dominant presence of Nb⁵⁺ with minor Nb⁴⁺ and an Nb⁵⁺/ΣNb ratio range from 0.59 to 1. In contrast, the Nb *K*-edge SXAS spectra of titanite and ilmenite with Nb/Ta < 30 indicate mixed valences of Nb⁵⁺ and Nb⁴⁺, with Nb⁵⁺/ΣNb in the range of 0.22 to 0.55. Similarly, XPS measurements of titanite and ilmenite further support the presence of mixed valences of Nb, with Nb⁵⁺/ΣNb in the range of 0.49 to 0.85. In addition, Ta *L*₃-edge SXAS spectra of titanite suggest the occupancy of Ta⁵⁺ at the octahedral site. Fitting results from Nb *K*-edge and Ta *L*₃-edge extended X-ray adsorption fine structure (EXAFS) data further suggest that both Nb and Ta replace Ti via coupled substitutions of the type 2Ti⁴⁺ ↔ (Nb⁵⁺, Ta⁵⁺) + (Al, Fe)³⁺ and an isovalent substitution Ti⁴⁺ ↔ Nb⁴⁺. A positive correlation between the oxidation states of Nb and the Nb/Ta values has been observed in titanite and ilmenite, but not for Ta. These results suggest that the extreme enrichment and large variations in Nb contents, as well as significant fractionation of Nb from Ta in titanite and ilmenite, are controlled by the prevailing oxygen fugacity in magmatic-hydrothermal systems. Given these complexities involving variable valence states, circumspection is required to use Nb and Ta anomalies to interpret geotectonic settings and apply Nb/Ta systematics to constrain magmatic-hydrothermal sources.

Keywords: Titanite, ilmenite, synchrotron X-ray adsorption spectroscopy, X-ray photoelectron spectroscopy, Nb/Ta fractionation, alkaline suites