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Contrasting Hydrothermal Complexation of Niobium and Tantalum: Insights from High-Resolution XAS and Thermodynamic Modelling

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Niobium (Nb) and tantalum (Ta) are critical metals for green technologies. These two elements have been called 'geochemical twins' because of their similar geochemical behaviours in geofluids (melts and hydrothermal solutions). This study integrates *in-situ* high-energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD-XAS) and thermodynamic modelling to unravel their contrasting coordination chemistry in fluoride (F)- and chloride (Cl)-rich hydrothermal fluids at temperatures up to 413°C and pressures of 800 bar.

For Nb, HERFD-XAS reveals a dynamic ligand competition: in acidic F-rich systems, Nb forms stable oxyfluoride complexes (e.g., $[NbF_6O_2]$), transitioning to Cl-O(H) species (e.g., $[NbCl_4O_2]$) in the chloride-rich systems. Our findings show that Cl becomes an important ligand for Nb transport in acidic brines, challenging previous assumptions. Conversely, Ta speciation is dominated by oxyfluoride complexes or high-order fluoride complexes (e.g., $[TaF_7]$, $[TaF_9]$) in relatively high-concentration F systems; there was no evidence of Cl coordination even in high-Cl (36 wt.% HCl) acidic solutions. Temperature-dependent structural transitions (e.g., $[TaF_9] \rightarrow [TaF_7]$ at >150°C) highlight fluoride's unique role in enhancing Ta solubility.

Thermodynamic simulations reconcile previous peer-reviewed solubility data with speciation models, demonstrating that Nb mobility is highly pH dependent, while Ta transport strictly requires F-rich fluids. These differences explain Nb-Ta fractionation trends in magmatic hydrothermal fluids associated with carbonatites and granitic systems. For instance, carbonate interactions buffer F/Cl activities, favoring Nb enrichment, whereas Ta precipitation is triggered by F depletion during fluid-rock reactions.

This work provides direct evidence of Nb-Ta complexation and resolves long-standing discrepancies in Ta-Nb speciation models and their transport in hydrothermal systems. The findings advance predictive frameworks for Nb-Ta ore formation and underscore the necessity of ligand-specific strategies in metallurgical extraction. By bridging molecular-scale insights with deposit-scale processes, this study enhances our ability to model critical metal cycles in Earth's crust.