Paragenesis and precipitation stages of Nb-Ta-oxide minerals in phosphorus-rich rare-element pegmatites (Buranga dike, Rwanda)

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ABSTRACT

Nb-Ta-oxide minerals (NTO) are commonly associated with rare-element pegmatites where they are interpreted to precipitate at magmatic to magmatic-hydrothermal conditions. Although high-temperature experiments show that phosphorus and other fluxing elements (e.g., Li, B, F) can affect the saturation of NTO in pegmatitic systems, it is still uncertain how NTO saturation occurs in natural, flux-rich pegmatitic melts and whether crystallization occurs at multiple stages during magmatic or subsolidus conditions. The lithium-cesium-tantalum (LCT) family P-rich Buranga granitic pegmatite (western Rwanda) is used as a type locality to address this question. NTO mineralization in the Buranga dike occurs in two mineralogical units: in mineralogically complex phosphatic nodules, and in albited parts. In the phosphatic nodules, Fe-Nb-Ta-rich rutile and columbite-group minerals (CGM) are observed, while in the albited parts, only CGM is found. Fe-Nb-Ta-rich rutile precipitates at the magmatic stage along with early primary phosphates (i.e., F-rich montebrasite, wollylite, and fluorapatite). Conversely, CGM mineralization occurs at the magmatic-hydrothermal stage in association with replacement phosphates like bertossaitite, after primary minerals (i.e., rutile, wollylite, rosemaryite, and trolleite) are destabilized due to crystal-melt-fluid interactions. NTO textures and chemical zoning show uneven evolution from core to rim and are related to localized alteration phenomena of the surrounding minerals. This indicates that local processes and element transfers are more important than dike-scale fractionation processes for NTO mineralization in P-rich granitic pegmatites. The restricted availability of Fe and Mn in the system, which is related to the competition between phosphate and oxide minerals, is identified as the main control on the CGM mineralization in the Buranga dike. CGM precipitation is only possible during the magmatic-hydrothermal stage when Fe and Mn are leached from the primary phosphates and remobilized to the Nb-Ta-bearing residual melt by the exsolved fluid.

Keywords: Nb-Ta mineralization, granitic pegmatite, pegmatitic phosphates, mineral paragenesis, Raman mapping, Buranga pegmatite

INTRODUCTION

Rare-element granitic pegmatites are commonly enriched in incompatible elements, e.g., Li, Rb, Cs, Be, Ta, Nb, P, and B (Černý et al. 1985; London 1987; Linnen and Cunev 2005; Simmons and Webber 2008). Most of the large-scale melt differentiation and element enrichment can be explained by fractional crystallization in a residual melt segregated from granitic mushes (Raimbault et al. 1995; Hulsbosch et al. 2014; Stepanov et al. 2014). However, the extreme elemental enrichment and fractional crystallization of particular geochemical ratios (i.e., Nb/Ta) observed in some pegmatites cannot be attributed to a pure equilibrium fractional crystallization model (Van Lichtervelde et al. 2018; Ballouard et al. 2020b; Kaeter et al. 2021). Therefore, additional mechanisms are required to explain this fractionation, especially on the scale of an individual pegmatite dike.

Due to their identical charge and similar ionic radius (i.e., usually labeled “geochemical twins”), Nb and Ta are not expected to fractionate extensively in most geological environments, requiring specific processes to fractionate (Green 1995). Nonetheless, niobium-tantalum-oxide minerals (NTO) commonly record considerable degrees of Nb/Ta fractionation in pegmatic systems (e.g., Černý and Erict 1985; Beurlen et al. 2008; Wise et al. 2012; Fuchsloch et al. 2019). This can be related to the lower solubility of MnNb2O6 to MnTa2O6 (Linnen 1998), suggesting that the melt Nb/Ta ratio decreases during magmatic differentiation until saturation of tantalite is reached. Contrarily, if saturation is not reached, the metals can be incorporated into other minerals (especially Fe-Ti oxides, micas, and phosphates).

Overall, the reported content of Nb and Ta in pegmatitic melts (Webster et al. 1997; Borisova et al. 2012) is mostly below the necessary saturation values for NTO (Linnen and Keppler 1997; Linnen 1998; London 2018; Van Lichtervelde et al. 2018; McNeil et al. 2020). This resulted in multiple hypotheses for the precipitation of NTO in pegmatites. The mineralization can be purely magmatic, originating from fractional crystallization (Černý et al. 1986; Llorens et al. 2017), due to extreme undercooling and disequilibrium crystallization (London 2018; Van Lichtervelde et al. 2018) or chemical quenching (Linnen et al. 2012). Alternatively, it can be triggered by interactions with an aqueous fluid