The effect of disequilibrium crystallization on Nb-Ta fractionation in pegmatites: Constraints from crystallization experiments of tantalite-tapiolite

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ABSTRACT

Tapiolite [FeTa2O6] and columbite-group minerals [(Fe,Mn)(Ta,Nb)O6] are common Nb-Ta-bearing accessory minerals in rare-element granites and pegmatites. Their compositional gap has inspired several experimental studies, but none of them have succeeded in reproducing the parameters that influence the compositional gap. In this study, tapiolite and columbite-group minerals (CGM) were crystallized from water-saturated, flux-rich granitic melts at various conditions of pressure, temperature, oxygen fugacity, and Ti contents. Crystals with a size as small as 500 nm were analyzed with a field emission gun (FEG) electron microprobe. The results show that temperature, pressure, and Ti content only slightly affect the compositional gaps between tapiolite and CGM, whereas high fO2 leads to complete solid solution between a rutile-structured component Fe4+TaO4 and (Fe,Mn)Ta2O6. The experimental CGM-tapiolite compositional gaps are compared with natural CGM-tapiolite pairs from rare-element granites and pegmatites worldwide. This study reveals that the crystallographic structure of tapiolite and CGM could be the dominant parameter that influences the position of the compositional gap. Order-disorder in CGM and tapiolite is tightly linked to disequilibrium crystallization triggered by supersaturation. Significant isothermal Nb-Ta fractionation is observed inside CGM crystals that grow at high degrees of supersaturation. The effect of supersaturation prevails over the solubility effect that is known to increase the Ta/(Ta+Nb) ratio in CGM and coexisting melts. Thus, even if global equilibrium in terms of the solubility of Nb-Ta-bearing minerals is attained, the Ta/(Nb+Ta) ratio in the crystals may differ significantly from equilibrium. It implies that Nb-Ta fractionation in Nb-Ta oxides is controlled by crystallization kinetics rather than equilibrium chemical fractionation (or any other processes such as F-complexing of Ta or fluid exsolution) in dynamic systems that can rapidly reach supersaturated conditions. These results have important implications for the understanding of crystallization processes in highly evolved and pegmatite-forming magmas.

Keywords: Crystallization experiments, disequilibrium crystallization, Nb/Ta fractionation, pegmatites, tapiolite; From Magmas to Ore Deposits

INTRODUCTION

Granitic pegmatites are sources of several strategic rare metals (e.g., Be, Li, and Ta) that have been classified as critical based on their economic importance and supply risk (Linnen et al. 2012). As these elements are generally incompatible and poorly mobilized by hydrothermal processes, their concentration mechanisms are controlled by extreme magmatic processes that involve low degrees of partial melting of pre-enriched sedimentary rocks and extreme fractional crystallization of fertile granites. Granitic pegmatites owe their spectacular textural features (e.g., giant crystal size) and geochemical signatures (e.g., extreme fractionation of the high field strength elements) to particular crystallization kinetics that prevail in pegmatite-forming melts at strong undercooling (London 2014a, 2014b). The fast crystal growth in high disequilibrium leads to boundary layer formation and/or melt-melt immiscibility, two mechanisms that are reviewed in recent partly controversial papers (Thomas and Davidson 2014; London 2014b, 2015). In addition to undercooling, the fast growth processes in pegmatite formation are enhanced by the presence of flux components such as fluorine (F), boron (B), and phosphorus (P), which considerably shift the pegmatitic melt properties toward those of an aqueous fluid, sharply depressing solidus temperature (Jaehn and Burnham 1969), viscosities (Bartels et al. 2013, 2015), and crystal nucleation rates (London et al. 1989). The presence of fluxes also results in an increase of the solubilities of high field strength element (HFSE) bearing minerals (Linnen and Cuney 2005; Bartels et al. 2010; Aseri et al. 2015). The main problem related to HFSE-bearing mineral saturation in granitic pegmatites is that experimentally determined solubilities indicate HFSE saturation values in pegmatite melts much higher than the concentrations determined in natural rocks. As an example, manganocolumbite and manganotantalite solubilities in water-saturated peraluminous granitic melt at 200 MPa and 800 °C (Linnen and Kepler 1997) give Nb and Ta saturation...