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

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Abstract

Tapiolite [$FeTa_2O_6$] and columbite-group minerals [$(Fe,Mn)(Ta,Nb)_2O_6$] 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 f_{O_2} leads to complete solid solution between a rutile-structured component $Fe^{3+}TaO_4$ and $(Fe,Mn)Ta_2O_6$. 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