Cassiterite crystallization experiments in alkali carbonate aqueous solutions using a hydrothermal diamond-anvil cell

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ABSTRACT

Ore-forming fluids enriched in alkali carbonate are commonly observed in natural melt and fluid inclusions associated with tin mineralization, particularly in granitic pegmatite. However, the roles of alkali carbonates remain unclear. Hence, to investigate the roles of alkali carbonate, herein, cassiterite (SnO₂) crystallization experiments in SnO₂-Li₂CO₃-H₂O and SnO₂-Na₂CO₃-H₂O systems were conducted using a hydrothermal diamond-anvil cell. The results showed that SnO₂ could dissolve into the alkali carbonate aqueous solution during heating, and long prismatic cassiterite crystals grew during the subsequent cooling stage at average rates of 0.61×10^{-6} to 8.22×10^{-6} cm/s in length and $3.40-19.07 \,\mu$ m³/s in volume. The mole fraction of cassiterite crystallized from the SnO₂-Li₂CO₃-H₂O system ranges from 0.03 to 0.41 mol%, which depends on the Li₂CO₃ content dissolved in the aqueous solution. In situ Raman analysis of the alkali carbonate-rich aqueous solution in the sample chamber suggests that the dissolution of SnO_2 can be attributed to the alkaline conditions produced by hydrolysis of alkali carbonate in which $Sn(OH)_{6}^{2}$ may be a potential tin-transporting species. The cassiterite crystallization conditions obtained in our SnO₂-alkali carbonate-H₂O systems primarily fell within the 400-850 °C and 300-850 MPa temperature and pressure ranges, respectively; furthermore, cassiterite crystallization ended in rare metal pegmatite-forming conditions. These crystallization features of cassiterite are similar to those formed in tin-mineralized granitic pegmatites. It indicates that an alkali carbonate-rich aqueous solution or hydrous melt can work as a favorable transport medium for tin and provides the necessary conditions for cassiterite crystallization in granitic pegmatite, bearing the roles in decreasing the viscosity of hydrous melts and enhancing the solubility of SnO₂ in ore-forming melts or fluids. These roles of alkali carbonate can also be extended for the mineralization of other rare metals (e.g., Li and Be) in granitic pegmatite.

Keywords: Cassiterite, alkali carbonate, pegmatite, crystallization, hydrothermal diamond-anvil cell