

## **In situ observation of the subsolidus reactions between petalite and spodumene + quartz in a hydrothermal diamond-anvil cell**

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### **ABSTRACT**

Spodumene and petalite are the primary minerals mined from pegmatites, which are the most important sources of hard-rock lithium resources. In Li-mineralized pegmatites, the subsolidus reaction of petalite  $\rightarrow$  spodumene + 2 quartz (1) and its reverse reaction: spodumene + 2 quartz  $\rightarrow$  petalite (2) produce secondary spodumene, usually in the form of spodumene and quartz intergrowths (SQI), and secondary petalite, respectively. The pressure-temperature ( $P$ - $T$ ) conditions under which these reactions occur have been investigated using quenching-type methods (e.g., with cold-seal pressure vessels). However, the kinetic parameters of the reactions are difficult to measure in these experiments and are thus frequently overlooked, even though their determination can significantly improve our understanding of the formation of spodumene and petalite in pegmatites. In this study, we employed a hydrothermal diamond-anvil cell to monitor the reaction process and crystallization dynamics in situ. The reaction rates ( $V_r$ ) of reaction 1 in sample systems with 5–95 wt% H<sub>2</sub>O ranged from  $10^{-6}$  to  $10^{-11}$  cm<sup>3</sup>/day at 355–753 MPa and 500–600 °C.  $V_r$  is driven by the Gibbs free energy change ( $\Delta G_r$ ) of the reaction, which is dependent on pressure and temperature. As  $\Delta G_r$  ( $<0$ ) decreases,  $V_r$  rises.  $V_r$  also correlates positively with the growth rate ( $V_g$ ) of secondary spodumene, though  $V_g$  is lower than that of primary spodumene formed in pegmatite-forming melts. Hence, by extrapolating experimental  $\Delta G_r$ - $V_r$  data to pressure-temperature ( $P$ - $T$ ) conditions of pegmatite formation, we can estimate  $V_r$  and thus assess  $V_g$  for secondary spodumene in natural SQI. For example, the formation of secondary spodumene in the Highbury pegmatite (South Africa) is attributed to reaction 1, which occurred at a  $V_r$  of  $10^{-8}$  to  $10^{-9}$  cm<sup>3</sup>/day under conditions of 370 MPa and 400–500 °C. This  $V_r$  could correspond to a high  $V_g$ , leading to secondary spodumene crystals reaching up to 0.5 cm in size. In contrast, the fine-grained secondary spodumene (e.g.,  $<0.2$  mm) in the Tanco pegmatite (Canada) is possibly attributed to a lower  $V_g$  under  $P$ - $T$  conditions of  $\sim 290$ – $260$  MPa and below 400 °C. Reaction 2 at 244 MPa and 600 °C yielded  $V_r$  of  $\sim 10^{-7}$  cm<sup>3</sup>/day, approaching the growth rate of petalite crystallized from pegmatite-forming melts. Thus, secondary petalite is easy to form via reaction 2 during pressure drops in pegmatite formation.

**Keywords:** Pegmatite, spodumene, petalite, spodumene and quartz intergrowths, hydrothermal diamond-anvil cell