

## **Ti-Al zoning of experimentally grown titanite in the system CaO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>-NaCl-H<sub>2</sub>O-(F): Evidence for small-scale fluid heterogeneity**

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### **ABSTRACT**

Chemical zoning according to the substitution  $\text{Al} + (\text{OH},\text{F}) = \text{Ti} + \text{O}$  is a common phenomenon in natural titanite and can be used to reconstruct its growth conditions. We synthesized titanite, which has a zoning pattern similar to that found in natural titanite that grew at the expense of rutile, visible in element distribution maps as a patchy irregular pattern. Run conditions in the system CaO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>-NaCl-H<sub>2</sub>O(-CaF<sub>2</sub>) were 600 °C, 0.4 GPa, 1 to 107 days duration. Natural rutile crystals were placed in a perforated Pt-tube within an outer Au-capsule containing wollastonite,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, optionally powdered CaF<sub>2</sub>, and a NaCl brine, to simulate conditions, where rutile is transformed into titanite by a hydrous Ca-Si-Al(-F) fluid, driven by a chemical potential gradient between inner and outer capsule. Spontaneous nucleation of titanite is restricted to a small number of crystals on the rutile surface in the inner capsule. Growth proceeds from sparse isolated titanite crystals after 1 day to assemblages of several 100  $\mu\text{m}$  large crystals in a reaction rim in the long-time runs. Titanite is strongly zoned in Al-Ti and shows up to  $\sim 0.5$  Al per formula unit (pfu) in experiments containing F; without F, substitution is limited to  $\sim 0.25$  Al pfu. The range of the Ti-Al exchange is already large in short run times and the same heterogeneity is observed in long-time runs. The Al-Ti distribution (with and without F) in compositional domains (up to several tens of micrometers) is patchy and irregular. No relation of the zoning with time (core-rim) or preferred growth directions was observed.

In the case of fluid-mediated growth, mineral growth zoning represents a disequilibrium at supersaturated conditions. The concentration of Ti in the fluid is likely the limiting factor for titanite growth considering the low solubility compared to that of Al, Ca, and Si. Titanium is not transported in significant amounts into the outer capsule, indicating low mobility, in contrast to Al, Ca, and Si, which are transported into the inner capsule. Assuming buffered Al concentration from dissolution of the Al-source, we speculate that the Ti/Al of the fluid at the precipitation site was controlled by the local Ti concentration, which varies over the distance from the rutile surface to the growing titanite crystal and produces the irregular patchy zoning.

**Keywords:** Dissolution-precipitation reaction, Al-Ti substitution, mineral zoning, experiments