

The petrological importance of accessory Ti-phases: experimental constraints on an activity model for titanite in the system $\text{CaTiSiO}_4\text{O} - \text{CaAlSiO}_4\text{F}$

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Experimental studies were carried out to evaluate phase relations involving titanite ($\text{CaTiSiO}_4\text{O}$) – F-Al titanite ($\text{CaAlSiO}_4\text{F}$) solid solution in the system $\text{CaSiO}_3 - \text{Al}_2\text{SiO}_5 - \text{TiO}_2 - \text{CaF}_2$. Piston-cylinder experiments at 900 – 1000°C and 1.1 – 4.0 GPa characterized the effect of excess fluorite on titanite composition for the equilibrium titanite + kyanite = anorthite + rutile (TARK). The reaction displacement experiments show that at high pressures the assemblage (Al + F) titanite + kyanite + rutile + fluorite is stable and at low pressures the assemblage (Al + F) titanite + anorthite + rutile + fluorite is stable.

The reduction in titanite activity resulted in shifts from the stoichiometric equilibrium of 1.60 GPa to 1.15 ± 0.05 GPa at 900°C, 1.79 GPa to 1.375 ± 0.025 GPa at 1000°C and from 1.98 GPa to 1.575 ± 0.025 GPa at 1100°C. The activity of $\text{CaTiSiO}_4\text{O}$ is closely approximated by an ideal molecular activity model (X_{Ti}) at 1100°C, but shows a negative deviation at 1000°C and 900°C from ideality. Since the chemical data at 900°C and 1000°C show large uncertainties, due to chemical heterogeneities in the experiments, the molecular activity model as an approximation is recommended for use in calculations for titanites with $X_{\text{Al}} = 0.1 - 0.4$, until more data are available. Although our data were obtained at high temperatures (900–1100°C), they provide important constraints on the use of a possible activity model for petrological calculations. The current data do *not* allow the extraction of meaningful values of the interaction parameter, W , of a regular solid solution model, due to the chemical

variations of the (Al + F) titanite compositions and the experimental uncertainties. For calculations involving natural (Al + F)-rich titanites in the compositional range of $X_{\text{Al}} = 0.1 - 0.3$, the molecular model seems to be the better approach to predict the activity of $\text{CaTiSiO}_4\text{O}$ in titanite than the ionic models at high temperatures.

Troitzsch and Ellis (2002) recently published a study on the thermodynamic properties of F-Al titanite. In contrast to this study by Tropper et al. (2002), the two studies differ in the choice of the activity model and the estimated values of the interaction parameter W for the solid solution. In our calculations we used a simple symmetrical model, which resulted in a negative deviation from ideality, in contrast to the slight positive deviation in their local balance and multi-site mixing models. The data for W obtained in our study are directly based on experiments and have definitive negative deviations. Recalculation of the P - T conditions of three eclogites illustrates the difference in pressure estimates resulting from the choice of different activity models (molecular vs. ionic) ranging from 0.05 to 2.1 GPa, depending on the $\text{CaAlSiO}_4\text{F}$ substitution in the natural titanites and the sensitivity of reactions to changes in the activity of $\text{CaTiSiO}_4\text{O}$ in titanite.

Troitzsch, U & Ellis, D.J., 2002: *Contrib. Mineral. Petrol.*, 142, 543-563.

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Some Insights on the geotectonic evolution of the central Southern Alps (Dolomites) along the Transalp-Traversal: Thermal maturity data and basin modelling

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The Permo-Mesozoic sedimentary succession along the TRANSALP-Traversal in the central Dolomites is very well

suited for combining thermal maturity investigations and basin modelling in order to unravel the thermal and