



Titanite thermobarometry in metamorphic rocks: the influence of titanite activity models in the system $\text{CaTiSiO}_4\text{O} - \text{CaAlSiO}_4\text{F}$ on phase equilibrium calculations in high- P rocks

Peter Tropper

Institute of Mineralogy and Petrography, Faculty of Geo- and Atmospheric Sciences,
University Innsbruck, Innrain 52, A-6020 Innsbruck, Austria (Peter.Tropper@uibk.ac.at)

Titanite is a common accessory mineral in mafic, pelitic and granitic rocks from many geologic environments which often deviates significantly from its ideal composition by the substitution Al and F, OH for Ti for O. The Al + OH (Ti + O substitution leads to the Al-OH end-member vuagnatite $\text{CaAlSiO}_4(\text{OH})$, which has a different structure than titanite and is typical of low temperature geologic environments. By contrast, the F-Al substitution is isostructural and is common at high metamorphic temperatures ($>500 - 600^\circ\text{C}$) and pressures. Since titanite is a common accessory mineral, it could reliably be used in phase equilibrium calculations, if the activity-composition relations in (Al + F)-bearing titanites were sufficiently known. Experimental investigations by Troitzsch and Ellis (2001, CMP, 142, 543) and Tropper et al. (2002, JPet., 43, 1787) derived non-ideal mixing models for solid solutions along the join $\text{CaTiSiO}_4\text{O} - \text{CaAlSiO}_4\text{F}$. Whereas Tropper et al. (2002) derived a negative interaction parameter, W , Troitzsch and Ellis (2001) obtained regular activity models, which included both positive and negative W 's, but they favored a positive W . These differences strongly influence calculated non-ideal titanite activities because the model of Troitzsch and Ellis (2001) yields higher $a(\text{CaTiSiO}_4\text{O})$ at $X_{\text{Al}} > 0.2$.

Although more experiments are needed to better constrain the activity-composition relationships along the join $\text{CaTiSiO}_4\text{O} - \text{CaAlSiO}_4\text{F}$ at lower temperatures, our result that the activity coefficients are < 1 at high T indicates a large degree of non-ideal behavior even at high T ($>900^\circ\text{C}$), which in turn will affect thermobarometric calculations involving titanite. Comparing available simple activity models with the regular

models shows that the $a(\text{CaTiSiO}_4\text{O})$ at these temperatures is substantially underestimated by the fully ionic model used by Manning and Bohlen (1991, CMP, 109, 1), in which $a_{\text{CaTiSiO}_4\text{O}} = X_{\text{Ca}}X_{\text{Ti}}X_{\text{Si}}X_{\text{O}}^5$. This model assumes independent mixing of Al for Ti and random mixing of F and O on all O sites. However, according to Oberti *et al.* (1991, EJM, 3, 777), F substitutes only in one O site (O1) and a fully ionic model should therefore be recast as $a_{\text{CaTiSiO}_4\text{O}} = X_{\text{Ca}}X_{\text{Ti}}X_{\text{Si}}X_{\text{O}}$, where X_{O} indicates the mole fraction of O on the (O1) site. The substitution of F on the O1 site is coupled with Al, so it is called the ideal coupled model. In contrast to the regular model, the two ionic models display a much stronger negative deviation from ideality, which is supported only by extrapolating the experimental results to much lower T ($<600^\circ\text{C}$). On the other hand, the data also show that the experimentally determined activity is very close to the ideal molecular activity model (X_{Ti}) at very high ($>900^\circ\text{C}$) temperatures and therefore the molecular activity model is recommended for use in high- T metamorphic rocks until more data are available. The activity of $\text{CaTiSiO}_4\text{O}$ in (Al + F) titanites is far better approximated by an ionic model for rocks at low T ($<600^\circ\text{C}$) and the molecular model at high T ($>900^\circ\text{C}$). Until similar experiments are obtained on $\text{CaTiSiO}_4\text{O}$ - $\text{CaAlSiO}_4\text{OH}$, the same mixing parameters may be applied provisionally to that join as well.

Recalculations of the $P - T$ conditions of three eclogites from Manning and Bohlen (1991, CMP, 109, 1), as well as calculations of simple phase equilibria in eclogites such as pyrope + 6 titanite = 3 diopside + grossular + 6 rutile, illustrate the difference in P estimates resulting from the choice of three different activity models (molecular vs. regular vs. ionic) ranging from 0.05 to 2.0 GPa, depending on the extent of $\text{CaAlSiO}_4\text{F}$ substitution in natural titanites and the sensitivity of titanite-bearing reactions to changes in the activity of $\text{CaTiSiO}_4\text{O}$.