



Titanite-rutile thermobarometry in ultrahigh-pressure metamorphic rocks

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Titanite, an important accessory mineral in ultrahigh-pressure (UHP) rocks, often deviates significantly from its ideal composition ($\text{CaTiSiO}_4\text{O}$) by the substitution Al and F, OH for Ti for O. Such compositional variability means that titanite could reliably be used in phase equilibrium calculations, if the activity-composition relations in (Al + F)-bearing titanites were sufficiently known. Schreinemakers analysis in the system $\text{CaO} - \text{MgO} - \text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ (CMTAS) involving the assemblage garnet + titanite + clinopyroxene + rutile + coesite yields two equilibria suitable for geothermobarometry. The equilibrium

Grossular + Rutile + Coesite = Titanite + Kyanite

has a dP/dT slope ($6.2 \cdot 10^{-5} \text{ GPaK}^{-1}$) and is potentially useful for geobarometry: The equilibrium

Grossular + Rutile + Diopside = Titanite + Pyrope

has a steep slope ($2.5 \cdot 10^{-4} \text{ GPaK}^{-1}$) in $P - T$ space and could therefore be used as geothermometer. Application of these two titanite-rutile-involving equilibria to rocks from four UHP terranes (Kokchetav Massif, Yinggelisay Area, Dora Maira Massif, Dabie Shan) shows that using ionic activity models for the calculations yields the best convergence with independently established P estimates. In terms of T estimates,

high-Al ($X_{Al} > 0.5$) titanites yield a large variation of up to 300°C in T and low-Al ($X_{Al} < 0.2$) titanites yield the best convergence with independently established T estimates. Until better activity constraints are available, the user is recommended to use either the ideal ionic model for titanite solid solutions involving mixing on the Ti and the O1-site and compare the results to an experimentally derived activity model, or use a range of different activity models (ionic and regular) to at least obtain a range of $P - T$ conditions. This study clearly shows that the difference in P and T estimates resulting from the choice of different activity models for $a_{CaTiSiO_4O}$ is large and ranges from 0.05 to 3.0 GPa and up to 300°C, depending on the extent of $CaAlSiO_4F$ substitution in natural titanites and the sensitivity of titanite-bearing reactions to changes in the activity of $CaTiSiO_4O$. Therefore titanite-rutile-involving thermobarometry should only be applied to UHP rocks if independent, more robust $P - T$ estimates are available.