The current status of titanite–rutile thermobarometry in ultrahigh-pressure metamorphic rocks: The influence of titanite activity models on phase equilibrium calculations

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ABSTRACT

Titanite, an important accessory mineral in ultrahigh-pressure (UHP) rocks, commonly deviates significantly from its ideal composition ($CaTiSiO_4O$) by the substitution of Al and (F, OH) for Ti for O. This compositional variability of titanite could 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 ([Troitzsch, U. and Ellis, D.J. (2002) Thermodynamic properties and stability of AlF-bearing titanite $CaTiOSiO_4$–$CaAlFSiO_4$. Contributions to Mineralogy and Petrology, 142, 543–563]) and Tropper et al. ([Tropper, P., Manning, C., Essene, E.J. 2002. The substitution of Al and F in Titanite at high pressure and temperature: experimental constraints on phase relations and solid solution properties. Journal of Petrology 43, 1787–1814.) derived non-ideal-mixing models for solid solutions along the join $CaTiSiO_4O$–$CaAlSiO_4F$. Tropper et al. [Troitzsch, U. and Ellis, D.J. (2002) Thermodynamic properties and stability of AlF-bearing titanite $CaTiOSiO_4$–$CaAlFSiO_4$. Contributions to Mineralogy and Petrology, 142, 543–563] derived a preliminary regular model in the *T* range 900–1100 °C, in which the *T*-dependent interaction parameter, W_G, was negative. In contrast, Troitzsch and Ellis ([Troitzsch, U. and Ellis, D.J. (2002) Thermodynamic properties and stability of AlF-bearing titanite $CaTiOSiO_4$–$CaAlFSiO_4$. Contributions to Mineralogy and Petrology, 142, 543–563]) favored a regular activity model with positive W_G. The different signs of the interaction parameter strongly influence calculated non-ideal titanite activities. Comparing available simple ideal ionic (coupled-ionic, non-coupled-ionic) activity models with the non-ideal models shows that $a_{CaTiSiO_4O}$, calculated with the ideal ionic models is substantially lower at almost all *T*. Calculation of two suitable titanite–rutile-involving equilibria for thermobarometry applied to literature data from rocks from four UHP terranes shows that ideal ionic models yield the best convergence with independently established *P* estimates. Although the literature data have to be treated with caution (e.g. retrogression, compositional disequilibrium etc.), the calculations nonetheless indicate that 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. This study shows that *P* and *T* estimates derived from ideal models and experimentally constrained non-ideal models for titanite activity may show large deviations at UHP conditions, ranging from 0.05 to 3.0 GPa and up to 300 °C. Therefore the current status of titanite–rutile-involving thermobarometry allows it only to be applied to Al-rich ($X_{Al}>0.2$) titanites from UHP rocks if independent, more robust *P–T* estimates are available. Until better activity constraints are available, it is recommended that the user employ either the ideal coupled-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 adopt a range of different activity models (ionic and regular) to obtain a range of *P–T* conditions.

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1. Introduction

At ultrahigh ultrahigh-pressure (UHP) metamorphic conditions (>2.5 GPa, Liou et al., 1994; Coleman and Wang, 1995; Liou et al., 1998), most silicate lithologies contain a similar eclogitic mineral assemblage, consisting of garnet, clinopyroxene, quartz/coesite, phengite, rutile±titanite, kyanite and zoisite (e.g. Liou et al., 1998). The low variance of eclogite mineral assemblages has long posed

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problems for derivation of intensive parameters attending metamorphism, such as temperature (T) and pressure (P). One strategy to solve this problem has been to use compositions of phengite in geothermobarometry (e.g. Page et al., 2007). However, phengite solid solutions are problematic because thermodynamic data for Si-rich micas are not well characterized, preservation of peak compositions can be problematic, and many potentially useful equilibria depend on H_2O activity, which is not known independently. An alternative approach to thermobarometry of UHP rocks is to take advantage of coexisting accessory phases such as titanite and rutile.

Titanite [$Ca(Ti,Al,Fe^{3+})SiO_4(O,F,OH)$] is a common accessory mineral in mafic, carbonate, pelitic and granitic rocks from many geologic environments (Higgins and Ribbe, 1976; Ribbe, 1982; Enami et al., 1993). Because of its participation in net-transfer equilibria, titanite can be useful for the evaluation of pressure (P), temperature (T), and the fugacities of volatile components associated with metamorphic and igneous processes (e.g. Manning and Bohlen, 1991; Ghent and Stout, 1994; Xirouchakis and Lindsley (1988); Frost et al., 2000; Troitzsch and Ellis, 2002; Tropper et al., 2002; Harlov et al., 2006; Page et al., 2007). Al–F-bearing titanites are also common in UHP rocks (Sobolev and Shatsky, 1990, Shatsky et al., 1995; Cong et al., 1995; Rubatto and Hermann, 2001; Ogasawara et al., 2002; Castelli et al., 2007). The association of F–Al-rich titanites with high high-pressure environments has led to the suggestion that equilibria involving titanite solid solutions may be useful for constraining intensive variables attending high-P metamorphism (Smith, 1977; Franz and Spear, 1985; Gibert et al., 1990, Manning and Bohlen, 1991; Enami et al., 1993; Ghent and Stout, 1994; Carswell et al., 1996; Markl and Piazolo, 1999; Rubatto and Hermann, 2001; Castelli and Rubatto, 2002; Tropper et al., 2002; Troitzsch and Ellis, 2002; Castelli et al., 2007).

Tropper et al. (2002) applied several titanite activity models to phase equilibrium calculations and concluded that choice of activity model has a significant effect on the results. Therefore, knowledge of appropriate activity models describing titanite solid solutions is essential. This study focuses on the thermodynamics of mixing of titanite solid solutions along the join $CaTiSiO_4O$–$CaAlSiO_4F$, the influence of activity models on phase equilibrium calculations, and the evaluation of the robustness of three titanite-involving equilibria used for thermobarometry and XCO_2 determinations in UHP rocks.

2. The a–X relations in titanite solid solutions in the system $CaTiSiO_4O$–$CaAlSiO_4F$

2.1. Crystal chemical constraints on activity–composition relations in titanite solid solutions

Titanite is an orthosilicate consisting of chains of TiO_6 octahedra which are linked by isolated Si-tetrahedra and CaO_7 polyhedra. At low T, synthetic, pure titanite has space group $P2_1/a$, but it transforms to $A2/a$ at 220±20 °C at 1 atm (Speer and Gibbs, 1976; Taylor and Brown, 1976, Ribbe, 1982). Experimental investigations have shown that the transition temperature is also a function of increasing P and the slope of the phase transition is −180 K/GPa (Kunz et al., 1996, 2000). In addition to T, substitution of other elements also yields the $A2/a$ structure (Higgins and Ribbe, 1976). Anion substitution is restricted to the under-bonded O1-site, of which there is one per formula unit (Taylor and Brown, 1976; Higgins and Ribbe, 1976; Oberti et al., 1991). Cation substitution can occur on any of the three distinct cation sites, the Ca-site, the Ti-site and the Si-site; however, substitution on the Si-site is very minor in crustal titanites (Oberti et al., 1991), only becoming significant above 4 GPa (Knoche et al., 1998), and substitution on the Ca-site (typically REE) is generally stoichiometrically negligible except in some pegmatites (Deer et al., 1992). Hence, only cation substitution on the octahedral Ti-site usually need be considered in activity models.

The main cations on the Ti-site in addition to Ti are Al and Fe^{3+}. Since these cations are trivalent, coupled substitutions are required. Examples include Al, $Fe^{3+}+F=Ti+O$ and Al, $Fe^{3+}+OH=Ti+O$ (Hollabaugh, 1980; Franz and Spear, 1985; Bernau et al., 1986; Fehr, 1991; Oberti et al., 1991; Enami et al., 1993; Carswell et al., 1996). Oberti et al. (1991) showed that the $Al+F=Ti+O$ substitution is isostructural since all Al-bearing titanites in their investigation showed $A2/a$ symmetry. Structural investigations by Oberti et al. (1991) have shown that the loss in charge due to Al substitution is balanced mainly by the presence of F and OH on the O1 position. The extent of the $Al+F$ substitution in natural titanites is high but complete solid solution in the system $CaTiSiO_4O$–$CaAlSiO_4F$ has only been observed in experimental investigations so far (Troitzsch et al., 1999a,b; Tropper et al., 2002). The $Al+OH=Ti+O$ substitution leads to the Al–OH end-member vuagnatite $CaAlSiO_4(OH)$, which has a different structure than titanite (space group $P2_12_12_1$; McNear et al., 1976) and is typical of low-T geologic environments (Enami et al., 1993). Oberti et al. (1991) and Troitzsch and Ellis (1999a) have shown that the unit cell volume of titanite solid solutions decreases with increasing Al content due to a strong contraction of the octahedral Ca-site geometry. This, and the occurrence of Al-bearing titanites in eclogites, led to the speculation that Al-rich titanites are a strong indicator of high-P conditions (e.g., Smith, 1988). However, Markl and Piazolo (1999), Troitzsch and Ellis (2002) and Tropper et al. (2002) showed that Al–F substitution in titanite may occur over a wide range of P, given the appropriate bulk chemical composition of the host rocks.

2.2. The chemical composition of titanite in UHP rocks

Titanite compositions in UHP rocks range from nearly stoichiometric $CaTiSiO_4O$ to compositions rich in Al, Fe, F and OH and the occurrence of the Al–F substitution titanites in UHP rocks is widespread (Sobolev and Shatsky, 1990; Shatsky et al., 1995; Cong et al., 1995; Carswell et al., 1996; Rubatto and Hermann, 2001; Ogasawara et al., 2002; Castelli et al., 2007). Most titanites in UHP terranes contain significant Al and F contents and the maximum value of Al and F reported so far are 0.42 a.p.f.u. from the Kokchetav Massif, Kazakhstan (Sobolev and Shatsky, 1990; Shatsky et al., 1995). Fig. 1A is a plot of $Al+Fe^{3+}$ vs. F of titanite compositions from the UHP rocks considered in this study (Castelli et al., 2007; Liu et al., 2004; Ogasawara et al., 2002; Shatsky et al., 1995). This figure shows that the data plot close to the 1:1 ($Al+Fe^{3+}$)+F substitution line, where most data lie slightly below the 1:1 line indicating a small degree of ($Al+Fe^{3+}$)+OH substitution. It is also interesting to note that titanites from rocks that experienced >6 GPa show an excess of F over Al on the order of 0.02–0.04 a.p.f.u. (Ogasawara et al., 2002). This indicates that the F-involving substitution is dominant in the titanites considered in this investigation. Fig. 1B illustrates the relations between X_F [$F/(F+OH)$] and X_{Al} [$Al/(Al+Fe^{3+})$]. This plot not only shows that the Al–OH substitution is usually small and ranges from 0 mol% to 25 mol% since calculated OH [($Al+Fe^{3+}$)−F] is <0.1 a.p.f.u. but also that Fe^{3+} plays a very minor role in the F and OH substitution in these titanite solid solutions since X_{Al} varies between 0.95 and 0.99. Therefore for the calculations presented below, very minor Fe^{3+} is neglected and only titanites with a small degree of OH substitution (<15 mol%), as close as possible to the Al–F join are used. In contrast to the substitution on the octahedral site, almost no substitution occurs on the Ca-site. The Ca values range from 0.98 (Liu et al., 2004) to 1.02 a.p.f.u. (Cong et al., 1995).

In addition to the Al–F substitution, some titanites from UHP rocks such as the Kokchetav Massif (Kumdy-kol) and the Yinggelisay area also show evidence for Si substitution on the Ti-site (Ogasawara et al., 2002; Liu et al., 2004), which will have an influence on activity calculations; however, no a–X data exist along the join $CaTiSiO_4O$–$CaTi_{1-X}Si_XSiO_4O$. In this study we will focus only on Al–F rich titanites
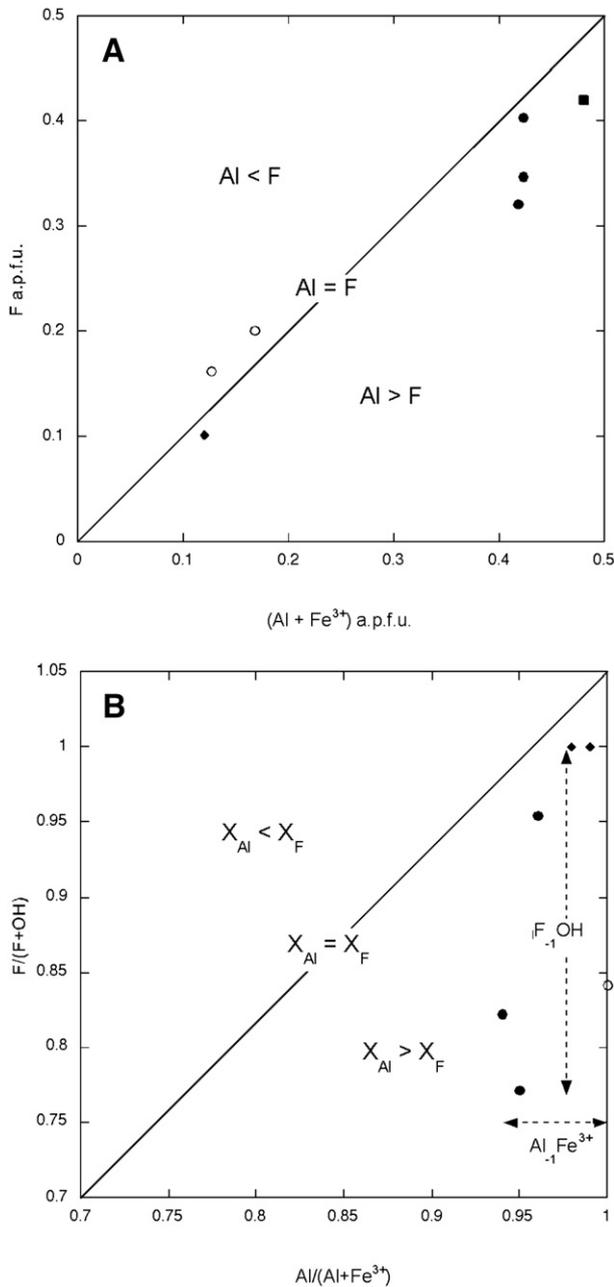
Fig. 1. (A): Plot of $(Al+Fe^{3+})$ a.p.f.u. vs. F a.p.f.u. of titanite compositions from a variety of UHP rocks considered in this study (black diamond: Castelli et al., 2007; black circle: Liu et al., 2004; open circle: Ogasawara et al., 2002; black square: Shatsky et al., 1995). (B): Plot of X_F [F/(F+OH)] vs. X_{Al} [Al/(Al+Fe^{3+})]. The symbols are the same as in (A).

to illustrate the influence of $a_{CaTiSiO_4O}$ on phase equilibrium calculations which are presented below.

2.3. Ideal activity–composition relations in titanite solid solutions

Ideal activities, applied to solid solutions, involve mixing of ions on one or more sites. If cation substitution only occurs on one Ti Ti-site per formula unit, the mole fraction of Ti on this octahedral site, X_{Ti}, is sufficient for an ideal activity model in which $a_{CaTiSiO_4O}=X_{Ti}$. This model will be called the molecular model; it usually yields an upper bound for $a_{CaTiSiO_4O}$. Ghent and Stout (1994) employed a two-site ideal-mixing model, where mixing takes place on the Ca- and the Ti-site only, and anion mixing was neglected. Thus, according to their model, $a_{CaTiSiO_4O}=X_{Ca}X_{Ti}$. If no substitution occurs on the Ca-site, this

reduces to the molecular model. Manning and Bohlen (1991) accounted for both cation and anion substitutions assuming an ideal fully ionic model in which $a_{CaTiSiO_4O}=X_{Ca}X_{Ti}X_{Si}X_O^5$. This model does not take into account the apparent coupling of anion substitution for Al+Fe on the Ti-site (e.g., Oberti et al., 1991) and also assumes random mixing of F and O on all O sites. We call it the ideal non-coupled-ionic model. However, because F substitutes only in one O site (O1), the ideal fully ionic model used by Manning and Bohlen (1991) should be recast as $a_{CaTiSiO_4O}=X_{Ca}X_{Ti}X_{Si}X_{O1}$, where X_{O1} indicates the mole fraction of O on the (O1) site. Since the substitution of F on the (O1) site is coupled with Al, this model is called the ideal coupled-ionic model and ("O et al., 1991 model in the figures following Oberti et al., 1991). Assuming there is no significant substitution in crustal rocks on the Ca-site and on the Si-site, this model reduces to $a_{CaTiSiO_4O}=X_{Ti}X_{O1}$. Although experimental data are lacking it is assumed that the energetics of the Al–OH exchange are equivalent to the Al–F exchange, since both anions show a similar crystal chemical behaviour (Oberti et al., 1991), thus it is possible to use the total Al content of titanite for the activity calculations. In addition, the lack of substitution on the Ca-site also allows application of the ideal coupled-ionic model. Unlike the molecular model, both ionic (coupled-ionic, non-coupled-ionic) models require a negative deviation of activity from the mole fraction (Fig. 2).

2.4. Non-ideal activity–composition relations in titanite solid solutions

Despite the importance of the F–Al substitution in titanite, there are few experimental data available which allow evaluation of the physical and chemical controls on this solid solution. The F–Al substitution was examined experimentally by Smith (1981), Troitzsch and Ellis (1999a,b, 2002) and Tropper et al. (2002). Smith (1981) synthesized titanite with about 50 mol% F–Al titanite substitution at 1000–1200 °C and 1.5–3.5 GPa, similar to the upper limit of substitution reported from various natural occurrences. He found an increase in the F–Al substitution with decreasing temperature and increasing pressure, but since his investigations only focused on the synthesis of Al–F rich titanites, no quantitative constraints on the solid solution behavior were deduced. Troitzsch and Ellis (1999a,b, 2002) and Tropper et al. (2002) synthesized F–Al-rich titanite with
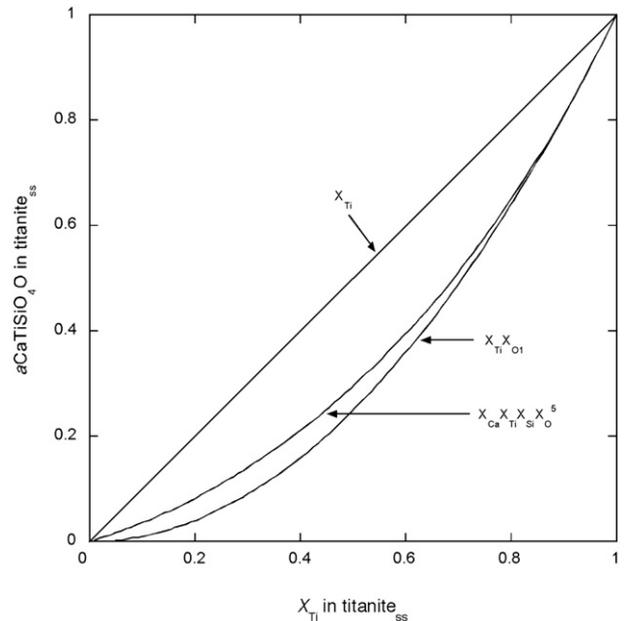

Fig. 2. Comparison between the ideal molecular model (X_{Ti}) and the ideal ionic models (coupled-ionic model $X_{Ti}X_{O1}$, non-coupled-ionic model $X_{Ca}X_{Ti}X_{Si}X_O^5$). X_{O1} indicates the mole fraction of O on the O1-position.

compositions ranging from $X_{Al}=0.5$ to $X_{Al}=1$ at 900–1100 °C and P ranging from 0.05–4 GPa. Both studies demonstrated complete solid solution in the system $CaTiSiO_4O$–$CaAlSiO_4F$ and also attempted to derive mixing properties of Al–F-bearing titanite solid solutions.

2.4.1. The study of Troitzsch and Ellis (2002)

Troitzsch and Ellis (2002) performed experiments in the range of 800–1000 °C and 0.5 to 2.1 GPa and measured the P- and T-dependence of X_{Al} in titanite solid solutions in the assemblage F–Al titanite+anorthite+fluorite based upon the reaction:

$$CaAl_2Si_2O_8 + CaF_2 = 2CaAlSiO_4F \qquad (1)$$

Anorthite + Fluorite = F–Al–Titanite

From these P–T–X_{Al} data, free-energy minimization allowed the simultaneous calculation of ΔH_f, S_{298} and (W_H–TW_S) involving two activity models, a multi-site mixing model (MM) and a local local-charge balance model (LCB). The MM model assumes independent distribution of Al and F on each site [$a_{CaTiSiO_4O}=(X_{Ti}^2)\gamma_{CaTiSiO_4O}$] and the LCB model assumes coupled substitution of Al and F [$a_{CaTiSiO_4O}=(X_{Ti})\gamma_{CaTiSiO_4O}$]. In addition, Troitzsch and Ellis (1999b) obtained XRD data on the complete solid solution, which showed a small negative deviation below $X_{Al}=0.15$ and a large positive deviation of the unit cell volume with a maximum at $X_{Al}=0.54$. These excess volume data allowed calculation of a positive W_V of 214.08 J kbar^{-1}. Depending on the activity model used, they obtained T-independent values for (W_H–TW_S) ranging from 13.6 kJ mol^{-1} (MM) to −9.1 kJ mol^{-1} (LCB). Since the MM model yielded a better fit to the data, as well as a value of W_V comparable to their XRD data, Troitzsch and Ellis (2002) favored the positive (W_H–TW_S) interaction parameter, thus indicating that there might be a tendency to unmix in this system. Fig. 3 shows activity–composition isotherms calculated using the MM and the LCB models at P of 2 GPa. The MM model shows a clear positive deviation from the molecular model at low T and $X_{Al}>0.5$ and a negative deviation at $X_{Al}<0.5$. Increasing T results in an increasingly negative deviation from X_{Ti} (Fig. 3A). In contrast, the LCB model shows an increasingly negative deviation from X_{Ti} with decreasing T (Fig. 3B). Troitzsch and Ellis (2002) derived a positive W_V, which leads to an increase in $a_{CaTiSiO_4O}$ in similar magnitude in both models with increasing P as shown at 700 °C in Fig. 4A, B. In the low X_{Al} region <0.1, the difference in $a_{CaTiSiO_4O}$ resulting from different P is negligible.

2.4.2. The study of Tropper et al. (2002)

These experimental investigations were conducted at 900–1100°°C and 1.1–4.0 GPa. The activity of $CaTiSiO_4O$ in titanite solid solution was obtained from the displacement of the end-member reaction curve

$$CaTiSiO_4O + Al_2SiO_5 = CaAl_2Si_2O_8 + TiO_2 \qquad (2)$$
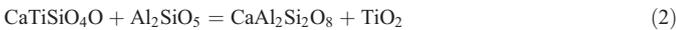
Titanite + Kyanite = Anorthite + Rutile

by adding fluorite to the experiments (e.g. Wood and Fraser, 1977; Schmid et al., 1978; Wood, 1988). This led to shifts from 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 $a_{CaTiSiO_4O}$ was obtained by using isothermal experiments and the activity of $CaTiSiO_4O$ in (Al+F) titanite was obtained from the relation

$$\int \Delta V_r dP = -RT \ln K \qquad (3)$$

where

$$K = a_{CaTiSiO_4O} \cdot a_{Al_2SiO_5} / a_{CaAl_2Si_2O_8} \cdot a_{TiO_2} \qquad (4)$$

and where ΔV_r is the average volume change of the reaction between the conditions of the end-member curve and the experimentally determined brackets. The activities of Al_2SiO_5 in kyanite, $CaAl_2Si_2O_8$ in anorthite and TiO_2 in rutile were assumed to be one. Solution of Eqs. (3) and (4) yielded the activity of $CaTiSiO_4O$ in (Al+F) titanite solid solutions of 0.42±0.04, 0.48±0.02 and 0.52±0.02 at 900 °C, 1000 °C and 1100 °C, respectively. These data indicate that $a_{CaTiSiO_4O}$ decreases with decreasing T. Assuming a local-charge balance (LCB) model, [$a_{CaTiSiO_4O}=(X_{Ti})\gamma_{CaTiSiO_4O}$], Tropper et al. (2002) obtained activity coefficients of 0.87±0.11 at 900 °C, 0.91±0.07 at 1000 °C and 1.02± 0.04 at 1100 °C. At the 1σ level, this showed nearly ideal mixing at 1100 °C and a negative deviation at 1000 °C and 900 °C (Fig. 5). Tropper et al. (2002) also used a symmetric mixing model which permitted calculation of the interaction parameter, W_G, which yielded −6.1±4.9 kJ/mole at 900°°C, −0.78±3.1 kJ/mole at 1000 °C and 0.93± 0.86 kJ/mole at 1100°°C for the calculations based on the midpoint of
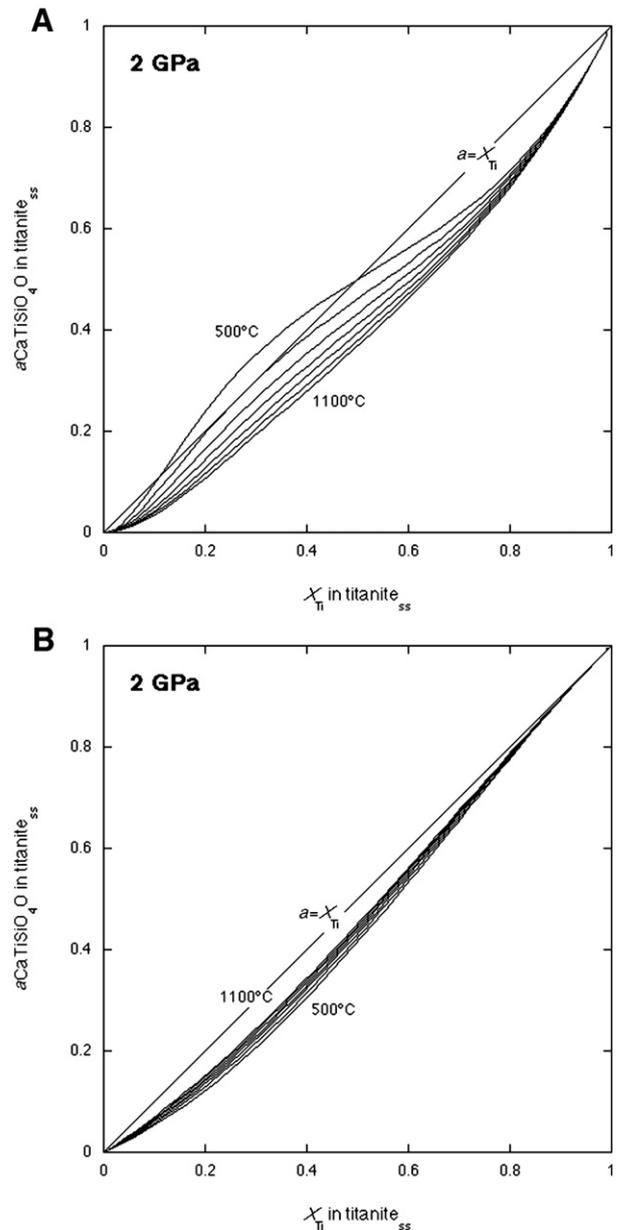

Fig. 3. Activity–composition (a–X) relationship in (Al+F)-bearing titanites from 500 °C to 1100 °C based on the regular mixing models derived by Troitzsch and Ellis (2002). (A): multi-site mixing model MM, (B): local local-charge balance model LCB. The ideal molecular model (X_{Ti}) is shown for comparison.

the brackets. In contrast to the results of Troitzsch and Ellis (2002), W_G derived in this study shows a strong T-dependence and the linear extrapolation of W_G leads to low $a_{CaTiSiO_4O}$ at $T<900$ °C (Fig. 5). As the errors indicate, the current data do *not* allow the extraction of meaningful values of the interaction parameter, W_G, of a regular solid solution model, due to the chemical variations of the (Al+F) titanite compositions and the experimental uncertainties. In addition, the experiments at 900 °C yielded the strongest negative deviation from ideality, probably due to sluggish reaction kinetics involving kyanite at this T (R. Newton, pers. Comm.), and these experiments should therefore be regarded with caution. It is possible that a large part of the Al+F substitution in titanite most likely occurred not according to reaction (2) but reaction (1) instead. Newton (1987) pointed out that overestimation of the T-dependence of thermodynamic properties of mixing is a common problem where the investigated T interval is small. Therefore extrapolation of this activity model should be regarded as preliminary and the low-T extrapolations will be shown
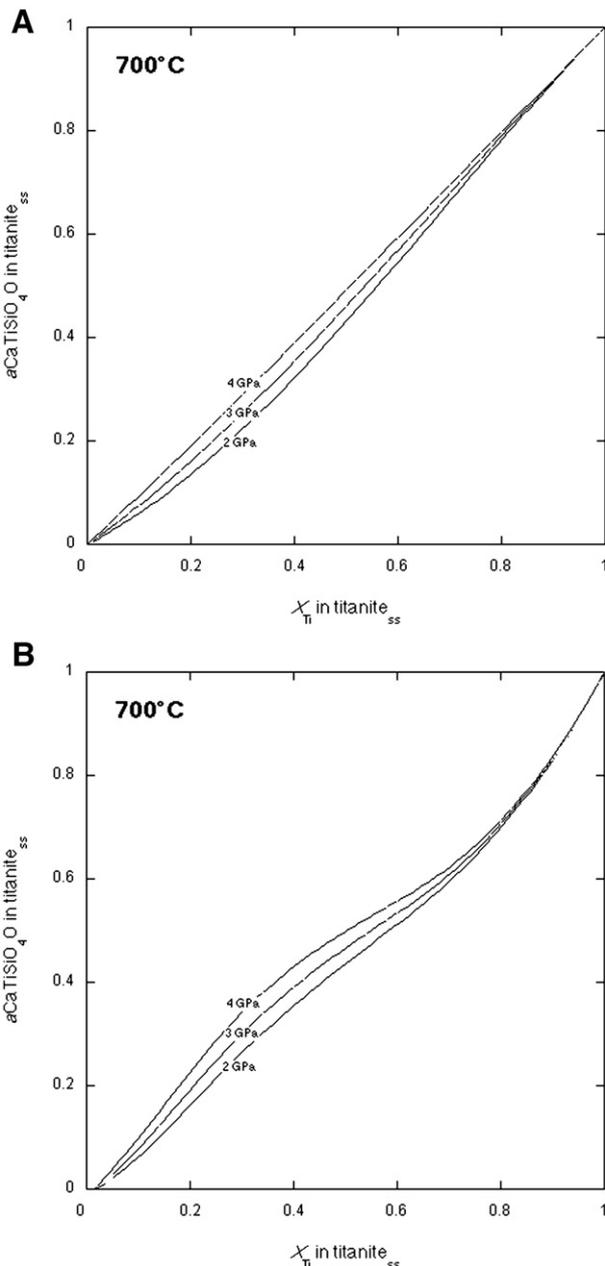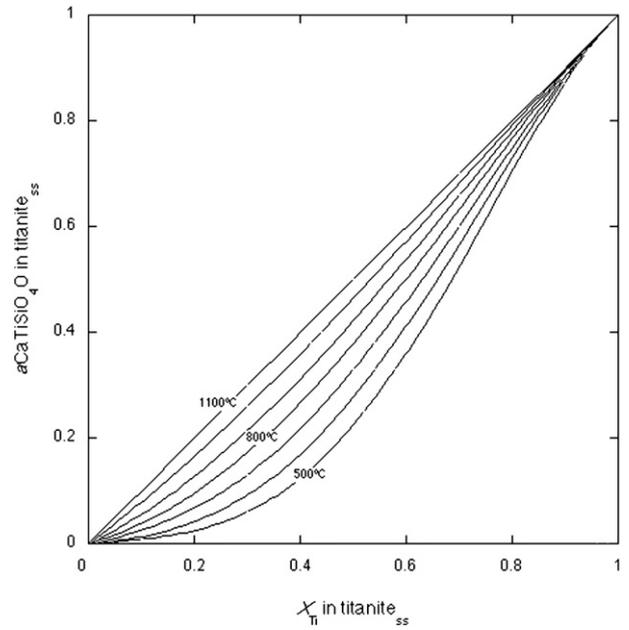

Fig. 5. Calculated a–X relations between 500 °C and 1100 °C based on the regular mixing model derived by Tropper et al. (2002).

only for comparison with the other models. Extrapolation of the model to low T as shown in Fig. 5 yields a very large deviation from the molecular model, which is much more pronounced than the LCB model of Troitzsch and Ellis (2002) as shown in Fig. 3B due to the strong T-dependence of W_G.

3. Geothermobarometry involving titanite solid solutions in UHP rocks

In high-pressure rocks, coexisting titanite and rutile form the basis for a set of equilibria useful for the determination of P (Manning and Bohlen, 1991; Tropper et al., 2002). Manning and Bohlen (1991) discussed the application of titanite-involving equilibria to two high-P localities (Glenelg, Scotland, and the Tauern Window, Austria) and one UHP locality (the Kokchetav Massif, Kazakhstan). Tropper et al. (2002) subsequently recalculated the P–T conditions of these three localities, comparing calculations with their activity model with calculations using ionic and molecular models. Rubatto and Hermann (2001) and Castelli et al. (2007) applied titanite–rutile-involving equilibria to the UHP rocks of the Dora Maira Complex in Italy. However, there has been no systematic attempt to assess the utility of titanite–rutile-based equilibria in calculation of P and T of UHP metamorphism so far. In the section below, we will discuss a set of H_2O-free titanite–rutile-involving equilibria usable for P–T calculations in UHP rocks. All calculations were performed with the program THERMOCALC v. 3.1. and the data base of Holland and Powell (1998). Activities of garnet and clinopyroxene were calculated with the program MacAX (Holland, 2000, written comm.). Rutile is assumed to be stoichiometric TiO_2.

3.1. Titanite–rutile equilibria useful for geothermobarometry in UHP rocks

Schreinemakers analysis in the system CaO–MgO–TiO_2–Al_2O_3–SiO_2 involving the assemblage garnet + titanite + clinopyroxene + rutile + coesite yields one invariant point as shown in Fig. 6. The equilibrium

$$Ca_3Al_2Si_3O_{12} + 3TiO_2 + SiO_2 = 3CaTiSiO_5 + Al_2SiO_5 \qquad (5)$$

Grossular + Rutile + Coesite = Titanite + Kyanite

Fig. 4. Pressure dependence of the activity models of Troitzsch and Ellis (2002) at 700 °C and P ranging from 2 GPa to 4 GPa. (A) MM model and (B) LCB model.
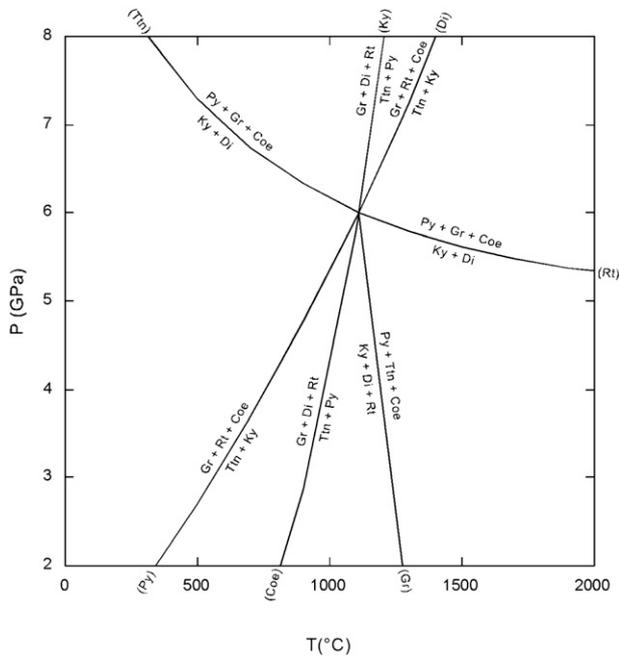
Fig. 6. Calculated end-member phase relations in the system CaO–MgO–TiO$_2$–Al$_2$O$_3$–SiO$_2$ (CMTAS) using the program THERMOCALC v. 3.1. and the data base of Holland and Powell (1998). Gr: grossular, Py: pyrope, Di: diopside, Ttn: titanite, Rt: rutile, Ky: kyanite, Coe: coesite.

shows an average dP/dT slope of 6.2·10^{-5} GPa K^{-1} and has been shown to be potentially useful for geobarometry: Fig. 6 also shows that the equilibrium

$$Ca_3Al_2Si_3O_{12} + 6TiO_2 + 3CaMgSi_2O_6 = 6CaTiSiO_5 + Mg_3Al_2Si_3O_{12} \quad (6)$$
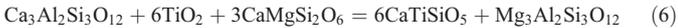
Grossular + Rutile + Diopside = Titanite + Pyrope

indicates an average steep slope (2.5·10^{-4} GPa K^{-1}) in P–T space and could therefore be used as a geothermometer. In the next section, we compare the positions of reactions (5) and (6) as calculated using six different activity models for $a_{CaTiSiO_4O}$, namely three ideal models (molecular, coupled-ionic, non-coupled-ionic) and three non-ideal models, the regular model by Tropper et al. (2002) and the LCB and MM models of Troitzsch and Ellis (2002). Since all compositional data presented in this section were taken from the literature, equilibration among the coexisting phases cannot be verified, which clearly leads to uncertainties in the absolute P–T determinations. Therefore it is the primary aim of this section to demonstrate the influence of changing $a_{CaTiSiO_4O}$ on the relative position of the titanite–rutile involving equilibria (5) and (6) and its possible use for geothermobarometric applications in UHP rocks.

3.2. Geothermobarometry using garnet + clinopyroxene + kyanite + titanite + rutile + coesite

3.2.1. Kokchetav Massif, Kazakhstan

The P–T conditions from Kokchetav Massif have been determined to be 900–1000 °C and >4 GPa based on garnet–cpx thermometry and titanite–rutile-involving phase equilibria (Manning and Bohlen, 1991; Shatsky et al., 1995). Although most of the T conditions from Kokchetav Massif have been determined to be in the range of 850–1000 °C, the overall spread in T based on garnet–clinopyroxene thermometry varies for the garnet–clinopyroxene–quartz sample from 670 °C to 1030 °C depending on the calibration used (Shatsky et al., 1995). Shatsky et al. (1995) report a complete assemblage from a garnet–pyroxene–quartz rock (sample 258) from the Kokchetav

Massif. Titanite from this sample is Al–F rich and contains 0.46 a.p.f. u. Al and 0.42 a.p.f.u F, indicating that almost all Al is involved in the Al–F substitution. The calculated $a_{CaTiSiO_4O}$ strongly varies with the activity model used, ranging from 0.308 (coupled coupled-ionic model) to 0.549 (LCB model of Troitzsch and Ellis, 2002). This results in enormous shifts of reaction (5) between 900 °C and 1000 °C, from 3.7 GPa to less than 0.5 GPa (Fig. 7). Manning and Bohlen (1991) and Tropper et al. (2002) calculated pressure using reaction (5) and the titanite-bearing mineral assemblage from sample 83/3 of Sobolev and Shatsky (1990), but had to use the titanite analysis from sample 258 since none was given for sample 83/3. These calculations resulted in much higher P estimates of up to 6 GPa, since the garnet in sample 83/3 showed a higher grossular component of ca. 30 mol% than in sample 258 which contains ca. 20 mol%.

Calculations of reaction (6), using the six activity models, results in a very large T range from 564 °C (ionic coupled model) to 840 °C (molecular model) at a P of 4 GPa as shown in Fig. 7. Due to the extreme shifts of reactions (5) and (6), almost no intersections could be calculated. Application of the regular models by Tropper et al. (2002) and the MM model of Troitzsch and Ellis (2002) yielded the only intersections, but at P below 0.5 GPa. It is interesting to note that calculation of reaction (5) using ionic models yields P close to the estimated value, whereas using the ionic models in the calculation of reaction (6), T is much too low. The latter result is likely due to the high reaction coefficient for titanite of six, which amplifies differences in $a_{CaTiSiO_4O}$ in the models.

3.2.2. Yinggelisay area, Altun Mountains, NW China

In the Yinggelisay area, P–T conditions of a granite gneiss were estimated to be ca. 1000 °C and 3.7–4.3 GPa based on the extent of Si substitution in titanite (Knoche et al., 1998) and ternary feldspar thermometry (Liu et al., 2004); however, they do not report a T range for the granite gneiss. In addition to this gneiss sample, Liu et al. (2004) report T from an UHP garnet lherzolite which range from
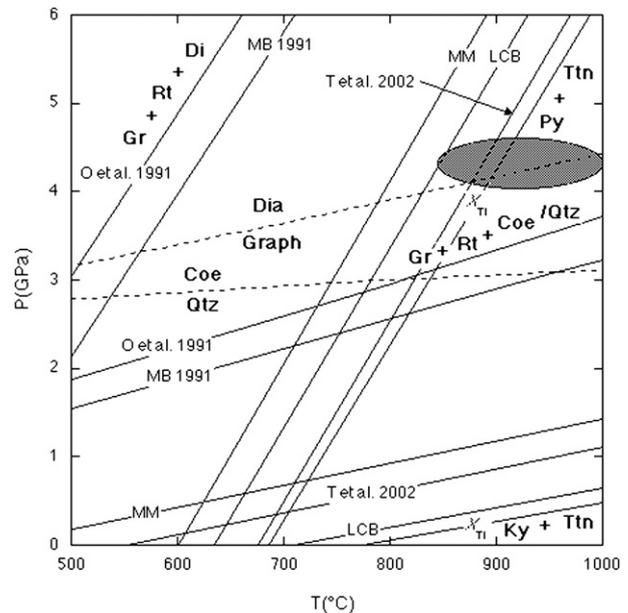

Fig. 7. Geobarometry of a garnet-bearing gneiss sample (258) from the Kokchetav Massif, Kazakhstan, using the mineral data from Shatsky et al. (1995). The labels on the curves indicate the three regular activity models (T et al., 2002, MM, LCB) and the three ideal activity models (molecular model X_{Ti}, coupled-ionic model O et al., 1991, non-coupled-ionic model MB 1991). Stippled lines indicate the solid–solid reactions α-quartz = coesite and graphite = diamond. The grey ellipse shows the independent P–T estimates by Manning and Bohlen (1991) and Shatsky et al. (1995). Mineral abbreviations: Gr: grossular, Rt: rutile, Di: diopside, Py: pyrope, Ttn: titanite, Ky: kyanite, Coe: coesite, Qtz: quartz, Dia: diamond, Graph: graphite.
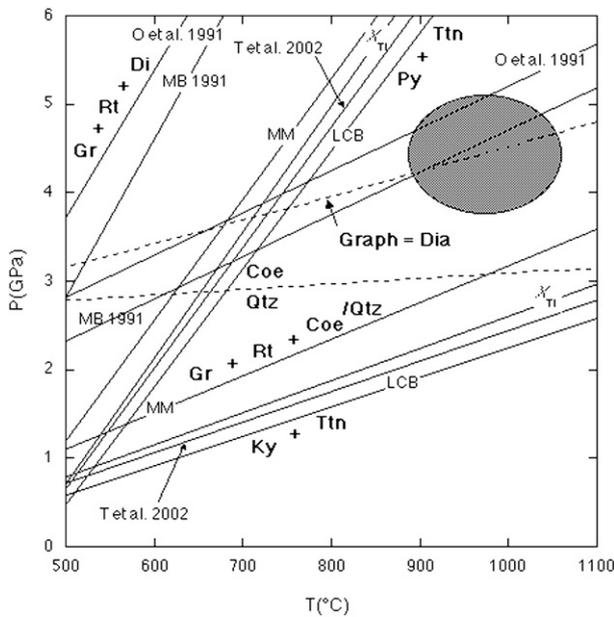
Fig. 8. Geobarometry of a garnet-bearing granite gneiss sample from the Yinggelisayi area, Altun Mountains, using the mineral data from Liu et al. (2004). The grey ellipse shows the independent P–T estimates from Liu et al. (2004). All other features are the same as in Fig. 7.

880 °C to 970 °C. Liu et al. (2004) derived UHP conditions in the Yinggelisayi area by using a granite gneiss with the UHP mineral assemblage garnet + clinopyroxene + perthitic feldspar + kyanite + zoisite + titanite + rutile + coesite. In contrast to the Kokchetav sample, titanite in these rocks shows abundant coesite exsolutions, although exsolution-free high-Al titanites also occur in this sample. These titanites contain ca. 0.40 a.p.f.u. Al and 0.32 to 0.40 a.p.f.u F, indicating that most Al is involved in the Al–F substitution. For the calculations we used a coesite-free titanite which contains equal amounts of Al and F. Activity calculations yielded a range of $a_{CaTiSiO_4O}$ values from 0.303 (coupled-ionic model) to 0.590 (LCB model of Troitzsch and Ellis, 2002), similar to the results from the Kokchetav sample. The shift in reaction (5) between 900 °C and 1100 °C is equally dramatic ranging from 5.5 GPa to 2.3 GPa as shown in Fig. 8.

Calculations of reaction (6) yielded a similar, but lower range of T at 4 GPa from 520 °C (ionic coupled model) to 810 °C (molecular model), like in the samples from the Kokchetav Massif. Although the T estimates from both samples are generally lower than the T reported, the large spread of the data of up to 300 °C also indicates that highly aluminous titanites ($X_{Al} > 0.4$) are unsuitable for a reliable application of reaction (6), owing to the combination of uncertainty in the activity models and the high stoichiometric coefficient of titanite of six in the reaction. Again, this also leads to an unusually large shift of the reactions to low T when multi-site mixing models are used in the calculations thus tainting the reliability of ionic models with geothermometric calculations, which have shown to be in good agreement with the results in terms of P. In order to test the reliability of reaction (6) as a thermometer in a more appropriate compositional range, the examples below were calculated using Al–F titanites with $X_{Al} < 0.2$.

3.3. Geothermometry using garnet + clinopyroxene + titanite + rutile

3.3.1. Dora Maira Massif, Western Alps, Italy

Rubatto and Hermann (2001) and Castelli et al. (2007) applied reaction (6) as an additional thermometric constraint to the UHP rocks of the Dora Maira Complex in Italy. Rubatto and Hermann (2001) investigated calc-silicate nodules in marbles. These nodules contain the UHP peak mineral assemblage calcite/aragonite + garnet +

clinopyroxene + epidote + titanite + rutile. The P–T conditions of the UHP event were determined to be 750–800 °C and 3.5 ± 0.5 GPa (Rubatto and Hermann, 2001). Titanite shows only minor Al–F substitution of ca. 10 mol% Al–F component. Rubatto and Hermann (2001) used an unspecified ideal-mixing model for titanite and obtained ca. 750 °C at 3.5 GPa in agreement with the garnet–phengite thermometer. Calculation of reaction (6) with the six activity models results in a range of T from 750 °C (ideal coupled- and non-coupled-ionic models and MM model) to 810 °C (molecular model, regular model and LCB model) at 3.5 GPa, which is in excellent agreement with the previous T estimates (Fig. 9).

Castelli et al. (2007) investigated two impure UHP marbles from the Brossasco-Isasca Unit in the southern Dora Maira Massif. The calcite marble contains the UHP mineral assemblage garnet + phengite + clinopyroxene + rutile + calcite/aragonite + titanite. According to textural evidence, titanite is part of a later, Alpine retrogression assemblage. Therefore, in this case, calculation of reaction (6) only yields a maximum T estimate. Titanite contains 0.1 F a.p.f.u. and due to an excess of Al over F, ca. 0.02 a.p.f.u. OH. Castelli et al. (2007) used the molecular model for their calculations and obtained ca. 730 °C and ca. 4 ± 0.3 GPa, slightly higher in P than the data of Rubatto and Hermann (2001). Recalculation of reaction (6) results in a range of T at 4 GPa from 800 °C (ideal coupled- and non-coupled-ionic models and MM model) to 880 °C (molecular model, regular model and LCB model). This range is higher than Rubatto and Hermann's (2001) T estimates of 730 °C based on garnet–clinopyroxene thermometry, consistent with the limitation that reaction (6) provides only a maximum T estimate in this instance.

3.3.2. Dabieshan area, Central China

The assemblage garnet + omphacite + phengite + epidote + titanite + rutile + calcite has been found in carbonate eclogites from Shuanghe in the Dabieshan area in Central China. P–T conditions for this area were estimated to be 700 ± 50 °C and > 2.7 GPa (Cong et al., 1995). Although these samples show textural evidence for the presence of Al-rich titanites (Al: 0.3–0.4 a.p.f.u.) in equilibrium with the UHP assemblage, titanite only contains rutile inclusions and it is not entirely clear if earlier rutile is replaced by titanite, or if both grew simultaneously. Although no F was measured in this study, we assume that the mixing
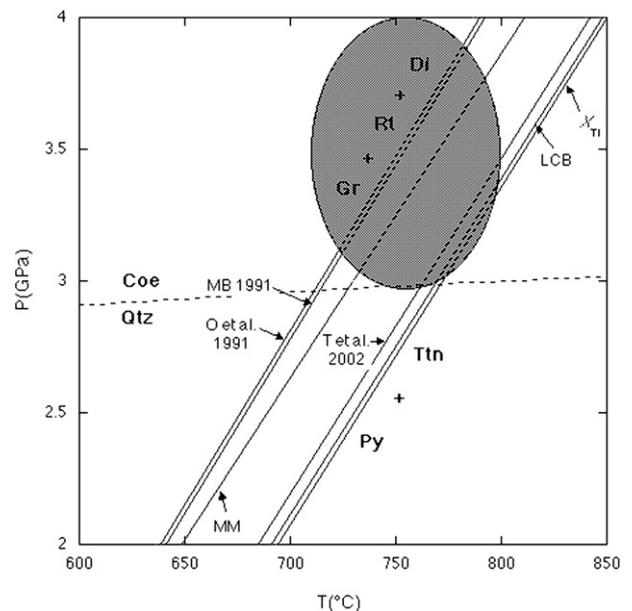

Fig. 9. Geothermometry of a garnet-bearing calc-silicate sample from the Dora Maira Massif, using the mineral data from Rubatto and Hermann (2001). The grey ellipse shows the previous P–T estimates from Compagnoni et al. (1995).

properties of F and OH are similar in the absence of experimental constraints. Recalculation of reaction (6) results in a range of T at 2.8 GPa from 480–600 °C (ideal coupled- and non-coupled-ionic models and MM model) to 560–670 °C (molecular model, regular model and LCB model), where the T estimates with the models of Tropper et al. (2002) and the MM model of Troitzsch et al. (2002) overlap. The calculations show that latter group is closer to the T estimates of Cong et al. (1995) involving garnet–clinopyroxene thermometry. The generally lower T estimates in this case could be due to the absence of rutile from the equilibrium assemblage since it only occurs as inclusions in titanite grains. Therefore these T estimates represent lower T limits.

3.3.3. Kumdy-kol area, Kokchetav Massif, Kazakhstan

Ogasawara et al. (2002) describe Al–F titanites with coesite exsolutions from the Kumdy-kol area in the Kokchetav Massif. The peak mineral assemblage of the calcite marble sample is garnet+ diopside+K-feldspar+titanite+calcite. Rutile is absent from these samples. Titanite without coesite exsolutions contains 0.16–0.2 a.p.f.u. F and 0.12–0.17 a.p.f.u. Al. Recalculation of coesite into the titanites yielded titanite compositions with ca. 0.07 a.p.f.u. F and 0.05–0.06 a.p.f.u. Al. The presence of coesite exsolutions in the titanites led to P estimates >6 GPa based on the experimental investigations on Si substitution in titanite at 1350 °C by Knoche et al. (1998). Okamoto et al. (2000) determined peak T of 950 °C to 1200 °C from this area based upon garnet–clinopyroxene thermometry. Since rutile is absent from these samples calculation of reaction (6) will only yield lower T limits. Using the coesite-free titanites, T estimates range from 660 °C (ideal coupled-ionic model) to 740 °C (LCB model). On the other hand, using the re-integrated titanite compositions and treating Si substitution on the Ti-site as an ideal diluent where $a_{CaTiSiO_4O}$ is multiplied by $(1-X_{Si})$, T increases only slightly and ranges from 720 °C (coupled-ionic model) to 740 °C (molecular model). Again these T estimates should only be viewed as a lower T limit.

4. Utility of titanite solid solutions in estimating fluid composition in UHP rocks

Calculation of volatile species in the binary system H_2O–CO_2 have shown that the fluid coexisting with the peak UHP assemblage in most impure UHP marbles is very rich in H_2O with $XCO_2<0.1$ (e.g. Omori et al., 1998; Ogasawara et al., 2002; Castelli et al., 2007). The most suitable equilibrium to estimate XCO_2 in titanite–rutile-bearing samples is the reaction:

$$CaTiSiO_5 + CO_2 = CaCO_3 + TiO_2 + SiO_2 \qquad (7)$$

$$Titanite + CO_2 = Calcite/Aragonite + Rutile + Quartz/Coesite$$

Application of reaction (7) to the impure calcite marbles from the Kumdy-kol area in the Kokchetav Massif from the study of Ogasawara et al. (2002) containing the titanites with coesite exsolutions, yields XCO_2 of <0.05 over a T range of 850 °C to 1000 °C at 6 GPa when calculated with the inclusion-free titanites. Due to the stoichiometric coefficient of titanite, the change in T, due to the change in the titanite activity model, is only very minor and for instance a change in $a_{CaTiSiO_4O}$ from 0.74 (MM model) to 0.85 (LCB model) results in a shift in T of only <20 °C indicating the robustness of this reaction towards activity variations (Fig. 10). Due to the absence of rutile from this sample these values have to be considered as maximum XCO_2 values, which are in agreement with previous estimates from dolomite-bearing marbles (Ogasawara et al., 2002).

Calculation of XCO_2 in the Brossasco calcite marble sample of Castelli et al. (2007) yields also very low XCO_2 of <0.01 at 720 °C and 4 GPa. Again, the overall change in $a_{CaTiSiO_4O}$ only results in a T change
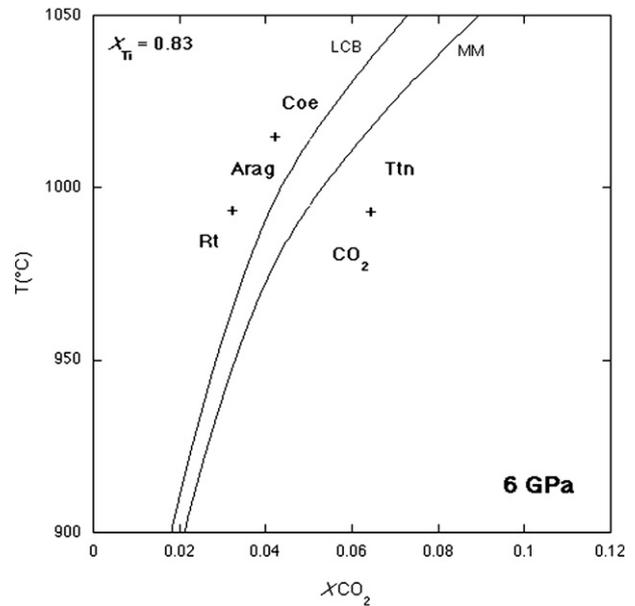

Fig. 10. P–XCO_2 diagram of an impure marble sample (J76) from the Kokchetav Massif, Kazakhstan, using the mineral data from Ogasawara et al. (2002).

of <10 °C. These results are also in very good agreement with the calculations of Castelli et al. (2007) which yielded XCO_2 of ca. 0.02 for the UHP peak conditions.

5. Discussion and conclusions

The calculations presented above in Figs. 7 and 8 clearly show that none of the activity models applied resulted in an intersection of reactions (5) and (6) at reasonable P–T conditions. The ideal molecular and non-ideal models yield reasonable T estimates while the ideal ionic models yield correct P estimates. This feature strongly implies that the problem in this case is less in the choice of the correct activity model but lies more in the fact that the literature data have to be treated with caution (e.g. retrograde reaction, non-equilibrium assemblages etc.) and the possibility of linking non-equilibrium compositions of titanite and garnet could be real. Nonetheless, even if textural and compositional equilibrium can be assured, the difference in the calculated shifts of the reactions as presented above in Figs. 7–9 clearly show that the choice of an appropriate titanite activity model is crucial when it comes to the application of titanite–rutile-bearing equilibria as geothermobarometers to Al-rich titanites in UHP rocks. Although experimentally determined activities should be preferred to empirically derived activity models because they provide more precise information on the behavior of a solid-solution by eliminating causes that may affect natural mineral assemblages. Experimental studies by Troitzsch and Ellis (2002) and Tropper et al. (2002) pose a problem since they show strongly contrasting results: Troitzsch and Ellis (2002) favor a positive deviation from ideality and Tropper et al. (2002) favor a negative deviation from ideality. Extrapolation of the thermodynamic data (W_G) beyond the experimental conditions is also problematic due to the restricted T range (200 °C) of the experimental investigations. Until further experimental investigations better constrain a–X relations in the system $CaTiSiO_4O$–$CaAlSiO_4F$, these non-ideal models should be applied with caution.

The positions of the two equilibria investigated display a strong dependence on the activity model used, which leads to large differences in results where $a_{CaTiSiO_4O}$ is low and the titanite reaction coefficient is high. Calculation of reaction (6) using samples in which Al–F substitution in titanite gives $X_{Al}>0.4$ yield a wide range of T. In contrast, application of reaction (6) to low Al–F titanites, where the

equilibrium assemblage contains rutile and titanite as in the study of Rubatto and Hermann (2001), yielded a reasonable T range, which is in very good agreement with previously established independent T estimates using the ideal coupled-ionic model with two-site mixing on the Ti- and O1-sites. Similar results were obtained for reaction (5).

Some UHP studies suggest that titanite and rutile are not in equilibrium, or that one of the two phases was not present during metamorphism. However, limiting constraints on T or P can still be derived. Calculations using reaction (6) and data from Castelli et al. (2007), Cong et al. (1995) and Ogasawara et al. (2002) confirm that titanite–rutile involving equilibria provide consistent limiting T constraints. Again, multi-site mixing models yield T closest to the independently derived estimates.

It is clear that more experimental data on the a–X relations in titanite solid solutions are needed in order to better understand and confirm the nature of the deviation from ideality, but until such constraints are available, it is recommended that the user employ either the ideal coupled-ionic model (e.g. Oberti et al., 1991) for titanite solid solutions and compare the results to an experimentally derived activity model, or use a range of different activity models to at least obtain a range of P–T conditions. Although Tropper et al. (2002) stated that the ideal molecular model can be used for calculations at high T and low X_{Al} (<0.2), the results from this study strongly indicate that the molecular model should not be applied for UHP rocks, since none of the thermobarometric results, calculated using the molecular model, were in agreement with independently established P–T data. For calculations in UHP rocks ionic models currently provide the best upper and lower limits on $a_{CaTiSiO_4O}$ for use in thermobarometry.

Acknowledgments

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