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Thermodynamic properties and stability of AlF-bearing titanite CaTiOSiO$_4$–Ca-AlFSiO$_4$

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Abstract Calorimetric and experimental data on AlF-bearing titanite are presented that yield thermodynamic properties of CaAlFSiO$_4$, as well as activity-composition relations of binary titanite CaTiOSiO$_4$–CaAlFSiO$_4$. The heat capacity of synthetic CaAlFSiO$_4$ was measured with differential scanning calorimetry between 170 and 850 K:

$$C_p = 689.96 - 0.386477 + 2911300T^{-2} - 8356.17T^{-0.5} + 0.000161797^2$$

Based on low-temperature heat capacity calculations with lattice vibrational theory (Debye model), the calorimetric entropy of CaAlFSiO$_4$ can be expected to lie between 104.7 and 118.1 J mol$^{-1}$ K$^{-1}$. The temperature of the $P2_1/a$ to $A2/a$ phase change was determined calorimetrically for a titanite with $X_{Al}=0.09$ ($T_{transition}=390$ K). The decrease of the transition temperature at a rate of about 11 K per mol% CaAlF-SiO$_4$ is in good agreement with previous TEM investigations. The displacement of the reaction anorthite + fluorite = CaAlFSiO$_4$ in the presence of CaTiOSiO$_4$ was studied with high P–T experiments. Titanite behaves as a non-ideal, symmetrical solid-solution. The thermodynamic properties of CaAlFSiO$_4$ consistent with a multi-site mixing model are:

- Enthalpy of formation (elements)<$d_e^0H^0$ = -2740.8 ± 3.0 kJ mol$^{-1}$
- Standard state entropy $S^0$ = 104.9 ± 1.1 J mol$^{-1}$ K$^{-1}$
- Margules parameter $|W_{PS-TW}|$ = 13.6 ± 0.4 J mol$^{-1}$

The pressure dependence of the Margules parameter ($W_{PS}$) was determined from the excess volume of mixing based on XRD measurements ($214 ± 18$ J mol$^{-1}$ kbar$^{-1}$), as well as refined from the piston-cylinder experimental results ($198 ± 114$ J mol$^{-1}$ kbar$^{-1}$), demonstrating consistency between crystal structure data and thermodynamic properties. The stability of AlF-bearing titanite Ca(Ti,Al)(O,F)SiO$_4$ was investigated by thermodynamic modelling in the system Ca–Al–Si–Ti–O–F–H–C and subsystems. The petrogenetic grids are in good agreement with natural mineral assemblages, in that very Al-rich titanite ($X_{Al} > 0.65 ± 0.15$) is generally absent because it is either unstable with respect to other phases, or its stability field lies outside the P–T conditions realised on Earth. The grids explain both the predominant occurrence of natural Al-rich titanite at high metamorphic grade such as eclogite facies conditions, as well as its scarcity in blueschist facies rocks. Wide spacing of the Al-isopleths for titanite of many high-grade assemblages prevents their use as geobarometers or thermometers. The instability of end-member CaAlFSiO$_4$ with respect to other phases in most assemblages modelled is consistent with the hypothesis that the presence of structural stresses in the crystal lattice of CaAlFSiO$_4$ influences its thermodynamic stability. The titanite structure is not well suited to accommodate Al and F instead of Ti and O, causing the relatively high Gibbs free energy of CaAlFSiO$_4$, manifested in its standard state properties. Thus, the increasing amount of CaAlFSiO$_4$ along the binary join is the reason why titanite with $X_{Al} > 0.65 ± 0.15$ becomes unstable in most petrogenetic grids presented here. The compositional limit of natural titanite ($X_{Al} = 0.54$) probably reflects the point beyond which the less stable end member begins to dominate the solid-solution, affecting both crystal structure and thermodynamic stability.

Introduction

Titanite (CaTiOSiO$_4$) is a common accessory phase in a range of igneous, metamorphic, and some sedimentary rocks. The widespread occurrence of titanite
throughout different geochemical environments and petrogenetic conditions is caused by the large number of other elements that can be substituted into its crystal structure (e.g. Sahama 1946; Oberti et al. 1991). Numerous studies based on natural assemblages, experiments and thermodynamic modelling proposed that titanite is a potential indicator for a range of metamorphic conditions (Kowallis et al. 1997), such as pressure and temperature (Essene and Bohlen 1985; Manning and Bohlen 1991; Mukhopadhyay et al. 1992; Ghent and Stout 1994), fluid composition (Hunt and Kerrick 1977; Valley and Essene 1980; Jacobs and Kerrick 1981; Itaya et al. 1985) and oxygen fugacity (Spear 1981; Wones 1989).

Its U–Pb content opens the exciting possibility to date the above metamorphic conditions (Frost et al. 2001). Understanding the stability of titanite in igneous and metamorphic rocks is important because it might play a dominant role in shaping their rare earth element patterns (Hellman and Green 1979; Green and Pearson 1986; Paterson and Stephens 1992; Dawson et al. 1994; Tribuzio et al. 1996). Moreover, the presence or absence of titanite in felsic igneous rocks could be used as an indicator for F contents of magmas (Price et al. 1999).

Because titanite commonly occurs in solid-solution with other end members, it is crucial to understand the mixing behaviour, and activity-composition relations of the most important end members. Although the thermodynamic data of the titanite end member (CaTiOSiO$_4$) are known, activity-composition relations of titanite solid-solution had never been determined, so that previous studies assumed either ideal mixing behaviour (Ghent and Stout 1994) or titanite to be pure CaTiOSiO$_4$ (Mukhopadhyay et al. 1992). Throughout the present paper ‘titanite’ stands for the phase titanite, thus including solid-solution, whereas pure titanite is referred to as ‘end member titanite’ or ‘CaTiOSiO$_4$’.

In the present study we investigated experimentally the activity–composition relations of Al-bearing titanite along the binary join CaTiOSiO$_4$–CaAlSiO$_4$, represented by the coupled substitution

$$\text{Ti}^{4+} + \text{O}^2- = \text{Al}^{3+} + \text{F}^- \quad (1)$$

The end member CaAlSiO$_4$ was chosen for several reasons. First, Al is one of the most common and abundant substituents for Ti in natural titanite, and thus most important for thermodynamic modelling of natural assemblages. Second, among the two main Al end members that occur in natural titanite, i.e. CaAlOHSiO$_4$ and CaAlSiO$_4$, the latter always dominates in the most Al-rich titanites, but never exceeds 54 mol% (Franz and Spear 1985, Markl and Piazolo 1999). The reasons for this compositional limit were the subject of much discussion (Smith 1981, Oberti et al. 1991). Crystal structure investigations along the join TiO–AlF indicated that, although complete solid-solution is observed, the titanite structure is not well suited to accommodate $X_{Al} > 0.5$ (Troitzsch et al. 1999). We examine whether these crystal structural problems are reflected in the thermodynamics of this system, for example as an activity anomaly at this composition. There has been no previous attempt to equilibrate more AlF-rich titanite in a minerallogically buffered phase assemblage. Although Smith (1981) determined qualitatively the dependence of the AlF content in titanite on pressure and temperature with experiments, the equilibrated phase assemblage contained met and, thus, was not minerallogically buffered, preventing a thorough thermodynamic interpretation of the results. Note, however, the recent study by Tropper et al. (1999, 2000) discussed below. Third, the unit-cell volume of titanite along the binary join TiO–AlF has recently been determined (Troitzsch and Ellis 1999; Troitzsch et al. 1999), permitting accurate thermodynamic calculations with this end member. Fourth, the Al content of titanite is pressure- and temperature-dependent, and thus of special interest for geothermobarometry (Smith 1981; Enami et al. 1993; Franz and Spear 1985).

The potential of Al-bearing titanite in geobarometry has long been recognised (Smith 1980; 1981). Many previous studies of natural (e.g. Franz and Spear 1985; Krogh et al. 1990; Enami et al. 1993; Carswell et al. 1996) and synthetic Al-rich titanite (Smith 1981) have suggested a strong pressure and mild temperature dependence of the Al content in titanite. However, the PTX relationship was never quantified for any assemblage, mainly because of the strong dependence of the system on fluorine, which, until more recently, was difficult to analyse quantitatively with standard equipment.

In the first part of this study we investigated, with differential scanning calorimetry, the heat capacity of synthetic CaAlFSiO$_4$ required for the subsequent interpretation of high P–T–experiments. Secondly, the $P_2J/a$ to $A2/a$ phase transition temperature of a synthetic titanite with $X_{AlF} = 0.09$ was determined calorimetrically to improve the resolution of the CaTiOSiO$_4$–CaAlFSiO$_4$ phase diagram. Thirdly, a series of piston-cylinder experiments was carried out in the system Ca–Ti–Al–Si–O–F, determining the displacement of the reaction

$$0.5\text{CaAl}_2\text{Si}_2\text{O}_8 + 0.5\text{CaF}_2 = \text{CaAlF}_4\text{SiO}_4$$

Anorthite + fluorite = AIF titanite

in the presence of CaTiOSiO$_4$. This gave the activity–composition relationship of titanite solid-solution, and the standard state entropy and enthalpy of formation of CaAlFSiO$_4$. These thermodynamic data were then used to investigate the stability of AIF-rich titanite.

### Differential scanning calorimetry details

The heat capacity of CaAlFSiO$_4$ was determined using the synthetic sample G-297 of Troitzsch and Ellis (1999). This sample contains small amounts of fluorine-rich zoisite, fluorite, and trace...