REVISION 1

LETTER

# Heat capacity measurements of $CaAlSiO_4F$ from 5 to 850K and its standard entropy

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## ABSTRACT

Heat capacity ($C_P$) data of Al-F-bearing titanite are presented that yield the standard entropy $S^{\circ}_{298.15}$ of F-Al-titanite $CaAlFSiO_4$ (FAT). $C_P$ of synthetic FAT was measured with relaxation calorimetry and differential scanning calorimetry between 5 and 764 K. The results constrain $S^{\circ}_{298.15}$ to be 115.4 ± 2.0 J/mol•K and subsequently the standard Gibbs free energy of formation from the elements, $\Delta_f G^{\circ}$ , of $CaAlSiO_4F$ to be between –2583 ± 3.0 kJ/mol and –2588 ± 3.0 kJ/mol, and the standard enthalpy of formation from the elements, $\Delta_f H^{\circ}$, to lie between –2728 ± 3.0 kJ/mol and –2733 ± 3.0 kJ/mol depending on the thermodynamic data retrieval approach. These data in turn can be used to quantitatively model high-grade and UHP fluid-rock interaction. The calculation of future petrogenetic grids involving F-bearing minerals and titanite solid solutions in the system $CaTiSiO_4O$ – $CaAlSiO_4F$ will only be

possible by expanding existing internally consistent thermodynamic databases to the F-system.

## INTRODUCTION

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; Frost et al. 2000; Troitzsch and Ellis 2002; Tropper et al. 2002; Tropper and Manning 2008; Hayden et al. 2008). Despite the importance of the F-Al content of titanite there are only few experimental data available with which to evaluate the physical and chemical controls on titanite solid solutions (Smith 1981; Troitzsch and Ellis 2002; Tropper et al. 2002). In high- and ultra high-pressure rocks, titanite and rutile also form the basis of a set of equilibria useful for the determination of pressure. Specific equilibria discussed by Manning and Bohlen (1991) and Tropper and Manning (2008) include:

$$CaAl_2Si_2O_8 + TiO_2 = CaTiSiO_5 + Al_2SiO_5 \qquad (1)$$

Anorthite + Rutile = Titanite + Kyanite

$$3Ca_3Al_2Si_3O_{12} + 5TiO_2 + 2SiO_2 + H_2O = 5CaTiSiO_5 + 2Ca_2Al_3Si_3O_{12}(OH) \qquad (2)$$

Grossular + Rutile + Quartz + $H_2O$ = Titanite + Zoisite

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

Grossular + Rutile + Quartz/Coesite = Titanite + Kyanite

The successful application of reactions (1)-(3) to geothermobarometry illustrates the utility of titanite-bearing equilibria in petrology. However, the accuracy of the results depends on the availability of precisely measured thermodynamic data such as $S°_{298.15}$, $\Delta_fG°$ and $\Delta_fH°$ which is the impetus of this study.

## PREVIOUS ENTROPY ESTIMATES AND CALORIMETRIC MEASUREMENTS

In absence of calorimetrically measured low-temperature heat capacity data, the standard entropy ($S^{°}_{298.15}$) of FAT can be estimated by applying additive techniques using $S°_{298.15}$ of simple silicates and oxides (Robinson and Haas 1983; Holland 1989). This can be illustrated by two simple estimates as shown by Tropper et al. (2002). The first estimate is based on a reaction among orthosilicates,

$2CaAlSiO_4F = Al_2SiO_4F_2 + 2CaMgSiO_4 - Mg_2SiO_4$ (4)

Al-F Titanite = Topaz + Monticellite – Forsterite

and yields $S^{°}_{298.15}$ for FAT (F-Al-titanite) of 105.2 J/mol•K. The second estimate uses a reaction among oxides and fluorides, where the data of the oxides were taken from Holland (1989) and fluorite was taken from Robie and Hemigway (1995)

$2CaAlSiO_4F = CaF_2 + CaO + Al_2O_3 + 2SiO_2$ (5)

Al-F Titanite = Fluorite + Lime + Corundum + Quartz

and gives $S^{°}_{298.15}$ = 109.6 J/mol•K after applying a volume correction (Fyfe et al. 1958). Troitzsch and Ellis (2002) also estimated the standard entropy of FAT by summing the entropies of its components, taking into account any volume or coordination differences between the phase and its constituents. They chose the simple reaction:

$2CaAlSiO_4F = CaAl_2Si_2O_8 + CaF_2$ (6)

Al-F Titanite = Anorthite + Fluorite

The data for anorthite and fluorite were taken from Robie and Hemingway (1995), and based on the method by Fyfe et al. (1958) with volume correction, they obtained entropy estimates of $CaAlFSiO_4$ between 105 and 112 J/mol•K with an uncertainty in all entropies discussed above on the order of ± 0.3 J/mol•K. Overall, the entropy estimates from both investigations are significantly lower than the entropy of titanite, $CaTiSiO_4O$, which has been inferred to vary strongly and range from 107.8 J/mol•K (Xirouchakis and Lindsley 1998) to 129.3 J/mol•K (King et al. 1954) to 131.2 J/mol•K (Holland and Powell 1998). On the other hand the FAT entropy estimates are comparable to $S^{\circ}_{298.15}$ = 107.8 J/mol•K for synthetic titanite estimated by Xirouchakis and Lindsley (1998) but their $S^{\circ}_{298.15}$ for titanite is too low to be consistent with the phase equilibrium constraints of Manning and Bohlen (1991). Manon et al. (2008) measured the heat capacity of synthetic titanite using PPMS (Physical Properties Measurement System) and obtained a value of 127.2 ± 0.2 J/mol•K and thus confirmed the adiabatic low-*T* data of King et al. (1954).

Troitzsch and Ellis (2002) determined the heat capacity of FAT using the synthetic sample G297 of Troitzsch and Ellis (1999). This sample contains small amounts of F-bearing zoisite, fluorite, and traces of kyanite as determined using Rietveld analysis (Table 1). All measurements were carried out with a Perkin Elmer differential scanning calorimeter DSC 2920 over the temperature range of 170 to 850 K. Their sample runs were performed at a heating rate of 20° $min^{-1}$, from 170 to 850 K and two scans of FAT were performed and the mean of which was taken as the final value. The experimentally determined $C_p$ of FAT increased smoothly with temperature (Fig. 1). Their experimental data were reproduced to within 1% (between 170 and 850 K) by the following equation based on Haas and Fisher (1976):

$$C_P = 689.96 - 0.38647T + 2911300T^{-2} - 8356.1T^{-0.5} + 0.00016179T^{2}$$

In a second step Troitzsch and Ellis extrapolated the FAT heat capacity data to the experimental temperatures (1073 to 1273 K). Because no melting was observed in the run products, the heat capacity of FAT was assumed to increase smoothly beyond 850 K to at least 1273 K approaching the 'Dulong Petit limit' (Gopal 1966, Berman and Brown 1985). Their Figure 2b shows the extrapolation of the heat capacity data (250 to 850 K) to 1300 K, with an extended Maier and Kelley (1932) heat capacity polynomial (Haas and Fisher 1976) as:

$$C_P = 272.54 - 0.01319T - 2055700T^{-2} - 1854.4T^{-0.5}$$

Troitzsch and Ellis (2002) then estimated the calorimetric entropy of FAT at standard state (1 bar, 298.15 K). This thermodynamic quantity can be calculated if the heat capacity is known between 0 K and 298.15 K. But because their FAT heat capacity data were limited to above 170 K, they were extrapolated to 0 K based on vibrational theory, using the Debye model (e.g. Gopal 1966). Two alternative extrapolations of the Debye temperature to 0 K were considered, in order to cover the entire possible range of entropy values. Their model 1 assumed a Debye temperature of 763 K, calculated from the lowest temperature data point and using it to compute $C_p$ between 0 and 170 K. Model 2 extrapolated the drop in the Debye temperature with a 2nd degree polynomial function fitted to the DSC data between 170 and 300 K. The calorimetric entropy estimated in this way was constrained to range between 104.7 and 118.1 J/mol·K (Troitzsch and Ellis 2002, Tab. 3).

## HEAT CAPACITY MEASUREMENTS

The heat-capacity option of the Physical Properties Measurement System (PPMS), produced by Quantum Design®, is based on the principles of relaxation calorimetry and allows measurement of $C_p$ values on milligram-sized samples enclosed in an aluminum pan (Dachs and Bertoldi 2005). The PPMS measurements were performed at the Department of Chemistry and Physics of Materials University of Salzburg, and were repeated three times at each temperature step. Fifty temperature set points between 5 and 300 K were measured for sample G-297 from Troitzsch and Ellis (1999) with a logarithmic spacing. Thirty set points between 3 and 10

K using a linear spacing were additionally measured for this sample. Sample weights used in the PPMS measurements were 21.39 mg. Heat capacities between 282 K and 764 K were measured using a Perkin Elmer Diamond DSC in the same calorimetry laboratory at Salzburg University. The data are given in the electronic supplementary materials. More details of measuring and calibration procedures are given in Benisek et al. (2010) or Dachs et al. (2012a, b) and will not be repeated here.

## RESULTS AND DISCUSSION

The agreement between PPMS and DSC $C_P$ data at ambient T is very good (the PPMS data are ~ 0.4 % larger). In order that the measured $C_P$ data can be compared to those obtained by Troitzsch and Ellis (2002), they were calculated to the same molar basis as used by these authors (i.e., the molar weight of 176.747 g/mol resulting from the microprobe analysis of synthetic FAT in sample G-297, Troitzsch and Ellis 1999, Tab. 1). As can be seen from Fig. 1, measured $C_P$ of this study is smaller by 1-3 % in the temperature range 170 – 550 K, whereas the deviation at higher temperatures is less than 0.5 %. The low-temperature $C_P$ values were fitted to a combination of Debye, Einstein and Schottky functions (Boerio-Goates et al. 2002) and smoothed values for selected temperatures between 5 and 298.15 K are given in the electronic supplementary data in addition to the experimental $C_P$ data. The standard entropy of FAT was then derived by numerically integrating $C_P/T$ between 0 K and 298.15 K and a value of $S^o_{298.15} = 115.4 \pm 2.0$ J/mol·K was obtained. This value lies within the range of 104.7 and 118.1 J/mol·K as estimated by Troitzsch and Ellis (2002) for $S^o_{298.15}$ by use of the Debye model to extrapolate their measured $C_P$ data from 170 K down to 0 K. We also tested the effect of impurities in sample G297 on the value of the derived standard entropy. Sample G297 is composed of 90 vol.% FAT, 6 vol.% F-bearing zoisite and 2 vol.% Fluorite (Tab. 1). In a first step vol.% were converted to mol % based on the molar volumes of the phases involved giving 92.5 mol% FAT, 2.3 mol% F-zoisite and 5.2 mol% fluorite (Tab. 1). The measured heat capacities were then recalculated to the molar weight of such a mechanical mixture (177.964 g/mol). Based on the relationship $C_P$(measured) = 0.925 $C_P$(FAT) + 0.023

$C_P$(Fzoi) + 0.052 $C_P$(Fluorite), the heat capacity of end-member FAT was then computed using $C_P$ values for fluorite from JANAF Tables (Chase et al. 1985) and those for F-zoisite from PPMS measurements on OH-zoisite and then taking into account the replacement of OH by F based on PPMS data measured on synthetic $Mg(OH)_2$ and $MgF_2$ (E. Dachs, unpublished data). The fit deviation, i.e. 100*[($C_P$(measured) – $C_P$(fit)]/ $C_P$(fit), amounts to 5 ± 2 % in the lowest temperature range of 5–10 K, to 0.5 ± 0.4 % between 10 K and 50 K and to 0.3 ± 0.2 % between 50 K and 298.15 K. The standard entropy of FAT derived from the so corrected Cp's amounts to $S^o_{298.15} = 114.5 \pm 2.0$ J/mol·K, which agrees within error with that derived above ignoring impurities (Geiger and Dachs 2018). The contents of impurities in sample G297 has thus only a minor effect on the derived final standard entropy value of FAT, as already suggested by Troitzsch and Ellis (2002). Fitting the DSC data to a polynomial as suggested by Berman and Brown (1985) yields:

$$C_P = 233.67 - 823.249 \cdot T^{-0.5} - 8.41356 \cdot 10^{6} \cdot T^{-2} + 1.15956 \cdot 10^{9} \cdot T^{-3}.$$

This polynomial, valid for calculating the heat capacity of FAT at temperatures > 298.15 K, can be used for extrapolation beyond the experimental range and replaces that given in Troitzsch and Ellis (2002).

Troitzsch and Ellis (2002) and Tropper et al. (2002) published studies on the thermodynamic properties of FAT. Based on displacement of reaction (6), Troitzsch and Ellis (2002) derived $\Delta_f H$ of –2740.8 ± 3 kJ/mol. This is in good agreement with the results of the study by Tropper et al. (2002) who performed reaction displacement experiments by adding fluorite to reaction (1) and this yielded $\Delta_f H$ of –2744 ± 3 kJ/mol. 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 on reaction (6). From these $P$-$T$-$X_{Al}$ data, free-energy minimization allowed the simultaneous calculation of $\Delta_f H$, $S^o_{298}$ and ($W_H$-T$W_S$) involving two activity models, a multi-site mixing model (MM) and a 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 [$a_{CaTiSiO_4O} = (X_{Ti})\gamma_{CaTiSiO_4O}$]. With this model, a $S^o_{298}$ = 111.13 J/mol·K for FAT was derived, close to the calorimetric value of this study (115.4 ± 2.0 J/mol·K). If the thermodynamic evaluation of the displacement experiments is repeated using this calorimetric value, a standard enthalpy of formation value $\Delta_f H = -2728.3 \pm 3.0$ kJ/mol is obtained for FAT.

Tropper et al. (2002) calculated $\Delta_f H$ of $CaAlSiO_4F$ based on the shift of the reversals of the TARK reaction reaction (1) in the presence of fluorite using a regular mixing model for titanite solid solutions. By using the newly obtained $S^o_{298}$ and $C_P$ data this yielded a slightly higher $\Delta_f H^\circ$ of $-2733 \pm 3.0$ kJ/mol. The slight discrepancies in the values of $\Delta_f G$ and $\Delta_f H$ of F-Al titanite between the two studies are the result of differences in (i) the choice of the activity model and the estimated values of the interaction parameter $W$ for the $CaTiSiO_4O$ – $CaAlSiO_4F$ solid solution and (ii) the experimental approach to determine the shift of the F-Al titanite involving reaction.

## IMPLICATIONS

Previous studies have shown that titanite is an important petrogenetic indicator as well as a frequently used petrochronological tool in metamorphic rocks (e.g. Frost et al. 2000; Hayden et al. 2008; Kohn 2017). The basic thermodynamic data ($S^o_{298}$, $\Delta_f H^\circ$,$\Delta_f G^\circ$) from this study and previously obtained $CaTiSiO_5$-$CaAlSiO_4F$ $a$-$X$ relations and mixing models (Troitzsch and Ellis 2002; Tropper et al. 2002) provide the basic framework for the calculation of phase diagrams and petrogenetic grids involving F-Al-bearing titanite solid solutions with respect to the use of titanite as petrogenetic indicator for high-grade and UHP fluid-rock interaction involving F-bearing fluids (e.g. Franz and Spear 1985; Carswell et al. 1996; Markl and Piazolo 1998, 1999; Sengupta et al. 2004). Tropper and Manning (2007) have shown that fluorite solubility is quite high in deep crustal fluids and this means that F must become quite concentrated before fluorite will saturate. That is, dissolved F in fluids and minerals may be large even in the absence of fluorite, as indicated by F-rich minerals associated with granulite-facies metamorphism (e.g. Chacko et al. 1987, Pan and Fleet 1996; Markl and Piazolo 1999; Tsunogae et al. 2003; Sengupta et al. 2004). Nonetheless first quantitative modeling of fluorite-F-Al titanite-involving reactions in the system $CaO$-$CaF_2$-$Al_2O_3$-$SiO_2$-$H_2O$±$CO_2$ became only possible with the first thermodynamic data of F-Al titanite by Troitzsch and Ellis (2002). Therefore it is desirable to extend the calculation of fluorite-F-Al titanite equilibria to other chemical systems using the revised thermodynamic data from this study, which can only be accomplished by expanding existing internally consistent databases (e.g., THERMOCALC, Holland and Powell 1998), which are are notably deficient in minerals with volatile components such as F, Cl, S, P to F-bearing systems. This in turn will be the first step towards future quantitative evaluation of F-bearing minerals as petrogenetic indicators for fluid-rock interaction during metamorphic processes.

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## FIGURE CAPTIONS

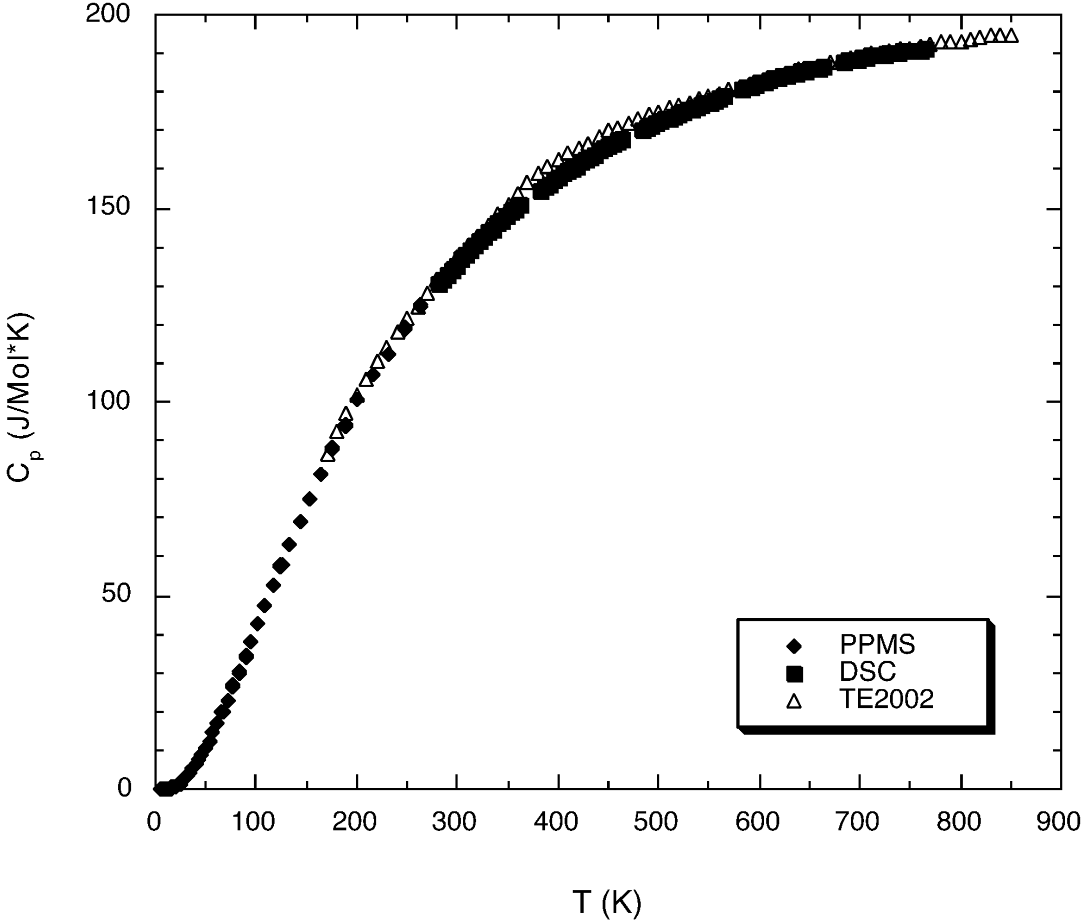
**FIGURE 1.** $C_P$ measurements of $CaAlSiO_4F$ of this study. The PPMS measurements are indicated with the black diamonds, DSC measurements with black squares and DSC data from Troitzsch and Ellis (2002, TE2002) with open triangles.

Table 1: Mineral and bulk composition of sample G-297

| Mineral | Si | Al | Ca | F | O | H | $M_{mineral}$ | Vol.% | Mol.% | $M_{sample}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| FAT | 0.999 | 1.005 | 0.996 | 0.916 | 4.016 | | 176.747 | 90.3 | 92.5 | 163.491 |
| F-zo | 2.968 | 3.010 | 2.021 | 0.330 | 12.531 | 0.448 | 452.777 | 5.8 | 2.3 | 10.414 |
| Fl | | | | | | | 78.075 | 2.4 | 5.2 | 4.060 |
| | | | | | | | Total | 98.5 | 100 | 177.964 |

The composition of F-bearing zoisite was taken from sample G295. $M_{mineral}$: molecular weight of the minerals, $M_{sample}$: total molecular weight of the sample corrected for the abundance of the minerals. The conversion of Vol.% to Mol.% was done based on the molar volumes of phases involved. The modal amounts of quartz, kyanite, AgO and PdO were below detection limits.

Fig. 1


200
150
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$C_p$ (J/Mol*K)
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900
T (K)
◆ PPMS
■ DSC
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