

Klaus-Dieter Grevel · Mirko Schoenitz · Volker Skrok
Alexandra Navrotsky · Werner Schreyer

Thermodynamic data of lawsonite and zoisite in the system CaO–Al₂O₃–SiO₂–H₂O based on experimental phase equilibria and calorimetric work

Received: 1 March 2001 / Accepted: 6 June 2001 / Published online: 3 August 2001
© Springer-Verlag 2001

Abstract The enthalpy of drop-solution in molten 2PbO·B₂O₃ of synthetic and natural lawsonite, CaAl₂(Si₂O₇)(OH)₂·H₂O, was measured by high-temperature oxide melt calorimetry. The enthalpy of formation determined for the synthetic material is $\Delta_f H^{\text{Oxides}} = -168.7 \pm 3.4$ kJ mol⁻¹, or $\Delta_f H^0_{298} = -4,872.5 \pm 4.0$ kJ mol⁻¹. These values are in reasonable agreement with previously published data, although previous calorimetric work yielded slightly more exothermic data and optimisation methods resulted in slightly less exothermic values. The equilibrium conditions for the dehydration of lawsonite to zoisite, kyanite and quartz/coesite at pressures and temperatures up to 5 GPa and 850 °C were determined by piston cylinder experiments. These results, other recent phase equilibrium data, and new calorimetric and thermophysical data for lawsonite and zoisite, Ca₂Al₃(SiO₄)(Si₂O₇)O(OH), were used to constrain a mathematical programming analysis of the thermodynamic data for these two minerals in the chemical system CaO–Al₂O₃–SiO₂–H₂O (CASH). The following data for lawsonite and zoisite were obtained: $\Delta_f H^0_{298}(\text{lawsonite}) = -4,865.68$ kJ mol⁻¹, $S^0_{298}(\text{lawsonite}) = 229.27$ J K⁻¹ mol⁻¹, $\Delta_f H^0_{298}(\text{zoisite}) = -6,888.99$ kJ mol⁻¹, $S^0_{298}(\text{zoisite}) = 297.71$ J K⁻¹ mol⁻¹. Additionally, a recalculation of the bulk modulus of lawsonite yielded $K = 120.7$ GPa, which is in good agreement with recent experimental work.

Introduction

During the last decade, the discoveries of high-pressure minerals such as coesite and diamond in metamorphic rocks have drastically changed our ideas concerning the limits of metamorphism. The process of ultrahigh-pressure metamorphism (UHPM), i.e. metamorphism at pressures >2.8 GPa, is now accepted in the scientific community. Early experimental studies in chemical model systems, like the system MgO–Al₂O₃–SiO₂–H₂O (MASH) representing material of crustal composition (e.g. Schreyer and Seifert 1969), offered guidelines for subsequent experimental work. Chatterjee et al. (1984) presented a detailed investigation of 14 univariant reactions in the system CaO–Al₂O₃–SiO₂–H₂O (CASH) covering pressures up to 4 GPa. The latter investigators were followed by Skrok (1993), Pawley (1994), Schmidt and Poli (1994), Schmidt (1995), and Poli and Schmidt (1998), who were particularly interested in studying reactions involving the hydrous Ca-bearing minerals zoisite, Ca₂Al₃(SiO₄)(Si₂O₇)O(OH), and lawsonite, CaAl₂(Si₂O₇)(OH)₂·H₂O. These minerals proved to be stable at pressures greater than 7 (zoisite) and 12 GPa (lawsonite) respectively, and are therefore potential carriers of water into the Earth's mantle during subduction.

In order to assess pressure and temperature conditions during subduction and subsequent exhumation of UHPM rocks, internally consistent thermodynamic data sets, as provided by Berman (1988), Holland and Powell (1998), and Chatterjee et al. (1998), are used extensively. The thermodynamic properties of lawsonite and zoisite are included in all data sets mentioned above, but they differ to some extent. As pointed out by Grevel (1998), the most significant differences can be found in the thermophysical data, i.e. data describing the volumetric behaviour of these minerals at high pressure and temperature. Due to the lack of P – V – T data, Berman (1988) estimated compressibility and thermal expansion of lawsonite and zoisite, whereas Holland and Powell

K.-D. Grevel (✉) · M. Schoenitz · V. Skrok · W. Schreyer
Institut für Geologie, Mineralogie und Geophysik,
Ruhr-Universität Bochum, 44780 Bochum, Germany
E-mail: Klaus-Dieter.Grevel@ruhr-uni-bochum.de
Tel.: +49-234-3223517
Fax: +49-234-3214433

K.-D. Grevel · M. Schoenitz · A. Navrotsky
Thermochemistry Facility, Department of Chemical
Engineering and Materials Science, University of California
at Davis, Davis,
CA 95616-8779, USA

Editorial responsibility: J. Hoefs

(1998) as well as Chatterjee et al. (1998) included compressibility data of Comodi and Zanazzi (1996, 1997) and measurements of thermal expansion provided by Pawley et al. (1996), and Comodi and Zanazzi (1996). Since then several more experimental studies on the P - V - T behaviour of lawsonite and zoisite have appeared in the literature (Pawley et al. 1998; Daniel et al. 1999, 2000; Chinnery et al. 2000; Grevel et al. 2000; Sinogeikin et al. 2000), still showing significant differences in the thermophysical properties.

In contrast to the amount of experimental work on the P - T stability fields of lawsonite and zoisite and the thermophysical data available, thermochemical data of these minerals are scarce and, especially in the case of lawsonite, based largely on the calculation of internally consistent data sets rather than on direct measurement (Halbach and Chatterjee 1984; Berman 1988; Holland and Powell 1998; Chatterjee et al. 1998). Experimental calorimetric data available for lawsonite are restricted to one measured value for the enthalpy of formation (Barany 1962), later recalculated by Hemingway and Robie (1977) based on new experimental data of quartz and gibbsite, and one publication of heat capacity and third-law entropy (Perkins et al. 1980). These data are the only sources for the current standard collection of thermodynamic data for minerals by Robie and Hemingway (1995). The experimental work of Barany (1962) and of Perkins et al. (1980) was performed on natural samples. While minor impurities in the sample material have negligible effect on heat capacity measurements, enthalpy of formation data can be biased by several kilojoules. Therefore, as the first objective of this paper, the enthalpy of formation of lawsonite, determined experimentally on synthetic material, is reported. In order to link the present result to the first measurement by Barany (1962), not only synthetic material but also a set of three natural samples has been analysed and measured.

Grevel et al. (2000) obtained the best agreement so far between calculated and experimentally determined equilibrium positions of mineral reactions in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at high pressures and temperatures by augmenting the Berman (1988) database with their P - V - T data for lawsonite and zoisite. In order to improve this agreement and to check the internal consistency of the modified Berman (1988) database, Grevel et al. (2000) recommend a more rigorous mathematical programming (MAP) analysis of the data based on a simultaneous treatment of calorimetric data, thermophysical data, and constraints given from relevant reaction reversal experiments. In the present study we performed this MAP analysis taking into account new calorimetric data for lawsonite (this study) and zoisite (Smelik et al. 2001) and the P - V - T measurements of Grevel et al. (2000). All relevant experimentally determined reversal brackets recently reported in the literature served as constraints for the MAP analysis. These brackets include some experiments on the dehydration of lawsonite to zoisite, kyanite and quartz/coesite reported by Skrok et al. (1994) in a short abstract. The final

objective of this paper is to describe these experiments, originally performed by Skrok (1993), in greater detail.

The enthalpy of formation of lawsonite

Synthesis and sample characterisation

Synthetic material

Up to now, the most successful synthesis of lawsonite was made by Schmidt and Poli (1994) who reported close to 100% yield, starting from anorthite at 2.3 GPa, 500 °C with a run duration of two days. Following this approach, synthetic anorthite as well as quenched glass with anorthite composition was used as starting material. Starting materials were produced by grinding together and firing analytical-grade commercial oxides. Lawsonite synthesis experiments were done with a girdle-anvil apparatus in a 500-ton uniaxial press at SUNY Stony Brook. The sample plus excess water, contained in a pressure-sealed silver capsule, was surrounded by boron nitride and inserted in a graphite tube furnace. The outer cell parts consisted of unfired pyrophyllite. The furnace was operated under power control, using previously established relations of power consumption vs. temperature. Synthesis conditions were chosen according to the phase diagram published by Pawley (1994) and fixed at 5 GPa and 600 °C, taking into account an uncertainty of about 100 degrees in our power-temperature calibration.

After the high-pressure synthesis experiments, no weight loss of the sample capsules was observed, indicating that the capsules were sealed effectively by pressure. Subsequent analyses of the products by X-ray powder diffraction, optical microscopy and electron microprobe analysis confirmed that the reaction yielded 100% lawsonite within 24 h with no detectable amounts of starting material or other phases.

Natural samples

Three natural samples were kindly provided by the Smithsonian Institution and Harvard University. The samples originated from Valley Ford, Sonoma, CA (S-97464-1), North Berkeley, CA (H91114), and the type locality Tiburon, Marin Co., CA (H95982). Electron microprobe analyses showed that iron was the only minor element in the otherwise stoichiometric samples. From mass balance calculations, it was concluded that the iron is trivalent and substitutes for aluminium in the structure. Thus, the compositional changes can be expressed by a single parameter, $\text{FFA} = \text{Fe}/(\text{Fe} + \text{Al})$, describing the variation along the $\text{Al}^{(\text{VI})}\text{-Fe}^{(\text{VI})}$ join. By electron microprobe analysis, FFA was found to vary locally between 0.5 and 6 mol%. Accordingly, samples were ground and homogenised prior to dissolution in the calorimeter. The bulk iron content was

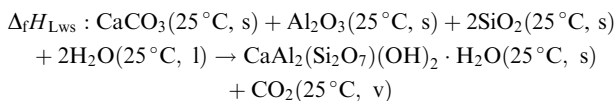
measured by an additional ICP analysis of the homogenised samples. Minute inclusions of epidote and sphene (<1%) were present in sample H-95982 only.

High-temperature oxide melt solution calorimetry

High-temperature oxide melt solution calorimetry has become a standard method to measure enthalpies of mineral reactions (Navrotsky 1977, 1997). In the present study, a Tian-Calvet-type twin calorimeter was used to determine heats of drop-solution. Sample pellets were dropped from ambient conditions into molten lead borate ($2\text{PbO}\cdot\text{B}_2\text{O}_3$) kept at constant temperature of 702 °C. The measured heat effect is the sum of the heat content (between 25 and 702 °C) and the heat of solution of the sample in lead borate at 702 °C. The final thermodynamic state for each sample drop is that of a dilute solution in lead borate at 702 °C. In order to control the final state of the volatile component (water), the atmosphere in the calorimeter was flushed with argon at a flow rate of about 5 ml s^{-1} . By flushing the atmosphere above the solvent, water is effectively expelled from the solvent, and the energy of interaction between water and the solvent is then negligible. The final state of water has thereby been fixed to that of water vapour at 702 °C and atmospheric pressure (Navrotsky et al. 1994).

Finally, the enthalpy of formation of lawsonite ($\Delta_f H_{\text{Lws}}$) can be calculated from its enthalpy of drop-solution ($\Delta H_{\text{ds,Lws}}$) and from the enthalpies of drop-solution of each of its components. In the present study the following thermodynamic cycle was used:

$\Delta H_{\text{ds,Lws}}$:	$\text{CaAl}_2(\text{Si}_2\text{O}_7)(\text{OH})_2 \cdot \text{H}_2\text{O}$ (25 °C,s)	→ solution (702 °C)
$\Delta H_{\text{ds,Crm}}$:	Al_2O_3 (25 °C,s)	→ solution (702 °C)
$\Delta H_{\text{ds,Qtz}}$:	2SiO_2 (25 °C,s)	→ solution (702 °C)
$\Delta H_{\text{ds,Cal}}$:	CaCO_3 (25 °C,s)	→ solution (702 °C)
ΔH_{CO_2} :	CO_2 (25 °C,v)	→ CO_2 (702 °C,v)
$\Delta H_{\text{H}_2\text{O}}$:	H_2O (25 °C,l)	→ H_2O (702 °C,v)



$$\Delta_f H_{298,\text{Lws}}^{\text{Oxides}} = -\Delta H_{\text{ds,Lws}} + \Delta H_{\text{ds,Crm}} + 2\Delta H_{\text{ds,Qtz}} + \Delta H_{\text{ds,Cal}} + 2\Delta H_{\text{H}_2\text{O}} + \Delta_f H_{298,\text{Cal}}^{\text{Oxides}} - \Delta H_{\text{CO}_2} \quad (1)$$

For each sample, pellets between 5 and 15 mg were introduced in the calorimeter. Following Kiseleva et al. (1996) and Bose and Navrotsky (1998), the calorimeter was calibrated with the heat content of pellets of similar weight of alpha-alumina (Aldrich, 99.99%, annealed at 1,500 °C for 24 h).

Table 1 and Fig. 1 show the enthalpy of drop-solution for all studied materials. The synthetic material has the most endothermic value, $474.8 \pm 2.1 \text{ kJ mol}^{-1}$. Data for the natural samples scatter somewhat, but the general trend goes to less endothermic values causing the

Table 1 Composition of the lawsonite samples used for calorimetry and their enthalpy of drop-solution (errors are two standard deviations of the mean)

Sample ID	Fe/(Fe + Al) (mol%)	ΔH_{ds} (kJ mol^{-1})
Lws5 (synth.)	0.00 ± 0.00	474.8 ± 2.1
H95982	1.39 ± 0.15	459.2 ± 9.4
S-97464-1	2.85 ± 0.15	465.6 ± 2.4
H91114	3.43 ± 0.15	458.5 ± 5.4

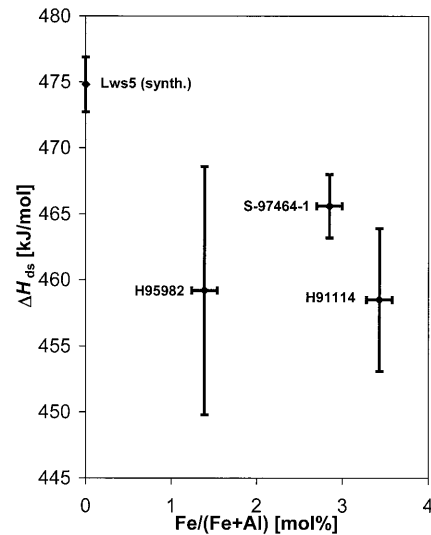


Fig. 1 Enthalpy of drop-solution for lawsonite. The error bars are two standard deviations of the mean

enthalpies of formation to become less exothermic with increasing iron content. This trend in ΔH_f is consistent with previous observations in our laboratory on Fe^{3+}/Al substitution in natural epidotes (Smelik et al. 2001). Errors associated with synthetic and natural samples are comparable, with the exception of sample H95982. This is attributed to phase impurities of epidote and sphene as described above.

The enthalpy of formation of lawsonite was calculated from the enthalpy of drop-solution of the synthetic material and from the data of the component oxides shown in Table 2, these data then being compared with previously published values (Table 3). The resulting values are $\Delta_f H^{\text{Oxides}}$ (lawsonite) = $-168.7 \pm 3.4 \text{ kJ mol}^{-1}$, and $\Delta_f H_{298}^0$ (lawsonite) = $-4,872.5 \pm 4.0 \text{ kJ mol}^{-1}$. The less exothermic $\Delta_f H^{\text{Oxides}}$ value reported by Barany (1962) is consistent with our observations for natural compositions. According to the chemical analysis reported by Barany (1962), the sample had an FFA value of 3.1%. The iron content and small levels of Ti and K impurities in Barany's sample might explain their less exothermic value although these authors corrected their direct measurements for impurities by -4.5 kJ mol^{-1} . On the other hand, the recalculated heat of formation reported by Hemingway and Robie (1977) is more

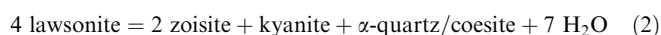
Table 2 Component values used in the thermodynamic cycle, calorimeter temperature: 701.7 °C = 974.85 K

Component	ΔH_{ds} (kJ mol ⁻¹)	Source
Al ₂ O ₃ (corundum)	108.0 ± 1.0	This study
SiO ₂ (quartz)	38.4 ± 0.8	This study
CaCO ₃ (calcite)	194.1 ± 0.9	This study
H ₂ O	69.0	Calculated from Robie and Hemingway (1995)
CO ₂	32.1	Calculated from Robie and Hemingway (1995)

exothermic than our value by 6.5 kJ mol⁻¹. The less exothermic values reported from calculations of internally consistent data sets generally are in good agreement with our measured value, only $\Delta_f H^{\text{Oxides}}$ calculated from the Berman (1988) database deviates notably from our measured value.

Reversal equilibrium experiments

The lawsonite dehydration



was first reversed by Newton and Kennedy (1963) in the stability field of quartz using natural materials and a piston-cylinder apparatus. In all but one experiment they mixed lawsonite and zoisite with aluminium hydroxide and silicic acid to satisfy reaction (2). Chatterjee et al. (1984) repeated the experiments of Newton and Kennedy (1963) using pure, synthetic phases with quartz and H₂O in excess, and located the equilibrium curve 30–40 °C below that obtained by Newton and Kennedy (1963). More recently, Schmidt and Poli (1994) studied the stability relation of zoisite and lawsonite at pressures from 1.7 to 9.2 GPa experimentally. Among other reactions, they re-examined reaction (2) in the stability fields of quartz and coesite up to 6.5 GPa. Their experiments were performed using mixtures of lawsonite–zoisite–grossular–cristobalite–corundum, lawsonite

–zoisite–cristobalite–corundum, or lawsonite–zoisite–kyanite–cristobalite, always with cristobalite and H₂O in excess. In the stability field of quartz, Schmidt and Poli (1994) confirmed the earlier results of Chatterjee et al. (1984). We also performed experiments on equilibrium (2) in a piston-cylinder apparatus at pressures up to 5 GPa using pure, synthetic phases with and without SiO₂ in excess. These experiments are described in detail below.

Experimental techniques

Independently of the lawsonite syntheses described above for enthalpy measurements, we prepared starting material for our equilibrium experiments at the high-pressure laboratory of the Institute for Mineralogy at Ruhr-University Bochum (Germany), using solid-media piston-cylinder presses described in detail by Massonne and Schreyer (1986). For the synthesis experiments gels were prepared from tetraethylorthosilicate (TEOS, Fluka, >99.99%), Al powder (Halewood Chemicals, >99.999%), and CaCO₃ (Merck, >99.5%). The gels, either of lawsonite composition, CaO:Al₂O₃:2SiO₂ (cf. Fig. 2), or lawsonite composition plus excess SiO₂, CaO:Al₂O₃:3SiO₂ (cf. Fig. 2), plus 20% distilled water were sealed in gold capsules (length = 16 mm, ϕ = 6 mm, wall thickness = 0.5 mm; cf. Fockenberg 1995). The capsules were placed in low-friction pressure cells consisting of rock salt and fired pyrophyllite with steel cylinders as resistance furnaces. Temperatures were measured using chromel–alumel thermocouples with the junction situated axially about 0.5 mm above the capsule.

All bracketing runs were also performed in a piston-cylinder press using an NaCl high-pressure cell with negligible friction effects (“type I”, Massonne and Schreyer 1986). Up to four gold capsules were run simultaneously. About 5 mg of reactants and products obtained from the synthesis experiments plus additional water were encapsulated and subjected to the desired *P–T* conditions. Here, the junction of the chromel–alumel thermocouple was placed in the centre between the four gold capsules (length = 10 mm, ϕ = 2 mm, wall thickness = 0.2 mm). In all experiments, the measured temperatures were corrected for the axial thermal gradient (Leistner 1979) as well as for the pressure effect on the emf of the thermocouple according to Getting and Kennedy (1970). After correction the overall accuracy is estimated to be about ±20 °C in synthesis experiments and ±10 °C in bracketing experiments. According to Chatterjee et al. (1984) the accuracy of the pressure measurement based on a simple force per area calibration is assumed to be ±1% of the stated pressure + 0.05 GPa.

All run products were examined optically and by standard X-ray powder diffraction. Detailed powder diffractograms of

Table 3 Enthalpy of formation of lawsonite at 25 °C (298.15 K) and 1 bar, comparison of available sources

Source	$\Delta_f H^{\text{Oxides}}$ (kJ mol ⁻¹)	$\Delta_f H^{\circ}_{298}$ (kJ mol ⁻¹)
Barany (1962): HF calorimetry	-155.6 ± 2.2	-4,797.1 ± 3.1
Hemingway and Robie (1977): recalculation of Barany's (1962) data using new experimental data of the components	-175.2 ± 3.0	-4,879.1 ± 3.7
Berman (1988): calculation of internally consistent data set by mathematical programming	-161.8	-4,865.67
Robie and Hemingway (1995): compilation of available data	-165.2 ± 3.0	-4,869.0 ± 2.1 ^a
Holland and Powell (1998): calculation of internally consistent data set by least squares refinement	-165.6 ± 2.5	-4,869.2 ± 0.9
Chatterjee et al. (1998): calculation of internally consistent data set using the Bayes method	-165.1 ^b	-4,866.3 ± 2.6
This work: high-temperature oxide melt calorimetry	-168.7 ± 3.4	-4,872.5 ± 4.0 ^c
This work: mathematical programming		-4,865.68

^aValue directly from Chatterjee et al. (1984), Halbach and Chatterjee (1984)

^bChatterjee et al. (1998) reported no errors for the constituent oxides CaO, Al₂O₃, SiO₂, and H₂O

^cCalculated using enthalpies of formation from the elements for the component oxides from Robie and Hemingway (1995)

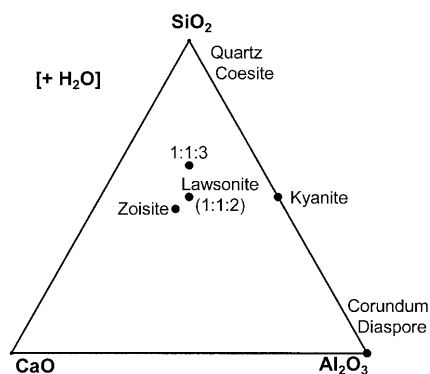


Fig. 2 Relevant phases of the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ projected from H_2O . 1:1:2 denotes the starting material of stoichiometric lawsonite composition, 1:1:3 denotes the starting material at SiO_2 -saturated conditions

synthetic lawsonite were obtained using an automated X-ray powder diffractometer (Siemens) with NBS Si ($a = 5.4208 \text{ \AA}$) as internal standard. The water content of synthetic lawsonite was determined by Karl-Fischer titration with an estimated uncertainty of $\pm 5\%$ (Johannes and Schreyer 1981), and by thermogravimetry/differential thermal analysis (TG/DTA) using a Linseis instrument, type 2045. Additionally, some of the run products obtained during the bracketing experiments were examined with a scanning electron microscope (Cambridge Instruments Stereoscan 250 M3).

Results

Synthesis experiments

Three different sets of synthesis runs (Table 4a) were performed. In order to obtain lawsonite \pm coesite or the reaction products zoisite, kyanite, and coesite, synthesis conditions were fixed at 4 GPa, 600–650 °C and 4 GPa, 800–850 °C respectively. While the runs performed with excess SiO_2 unequivocally resulted in either lawsonite + coesite or zoisite + kyanite + coesite, coesite could not be clearly identified in the run products of experiments performed using the stoichiometric gel ($\text{CaO}:\text{Al}_2\text{O}_3:2\text{SiO}_2$). The lattice parameters of the resulting lawsonite samples were obtained by X-ray powder diffraction:

$$\text{No. 241 } a = 5.841(1)\text{\AA}, \quad b = 8.787(2)\text{\AA}, \quad c = 13.126(3)\text{\AA}, \\ V = 673.7(2)\text{\AA}^3$$

$$\text{No. 155 } a = 5.835(1)\text{\AA}, \quad b = 8.782(1)\text{\AA}, \quad c = 13.119(2)\text{\AA}, \\ V = 672.3(2)\text{\AA}^3$$

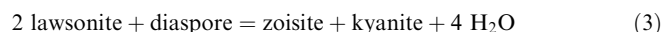
The cell parameters are in reasonable agreement with recent determinations (Libowitzky and Armbruster 1995; Grevel et al. 2000). In comparison, the molar volume of sample 155 obtained at SiO_2 -saturated conditions is slightly smaller, and that of the stoichiometric sample 241 is slightly greater than the volume reported by Chatterjee et al. (1984), $V(\text{lawsonite}) = 672.99(17) \text{ \AA}^3$. Sample 241 has a bulk water content of 11.48 wt% obtained by Karl-Fischer titration (Johannes and Schreyer 1981), which is very close to the ideal water

content of 11.466 wt%. A TG analysis of sample 246 yielded a similar bulk water content within experimental errors. However, the DTA showed a first endothermic event slightly above 500 °C, followed by a second peak between 610 and 810 °C. The second peak corresponds to the dehydration of lawsonite whereas the first peak indicates the presence of a small amount of diaspore below the detection limit of X-ray diffraction methods.

In the stability field of quartz, only synthesis experiments using a gel with excess SiO_2 ($\text{CaO}:\text{Al}_2\text{O}_3:3\text{SiO}_2$) were performed (Table 4a). At 2 GPa, 700 °C the reaction products zoisite, kyanite and quartz were obtained, whereas lawsonite + quartz were synthesised in a two-step process. At 4 GPa and 600 °C lawsonite + coesite were produced and subsequently recrystallised to lawsonite + quartz at 2 GPa, 500 °C.

Bracketing runs

A number of bracketing experiments was performed, either with a mixture of lawsonite and its decomposition products in stoichiometric proportions, or with excess SiO_2 . The direction of the reaction was determined by comparing the X-ray powder diffractograms of the run products with those of the starting mixtures. After each run the capsules were checked for leakage; the presence of water was confirmed in all cases. The results are listed in Table 4b (bulk composition 1:1:2), and Table 4c (bulk composition 1:1:3). Only increase or decrease of lawsonite is listed in Table 4b, because coesite could not be detected in the starting material and it was quite possible that diaspore was present during the experiments. Electron microscopy of some of the run products (runs 133, 136, 190, 215, cf. Table 4) showed the presence of unidentified aluminous phases in the experiments performed with the stoichiometric mixture, while coesite or quartz were clearly present in all runs listed in Table 4c. The results of the bracketing experiments are shown in Figs. 3 and 4. The experiments performed on stoichiometric composition, $\text{CaO}:\text{Al}_2\text{O}_3:2\text{SiO}_2$ (Fig. 3), showed lawsonite breakdown at 20–75 °C below the equilibrium position obtained at SiO_2 -saturated conditions ($\text{CaO}:\text{Al}_2\text{O}_3:3\text{SiO}_2$). The latter experiments (Fig. 4) are in very good agreement with the investigations of Chatterjee et al. (1984) and Schmidt and Poli (1994). Due to the possible presence of diaspore in our starting material, and the observations of aluminous phases instead of coesite or quartz in the run products of some experiments on the stoichiometric composition (Table 4b), we conclude that we have observed the reactions



or



during these experiments. Probably, in all synthesis and bracketing experiments some SiO_2 was dissolved in the

Table 4 Results of the piston-cylinder experiments. Mineral abbreviations were taken from Kretz (1983), modified by Bucher and Frey (1994). *Cs* Coesite, *Dsp* diaspore, *Ky* Kyanite, *Lws* lawsonite,

Qtz quartz, *Zo* zoisite. 1:1:2 or 1:1:3 denote the composition of the starting material CaO: Al₂O₃:2SiO₂, or CaO:Al₂O₃:3SiO₂. – Decrease, + increase in phase

Run ID	Starting material	P (GPa)	T (°C)	Duration (days)	Result
(a) Synthesis experiments					
241, 246	Gel 1:1:2	4	600	3	Lws, Dsp (?)
82	Gel 1:1:2	4	850	3	Zo, Ky, Cs (?)
155	Gel 1:1:3	4	650	3	Lws, Cs
156	Gel 1:1:3	4	800	3	Zo, Ky, Cs
214	Gel 1:1:3	4+2	600+500	2+2	Lws, Qtz ^a
181	Gel 1:1:3	2	700	3	Zo, Ky, Qtz
(b) Bracketing experiments on phase mix received from experiments 82 and 241 or 246					
117	Phase mix 1:1:2	4.5	750	1	Lws (+)
133 ^b	Phase mix 1:1:2	4.5	775	1	Lws (-)
136 ^b	Phase mix 1:1:2	4.5	800	1	Lws (-)
120	Phase mix 1:1:2	4	725	1	Lws (+)
102	Phase mix 1:1:2	4	750	1	Lws (-)
96	Phase mix 1:1:2	3.5	675	2	Lws (+)
139	Phase mix 1:1:2	3.5	700	2	Lws (-)
123	Phase mix 1:1:2	3	625	2	Lws (+)
110	Phase mix 1:1:2	3	650	2	No reaction
99	Phase mix 1:1:2	3	700	2	Lws (-)
143	Phase mix 1:1:2	2.5	575	2	Lws (+)
140	Phase mix 1:1:2	2.5	625	2	Lws (-)
(c) Bracketing experiments ^c on phase mix received from experiments 155 and 156 or 181 and 214					
196 ^b	Phase mix 1:1:3	5	850	2	Lws (+), Zo (-), Ky (-), Cs (-)
211	Phase mix 1:1:3	5	875	2	Lws (-), Zo (+), Ky (+), Cs (+)
199	Phase mix 1:1:3	4.5	825	2	Lws (+), Zo, Ky, Cs
208	Phase mix 1:1:3	4.5	850	2	no Lws, Zo (+), Ky (+), Cs (+)
194	Phase mix 1:1:3	4.3	800	1	Lws (+), Zo, Ky, Cs
202	Phase mix 1:1:3	4	775	3	Lws (+), Zo, Ky, Cs
215	Phase mix 1:1:3	4	800	2	No Lws, Zo (+), Ky (+), Cs (+)
190 ^b	Phase mix 1:1:3	4	825	3	No Lws, Zo (+), Ky (+), Cs
221	Phase mix 1:1:3	3.5	725	2	Lws (+), no Zo, Ky, Cs
242	Phase mix 1:1:3	3.5	750	2	Lws (-), Zo, Ky, Cs
224	Phase mix 1:1:3	3	675	3	Lws (+), Zo, Ky, Cs
204	Phase mix 1:1:3	3	700	4	Lws (-), Zo, Ky, Cs
195	Phase mix 1:1:3	2.8	640	4	Lws (+), Zo, Ky, Cs, Qtz (+)
231	Phase mix 1:1:3	2.5	625	3	Lws (+), Zo, Ky, no Cs, Qtz (+)
236	Phase mix 1:1:3	2.5	650	4	Lws (-), Zo (+), Ky (+), no Cs, Qtz (+)
251	Phase mix 1:1:3 ^d	2	550	4	Lws (+), Zo, Ky, Qtz
247	Phase mix 1:1:3 ^d	2	575	4	Lws (-), Zo, Ky, Qtz

^aRun 214 was a two-step experiment: Lws + Cs were synthesized at 4 GPa, 600 °C, and recrystallized to Lws + Qtz at 2 GPa, 500 °C

^bThe products of these experiments were investigated with an electron microscope

^cNot all experiments of Skrok (1993) are reported; only brackets close to the equilibrium position (I) are listed here

^dFor experiments at 2 GPa, a phase mix with Qtz instead of Cs was used

fluid which – for the stoichiometric starting composition – led to Al₂O₃ excess in the solid material (cf. Fig. 2). The brackets shown in Fig. 3 agree well with experiments on reactions (3) and (4) for Al₂O₃ saturated conditions (Schmidt and Poli 1994). For comparison, the equilibrium position of the reaction



as obtained by Fockenberg et al. (1996) is included in Fig. 3. At 5 GPa this equilibrium occurs at temperatures 100 °C lower than calculated with the Berman (1988) database. The equilibrium position reported by Fockenberg et al. (1996) is supported by observations of Schmidt and Poli (1994) in the Al₂O₃-saturated system. Evidently, several of our experiments were outside the

stability field of diaspore, i.e. in these cases presumably reaction (4) took place.

Quartz was found in the reaction products of experiments performed at pressures below 3 GPa with coesite in the starting material (runs 195, 231, 236). At 2.8 GPa and 640 °C this result supports recent experiments of Bose and Ganguly (1995), who have located the quartz/coesite reaction boundary approximately 1.5 GPa above the position reported earlier by Bohlen and Boettcher (1982) or Mirwald and Massonne (1980).

The cell parameters of different lawsonite samples obtained from equilibrium experiments were calculated from X-ray diffraction patterns. The molar volumes range from 672.3 ± 0.2 to $675 \pm 0.5 \text{ \AA}^3$ and do not show any significant dependence on the *P-T* conditions of the experiments.

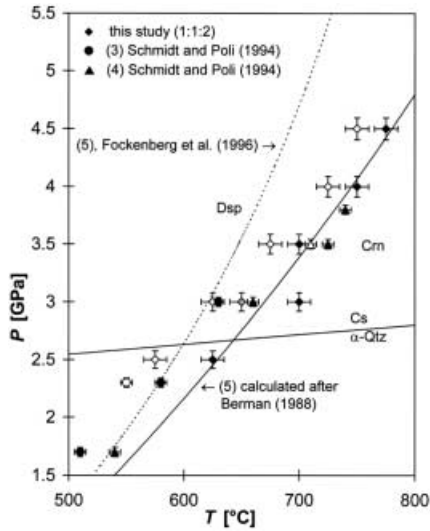


Fig. 3 Pressure-temperature diagram showing our experimental reversals using starting material of stoichiometric lawsonite composition, $\text{CaO}:\text{Al}_2\text{O}_3:2\text{SiO}_2$ (*diamonds*). Also included are the experimental reversals obtained by Schmidt and Poli (1994) for lawsonite breakdown reactions in the SiO_2 -undersaturated system, Eq. (3) (*circles*) and Eq. (4) (*triangles*), *Open symbols* indicate stability of lawsonite. *Filled symbols* indicate growth of the phases on the right-hand side of the equations. The *shaded symbol* indicates no reaction. *Error bars* are shown as cited by the respective authors. The *dashed line* delineates a fit to experiments on the dehydration of diaspore to corundum [reaction (5); Fockenberg et al. 1996]. Also included are calculated curves of reaction (5) and the coesite–quartz equilibrium (Berman 1988). For mineral abbreviations, see Table 5; for further explanation, see text

Mathematical programming analysis

As recommended by Grevel et al. (2000), we performed a mathematical programming analysis (MAP) of the thermodynamic data of lawsonite and zoisite in the chemical system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, based on all reliable reversal experiments on lawsonite and zoisite stability, and on the best calorimetric and equation of state data available now. A similar optimisation technique as described by Berman et al. (1986) was used. Our calculations were based on the data set of Berman (1988) with the following changes. For lawsonite and zoisite we have used $\Delta_f H_{298}^0$ (lawsonite) obtained in this study (Table 3), $\Delta_f H_{298}^0$ (zoisite) (Smelik et al. 2001), and the entropy values S_{298}^0 (lawsonite) = $230.04 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$, S_{298}^0 (zoisite) = $295.85 \pm 2.09 \text{ J mol}^{-1} \text{ K}^{-1}$, provided by Perkins et al. (1980)¹ as input. These parameters were allowed to vary within twice their error limits during the MAP analysis.

Molar volumes and the parameters describing thermal expansion and compressibility of the two phases were taken from Grevel et al. (2000). Berman (1988) uses

¹The error limits were reported by Berman (1988) for the original S_{298}^0 data; they were not included by Perkins et al. (1980).

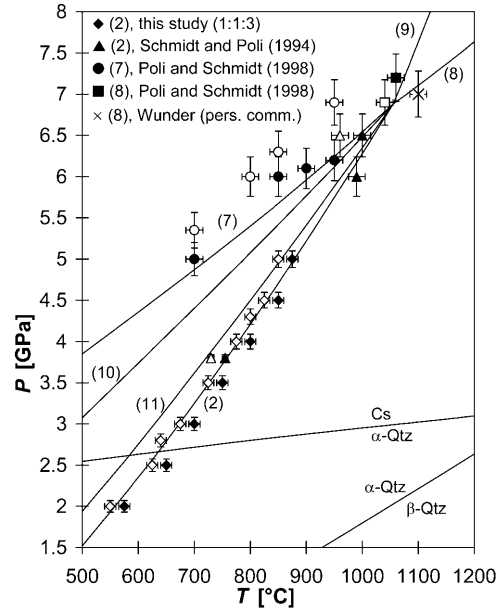
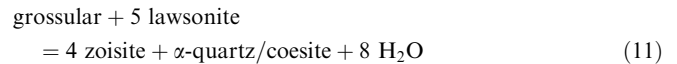
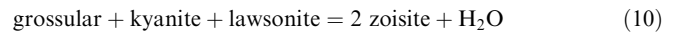
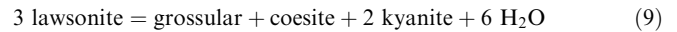
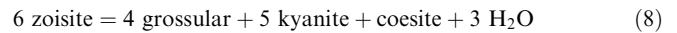
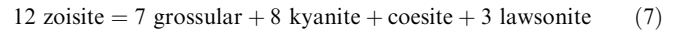
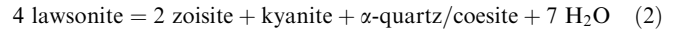


Fig. 4 Pressure-temperature diagram showing selected lawsonite and zoisite breakdown reactions in the SiO_2 saturated system at high pressures



as calculated with the Berman (1988) data set augmented by the data listed in Table 6. Also included are the experimental reversals on reaction (2) described in this study (*diamonds*) as well as selected reversal brackets from Schmidt and Poli (1994), and Poli and Schmidt (1998) on reactions (2) (*triangles*), (7) (*circles*), and (8) (*squares*). Also, Wunder (personal communication) obtained a bracket on reaction (8) performing experiments in a multi-anvil apparatus: 890.00 °C, 6 GPa (growth of zoisite), and 1,100.00 °C, 7 GPa (growth of products). The upper half-bracket is shown by a *cross*. Generally, *open symbols* indicate stability of lawsonite (2), or zoisite (7), (8), respectively; *filled symbols* indicate growth of the phases on the right-hand side of Eqs. (2), (7), and (8). *Error bars* are shown as cited by the respective authors. For mineral abbreviations, see Table 5

a simple polynomial to describe the P - V - T behaviour of the solid phases in his database:

$$\begin{aligned} V(P, T) = V_{298}^0 \times (1 + v_1(P - 1) + v_2(P - 1)^2 + v_3(T - T^0) \\ + v_4(T - T^0)^2), \quad T^0 = 298.15 \text{ K} \end{aligned} \quad (6)$$

Grevel et al. (2000) have fitted v_1 and v_3 [Eq. (6)] to their P - V - T data of lawsonite and zoisite. The measured volumes scattered too much to obtain precise values of v_2 and v_4 , and therefore these parameters were set equal

Table 5 Mineral equilibria used for the MAP analysis. Mineral abbreviations were taken from Kretz (1983), modified by Bucher and Frey (1994). *An* Anorthite, *Cs* coesite, *Crn* corundum, *Dsp* diaspore, *Gr*s grossular, *Ky* kyanite, *Lws* lawsonite, *Mrg* margarite, *Prh* prehnite, *Prl* pyrophyllite, *Qtz* quartz, *Sil* sillimanite, *Zo* zoisite

Reaction	No. of half brackets	References
6Zo = 4Gr _s + 5Ky + 1Cs + 3H ₂ O	4	Poli and Schmidt (1998), Wunder (personal communication)
4Lws = 2Zo + 1Ky + 1Cs + 7H ₂ O	22	This study, Schmidt and Poli (1994)
4Lws = 2Zo + 1Ky + 1 α -Qtz + 7H ₂ O	13	This study, Chatterjee et al. (1984), Schmidt and Poli (1994)
3Lws = 1Gr _s + 1Cs + 2Ky + 6H ₂ O	2	Schmidt and Poli (1994)
2Lws + 1Dsp = 1Zo + 1Ky + 4H ₂ O	4	Schmidt and Poli (1994)
4Lws + 1Crn = 2Zo + 2Ky + 7H ₂ O	5	Schmidt and Poli (1994)
1Lws = 1An + 2H ₂ O	5	Perkins et al. (1980), after Crawford and Fyfe (1965)
12Lws = 6Zo + 2Ky + 1Prl + 20H ₂ O	4	Nitsch (1972)
4Lws + 2 α -Qtz = 2Zo + 1Prl + 6H ₂ O	3	Nitsch (1972)
4Zo + 1 α -Qtz = 5An + 1Gr _s + 2H ₂ O	29	Newton (1966), Boettcher (1970), Chatterjee et al. (1984)
6Zo = 6An + 2Gr _s + 1Crn + 3H ₂ O	21	Newton (1965), Boettcher (1970), Chatterjee et al. (1984)
2Zo + 1Ky + 1 α -Qtz = 4An + 1H ₂ O	42	Goldsmith (1981), Johannes (1984), Chatterjee et al. (1984), Jenkins et al. (1985)
2Zo + 1Sil + 1 α -Qtz = 4An + 1H ₂ O	14	Newton and Kennedy (1963), Newton (1966)
4Mrg = 2Zo + 2Ky + 3Co + 3H ₂ O	4	Chatterjee et al. (1984)
4Mrg + 3 α -Qtz = 2Zo + 5Ky + 3H ₂ O	8	Jenkins (1984)
5Prh = 2Zo + 2Gr _s + 3 α -Qtz + 4H ₂ O	10	Chatterjee et al. (1984), Connolly and Kerrick (1985)
12Zo = 7Gr _s + 8Ky + 1Cs + 3Lws	8	Poli and Schmidt (1998)

to 0. Whereas the molar volumes were kept at a fixed value (cf. Table 6), the parameters v_1 and v_3 were also treated as variables in the MAP analysis.

The heat capacity data of lawsonite and zoisite as well as all other thermodynamic data of the pertinent minerals in the CASH system were taken from Berman (1988).

To calculate the properties of water, the equation of state (EOS) proposed by Grevel and Chatterjee (1992) was used. As demonstrated by Theye et al. (1997), calculations of mineral equilibria based on this EOS are very similar to the Berman (1988) formalism at pressures < 5 GPa. At higher pressures the calculated temperature of equilibrium is approximately 30–40 °C lower if the EOS of Grevel and Chatterjee (1992) is used, but this is still well within the experimental uncertainties reported in the studies cited above (e.g. Schmidt and Poli 1994).

The MAP analysis was constrained by all equilibria listed in Table 5. These brackets were chosen, because Berman (1988) already demonstrated the reliability of the underlying experiments or because they were obtained more recently. Although our results using the stoichiometric mixture most likely reflect the position of reactions (3) and (4), they were not used as constraints for our calculations, because it was not possible to un-

equivocally prove equilibrium conditions during the experiments. Prior to fixing the phase equilibrium constraints of the MAP analysis, the P – T co-ordinates of each half bracket were adjusted away from the estimated position of equilibrium by an amount equal to the experimental uncertainties in pressure and temperature (cf. Berman et al. 1986). For the mathematical procedure Fortran routines of the NAG Fortran library (Numerical Algorithms Group Ltd., Oxford) were applied.

Based on the constraints described above, it was possible to solve the optimisation problem. All reversal experiments listed in Table 5 are consistent with the Berman (1988) data set modified by the resulting thermodynamic data of lawsonite and zoisite listed in Table 6. The final value of $\Delta_f H^0_{298}$ (lawsonite), $-4,865.68 \text{ kJ mol}^{-1}$, is 6.8 kJ mol^{-1} less exothermic than the measured value, whereas $\Delta_f H^0_{298}$ (zoisite), $-6,888.99 \text{ kJ mol}^{-1}$, now is 10.5 kJ mol^{-1} more exothermic than the value of Smelik et al. (2001). Smelik et al. (2001) based their enthalpy measurements on calibrations of the calorimeter using the heat content of Pt pieces (cf. Navrotsky 1997). During most other similar studies performed in this laboratory recently (e.g. Kiseleva et al. 1996; Bose and Navrotsky 1998; this study), the calorimeter was calibrated with Al_2O_3 pellets of known heat content. A recalculation of the drop-solu-

Table 6 Refined thermodynamic data for lawsonite and zoisite (the notation follows Berman 1988). Molar volumes were used by Grevel et al. (2000) for initial calculations: V^0_{298} (lawsonite) is the mean value of several observations of Grevel et al. (2000) whereas

V^0_{298} (zoisite) is based on data of Smith et al. (1987). The volumes as well as the heat capacity data taken from Berman (1988) were not refined during the MAP analysis. To be compatible to the Berman (1988) data set, pressure units are given in kilobar here

Phase	$\Delta_f H^0_{298}$ (kJ mol ⁻¹)	S^0_{298} (J K ⁻¹ mol ⁻¹)	V^0_{298} (cm ³ mol ⁻¹)	$v_1 \times 10^5$ (bar ⁻¹) ^a	$v_3 \times 10^5$ (K ⁻¹) ^a
Lawsonite	-4,865.68	229.27	101.55	-0.08141	3.340
Zoisite	-6,888.99	297.71	135.65	-0.06899	2.733

^a $v_2 = 0$ and $v_4 = 0$ for both phases

tion values reported by Smelik et al. (2001) with a calibration constant obtained from alumina calibrations finally resulted in $\Delta_r H_{298}^0$ (zoisite) = $-6,886.6 \pm 6.8$ kJ mol⁻¹, which is much closer to the result obtained from the MAP analysis. The refined standard entropy values, S_{298}^0 (lawsonite) = 229.27 and S_{298}^0 (zoisite) = 297.71 J mol⁻¹ K⁻¹, changed well within the error limits reported for the calorimetric measurements. All these refined values are very similar to Berman's (1988) original values, which is not surprising because all entropy and enthalpy values are highly correlated, and all other calorimetric data were restricted to the Berman (1988) data set prior to the MAP analysis.

The changes of the parameters v_1 and v_3 describing the P - V - T behaviour of zoisite are negligible, whereas v_1 (lawsonite) is slightly smaller than the input value, indicating a smaller compressibility of lawsonite than observed by Grevel et al. (2000). On the other hand, v_3 (lawsonite) is somewhat greater than reported by Grevel et al. (2000). As published recently by Sinogeikin et al. (2000), the bulk modulus of lawsonite obtained by Grevel et al. (2000), 106.7 GPa, seems to be slightly too small. This observation is supported by the MAP analysis in this study. A re-fit of the bulk modulus of lawsonite, using the Birch-Murnaghan equation of state ($K' = 4$) to P - V values calculated with Eq. (6) and v_1 (lawsonite) = -0.08141×10^{-5} bar⁻¹, resulted in 120.7 GPa which is very close to recent observations from Brillouin spectroscopy, K (lawsonite) = 123.2 GPa (Sinogeikin et al. 2000), and diamond-anvil cell experiments by Daniel et al. (1999) who obtained 124.1 GPa.

Figure 4 shows some calculated equilibria in the SiO₂-saturated part of the CASH system at high pressures. For the calculations the Berman (1988) data augmented by all data listed in Table 6 were used. The calculations were performed with TWEEQU (Berman 1991). They were limited to 8 GPa because data for stishovite, which becomes the stable SiO₂ modification above 8 GPa, are not included in the Berman (1988) database. The thermodynamic data for lawsonite and zoisite obtained by the MAP analysis are consistent with the reversals of Schmidt and Poli (1994), Poli and Schmidt (1998), and the reversals described in this study for the SiO₂-saturated system (Table 4c). The effect of the modification of the lawsonite and zoisite data on the position of all other equilibria listed in Table 5 was negligible, because the calorimetric data for zoisite and lawsonite changed only slightly in relation to the Berman (1988) database. The more significant changes to the P - V - T data of these phases have less impact at lower pressure, where most of the reactions not depicted in Figs. 3 and 4 take place.

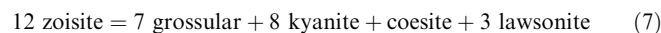
Conclusion

It has been shown that reliable thermobarometric estimates in the CASH system at pressure temperature conditions of UHPM can now be obtained using the

TWEEQU program (Berman 1991) and the Berman (1988) database augmented by our new data for lawsonite and zoisite. In order to improve the thermodynamic database of Berman (1988) further, a complete optimisation procedure varying all input data simultaneously is required. Additionally, a more sophisticated EOS approach for solids is needed, if an extension of the data-base to phases relevant for the Earth's mantle is desired.

In addition, the low-temperature calorimetric data obtained by Perkins et al. (1980) are somewhat problematic. These investigators attributed anomalies in their measurements at -143 and 0 °C to the influence of fluid inclusions. Libowitzky and Armbruster (1995) detected two phase transitions at -118 and 0 °C, indicating that new calorimetric measurements at low temperatures, especially in the vicinity of the phase transitions, are desirable. Such measurements would improve the accuracy of the standard entropy and the heat capacity data of lawsonite, which can be included into internally consistent thermodynamic databases.

Finally, it should be noted that a large number of geoscientists uses the database provided by Holland and Powell (1998). The calculated position of the reaction



using this data set (cf. Fig. 6c of Grevel et al. 2000) is 0.3–0.8 GPa below the experimentally determined equilibrium (Poli and Schmidt 1998). Presumably, this behaviour is caused by the parameters describing the P - V - T properties of zoisite and lawsonite in the Holland and Powell (1998) data set. In order to improve the database, it must be augmented by the most recent experimental thermodynamic data for zoisite and lawsonite. Then, a regression analysis has to be performed to obtain internal consistency (Holland and Powell 1998), which is beyond the scope of this paper.

Acknowledgements The authors thank R. Liebermann and T. Gasparik for help with the girdle anvil press at SUNY Stony Brook. J. Post of the Smithsonian Institution and V. Francis of Harvard University kindly provided the natural samples. E. Vicenzi assisted with electron microprobe analyses of lawsonite, and M. Borcsik with ICP analyses. Detailed reviews by J. Connolly and an anonymous reviewer helped to improve the manuscript. This work was supported by the Deutsche Forschungsgemeinschaft (Grants Gr 1586/1-1 bis 1-5, Schr 64/59-3), and by CHiPR, the Center for High-Pressure Research, a US National Science Foundation Science and Technology Center.

References

- Barany R (1962) Heats and free energies of formation of some hydrated and anhydrous sodium- and calcium-aluminum silicates. US Bureau Mines Rep Inv 5900
- Berman RG (1988) Internally-consistent thermodynamic data for minerals in the system Na₂O-K₂O-CaO-MgO-FeO-Fe₂O₃-Al₂O₃-SiO₂-TiO₂-H₂O-CO₂. J Petrol 29:445–522
- Berman RG (1991) Thermobarometry using multi-equilibrium calculations: a new technique, with petrological applications. Can Mineral 29:833–855

- Berman RG, Engi M, Greenwood HJ, Brown TH (1986) Derivation of internally-consistent thermodynamic data by the technique of mathematical programming: a review with application to the system MgO-SiO₂-H₂O. *J Petrol* 27:1331–1364
- Boettcher AL (1970) The system CaO-Al₂O₃-SiO₂-H₂O at high pressures and temperatures. *J Petrol* 11:337–379
- Bohlen SR, Boettcher AL (1982) The quartz <=> coesite transformation: a precise determination and the effects of other components. *J Geophys Res* 87:7073–7078
- Bose K, Ganguly J (1995) Quartz-coesite transition revisited: Reversed experimental determination at 500–1200 °C and retrieved thermochemical properties. *Am Mineral* 80:231–238
- Bose K, Navrotsky A (1998) Thermochemistry and phase equilibria of hydrous phases in the system MgO-SiO₂-H₂O: Implications for volatile transport to the mantle. *J Geophys Res* 103(B5):9713–9719
- Bucher K, Frey M (1994) *Petrogenesis of metamorphic rocks*, 6th edn. Springer, Berlin Heidelberg New York
- Chatterjee ND, Johannes W, Leistner H (1984) The system CaO-Al₂O₃-SiO₂-H₂O: new phase equilibria data, some calculated phase relations, and their petrological applications. *Contrib Mineral Petrol* 88:1–13
- Chatterjee ND, Krüger R, Haller G, Olbricht W (1998) The Bayesian approach to an internally consistent thermodynamic database: theory, database, and generation of phase diagrams. *Contrib Mineral Petrol* 133:149–168
- Chinnery N, Pawley AR, Clark SM (2000) The equation of state of lawsonite to 7 GPa and 873 K, and calculation of its high pressure stability. *Am Mineral* 85:1001–1008
- Comodi P, Zanazzi PF (1996) Effects of temperature and pressure on the structure of lawsonite. *Am Mineral* 81:833–841
- Comodi P, Zanazzi PF (1997) The pressure behavior of clinozoisite and zoisite: An X-ray diffraction study. *Am Mineral* 82:61–68
- Connolly JAD, Kerrick DM (1985) Experimental and thermodynamic analysis of prehnite stability. *Trans Am Geophys Union* 66:388
- Crawford WA, Fyfe WS (1965) Lawsonite equilibria. *Am J Sci* 263:262–270
- Daniel I, Fiquet G, Gillet P, Schmidt MW, Hanfland M (1999) *P-V-T* equation of state of lawsonite. *Phys Chem Minerals* 26:406–414
- Daniel I, Fiquet G, Gillet P, Schmidt MW, Hanfland M (2000) High-pressure behaviour of lawsonite: a phase transition at 8.6 GPa. *Eur J Mineral* 12:721–733
- Fockenberg T (1995) Synthesis and chemical variability of Mg-stauroilite in the system MgO-Al₂O₃-SiO₂-H₂O as a function of water pressure. *Eur J Mineral* 7:1373–1380
- Fockenberg T, Wunder B, Grevel K-D, Burchard M (1996) The equilibrium diaspore-corundum at high pressures. *Eur J Mineral* 8:1293–1299
- Getting IC, Kennedy G (1970) Effect of pressure on the emf of chromel-alumel and platinum-platinum 10% rhodium thermocouples. *J Appl Phys* 41:4552–4562
- Goldsmith JR (1981) The join CaAl₂Si₂O₈-H₂O (anorthite-water) at elevated pressures and temperatures. *Am Mineral* 66:1183–1188
- Grevel K-D (1998) The importance of P-V-T data for internally consistent data bases – some examples. *Petrology* 6:527–534
- Grevel K-D, Chatterjee ND (1992) A modified Redlich-Kwong-equation of state for H₂-H₂O fluid mixtures at high pressures and at temperatures above 400°C. *Eur J Mineral* 4:1303–1310
- Grevel K-D, Nowlan EU, Faßhauer DW, Burchard M (2000) In situ X-ray diffraction investigation of lawsonite and zoisite at high pressures and temperatures. *Am Mineral* 85:206–216
- Halbach H, Chatterjee ND (1984) An internally consistent set of thermodynamic data for twenty one CaO-Al₂O₃-SiO₂-H₂O phases by linear parametric programming. *Contrib Mineral Petrol* 88:14–23
- Hemingway BS, Robie RA (1977) Enthalpies of formation of low albite (NaAlSi₃O₈), gibbsite (Al(OH)₃), and NaAlO₂; revised values for $\Delta H^0_{f,298}$ and $\Delta G^0_{f,298}$ of some aluminosilicate minerals. *J Res US Geol Surv* 5:413–429
- Holland TJB, Powell R (1998) An internally-consistent thermodynamic dataset for phases of petrological interest. *J Metamorph Geol* 16:309–343
- Jenkins DM (1984) Upper-pressure stability of synthetic margarite plus quartz. *Contrib Mineral Petrol* 88:332–339
- Jenkins DM, Newton RC, Goldsmith JR (1985) Relative stability of Fe-free zoisite and clinozoisite. *J Geol* 93:663–672
- Johannes W (1984) Beginning of melting in the granite system Qz-Or-Ab-An-H₂O. *Contrib Mineral Petrol* 86:264–273
- Johannes W, Schreyer W (1981) Experimental introduction of CO₂ and H₂O in Mg-cordierite. *Am J Sci* 281:299–317
- Kiseleva I, Navrotsky A, Belitsky IA, Fursenko BA (1996) Thermochemistry and phase equilibria in calcium zeolites. *Am Mineral* 81:658–667
- Kretz R (1983) Symbols of rock-forming minerals. *Am Mineral* 68:277–279
- Leistner H (1979) *Temperaturgradienten-Messungen in Piston-Zylinder Pressen*. Fortschr Mineral 57(Beiheft 1):81–82
- Libowitzky E, Armbruster T (1995) Low-temperature phase transitions and the role of hydrogen bonds in lawsonite. *Am Mineral* 80:1277–1285
- Massonne H-J, Schreyer W (1986) High-pressure syntheses and X-ray properties of white micas in the system K₂O-MgO-Al₂O₃-SiO₂-H₂O. *N Jahrb Mineral Abh* 153:177–215
- Mirwald PW, Massonne H-J (1980) Quartz→coesite transition and the comparative friction measurements in piston-cylinder apparatus using talc-alsimag-glass (TAG) and NaCl high pressure cells: a discussion. *N Jahrb Mineral Mh*:469–477
- Navrotsky A (1977) Progress and new directions in high temperature calorimetry. *Phys Chem Minerals* 2:89–104
- Navrotsky A (1997) Progress and new directions in high temperature calorimetry revisited. *Phys Chem Minerals* 24:222–241
- Navrotsky A, Rapp RP, Smelik E, Burnley P, Circone S, Chai L, Bose K, Westrich HR (1994) The behavior of H₂O and CO₂ in high-temperature lead borate solution calorimetry of volatile-bearing phases. *Am Mineral* 79:1099–1109
- Newton RC (1965) The thermal stability of zoisite. *J Geol* 73:431–441
- Newton RC (1966) Some calc-silicate equilibrium relations. *Am J Sci* 264:204–222
- Newton RC, Kennedy GC (1963) Some equilibrium reactions in the join CaAl₂Si₂O₈-H₂O. *J Geophys Res* 68:2967–2983
- Nitsch K-H (1972) Das *P-T-X*_{CO₂}-Stabilitätsfeld von Lawsonit. *Contrib Mineral Petrol* 34:116–134
- Pawley AR (1994) The pressure and temperature stability limits of lawsonite: implications for H₂O recycling in subduction zones. *Contrib Mineral Petrol* 118:99–108
- Pawley AR, Redfern SAT, Holland TJB (1996) Volume behavior of hydrous minerals at high pressure and temperature. I. Thermal expansion of lawsonite, zoisite, clinozoisite, and diaspore. *Am Mineral* 81:335–340
- Pawley AR, Chinnery NJ, Clark SM (1998) Volume measurements of zoisite at simultaneously elevated pressure and temperature. *Am Mineral* 83:1030–1036
- Perkins III D, Westrum EF, Essene EJ (1980) The thermodynamic properties and phase relations of some minerals in the system CaO-Al₂O₃-SiO₂-H₂O. *Geochim Cosmochim Acta* 44:61–84
- Poli S, Schmidt MW (1998) The high pressure stability of zoisite and phase relationships of zoisite-bearing assemblages. *Contrib Mineral Petrol* 130:162–175
- Robie RA, Hemingway BS (1995) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10⁵ Pascals) pressure and at higher temperatures. *US Geol Surv Bull* 2131
- Schmidt MW (1995) Lawsonite: upper pressure stability and formation of higher density hydrous phases. *Am Mineral* 80:1286–1292
- Schmidt MW, Poli S (1994) The stability of lawsonite and zoisite at high pressures: Experiments in CASH to 92 kbar and implications for the presence of hydrous phases in subducted lithosphere. *Earth Planet Sci Lett* 124:105–118

- Schreyer W, Seifert F (1969) High-pressure phases in the system MgO-Al₂O₃-SiO₂-H₂O. *Am J Sci* 267(A):407-443
- Sinogeikin SV, Schilling FR, Bass JD (2000) Single crystal elasticity of lawsonite. *Am Mineral* 85:1834-1837
- Skrok V (1993) Synthese und Stabilität von Lawsonit im System CaO-Al₂O₃-SiO₂-H₂O unter hohen Drücken. Dipl Thesis, Ruhr-Universität Bochum
- Skrok V, Grevel K-D, Schreyer W (1994) Die Stabilität von Lawsonit, CaAl₂[Si₂O₇](OH)₂·H₂O, bei Drücken bis zu 50 kbar. *Ber Dtsch Mineral Gesell, Eur J Mineral* 6(Beiheft 1):270
- Smelik EA, Franz G, Navrotsky A (2001) A calorimetric study of zoisite and clinozoisite solid solutions. *Am Mineral* 86:80-91
- Smith JV, Pluth JJ, Richardson JW Jr, Kvik Å (1987) Neutron diffraction study of zoisite at 15 K and X-ray study at room temperature. *Z Kristallogr* 179:305-321
- Theye T, Chopin C, Grevel K-D, Ockenga E (1997) The assemblage diaspore + quartz in metamorphic rocks – a petrological, experimental and thermodynamic study. *J Metamorph Geol* 15:17-28