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Volume behavior of hydrous minerals at high pressure and temperature: I. Thermal expansion of lawsonite, zoisite, clinozoisite, and diaspore

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ABSTRACT

The temperature dependence of the lattice parameters of synthetic lawsonite [$CaAl_2Si_2O_7(OH)_2 \cdot H_2O$], natural zoisite [$Ca_2Al_3Si_3O_{12}(OH)$], natural clinozoisite [$Ca_2Al_3Si_3O_{12}(OH)$], and synthetic diaspore [$AlO(OH)$] have been measured at ambient pressure. The volume thermal expansion coefficients for lawsonite, zoisite, and clinozoisite are approximately constant over the measured temperature ranges (25–590 °C for lawsonite, 25–750 °C for zoisite, and 25–900 °C for clinozoisite), whereas the thermal expansion of diaspore increases slightly over the range 25–300 °C. Interestingly, the room-temperature volume of clinozoisite is greater than that of zoisite, but this situation is reversed above ~300 °C. The experimental results may be summarized as follows: lawsonite: $V/V_0 = 1 + 3.16\ (\pm 0.05) \times 10^{-5}\ (T - 298)$, $V_0 = 101.51\ (\pm 0.01)$ cm³/mol; zoisite: $V/V_0 = 1 + 3.86\ (\pm 0.05) \times 10^{-5}\ (T - 298)$, $V_0 = 136.10\ (\pm 0.02)$ cm³/mol; clinozoisite: $V/V_0 = 1 + 2.94\ (\pm 0.05) \times 10^{-5}\ (T - 298)$, $V_0 = 136.42\ (\pm 0.05)$ cm³/mol; diaspore: $V/V_0 = 1 + 7.96\ (\pm 0.28) \times 10^{-5}\ [T - 298 - 20\ (\sqrt{T} - \sqrt{298})]$, $V_0 = 17.74\ (\pm 0.01)$ cm³/mol.

INTRODUCTION

Hydrous minerals play a major role in transporting and storing H_2O in the Earth. They may be involved in metamorphic and melting reactions from the crust through the upper mantle. Knowledge of their stability at high pressures and temperatures is therefore important for interpreting the conditions of formation of natural mineral assemblages and for indicating processes at depth in the Earth that involve water, such as mantle melting above subducting slabs and the generation of arc magmas. Stabilities can be determined from phase-equilibrium experiments, but substantially more information is obtainable if thermodynamic properties of the phases are known. For example, the pressure-temperature positions of reactions not determined experimentally can be calculated, and data on the molar volume of H_2O can be extracted from phase-equilibrium experiments on dehydration reactions, if thermodynamic data for the solid phases are available. An accurate equation of state for H_2O is essential for calculating its properties at depth in the Earth, and so any method of determining its molar volume at high pressure is useful, particularly considering that most currently used equations of state for H_2O are based on extrapolations of low-pressure data and tend to diverge from each other at high pressures. However, although a comprehensive set of thermodynamic data exists for anhydrous mantle minerals such as pyroxenes, olivines, garnets, and the silica polymorphs, there are few data for high-pressure hydrous phases, with thermal expansivities and compressibilities most lacking. This situation needs to be remedied, particularly because recent studies have shown that a wide variety of hydrous phases may be stable at high pressures in the Earth, especially in subduction zones, where temperatures are considerably lower than in average mantle, and where a significant amount of H_2O is initially incorporated into the subducting slab. Four such mineral phases are lawsonite, zoisite, clinozoisite-epidote solid solutions (likely to be present in hydrated basalt), and diaspore (a possible component of aluminous sediments). The stabilities of lawsonite, zoisite, and diaspore have recently been shown to extend to very high pressures (Pawley 1994; Schmidt and Poli 1994). Thermal expansivities of these phases have not previously been measured, and compressibility has been determined only for diaspore (Xu et al. 1994). In this paper we present measurements of the thermal expansivity of lawsonite, zoisite, clinozoisite, and diaspore, and in the companion paper (Holland et al. 1996) we present measurements of the compressibility of lawsonite, zoisite, clinozoisite, and epidote. These new data allow more reliable calculation of the *P-T* positions of reactions involving these phases, indicating metamorphic parageneses and the conditions under which H_2O might be released from a subducting slab. The thermodynamic data may also be combined with experimental data on dehydration reactions to determine the molar volume of H_2O along the reactions.

Lawsonite (*Ccmm*), $CaAl_2Si_2O_7(OH)_2 \cdot H_2O$, is com-

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mon in blueschist-facies metabasalts and metagreywackes, where abundances may be up to 20 vol% (e.g., Hermes 1973). It is also occasionally found in eclogites, e.g., in eclogite nodules within kimberlite at Garnet Ridge, Arizona (Watson and Morton 1969). Lawsonite was shown experimentally by Pawley (1994) and Schmidt and Poli (1994) to be stable to very high pressure but at low temperature. In experiments on its composition, Pawley (1994) found that its maximum thermal stability was reached at 1080 °C at 9.4 GPa. The highest pressure at which it was synthesized was 12 GPa, at which pressure it was stable to a temperature of 1010 °C. At 14 GPa and 740 °C it was no longer stable. Schmidt and Poli (1994) determined its stability to 9.2 GPa, at which pressure it broke down at 1040 °C. The high-pressure, low-temperature stability of lawsonite, and its high H_2O content (11.5 wt%), make it a likely candidate for transporting H_2O deep into the mantle in subduction zones.

Zoisite (*Pnma*), $Ca_2Al_3Si_3O_{12}(OH)$, is one of the dehydration products of lawsonite at moderate pressures. Thus, it often occurs as an alteration product of lawsonite in rocks that have been subjected to high-pressure–low-temperature conditions in a subduction zone, followed by heating before or during exhumation (e.g., Watson and Morton 1969). It is a very common mineral in metabasaltic rocks of high-pressure amphibolite and, particularly, eclogite-facies metamorphism (e.g., Holland 1979; Franz and Selverstone 1992). The high-pressure stability of zoisite has been experimentally determined to occur at 6.7 GPa at ~1000 °C (Schmidt and Poli 1994), and therefore it too is capable of transporting H_2O to considerable depth in subduction zones. Clinozoisite ($P2_1/m$), $Ca_2Al_3Si_3O_{12}(OH)$, is the monoclinic form of zoisite.

Diaspore (*Pbnm*), AlO(OH), occurs principally as a low-pressure, low-temperature alteration product of Al-rich minerals and rocks. The breakdown of diaspore to corundum + H_2O has been determined up to 5 GPa, where the reaction occurs at ~720 °C (Grevel et al. 1994). Reaction with silica occurs at a lower temperature, and Wunder et al. (1993) showed that at ~400 °C and 5 GPa diaspore reacts with coesite to produce hydrous aluminosilicate phase pi, $Al_3Si_2O_7(OH)_3$. Diaspore has also been found to occur as a breakdown product of lawsonite in experiments at 14 GPa, 740 °C (Pawley 1994).

SAMPLES AND EXPERIMENTAL TECHNIQUE

The sample of natural zoisite came from the Moine Schist, Glenurquhart, Scotland (powdered sample kindly provided by C.M. Graham), and contained 2.3–4.3% of the ferric end-member, $Ca_2Al_2Fe^{3+}Si_3O_{12}(OH)$. Our natural colorless clinozoisite came from the Willsboro wollastonite deposit, New York, described initially by DeRudder and Beck (1964) and subsequently used in the single-crystal structure refinement by Dollase (1968). It is very close to end-member clinozoisite in composition, containing only about 2% epidote [$Ca_2Al_2Fe^{3+}Si_3O_{12}(OH)$] component (analysis tabulated in the companion paper, Holland et al. 1996). The lawsonite was synthesized at 6 GPa, 800 °C in a multi-anvil apparatus at Arizona State University. The diaspore was synthesized at 3 GPa, 550 °C in a piston-cylinder apparatus at Bristol University. Both synthetic samples were well crystallized and comprised 100% of the experimental products.

Clean and colorless individual crystals of zoisite and clinozoisite were hand-picked from the natural samples, and they and batches of the synthetic lawsonite and diaspore were crushed and ground to a fine powder for X-ray analysis. Two instruments were used to collect X-ray diffraction patterns at high temperature, allowing measurements to be made for more than one sample at a time. The individual powder samples of lawsonite and clinozoisite were mixed with Si as an internal standard and spread as a thin film on a platinum heating strip in a newly designed, high-temperature powder diffractometer [see Salje et al. (1993) for experimental details and design]. A strictly monochromatic ($CuK\alpha_1$) focused X-ray beam with a diameter of 0.1 × 10 mm was incident on the sample, and the diffraction pattern was collected over a 120° 2θ angle by a 4 K-PSD detector (INEL). Temperature calibration, uncertainties, and control are described by Salje et al. (1993). All readily detectable diffraction signals between $2\theta = 18°$ and $2\theta = 110°$ were measured. The position of each Bragg peak was measured individually and indexed to allow refinement of the lattice parameters. Typically, 35–48 peaks were used. Indexed diffraction patterns are shown in Figure 1.

The expansivities of the diaspore and zoisite samples were measured with the use of a high-temperature Guinier camera in transmission geometry, with the sample (with internal standard) held as a thin film in a small platinum loop. The experimental arrangement is described in greater detail by Redfern and Salje (1987). Films were scanned on a flatbed scanner similar to that described by O'Neill et al. (1993). Peak positions were determined by subsequent inspection of the individual intensity -2θ data at each Bragg reflection using a standard graph package. Typical diffraction patterns are shown in Figure 1. Most diffraction maxima between 10 and 60° 2θ were readily indexed, and their positions were used for refinement of the lattice parameters. The nonlinear least-squares program UnitCell (Holland and Redfern in preparation) was used for cell refinement, allowing refinement on the basis of the actual measured values of 2θ and providing a check on data quality through the use of regression diagnostics.

RESULTS

Values of cell parameters as a function of temperature are listed in Table 1 and plotted in Figures 2–5 (as relative expansion, normalized to 298 K values). The lawsonite, zoisite, and clinozoisite data show an essentially linear variation of molar volume with temperature, but the diaspore volumes indicate some curvature. The temperature evolution of the *a* parameter of diaspore, which has more significant curvature than either the *b* or *c* parameters, justifies the nonlinear fit for the dependence of

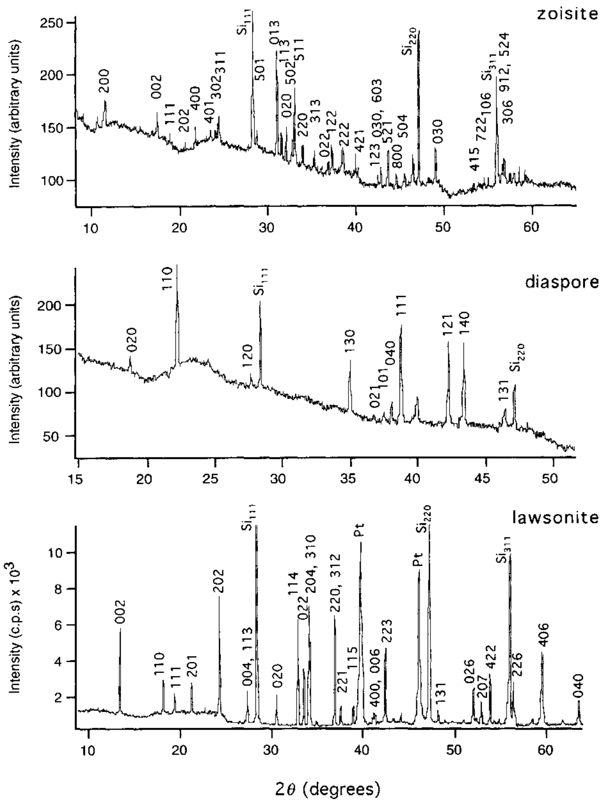

FIGURE 1. X-ray diffraction patterns of zoisite, diaspore, and lawsonite at room temperature (the original data for clinozoisite were mislaid and are not available, although lists of indexed reflections are available from the authors). The zoisite and diaspore patterns are scans of Guinier films (with resultant varying background), and the lawsonite and clinozoisite patterns were collected on the 120° position-sensitive detector. Reflections were indexed, and peaks from the silicon internal standard are shown. Peaks from the platinum strip heater (marked Pt) also appear in the pattern of lawsonite.

TABLE 1. High-temperature cell parameters

T (°C)	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
Clinozoisite					
25	8.861(3)	5.583(1)	10.141(3)	115.46(2)	452.9(1)
100	8.860(3)	5.590(1)	10.159(3)	115.50(2)	454.1(1)
200	8.863(3)	5.596(2)	10.172(3)	115.49(2)	455.4(2)
300	8.873(3)	5.604(1)	10.185(3)	115.56(2)	456.9(1)
400	8.880(2)	5.612(1)	10.195(2)	115.64(1)	458.0(1)
500	8.881(2)	5.619(1)	10.210(2)	115.67(1)	459.2(1)
600	8.881(2)	5.625(1)	10.221(2)	115.66(1)	460.3(1)
650	8.884(2)	5.630(1)	10.235(2)	115.68(2)	461.3(1)
700	8.883(2)	5.633(1)	10.239(2)	115.68(1)	461.7(1)
800	8.893(2)	5.639(1)	10.249(2)	115.72(1)	463.0(1)
900	8.903(3)	5.651(2)	10.273(3)	115.76(2)	465.5(2)
Zoisite					
25	16.210(2)	5.5552(8)	10.041(1)		904.2(2)
70	16.214(2)	5.5582(8)	10.048(1)		905.5(2)
120	16.213(2)	5.5644(8)	10.053(1)		906.9(2)
170	16.210(2)	5.5692(7)	10.067(1)		908.8(2)
220	16.209(2)	5.5749(7)	10.077(1)		910.6(2)
270	16.211(2)	5.5819(6)	10.088(1)		912.9(1)
320	16.209(2)	5.5861(6)	10.098(1)		914.4(1)
370	16.197(4)	5.5897(10)	10.109(2)		915.3(2)
420	16.206(2)	5.5962(8)	10.120(1)		917.8(2)
470	16.207(3)	5.6016(8)	10.131(1)		919.7(2)
520	16.198(3)	5.6064(9)	10.142(2)		921.0(2)
570	16.195(3)	5.6120(8)	10.152(2)		922.7(2)
650	16.189(4)	5.6223(8)	10.173(2)		925.9(2)
700	16.194(4)	5.6233(9)	10.180(2)		927.1(2)
750	16.195(4)	5.6282(9)	10.184(2)		928.3(2)
Diaspore					
25	4.397(2)	9.421(2)	2.8439(7)		117.80(4)
50	4.398(3)	9.424(3)	2.8458(11)		117.94(5)
80	4.399(3)	9.428(3)	2.8460(10)		118.03(5)
110	4.400(3)	9.432(3)	2.8496(11)		118.25(5)
140	4.403(2)	9.435(2)	2.8478(6)		118.30(4)
170	4.404(1)	9.438(1)	2.8490(6)		118.43(3)
200	4.406(2)	9.443(2)	2.8507(9)		118.62(4)
230	4.411(2)	9.447(2)	2.8505(9)		118.78(4)
260	4.414(3)	9.450(3)	2.8516(12)		118.94(6)
Lawsonite					
25	8.790(1)	5.840(1)	13.133(2)		674.1(1)
50	8.788(2)	5.840(1)	13.138(2)		674.3(2)
80	8.794(2)	5.845(1)	13.143(2)		675.5(2)
110	8.795(2)	5.849(1)	13.145(2)		676.2(2)
140	8.796(2)	5.850(1)	13.150(2)		676.7(2)
170	8.800(2)	5.852(1)	13.154(2)		677.3(2)
200	8.806(1)	5.853(1)	13.157(2)		678.2(1)
230	8.807(1)	5.856(1)	13.160(2)		678.7(2)
260	8.811(1)	5.858(1)	13.163(2)		679.3(2)
290	8.814(2)	5.860(1)	13.168(2)		680.1(2)
320	8.813(2)	5.863(1)	13.170(2)		680.4(2)
350	8.829(2)	5.863(1)	13.167(3)		681.6(2)
380	8.826(2)	5.865(1)	13.170(2)		681.7(2)
410	8.827(2)	5.867(1)	13.178(3)		682.5(2)
440	8.830(2)	5.868(1)	13.179(2)		682.9(2)
470	8.833(2)	5.870(1)	13.184(2)		683.6(2)
500	8.835(3)	5.871(2)	13.190(3)		684.1(2)
530	8.835(3)	5.875(1)	13.193(3)		684.8(2)
560	8.841(3)	5.872(2)	13.210(3)		685.8(3)
590	8.848(3)	5.869(2)	13.201(4)		685.5(3)

the volume (Fig. 5). As discussed in the review of Anderson et al. (1992) and Redfern et al. (1993), the thermal expansion coefficient α is expected to increase with temperature with a temperature-dependence that is small above the Debye temperature (similar to the well-known behavior of heat capacity). We wish to represent the diaspore expansion data with an equation containing as few adjustable parameters as possible but that extrapolates reasonably to higher temperatures. Although an equation such as $\alpha = a + bT + c/T^2$ can reproduce high-temperature data for minerals such as MgO, it is our experience that high-temperature expansion data are often not known precisely enough to justify fitting with three adjustable parameters. In a survey of minerals with expansivities measured to very high temperatures, we find that a reasonable fit can be obtained, within the uncertainties, with the expression $\alpha = \alpha_0 - \alpha_1 T^{-1/2}$. This expression has several advantages: (1) It requires only two adjustable parameters, (2) it allows α to increase with temperature, (3) α is bounded at high temperatures to the value α_0, and (4) of the two parameter equations investigated, it best fits the measured experimental data to high temperatures. In practice, a further simplification may often be made because we find that α_0 and α_1 occur in approximately constant ratio. For the minerals forsterite, diamond, ak-

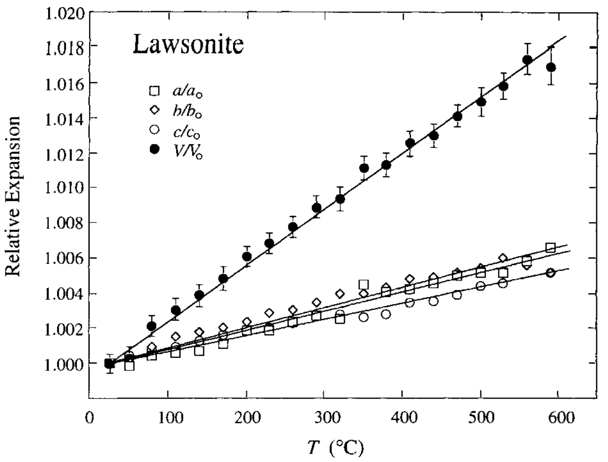

FIGURE 2. Relative expansion of lawsonite. Variation of cell parameters normalized to values at 298 K as a function of temperature. The curve for volume is a least-squares fit, giving $V/V_0 = 1 + 3.16\ (\pm 0.05) \times 10^{-5}\ (T - 298)$; the cell-parameter curves are just guides for the eye. Error bars for V/V_0 are two standard deviations; error bars on individual axial ratios are slightly larger than symbols.

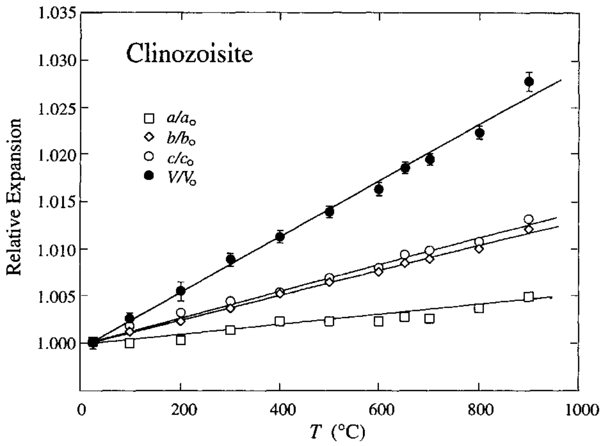

FIGURE 4. Relative expansion of clinozoisite. Variation of cell parameters normalized to values at 298 K as a function of temperature. The curve for volume is a least-squares fit, giving $V/V_0 = 1 + 2.94\ (\pm 0.05) \times 10^{-5}\ (T - 298)$; the cell-parameter curves are just guides for the eye. Error bars for V/V_0 are two standard deviations; error bars on individual axial ratios are as large as symbols.

ermanite, corundum, spinel, gehlenite, merwinite, monticellite, pseudowollastonite, lime, diopside, and albite, the values for α_1 are simply proportional to α_0, with $\alpha_1 = 10(\pm 2)\alpha_0$. Thus, if the thermal expansion measurements of a phase are available only over a small temperature interval, or if the uncertainties do not allow a precise value to be obtained for α_1 (as in diaspore), we assume that $\alpha = \alpha_0(1 - 10T^{-1/2})$.

With the assumptions discussed above, the volumes can then be represented by the expression $V/V_0 = 1 + \alpha_0(T - 298) - 2\alpha_1\ (\sqrt{T} - \sqrt{298})$, where $\alpha_1 = 0$ for zoisite, clinozoisite, and lawsonite, and $\alpha_1 = 10\alpha_0$ for diaspore. Least-squares regressions of the data in Table 1 give the following: lawsonite: $V/V_0 = 1 + 3.16\ (\pm 0.05) \times 10^{-5}\ (T - 298)$, $V_0 = 101.51\ (\pm 0.01)$ cm³/mol; zoisite: $V/V_0 = 1 + 3.86\ (\pm 0.05) \times 10^{-5}\ (T - 298)$, $V_0 = 136.10\ (\pm 0.02)$ cm³/mol; clinozoisite: $V/V_0 = 1 + 2.94\ (\pm 0.05) \times 10^{-5}\ (T - 298)$, $V_0 = 136.42\ (\pm 0.05)$ cm³/mol; diaspore: $V/V_0 = 1 + 7.96\ (\pm 0.28) \times 10^{-5}\ [T - 298 - 20(\sqrt{T} - \sqrt{298})]$, $V_0 = 17.74\ (\pm 0.01)$ cm³/mol.

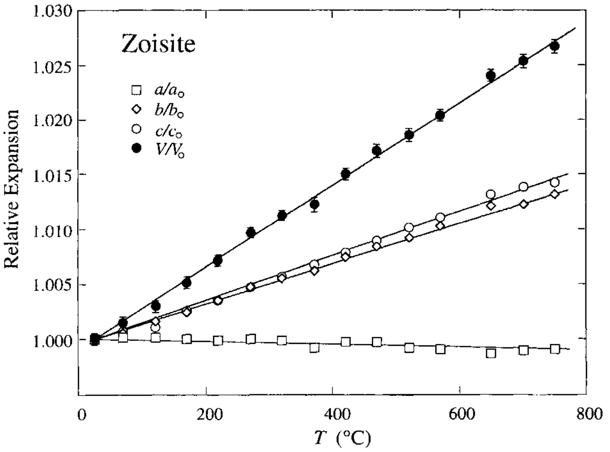

FIGURE 3. Relative expansion of zoisite. Variation of cell parameters normalized to values at 298 K as a function of temperature. The curve for volume is a least-squares fit, giving $V/V_0 = 1 + 3.86\ (\pm 0.05) \times 10^{-5}\ (T - 298)$; the cell-parameter curves are just guides for the eye. Error bars for V/V_0 are two standard deviations; error bars on individual axial ratios are as large as symbols.

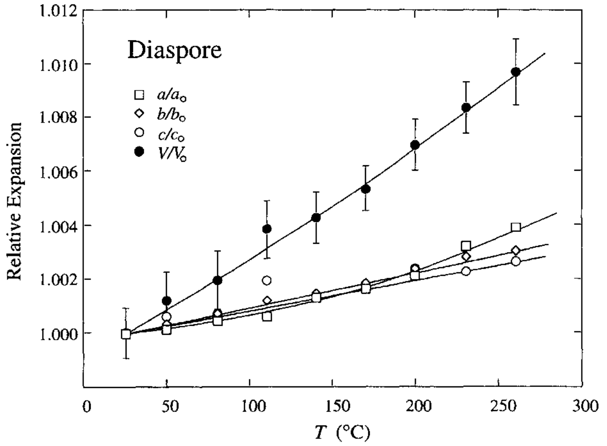

FIGURE 5. Relative expansion of diaspore. Variation of cell parameters normalized to values at 298 K as a function of temperature. The curve for volume is a least-squares fit, giving $V/V_0 = 1 + 7.96\ (\pm 0.28) \times 10^{-5}\ [T - 298 - 20\ (\sqrt{T} - \sqrt{298})]$; the cell-parameter curves are just guides for the eye. Error bars for V/V_0 are two standard deviations; error bars on individual axial ratios are much larger than symbols.

DISCUSSION

The structures of lawsonite, clinozoisite, and zoisite are related, each containing chains of AlO_6 octahedra parallel to *y*, cross-linked by Si_2O_7 tetrahedral groups parallel to *z*. Clinozoisite and zoisite differ mainly in the nature of the octahedral chains (Dollase 1968, Fig. 1), and the unit cell of zoisite is approximately related to that of clinozoisite by a unit-cell twinning such that a (zo) = $2a \sin \beta$ (cz). Thus, although the overall volume expansion of zoisite is a little greater than that of clinozoisite, the similarities of structure are evident in the expansions of the individual cell parameters. For both minerals the b and c parameters expand much more than the a parameter, with the zoisite a parameter remaining essentially constant. Because β increases with temperature in clinozoisite, the values for $2a \sin \beta$ (equivalent to a for zoisite) show only a very small temperature-dependence (about one-half that of the a parameter). The implication must be that the Al octahedra expand on heating, forcing the chains to lengthen (parallel to b), but presumably rotation of the cross-linkages, by means of the Si tetrahedral pairs, occurs and prevents the a axis from enlarging significantly. Details and confirmation of this would require single-crystal refinements at high temperature. Of much more interest, from a phase-equilibrium perspective, is the swapping of the relative volumes of ortho- and clinozoisite in the region of 300–350 °C, with clinozoisite becoming more dense than orthozoisite at the higher temperatures. The relative compressibilities, discussed in the companion paper (Holland et al. 1996), have a bearing on the possible dP/dT slope of the clino-ortho phase transition.

The expansion of lawsonite is approximately equal along all three axes, with c slightly less expansive than a and b. In contrast, zoisite shows no expansion along a, and expansion along b and c is approximately double that for lawsonite; presumably the presence of H_2O molecules accompanying the Ca cations in the cages between the Si_2O_7 cross-linking braces (Baur 1978, Fig. 1) helps prevent rotation of these polyhedra and thus causes lawsonite to expand in the a dimension, whereas zoisite does not.

The thermal expansivity of diaspore is also quite anisotropic, with a-axis expansion approximately double that of the b and c dimensions. Interestingly, a is also most sensitive to changes in pressure, being twice as compressible as b and c (Xu et al. 1994).

As an example of the use of the new data for diaspore, we compared calculated and experimental results on the breakdown reactions of diaspore and pyrophyllite + diaspore in the system Al_2O_3-SiO_2-H_2O. We used the program THERMOCALC (initially described in Powell and Holland 1988 and continuously upgraded since) and the thermodynamic data of Holland and Powell (1990), updated to allow for the new thermal expansion of diaspore presented in this paper. The fugacity of H_2O at high pressure was calculated using the CORK equation of state (Holland and Powell 1991). The agreement of calculations with the diaspore + pyrophyllite breakdown experiments of Haas and Holdaway (1973) below 1.0 GPa is excellent (Fig. 6a), as is the agreement with the experiments on diaspore breakdown up to 3 GPa (Fig. 6b). Above 3 GPa the calculated equilibrium temperatures are a little higher than the experimental brackets, a feature also noticed for other reactions in the companion paper (Holland et al. 1996). The origin of this discrepancy with the very-high-pressure data is not clear and could

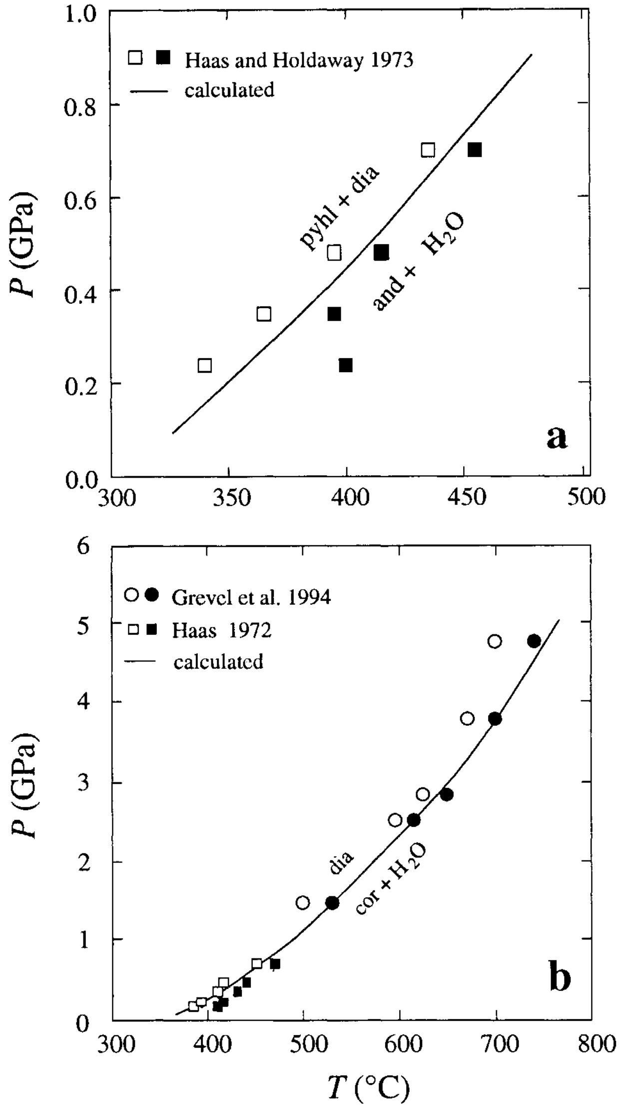

FIGURE 6. (**a**) Calculated *P-T* curve and experimental brackets for the reaction pyrophyllite + diaspore = andalusite + H_2O. (**b**) Calculated *P-T* curve and experimental brackets for the reaction diaspore = corundum + H_2O. Abbreviations: diaspore = dia, pyrophyllite = pyhl, andalusite = and, and aqueous fluid = H_2O. Thermodynamic data used in the calculations are from Holland and Powell (1990, updated) and from data on the thermal expansion of diaspore from this study, compressibility of diaspore from Xu et al. (1994), and H_2O properties from Holland and Powell (1991).

be due to pressure calibrations in the very-high-pressure experiments or to errors in some of the thermodynamic data for solid phases, H_2O, or both. Assuming that the thermodynamic properties of corundum are accurately known, removing the discrepancy would require lowering the entropy, compressibility, or heat capacity of diaspore or raising its thermal expansivity. All these thermodynamic data for diaspore are now quite well known from experimentation, except for the high-temperature heat capacities. The measured heat capacity of diaspore may, however, be extrapolated to high temperatures with reasonable accuracy using the methods outlined in Saxena et al. (1993), and errors in these data contribute little to the uncertainties in calculated temperatures. Use of the molar volumes for H_2O from the MD-simulation and fluid-inclusion studies of Brodholt and Wood (1993, 1994) exacerbates the disagreement. The high-pressure experiments shown in Figure 6b were already corrected for possible friction in the piston-cylinder device by −5%, and changing this to −10% would just bring the calculated curve to within the brackets. Stabilities of the Ca-bearing phases (lawsonite, clinozoisite, and zoisite) are investigated in the companion paper (Holland et al. 1996).

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