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ORIGINAL PAPER

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Molar volume and thermal expansion of glaucophane

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Abstract The molar volume of glaucophane [$Na_2Mg_3Al_2Si_8O_{22}(OH)_2$] has been determined in this study by correcting synthetic glaucophane-rich amphiboles made in the system Na_2O–MgO–Al_2O_3–SiO_2–H_2O for very small deviations from ideal glaucophane composition using recent volume data on key amphibole components. The derived unit-cell volume for end-member glaucophane is 862.7 ± 1.6 Å^3, which gives a molar volume of 259.8 ± 0.5 cm^3/mol and a calculated density of 3.016 ± 0.006 g/cm^3. This value has been corroborated through an essentially independent method by correcting the volumes of natural sodic amphiboles reported in the literature for non-glaucophane components, particularly including calcium-rich components, to yield a value of 861.2 ± 1.9 Å^3. The unit-cell volume derived from the synthetic amphiboles, which is considered here to be more reliable, is somewhat smaller than that reported previously in the literature. A thermal expansion (α_V) at 298 K of $1.88 \pm 0.06 \times 10^{-5}$/K was derived from unit-cell volumes measured in the range of 25–500°C for a synthetic glaucophane sample, which is noticeably smaller than previously reported.

Keywords Glaucophane · Sodic amphibole · Volume · Thermal expansion · Nyböite

Introduction

The inability to synthesize ideal, pure magnesian glaucophane is well documented in the literature (e.g. Maresch 1977; Carman and Gilbert 1983; Welch and Graham 1992; Tropper et al. 2000) and has posed the greatest impediment to investigating either its stability in pressure–temperature space or its physical properties. Without a good understanding of one of the most basic parameters of a mineral, its molar volume, one cannot make accurate calculations of the stability field of a mineral. The lack of an accurate molar volume is particularly detrimental for minerals having a high-pressure stability field, where small changes in volume can translate to relatively large changes in their upper-pressure stability limit. It has recently been shown (Jenkins and Corona 2006) that essentially pure glaucophane can be synthesized without the intervention of the sheet silicate that has long been encountered (Ernst 1961; Koons 1982) by maintaining the water content within the strict limits of 4–5 wt%. With the production of such glaucophane-rich amphiboles it is now possible to extract the molar volume of ideal glaucophane with only very small adjustments for non-glaucophane components. Because there is very little information on the bulk-volume thermal expansion (α_V) of glaucophane, this parameter was also measured here.

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Experimental methods

Unit-cell volumes at room temperature were determined from Rietveld refinements of powder X-ray diffraction patterns made on a Philips PW3040-MPD X-ray diffractometer (XRD) operated at 40 kV and 20 mA using Cu Kα radiation with a graphite diffracted-beam monochromator. Step scans were made over the range of 8–100 °2Θ at step sizes of 0.05 °2Θ for counting times sufficient to achieve at least a thousand counts on the maximum reflections. Samples were mounted on zero-background quartz plates with care taken to ensure that the X-ray beam remained on the sample at all angles. Refinements were made using the program DBWS-9807 (Young et al. 1995). The accuracy of the diffractometer, which is calibrated using silicon, was independently assessed by determining the cell dimensions of the corundum plate (SRM 1976) distributed by the National Institute of Standards and Technology (Gaithersburg, MD, USA). Using the same scan range as that used for the samples reported here, the cell dimensions were

found to be underestimated by 0.025% compared to the standard values, which translates to an uncertainty of 0.6 $Å^3$ (about six times the precision) in the accuracy of the unit-cell volume of glaucophane. Rietveld refinements were made on the synthesis products using the structure of glaucophane (Papike and Clark 1968) and the structures of any coexisting quartz (Lager et al., 1982), jadeite (Prewitt and Burnham 1966), and talc (Perdikatsis and Burzlaff 1981) to start the refinement. It should be noted that only the *c* dimension of talc was refined because of the low abundance and very strong (001) preferred orientation of this phase. The amphibole yields in these syntheses ranged from 90–100 wt%.

High-temperature X-ray diffraction powder patterns were obtained using an Anton Paar HTK 10 heating stage mounted on the Philips diffractometer. Heating-stage temperatures were calibrated against the melting point of lead (327°C). Samples were mounted on flat aluminum plates that were centered on the hot spot of the heating filament. The accuracy of thermal expansion measurements using this configuration was assessed by determining the linear thermal expansion $\left(\alpha_a = 1/a_0(da_0/dT)_P\right)$of aluminum (the sample holder), which was found at 298 K to be $21.9 \pm 1.6\times10^{-6}$ K^{-1}. This value is, within error, the same as the value of 23.1×10^{-6} K^{-1} recommended by Touloukian et al. (1975).

Results

The method used for extracting the volume of ideal glaucophane is as follows. Amphiboles synthesized in the five-component chemical system Na_2O–MgO–Al_2O_3–SiO_2–H_2O can be uniquely expressed as a combination of four independent amphibole compositions (assuming the water contents of the amphiboles are all constant). The exact choice of amphibole components is arbitrary; however, using components for which unit-cell volumes are known places much better constraints on the volumes of the components that are derived. In this study, the four components chosen were glaucophane ($Na_2Mg_3Al_2Si_8O_{22}(OH)_2$ = GL) and the non-glaucophane components, nyböite ($Na_3Mg_3Al_3Si_7O_{22}(OH)_2$ = NY), cummingtonite ($Mg_7Si_8O_{22}(OH)_2$ = CM), and sodian-cummingtonite ($Na_2Mg_6Si_8O_{22}(OH)_2$ = SC), all with the same monoclinic (*C*2/m) structure. Using simple matrix algebra one can transform the composition of a mineral expressed in terms of the moles of the oxides into the equivalent mole fractions (X_i) of the amphibole components. Assuming that the volume of an amphibole solid solution (V) is the linear sum of its constituent end members, the volume of a particular end-member component (V_i) is derived by solving the equation:

$$V = \sum (X_i V_i). \quad (1)$$

Table 1 lists the compositions, determined from electron microprobe analysis, of the most glaucophane-rich amphiboles synthesized previously (Jenkins and Corona 2006). The compositions are expressed in terms of the number of cations per 23 oxygens. Also shown in Table 1 is the composition of each amphibole expressed in terms of the mole fractions of the components GL, NY, CM, and SC.

The cell dimensions and unit-cell volumes of the amphiboles listed in Table 1 are given in Table 2, along with the agreement indices from the Rietveld refinements. Although unit-cell volume is the principal information sought in this study, the refinements also included the amphibole atomic coordinates, which yielded interatomic distances comparable to those reported for the single-crystal structure refinement of glaucophane (Papike and Clark 1968).

In this study, the volumes of end-member cummingtonite and sodian cummingtonite were considered to be known, while the volumes of glaucophane and nyböite

Table 1 Cation compositions (per 23 oxygens) from electron microprobe analyses and the equivalent mole fractions of glaucophane (GL), nyböite (NY), cummingtonite (CM), and sodian-cummingtonite (SC) for synthetic glaucophane-rich amphiboles

Cations	Sample					
	Ideal	FEGL 1-11-4	FEGL 1-14-8	FEGL 5-2-3	GL 4-R5	GL 7-R6
n		12	13	23	9	16
Si	8.00	7.85(9)	7.97(7)	7.99(5)	7.81(7)	8.02(4)
Al	2.00	1.98(10)	1.97(9)	1.94(9)	2.17(6)	1.97(3)
Mg	3.00	3.40(24)	3.09(10)	3.09(14)	3.20(10)	3.03(7)
Na	2.00	1.86(10)	2.02(10)	2.03(14)	1.85(9)	1.95(4)
Total components	15.00	15.08(11)	15.05(8)	15.05(9)	15.04(10)	14.97(4)
GL	1.00	0.765	0.943	0.958	0.800	1.015
NY	0.0	0.150	0.028	0.008	0.190	-0.020
CM	0.0	0.145	0.004	-0.011	−0.160	0.015
SC	0.0	−0.060	0.025	0.045	0.170	-0.010

The composition of ideal glaucophane for comparison is also shown. Values shown are averages of *n* number of analyses, and 1 SD uncertainties in the last digit are given in parentheses.
Synthetic glaucophane-rich amphibole samples were made by multiple treatments of reagent-grade oxide/glass or oxide/hydroxide mixtures with bulk water contents of 4–5 wt% at 750°C and 2.5 GPa for durations ranging from 389 to 954 h, as reported by Jenkins and Corona (2006)

Table 2 Unit-cell dimensions and volumes of synthetic amphiboles (all at 1 atm, 298 K) derived from Rietveld structure refinements of the synthetic amphiboles reported in Table 1

Cell dimensions	Sample				
	FEGL 1-11-4	FEGL 1-14-8	FEGL 5-2-3	GL 4-R5	GL 7-R6
a (Å)	9.5304(7)	9.5213(7)	9.5208(8)	9.5323(9)	9.519(1)
b (Å)	17.678(1)	17.680(2)	17.686(2)	17.669(2)	17.681(2)
c (Å)	5.2845(4)	5.2882(4)	5.2885(4)	5.2857(6)	5.2867(7)
β (°)	103.644(5)	103.609(5)	103.573(5)	103.654(8)	103.60(1)
V (Å^3)	865.2(1)	865.2(1)	865.6(1)	865.1(2)	864.8(2)
Agreement indices					
R_p	8.1	9.8	9.4	12.3	13.0
R_{wp}	10.8	13.5	12.3	16.6	17.46
DWD	1.20	1.30	1.42	1.30	1.57
GoF	1.63	1.46	1.65	1.93	1.57
R_{Bragg}	5.6	7.3	7.1	9.6	9.0

$R_p = 100\sum|y_i - y_{ci}|/\sum|y_i|$, $R_{wp} = 100\{\sum w_i(y_i - y_{ci})^2/\sum w_i y_i{}^2\}^{1/2}$, GoF = goodness-of-fit = $R_{wp}/(100\ \{(N-P)/\sum\ w_i\ y_i\}^{1/2})$, and $R_{Bragg} = 100\sum|I_o - I_c|/\sum|I_o|$, where y_i and y_{ci} are the observed and calculated intensities, respectively, at the ith step, $w_i = 1/y_i$, N = total number of steps, P = number of parameters being refined, I_o and I_c are the observed and calculated intensities, respectively, for the Bragg reflections of each phase
DWD Durbin–Watson d statistic

were considered unknown. The volume of pure (magnesian) cummingtonite extracted from natural (iron-bearing) cummingtonites has been reported as 874 Å^3 (Hirschmann et al. 1994), while the volume of sodian-cummingtonite in the $C2/m$ structure was extrapolated from high-temperature data (Cámara et al. 2003) down to room temperature as 901 Å^3. Because the amphiboles listed in Table 1 are very low in nyböite component, two nyböite-rich samples that were synthesized in the same chemical system as was studied here and that were reported earlier in the literature (OH-NY9 and OH-Q6 of Pawley 1992) were included, making the total number of samples in this analysis 7. Solving for the values of V_{GL} and V_{NY} in the equation,

$$V = X_{GL}\,V_{GL} + X_{NY}\,V_{NY} + X_{CM}(874) + X_{SC}(901), \qquad (2)$$

by regression ($n = 7$, $r = 0.997$), one obtains volumes of end-member glaucophane and nyböite of 862.7 ± 1.6 Å^3 and 873.9 ± 3.1 Å^3, respectively. The derived volume of nyböite, aside from being quite small compared to that of natural nyböitic amphiboles (Ungaretti et al. 1981), is not considered very reliable because of the relatively small number of nyböite-bearing samples included in this analysis and the relatively large extrapolation to end-member nyböite. The derived glaucophane volume is considered reliable and can be corroborated independently using natural sodic amphiboles, as discussed below.

The unit-cell dimensions of sample FEGL 1-14-8 at elevated temperatures are given in Table 3 and plotted in Fig. 1. The open symbols are the cell dimensions in the heating series, while the solid symbols represent the cell dimensions at 25°C after the heating series (after 500°C) to see if any hysteresis effects were discernible. Only the c parameter showed any significant hysteresis; the source of this discrepancy is not known and not expected in view of the lack of statistically significant hysteresis in any of the other parameters. All of the cell dimensions, with the possible exception of β, show a simple linear change with increasing temperature, as shown by the solid lines. A slight increase in the correlation coefficient (from 0.967 to 0.982) was obtained when β was fitted to a second-order polynomial in temperature. The dV/dT slope derived from the bottom plot in Fig. 1 is

Table 3 Unit-cell dimensions of synthetic glaucophanic amphibole sample FEGL 1-14-8 at elevated temperatures and 1 atm

Parameter	Temperature (°C)						
	25[a]	100	200	300	400	500	25[b]
a (Å)	9.5148(6)	9.5203(6)	9.5276(7)	9.5368(7)	9.5463(8)	9.5547(11)	9.5169(9)
b (Å)	17.664(1)	17.673(1)	17.682(1)	17.695(1)	17.707(2)	17.720(2)	17.669(2)
c (Å)	5.2836(4)	5.2837(4)	5.2851(4)	5.2864(4)	5.2883(4)	5.2910(6)	5.2815(5)
β (°)	103.609(6)	103.601(3)	103.576(6)	103.569(7)	103.56(1)	103.55(1)	103.624(8)
V (Å^3)	863.1(1)	864.0(1)	865.5(1)	867.2(1)	869.0(1)	870.9(2)	863.1(1)

[a]Unit-cell dimensions determined on the heating stage before the heating cycle. The heating stage alignment was not calibrated so accurately as the normal stage goniometer which leads to differences in the absolute, not relative, cell dimensions from those given in Table 2
[b]Unit-cell dimensions determined after the heating cycle to look for hysteresis effects

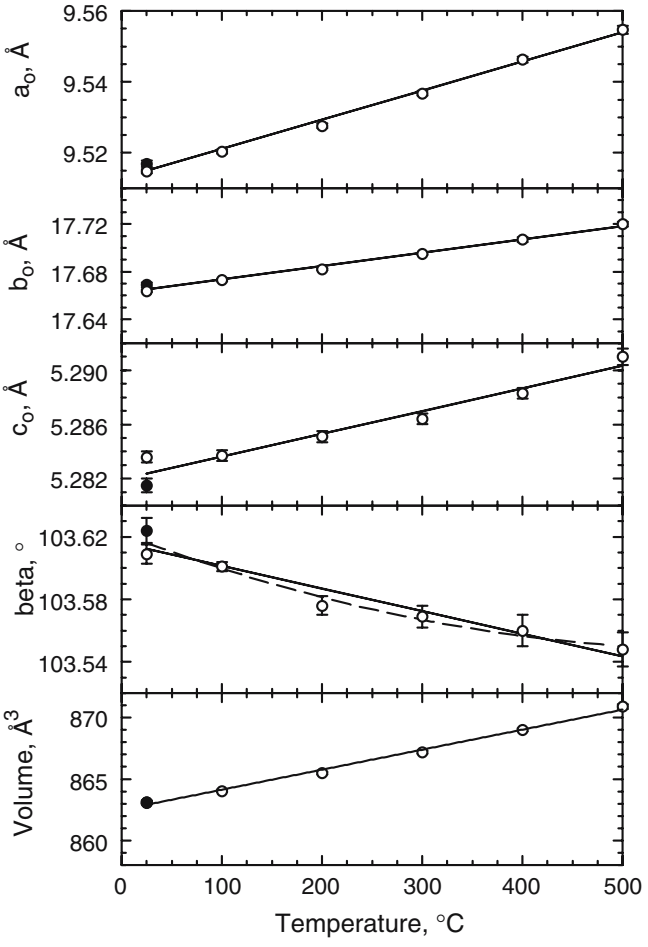

Fig. 1 Unit-cell dimensions of amphibole in sample FEGL 1-14-8 at 1 atm and temperatures up to 500°C. *Solid symbols* indicate cell dimensions measured at 25°C after the heating series (*open symbols*). Errors are less than the size of the symbol if not shown explicitly

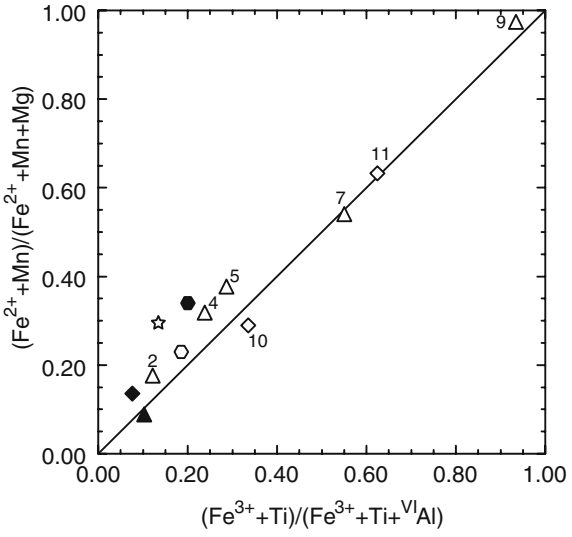

Fig. 2 Compositions of natural sodic amphiboles reported in the literature that were used for the derivation of the volume of glaucophane. Symbols are as follows: *open triangle* Borg (1967), *numbers* indicate sample number; *open diamond* Coleman and Papike (1968), *numbers* indicate sample number; *open hexagon* Papike and Clark (1968); *closed triangle* Holland (1988); *closed diamond* Gillet et al. (1989); *closed hexagon* Comodi et al. (1991); *star* Smelik and Veblen (1991), average of samples Veb1-Da, -Db, -Dc, -B, -A, -Dd, -De, and -E

$1.63(5)\times10^{-2}$ Å^3/K, which for a cell volume of 865.2 Å^3 gives a thermal expansion α_V of $1.88\pm0.06\times10^{-5}$/K.

Discussion

The derived volume of 862.7 ± 1.6 Å^3 ($=259.8\pm0.5$ cm^3/mol) for glaucophane is slightly lower than the currently accepted value of 865.2 Å^3 which had been derived by Holland (1988) from the volumes of natural sodic amphiboles. It is suggested here that the earlier (larger) volume for glaucophane has been over estimated. We have repeated the type of volume analysis done in earlier studies (Borg 1967; Coleman and Papike 1968; Hoffman and Katz 1982; Holland 1988), which uses essentially the same approach as that expressed in Eq. (1), for extracting the volume of ideal glaucophane from natural sodic amphiboles. Unlike earlier studies, which have sought to contour the entire Miyashiro diagram of common sodic amphiboles (Fig. 2), we have restricted our choice of natural amphiboles to those that lie close to the glaucophane-riebeckite join. By doing this we minimize the dependence of the volume analysis on the poorly constrained volumes of ferroglaucophane and magnesioriebeckite (Della Ventura et al. 2005) and take advantage of the recently determined volume of riebeckite ($Na_2Fe_3^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2$ = RB) of 916.5 Å^3 (Iezzi et al. 2003). The additional components that were chosen are tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$ = TR, 907 Å^3, Yang and Evans 1996), magnesiohornblende ($Ca_2Mg_4Al_2Si_7O_{22}(OH)_2$ = HB, 899 Å^3, Smelik et al. 1994), grunerite ($Fe_7Si_8O_{22}OH_2$ = GR, 924.5 Å^3, Hirschmann et al. 1994), and cummingtonite and sodian-cummingtonite that were discussed above. Natural sodic amphiboles reported in the literature that were used in this study (Borg 1967; Coleman and Papike 1968; Papike and Clark 1968; Holland 1988; Gillet et al. 1989; Comodi et al. 1991; Smelik and Veblen 1991) are shown in Fig. 2. Their compositions were recast into the seven amphibole components identified above (Table 4) and the equation:

$$V = X_{GL}V_{GL} + X_{CM}(874) + X_{SC}(901) + X_{TR}(916.5) + X_{TR}(906) + X_{HB}(899) + X_{GR}(924.5)$$

was solved by regression ($n=12$, $r=0.941$) to yield a volume for ideal glaucophane of 861.2 ± 1.9 Å^3. Note that this volume determination is essentially independent of the analysis using synthetic amphiboles (though they both use the same volumes for the CM and SC components) but gives virtually identical results. A comparison of all of the observed and calculated volumes for synthetic (based on the derived volumes of glaucophane

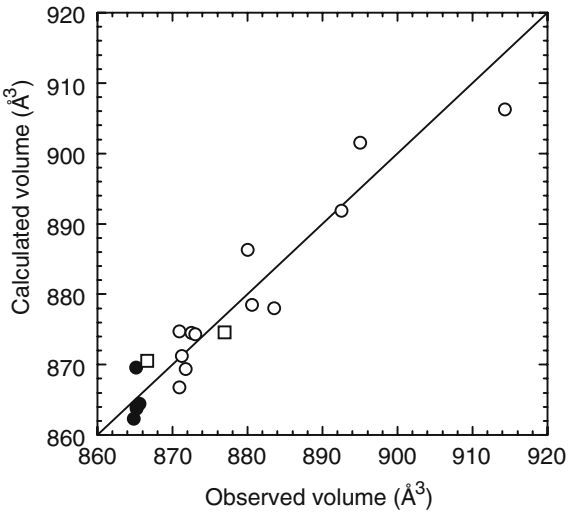

Fig. 3 Comparison of observed and calculated unit-cell volumes for natural sodic amphiboles from Table 4 (*open circles*), synthetic glaucophane-rich amphiboles from this study (*solid circles*), and synthetic sodic amphiboles along the glaucophane–nyböite join (*open squares*, Pawley 1992) based on the derived volumes of glaucophane and nyboite for synthetic amphiboles and on the derived volume of glaucophane for natural amphiboles from this study. The *diagonal line* represents the line of 1:1 correlation and the uncertainty in the individual volumes is within the size of the symbol

and nyböite) and natural (based on the derived volume of glaucophane) sodic amphiboles is shown in Fig. 3.

The only previous measurement of the thermal expansion of glaucophane is that of Gillet et al. (1989) who reported preliminary high-temperature X-ray data for natural glaucophane sample EM-A in Table 4 and Fig. 2. They reported a value for α_V of $2.6 \pm 0.3 \times 10^{-5}$/K, which is significantly higher than the value of $1.88 \pm 0.06 \times 10^{-5}$/K reported here. As noted by Gillet et al. (1989), the thermal expansion reported in their study was based on preliminary X-ray diffraction data and may be subject to revision. For comparison, the thermal expansion of tremolite can be derived from the *P–V–T* equation reported by Grevel et al. (1998), which is 2.06×10^{-5}/K at 298 K. It is interesting to compare the thermal expansions of glaucophane and tremolite to the thermal expansions of jadeite (2.47×10^{-5}/K) and diopside (3.33×10^{-5}/K) reported by Cameron et al. (1973). For both amphibole and pyroxene, the substitution of Ca for Na in the larger 8-coordinated sites and of Mg for Al within the octahedral slab joining the silicate chains of the "I-beam" structure promotes an increase in the thermal expansion of the structure, though it is a much larger percentage increase for pyroxene compared to amphibole.

The preferred volume for ideal glaucophane is that derived from the synthetic sodic amphiboles, namely 862.7 ± 1.6 Å^3 ($= 259.8 \pm 0.5$ cm^3/mol). This is because of the simpler chemistry of the synthetic amphiboles (devoid of Ca, Ti, Mn, etc.) and the consequent smaller compositional range over which the fundamental assumption of volume linearity must be applied. The only negative aspect of using the synthetic sodic amphiboles is that the volume of nyböite is derived and not independently fixed. Based on the above volume the calculated density for ideal glaucophane is 3.016 ± 0.006 g/cm^3. The

Table 4 Cation compositions (per 23 oxygens) of natural sodic amphiboles near the glaucophane-riebeckite join reported in the literature and their equivalent mole fractions of glaucophane (GL), cummingtonite (CM), sodian-cummingtonite (SC), riebeckite (RB), tremolite (TR), magnesian-hornblende (HB), and grunerite (GR)

Cations	Sample[a]											
	B2	B4	B5	B7	B9	CP10	CP11	Tib	THG	EM-A	Sval	VEB1
Si	7.78	7.86	7.94	8.00	7.93	7.95	7.99	7.92	7.95	7.92	8.00	7.91
Ti	0.02	0.01	0.01	0.04	0.07	0.01	0.00	0.06	0.01	0.00	0.00	0.01
Al	1.98	1.56	1.40	0.90	0.20	1.38	0.79	1.66	1.88	1.91	1.60	1.65
Fe^{3+}	0.23	0.44	0.53	1.06	1.77	0.67	1.34	0.30	0.20	0.15	0.40	0.24
Fe^{2+}	0.56	1.00	1.11	1.58	2.39	0.88	1.73	0.70	0.27	0.43	1.02	1.07
Mg	2.61	2.18	1.87	1.36	0.07	2.21	1.10	2.38	2.76	2.60	1.98	2.26
Mn	0.00	0.02	0.02	0.02	0.37	0.02	0.10	0.01	0.00	0.00	0.00	0.00
Ca	0.06	0.17	0.20	0.17	0.13	0.18	0.09	0.20	0.11	0.05	0.00	0.10
Na	1.75	1.76	1.85	1.79	1.89	1.74	1.89	1.84	1.87	1.93	1.98	1.77
K	0.01	0.01	0.01	0.01	0.14	0.01	–	–	0.01	–	–	0.01
Volume	871.7	880.6	883.5	892.5	914.3	880	895	870.92	871.2	870.92	872.5	873.0
GL	0.769	0.649	0.672	0.443	0.084	0.588	0.336	0.727	0.857	0.884	0.803	0.748
CM	0.067	−0.017	−0.071	0.027	−0.018	0.064	0.042	−0.045	0.018	−0.020	−0.050	−0.038
SC	−0.017	0.009	−0.018	−0.097	−0.062	−0.058	−0.061	0.013	−0.022	0.006	−0.013	0.019
RB	0.122	0.222	0.270	0.549	0.921	0.340	0.670	0.180	0.100	0.075	0.200	0.118
TR	−0.188	−0.042	0.068	0.078	0.049	−0.012	−0.014	0.037	−0.028	−0.046	0.003	−0.027
HB	0.219	0.128	0.030	0.007	0.017	0.102	0.059	0.063	0.083	0.071	−0.003	0.076
GR	0.027	0.051	0.046	−0.007	0.001	−0.017	−0.026	0.023	−0.004	0.029	0.060	0.102

[a] *B2, B4, B5, B7, B9* samples 2, 4, 5, 7, 9 of Borg (1967); *CP10, CP11* samples 10 and 11 of Coleman and Papike (1968); *Tib* sample from Tiburon Peninsula, California, USA (Papike and Clark 1968); *THG* sample THGW2 of Holland (1988); *EM-A* sample EM-A of Gillet et al. (1989); *Sval* sample from Svalbard Islands, Norway of Comodi et al. (1991); *VEB1* average of samples VEB1-A, -B, -D, and -E of Smelik and Veblen (1991)

smaller volume obtained in this study also implies a higher-pressure stability field for glaucophane, particularly for water-conserving reactions that involve relatively small entropy changes. For example, Fig. 4 shows how the calculated location of the high-pressure stability curve for glaucophane, breaking down to 2 jadeite + talc, will increase from about 3.6–4.0 GPa in the range of 700–1,000°C (an increase in depth from about 108–120 km) if one simply substitutes the new volume derived in this study (259.8 cm^3/mol) with the previous volume for glaucophane (260.5 cm^3/mol) while keeping all of the remaining thermodynamic data constant (Holland and Powell 1998). With a stability of up to 4.0 GPa, magnesium-rich glaucophane could well be added to the list of indicator minerals for ultrahigh-pressure metamorphic terranes (Chopin 2003). The lower-pressure stability of glaucophane defined by the reaction glaucophane + 2 quartz breaking down to 2 albite + talc is also shown in Fig. 4. In this case the boundary is shifted only slightly to lower pressures (expanding the glaucophane stability field) because the volume of glaucophane contributes less to the overall volume change of this reaction and because the Gibbs free-energy change associated with the $P\Delta V$ term is inherently smaller at these lower pressures. It is stressed, however, that the impact of this study is less on the effect that the newly revised volume will have on the placement of reaction boundaries and more on establishing a fundamental parameter for the key index mineral of blueschist-facies rocks.

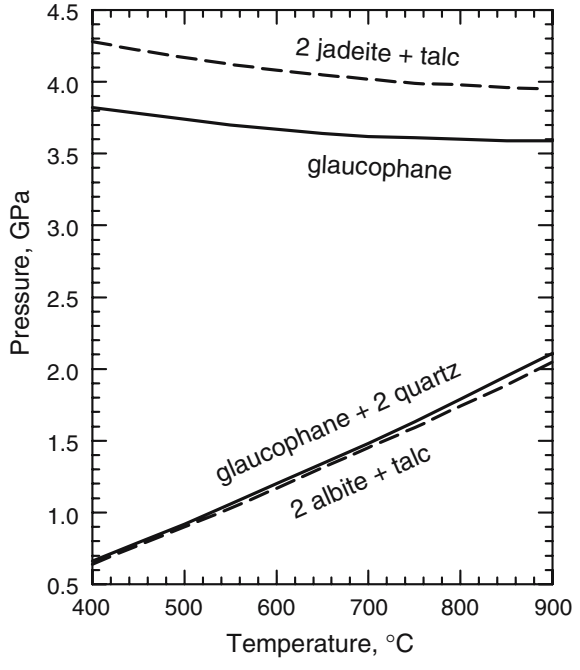

Fig. 4 Calculated locations of the reaction boundaries defining the upper- and lower-pressure limits of glaucophane using the program Thermocalc of Holland and Powell (1998) (*solid curves*). The *dashed curves* show the same boundaries after substituting the volume of glaucophane in the Holland and Powell (1998) database (260.5 cm^3/mol) for the preferred value derived in this study (259.8 cm^3/mol)

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