The thermodynamic properties and phase relations of some minerals in the system CaO–Al$_2$O$_3$–SiO$_2$–H$_2$O*

Dexter Perkins III†

Institute für Kristallographie und Petrographie, Eidgenossische Technische
Hochschule, Zürich, Switzerland

and

Edgar F. Westrum, Jr

The Department of Chemistry, The University of Michigan,
Ann Arbor, MI 48109, U.S.A.

and

Eric J. Essene

The Department of Geology and Mineralogy, The University of Michigan,
Ann Arbor, MI 48109, U.S.A.

Abstract—The heat capacities of lawsonite, margarite, prehnite and zoisite have been measured from 5 to 350 K with an adiabatic-shield calorimeter and from 320 to 999.9 K with a differential-scanning calorimeter. At 298.15 K, their heat capacities, corrected to end-member compositions, are 66.35, 77.30, 79.13 and 83.84 cal K^{-1} mol^{-1}; their entropies are 54.98, 63.01, 69.97 and 70.71 cal K^{-1} mol^{-1}, respectively. Their high-temperature heat capacities are described by the following equations (in calories, K, mol):

Lawsonite (298–600 K):
$$Cp° = 66.28 + 55.95 \times 10^{-3} T - 15.27 \times 10^5 T^{-2}$$
Margarite (298–1000 K):
$$Cp° = 101.83 + 24.17 \times 10^{-3} T - 30.24 \times 10^5 T^{-2}$$
Prehnite (298–800 K):
$$Cp° = 97.04 + 29.99 \times 10^{-3} T - 25.02 \times 10^5 T^{-2}$$
Zoisite (298–730 K):
$$Cp° = 98.92 + 36.36 \times 10^{-3} T - 24.08 \times 10^5 T^{-2}$$

Calculated Clapeyron slopes for univariant equilibria in the CaO–Al$_2$O$_3$–SiO$_2$–H$_2$O system compare well with experimental results in most cases. However, the reaction zoisite + quartz = anorthite + grossular + H$_2$O and some reactions involving prehnite or margarite show disagreements between the experimentally determined and the calculated slopes which may possibly be due to disorder in experimental run products. A phase diagram, calculated from the measured thermodynamic values in conjunction with selected experimental results places strict limits on the stabilities of prehnite and assemblages such as prehnite + aragonite, grossular + lawsonite, grossular + quartz, zoisite + quartz, and zoisite + kyanite + quartz. The presence of this last assemblage in eclogites indicates that they were formed at moderate to high water pressure.

1. INTRODUCTION

Minerals whose compositions fall within the CaO–Al$_2$O$_3$–SiO$_2$–H$_2$O (CASH) system are found in a wide variety of metamorphic and igneous rocks. Knowledge of their stabilities with respect to each other and, perhaps more important, knowledge of their stabilities with respect to minerals of larger systems involving MgO, FeO, or CO$_2$ can give valuable insight into the origin of metamorphic and igneous rocks.

Many experimental investigations have been conducted on reactions within the CASH and larger systems, but there are many more yet to be studied. In addition, some apparent inconsistencies and contradictory results obtained in the past require clarification. Rather than conducting lengthy experiments, it is possible, given accurate thermodynamic data, to check experimental results or to calculate the location of reactions for which no experiments have been conducted. In order to fill lacunae in our knowledge of the thermodynamic properties of minerals in the CASH system, we have undertaken a study of the heat capacities of lawsonite [CaAl$_2$Si$_2$O$_7$(OH)$_2$·H$_2$O], margarite [CaAl$_4$Si$_2$O$_{10}$(OH)$_2$], prehnite [Ca$_2$Al$_2$Si$_3$O$_{10}$(OH)$_2$], and zoisite [Ca$_2$Al$_3$Si$_3$O$_{12}$(OH)]. Natural samples were used for

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our experiments because of the prohibitive difficulties in synthesizing large quantities of phase-pure materials and the greatly decreased thermal equilibration times of coarsely crystalline materials. Although the presence of impurities in our samples required that our experimental results be adjusted slightly to represent values of end-member minerals, the near end-member composition of most of our specimens usually made such adjustments minor. In conjunction with data obtained for grossular (WESTRUM et al., 1979), anorthite (ROBIE et al., 1978b; KRUPKA et al., 1979), Ca-Al pyroxene (THOMPSON et al., 1978), and gehlenite (WELLER and KELLEY, 1963; ROBIE, personal communication) these data complete our knowledge of the heat capacities and related properties of the most important calcium-aluminum silicates.

2. EXPERIMENTAL

Sample provenance

The silver-pink margarite (originally collected at Chester, Massachusetts) and the light-green, botryoidal, prehnite (originally collected at Dunbartonshire, Scotland) were obtained from the Mineralogy Collection of The University of Michigan. The margarite consisted of coarse books in a vein which graded into an intimate mixture of chlorite and magnetite at the edges. After removing the surround-margarite was crushed to flakes of 5 mm in longest dimension. Hand picking on a light table allowed rapid removal of all remaining foreign phases. The prehnite sample was crushed to millimeter size; careful examination revealed no impurities.

The zoisite, of which 24 g were purchased from Mr G. Vargas, a gem dealer, and an additional 29 g borrowed from Mr E. D. Swoboda of the Gemological Institute of America, was of the gem variety 'Tanzanite'. The brown to blue euhedral crystals were carefully washed in dilute HCl to remove adherent calcite. No other impurities were visible in the transparent crystals.

The lawsonite, collected from veins at Valley Ford, California, and purchased from the Minerals Unlimited Company, was light tan in color. Careful examination using an optical microscope revealed minor inclusions of calcite, aragonite, glaucophane, albite, and quartz. The contaminants were removed by floating the sample in tetrabromoethane and by using a magnetic separator. Both processes were repeated several times after X-ray and optical examination revealed no impurities.

After final preparation, the samples were examined with an X-ray powder diffractometer (Cu Kα, 0.25 deg 2θ min^{-1}) using quartz (a = 4.913 Å, C = 5.405 Å) and fluorite (a = 5.4626 Å) as internal standards. In addition, the margarite was examined using a 57.3 mm radius Gandolfi X-ray camera. No anomalous peaks were observed. Cell parameters, listed in Table 1, were regressed by the computer program LCLSQ and agree well with values cited in the literature.

All four samples were analyzed for major and minor elements using an ARL-EMX electron microprobe equipped with LIF, PET and TAP crystal spectrometers. Accelerating potential, emission current, and (digitized) beam current were typically 12–15 keV, 150 μA and 0.005–0.008 μA respectively. For each mineral, at least five spots on 10–15 grains were analyzed to check of heterogeneities; no significant variations were observed.

The analyses and normalized formulas (Table 1) indicate that the lawsonite, prehnite, and zoisite are approximately 95, 98, and 99% pure with respect to end-member com-

Table 1. Chemical analyses and unit cell parameters for the samples studied. The water analyses were determined by weight loss upon heating from 70°C (343.15 K) to 1100°C (1373.15 K) and subtracting F and Cl. The lithium analysis was obtained by atomic absorption; all others analyzed by electron microprobe. Lawsonite, prehnite, and zoisite are normalized to cations; margarite is normalized to (O + OH + Cl + F) = 24. The notation 'n.a.' indicates no analysis made. Values in parentheses are one standard deviation; units are angstroms and degrees

Ions	Lawsonite Oxide wt %	moles	Margarite Oxide wt %	moles	Prehnite Oxide wt %	moles	Zoisite Oxide wt %	moles
Si	37.61	4.03	29.90	4.00	43.54	5.99	39.55	6.01
Al	30.07	3.80	50.40	7.95	24.21	3.92	33.20	5.96
Ti	0.50	0.03	0.03	0.00	0.00	0.00	0.03	0.00
Fe^{3+}	1.70	0.14	0.62	0.06	0.46	0.06	0.01	0.00
V	0.00	0.00 3.98	0.00	0.00 8.22	<0.01	0.00 4.01	0.23	0.01 5.99
Mg	0.05	0.01	0.27	0.05	0.13	0.03	0.08	0.02
Mn	<0.01	0.00	0.01	0.00	0.04	0.00	0.03	0.00
Cr	<0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Li	n.a.	----	0.30	0.16	n.a.	----	n.a.	----
Ca	17.29	1.98	11.05	1.58	27.00	3.97	24.53	4.00
Na	0.01	0.01	1.77	0.46	0.19	0.05	0.02	0.00
K	0.00	0.00 1.99	0.00	0.00 2.04	0.00	0.00 4.02	0.00	0.00 4.00
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00
Cl	0.05	0.01	0.08	0.02	0.01	0.00	0.03	0.01
F	0.01	0.00 8.36	0.01	0.00 4.08	<0.01	0.00 3.88	0.02	0.01 2.04
OH	11.70	8.35	4.55	4.06	4.23	3.88	1.99	2.02
Total	98.98		98.99		99.81		99.82	
O≡F, Cl	-0.01		-0.02		-0.00		-0.02	
Total	98.97		98.97		99.81		99.80	

Unit Dimensions

Parameters								
a	8.796	(02)	5.162	(08)	4.617	(03)	16.201	(03)
b	13.125	(03)	8.882	(24)	5.473	(03)	5.551	(01)
c	5.849	(02)	19.062	(02)	18.435	(19)	10.036	(05)
β	90.000	(00)	95.19	(12)	90.000	(00)	90.000	(00)
V	675.16	(22)	870.5	(19)	465.86	(34)	902.65	(41)

positions (neglecting deficiencies or excesses in the hy-droxyl sites). However, the margarite analysis shows it to be approximately 75% end-member only. It may be compared with an analysis of margarite from the same locale (No. 1 in DEER et al., 1962); the only major difference between the two analyses is the amount of Fe_2O_3 present. This disagreement is not surprising because the samples probably came from different veins. The major solid solution in the margarite is Na, but it does not appear to be present as a paragonite solid solution because Si normalizes exactly to 4.0. The charge deficiency of the Ca site is partially compensated by the excess in the octahedral sites. This solid solution towards a trioctahedral mica has been reported in some other margarite analyses (DEER et al., 1962).

Calorimetric technique

Low-temperature heat-capacity measurement (5–350 K) were made in the Mark II cryostat, details of which have been described elsewhere (WESTRUM et al., 1968). The lawsonite sample (129.24 g), margarite sample (90.92 g), prehnite sample (172.10 g), and zoisite sample (54.74 g) were determined separately in a cylindrical, gold-plated copper calorimeter (laboratory designation W-54) with an axial entrant well for the thermometer/heater assembly. After evacuation of a calorimeter containing a sample, 15 kPa (0.15 bar) of helium gas were added to enhance thermal contact between the calorimeter, sample, and thermometer assembly. All determinations of mass, potential, current, time, and temperature were based ultimately upon calibrations by the National Bureau of Standards.

Super-ambient (above 300 K) heat-capacity measurements were conducted using a Perkin–Elmer Model DSC-2, differential scanning calorimeter (D.S.C.). Samples of approximately 40 mg were contained in gold pans of 130 mg mass. Overlapping scans of 60–120 K were made at a heating rate of 5–10 K min^{-1}. Corundum (NBS Heat-Capacity Standard Reference Material No. 720) was used as a heat-capacity standard; values for its heat capacity came from DITMARS and DOUGLAS (1971). Temperatures were calibrated against the known transition temperatures of $KClO_4$ and In. Samples were carefully weighed before and after each scan; any mass change of greater than 0.005 mg was considered an indication of dehydration and no subsequent measurements were made at higher temperatures.

3. RESULTS AND DISCUSSION

Heat capacity of samples

Results of the heat-capacity measurements are listed in Appendix 1 in chronological sequence so that the temperature increments used can be inferred from adjacent mean temperatures. These data have been corrected for curvature in non-transition regions—i.e., the average heat capacity over a temperature interval has been adjusted for non-linearity in the heat-capacity curve. The values in Appendix 1 represent those on the samples as run. They have, however, been calculated for a molecular mass corresponding to that of the pure end-member phase (derived from elemental masses cited in WEAST et al., 1972), not for the solid-solution composition.

For our adiabatic calorimetric experiments, the heat-capacity of the empty calorimeter (determined in a separate series of experiments) was approximately 60% of the total at 15 K, 45% of the total at 100 K, and 35% from 150 to 350 K. For D.S.C. measurements, the heat capacities of the sample and the standard were within 10% of each other and represented approximately 80% of the total sample/container assembly. The curves of heat capacity versus temperature are all sigmate in shape and, with the exception of the lawsonite (discussed below), without anomalies.

Apart from the question of chemical composition, the heat capacity values given in Appendix 1 are considered to be characterized by standard deviations of 10% at 5 K, rapidly decreasing to 0.1% at 20 K and staying at this level through 350 K. The uncertainties at lower temperatures are due to the decreasing sensitivity of the platinum resistance thermometer. The D.S.C.-determined heat capacities were reproducible to 0.5% at 320 K, but precision gradually decreased to 1% at 1000 K as thermal equilibrium became more difficult to maintain.

The experimental values of the heat capacity of lawsonite do not form a completely smooth curve. Several deviations are present, the most marked of which occurs in the vicinity of 270–275 K. The same anomaly was reported by KING and WELLER (1961) in an earlier investigation of the heat capacity of lawsonite. We interpret this anomaly as being the fusion peak of water inclusions in the sample. This conclusion is supported by: (1) the small anomaly near 130 K which corresponds to one in the heat capacity of ice determined by GIAUQUE and STOUT (1936), (2) the slight concavity upwards in the heat-capacity curve as the temperature approaches the vaporization temperature of water, and (3) optical examination which revealed a myriad of small inclusions. The amount of water present, determined by calculating the area under the fusion peak, was approximately (0.50 ± 0.01) mass % of the sample. In a separate series of experiments, a 10 g sample of the same lawsonite was found to lose (0.40 ± 0.05) % of its mass between 70 and 200°C without undergoing any structural damage.

Thermodynamic functions

Values of selected thermodynamic functions for the sample compositions were calculated for the four minerals on the basis of smoothed curves fitted to the empirical data by digital computer (Appendix 2 and Tables 2–5). Figures 1–4 show the residuals (i.e., the difference between the values of the samples as measured and those of the smooth curve). For margarite, prehnite, and zoisite no corrections were made to the data prior to curve fitting. For lawsonite, however, minor corrections were made as follows: a smooth curve was fit across the H_2O fusion peak, adjustments were made at 300–350 K to compensate for the effect of water vaporization (using vapor-pressure data of WEAST, 1962), and the heat-capacity of the appropriate amount of ice/water (values from GIAUQUE and STOUT, 1936) was subtracted from the remaining curve. Although there is larger uncertainty at lower temperatures, the values of all functions are considered to be reliable to 0.1% for temperatures between 50 and 350 K. It should again be emphasized that these values are based upon the ideal atomic weights of lawsonite, margarite, prehnite, and zoisite; the values have not been corrected for solid solution components.

Super-ambient thermodynamic functions

Values of selected thermodynamic functions above 298.15 K are given in Tables 2–5 for the minerals studied, along with equations for their high-temperature heat capacities. Also included in the tables are calculated values for the end-member minerals based upon our measured values, the analyses in Table 1, and a previously described (WESTRUM et al., 1979) correction scheme. (The scheme consists of calculating the effects of impurities by similar substitutions in comparable phases for which heat-capacity data are available.) The magnitudes of the corrections (shown in Fig. 1–4) are generally less than 0.5% for lawsonite, prehnite, and zoisite due to the near end-member composition of our samples. The margarite values were adjusted to a greater extent.
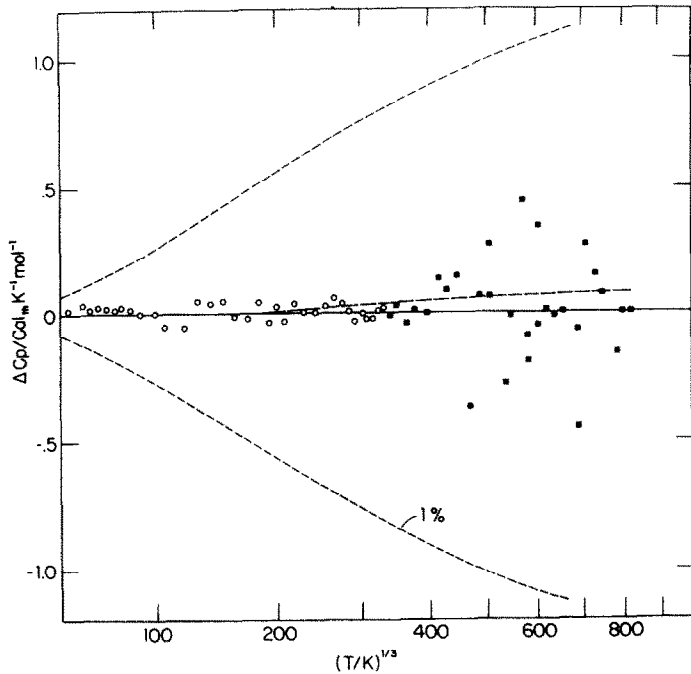
Fig. 1. Deviation plot for lawsonite. The fine dotted line represents the difference between the smooth curve of Weller and King (1961) and that of the present study. In this and the following figures, the dots and squares represent the adiabatic and D.S.C. experimental determinations, respectively, the finer dashed line represents a deviation of 1%; the coarser dashed line shows the correction added to the experimental curve to correct the heat capacity to end-member composition. Note, also, that in this and the following figures the horizontal scale is not linear.
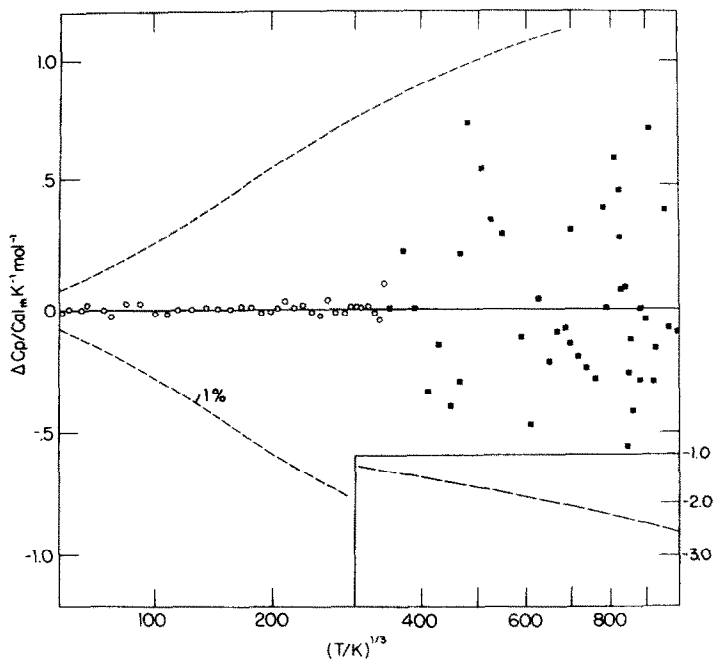
Fig. 2. Deviation plot for margarite. All symbols as in Fig. 1. Note the expanded scale of the inset, showing the correction made for composition.
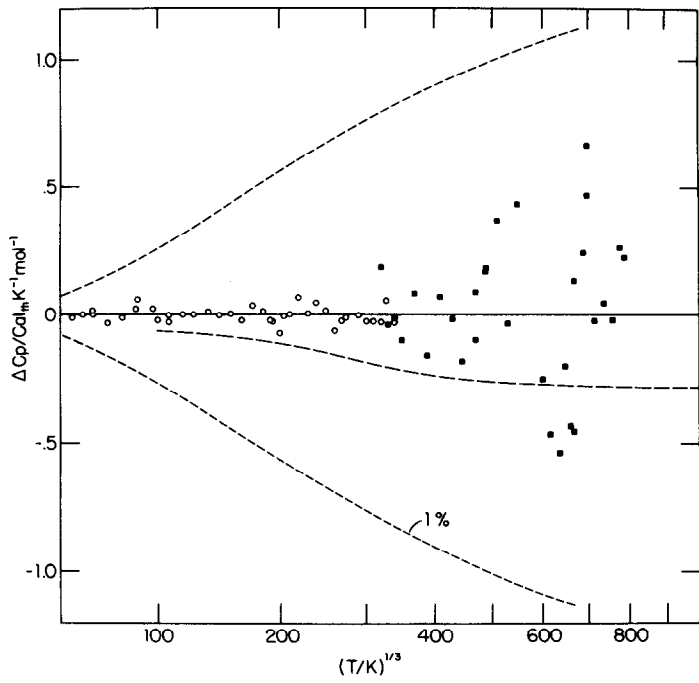
Fig. 3. Deviation plot for prehnite. All symbols as in Fig. 1.
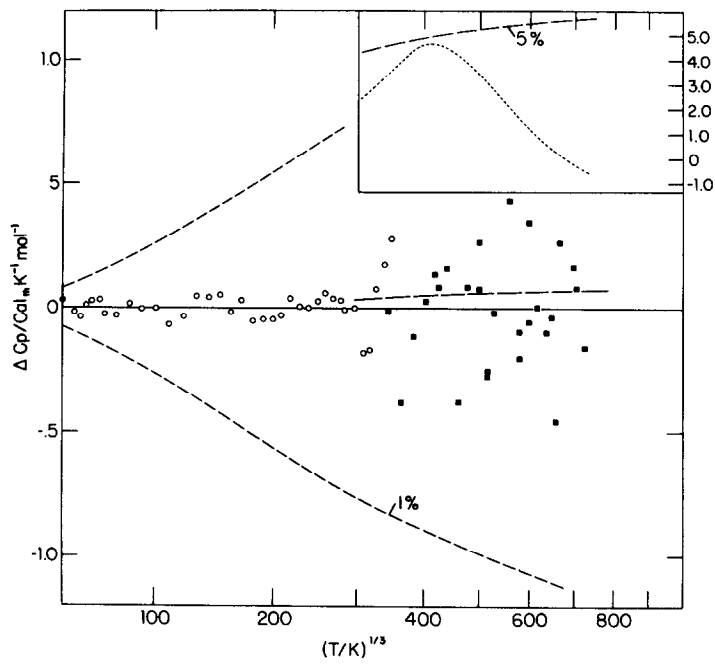
Fig. 4. Deviation plot for zoisite. The dotted curve on the expanded scale in inset shows the difference between the smooth values of KISELEVA et al. (1974) and those of the present study. All other symbols as in Fig. 1.

Table 2. Smoothed thermodynamic functions of lawsonite in cal, K, and mol with and without adjustment to end-member composition. In this and the following three tables, the values in columns with an asterisk are adjusted to end-member composition; the others are not; both are based upon a mol defined in terms of end-member formula weight

T	C_p	C_p^*	S°	$S^{\circ*}$	$(H_T^\circ - H_{298}^\circ)$	$(H_T^\circ - H_{298}^\circ)^*$	G	G*
298.15	66.37	66.35	55.45	54.98	0	0	55.45	54.98
300	66.64	66.66	55.86	55.39	124	124	55.45	54.98
350	73.33	73.38	66.65	66.17	3627	3626	56.29	55.81
400	79.01	79.10	76.82	76.34	7438	7437	58.23	57.75
450	83.83	83.94	86.41	85.94	11512	11524	60.83	60.33
500	88.21	88.35	95.47	95.01	15815	15842	63.84	63.33
550	91.95	92.10	104.06	103.62	20395	20420	66.98	66.49
600	94.47	94.63	112.18	111.75	24987	25009	70.54	70.07

$$C_p^* = 66.28 + 55.95 \times 10^{-3}\, T - 15.27 \times 10^5\, T^{-2}$$

[a] The numbers in the columns headed 'G' are values of the Gibbs function: $-(G_T - H_0^c)/T$. All units are calories, K and mol.

Table 3. Smoothed thermodynamic functions of margarite in cal, K, and mol with and without adjustment to end-member composition (see also Table 2)

T	C_p	C_p^*	S°	$S^{\circ*}$	$(H_T^\circ - H_{298}^\circ)$	$(H_T^\circ - H_{298}^\circ)^*$	G	G*
298.15	78.54	77.30	64.63	63.01	0	0	64.63	63.01
300	78.88	77.64	65.12	63.49	145	142	64.64	63.02
350	86.91	85.59	77.92	76.10	4305	4238	65.62	63.99
400	93.09	91.69	89.92	87.91	8801	8669	67.92	66.24
450	98.94	97.43	101.24	99.07	13606	13399	71.00	69.29
500	103.67	102.06	111.91	109.58	18676	18393	74.56	72.79
550	107.28	105.58	121.97	119.48	23954	23585	78.42	76.60
600	110.09	108.29	131.43	128.78	29391	28936	82.45	80.55
650	112.41	110.52	140.34	137.55	34955	34441	86.56	84.56
700	114.50	112.52	148.75	145.81	40623	40049	90.72	88.60
750	116.47	114.40	156.71	153.63	46403	45690	94.84	92.71
800	118.38	116.22	164.29	161.08	52273	51420	98.95	96.81
850	120.20	117.94	171.52	168.17	58243	57278	103.00	100.78
900	121.93	119.57	178.44	174.96	64293	63216	107.00	104.72
950	123.53	121.10	185.08	181.50	70433	69236	110.94	108.62
1000	124.91	122.41	191.45	187.78	76643	75326	114.81	112.45

$$C_p^* = 101.83 + 24.17 \times 10^{-3}\, T - 30.24 \times 10^5\, T^{-2}$$

[a] Numbers in columns headed 'G' are values of the Gibbs function: $-(G_T - H_0^c)/T$. All units are calories, K and mol.

Table 4. Smoothed thermodynamic functions of prehnite in cal, K, and mol with and without adjustment to end-member composition (see also Table 2)

T	C_p	C_p^*	$S°$	$S°*$	$(H_T° - H_{298}°)$	$(H_T° - H_{298}°)*$	G	G*
298.15	79.20	79.13	70.09	69.97	0	0	70.09	69.97
300	79.52	79.45	70.58	70.46	147	146	70.09	69.97
350	87.15	87.07	83.44	83.31	4320	4315	71.10	70.98
400	93.09	93.01	95.47	95.33	8831	8823	73.39	73.27
450	97.99	97.91	106.73	106.58	13612	13600	76.48	76.36
500	102.10	102.03	117.27	117.11	18617	18601	80.04	79.91
550	105.58	105.51	127.17	127.02	23811	23791	83.88	83.76
600	108.53	108.44	136.49	136.32	29166	29142	87.88	87.75
650	111.00	110.87	145.28	145.10	34656	34627	91.96	91.83
700	113.02	112.90	153.58	153.39	40259	40224	96.07	95.93
750	114.63	114.51	161.43	161.23	45952	45911	100.16	100.02
800	115.90	115.78	168.76	168.67	51716	51669	104.12	104.08

$$C_p^* = 97.04 + 29.99 \times 10^{-3} T - 25.02 \times 10^5 T^{-2}$$

[a] Numbers in the columns headed 'G' are values of the Gibbs function: $-(G_T - H_0°)/T$. All units are calories, K and mol.

Table 5. Smoothed thermodynamic functions of zoisite in cal, K, and mol with and without adjustment to end-member composition (see also Table 2)

T	C_p	C_p^*	$S°$	$S°*$	$(H_T° - H_{298}°)$	$(H_T° - H_{298}°)*$	G	G*
298.15	83.80	83.84	70.74	70.71	0	0	70.74	70.71
300	84.16	84.20	71.26	71.30	155	155	70.74	70.78
350	92.29	92.34	84.89	84.86	4581	4584	71.80	71.76
400	98.01	98.06	97.58	97.55	9336	9341	74.24	74.20
450	103.28	103.34	109.44	109.42	14374	14382	77.50	77.46
500	107.30	107.36	120.54	120.52	19642	19653	81.26	81.21
550	110.92	110.99	130.94	131.02	25098	25113	85.31	85.36
600	114.42	114.49	140.74	140.73	30733	30751	89.52	89.48
650	117.90	117.97	150.01	150.01	36525	36547	93.82	93.78
700	118.91	118.99	158.76	158.76	42425	42451	98.15	98.12
730	119.78	119.86	163.77	163.78	46005	46033	100.75	100.72

$$C_p^* = 98.92 + 36.36 \times 10^{-3} T - 24.08 \times 10^5 T^{-2}$$

[a] Numbers in the columns headed 'G' are values of the Gibbs function: $-(G_T - H_0°)/T$. All units are calories, K and mol.

Comparison with other data

KING and WELLER (1961) have measured the heat capacity of lawsonite over the range 50–300 K. The differences between their values and ours are shown in Fig. 1. Although they noted an anomaly in their data near 273 K, they did not correct their values for water as we did. Accordingly, their heat-capacity values are all slightly greater than ours. Their value of $S^\circ_{298.15}$ is, however, 2% greater than ours. This disagreement is primarily due to the large extrapolation that they made (from 50 to 0 K) in the absence of data. Once again (cf. ROBIE et al., 1978b), it is emphasized that significant errors may be present in the tabulated entropy values for minerals whose heat-capacities have not been determined to very low temperatures. Such minerals include many important silicates (e.g. almandine, diopside, enstatite, fayalite, wollastonite); low-temperature heat-capacities must be determined for them before their entropies can be reliably known.

KISELEVA et al. (1974) have measured the heat-capacity of zoisite from 335 K through 1000 K using a Tian-Calvet microcalorimeter and natural samples of 4–6 mg. Their values do not accord well with ours, reaching a maximum deviation of almost 5% near 400 K (Fig. 4). Although this disagreement may seem large, their small sample mass, large corrections for impurities (up to 5%) and the inherent uncertainties of their technique may account for the deviations. It has also been noted (PERKINS et al., 1977) that their values do not fit well with current experimental results on the stability of zoisite.

Standard entropies

Crystal structure refinements of lawsonite and zoisite (BAUR, 1978; DOLLASE, 1968) preclude a zero-point contribution to the entropy of these phases. In margarite and prehnite, however, the possibility of disorder amongst tetrahedral Al and Si is not excluded.

An early investigation (TAKEUCHI, 1965) suggested that Si^{IV} and Al^{IV} were disordered in margarite, but recent studies refute the idea. FARMER and VELDE (1973) examined the infrared spectra of brittle micas and concluded that margarites (unlike clintonites) are completely ordered in Al^{IV} and Si^{IV}. GUGGENHEIM and BAILEY (1975) showed that the structure of margarite could be refined more precisely in the space group Cc (ordered) than in the space group C2/c (disordered), and pointed out that T-O bond lengths indicated nearly complete order. BISH and HORSEY (1978), on the basis of optical second harmonic analysis, concluded that the margarite structure must be acentric—and thus ordered. It is reasonable, then, to assume that natural margarite is a completely ordered structure, having no zero-point contribution to its entropy.

The structure of prehnite has been investigated by PAPIKE AND ZOLTAI (1967). Although equivocal as to

the exact space group of a natural prehnite, their results indicate that Al^{IV} is ordered on two distinct T_2 positions. We have, therefore, not attributed zero-point entropy to prehnite. It should be emphasized that we have not excluded the possibility that synthetic margarite and phrehnite may be metastably disordered or that disorder may occur at super-ambient temperatures. We have concluded that in the natural, stable form they are ordered at ambient temperatures.

Clapeyron slopes

In an earlier paper (PERKINS et al., 1977) we calculated theoretical Clapeyron slopes for some reactions in the CASH system and compared them to experimentally determined ones. We have now recalculated the slopes of those and several other reactions using the same computer program and input data with the following exceptions: the entropy values for lawsonite, margarite, prehnite, and zoisite were those presented in this paper; the entropy of anorthite was taken from ROBIE et al. (1978b). For most of the reactions the recalculated slopes are not significantly different than those presented by Perkins et al. However, reactions involving both anorthite and zoisite bear special comment as modifications in the entropies of both phases has led to significant changes in the calculated slopes.

Three such reactions were discussed by PERKINS et al. (1977): ·

2 zoisite + sillimanite + quartz
$$= 4 \text{ anorthite} + H_2O \quad (1)$$

6 zoisite = 6 anorthite + 2 grossular
$$+ \text{ corundum} + 3 H_2O \quad (2)$$

4 zoisite + quartz = 5 anorthite
$$+ \text{grossular} + 2 H_2O \quad (3)$$
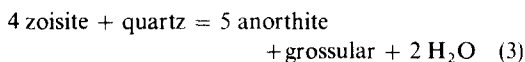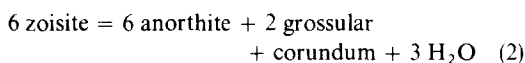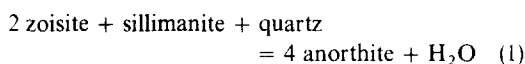
In the present calculations, the entropy of zoisite is greater and the entropy of anorthite is less than those values previously used. Because zoisite and anorthite are on opposite sides of reactions (1)–(3), the recalculated slopes extend the stability of the zoisite-bearing side of the reactions at elevated temperatures. For reactions (1) and (2) the effect is to bring the calculated slopes into better agreement with the experimentally determined ones (Fig. 5). For reaction (3), however, the recalculated slope does not agree well with experiments by NEWTON (1966) and by BOETTCHER (1970) (Fig. 6). We have calculated slopes for reactions (1), (2), and (3) for a partially disordered anorthite $(0.7 \text{ cal K}^{-1} \text{ mol}^{-1})$ as well as for an ordered one (cf. CHARLU et al., 1978; see section on Gibbs energies, below). The agreement is slightly better for reaction (3) if anorthite is disordered, but is worse for the other reactions. The cause of this discrepancy between the experimental and calculated slope is unknown.
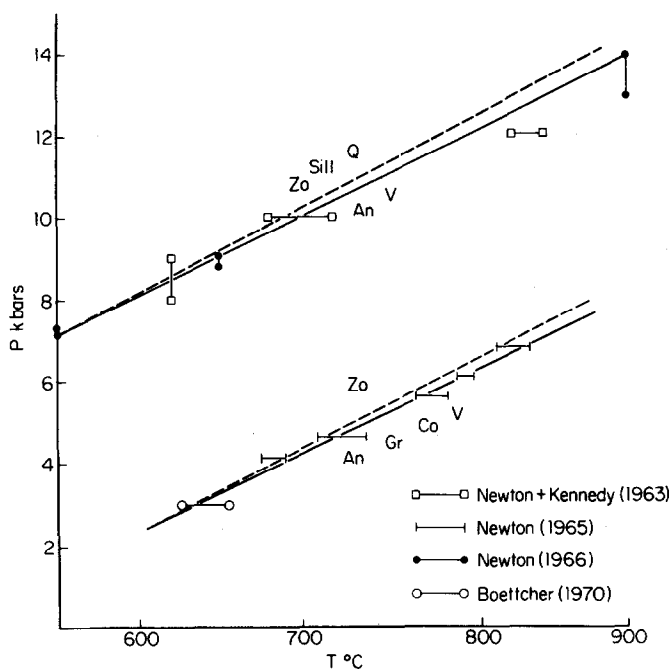
Fig. 5. Experimental reversals and calculated slopes for two reactions involving zoisite and anorthite. In this and the following figure the solid line is for ordered anorthite while the dashed line refers to partially disordered anorthite. Zo = zoisite, Sill = sillimanite, Q = quartz, An = anorthite, Gr = grossular, Co = corundum, v = water.

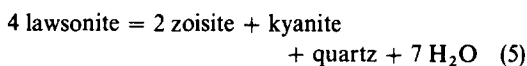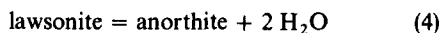Two reactions involving lawsonite that have been investigated experimentally are:

$$\text{lawsonite} = \text{anorthite} + 2\,H_2O \qquad (4)$$

$$\begin{aligned} 4\,\text{lawsonite} &= 2\,\text{zoisite} + \text{kyanite} \\ &\quad + \text{quartz} + 7\,H_2O \end{aligned} \qquad (5)$$

Figure 6 shows the limiting experiments conducted on these reactions and a calculated slope for each. For both reactions, the calculated curves are in good agreement with the experiments. In addition, if reactions (4) and (5) are combined, eliminating lawsonite, the calculated location of reaction (1) is identical with
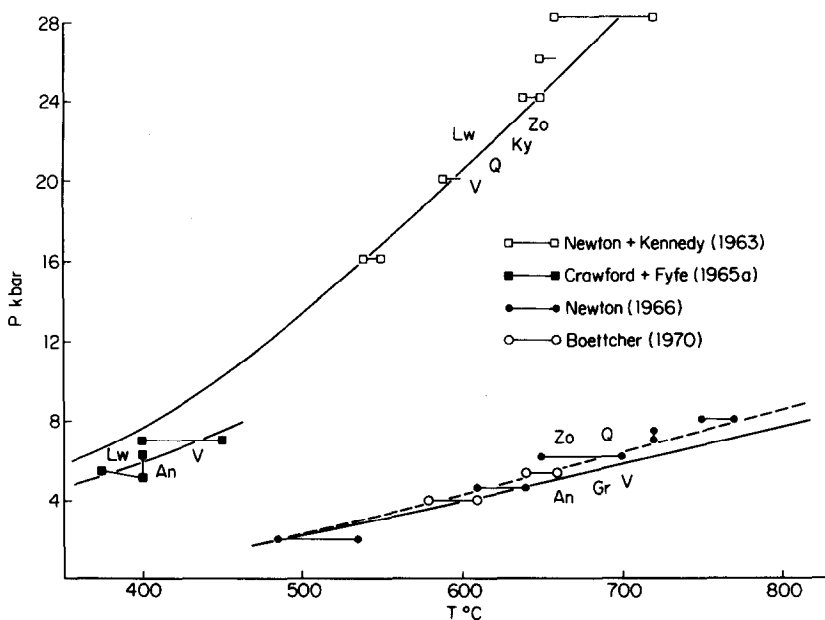
Fig. 6. Comparison of experimental reversals and calculated slopes. See Fig. 5. Lw = lawsonite, Ky = kyanite. Note that the reversals for the reaction lawsonite = anorthite + 2 H₂O have been adjusted for errors in the original publication of Crawford and Fyfe (c.f. CRAWFORD, 1972, personal communication).

that shown in Fig. 6 within the uncertainties (after correcting for the different Al_2SiO_5 polymorphs), indicating reasonable internal consistency within the three reactions.

The stability limits of prehnite have been studied by LIOU (1971):

$$prehnite = anorthite + wollastonite + H_2O \quad (6)$$

$$5\ prehnite = 2\ oisite + 2\ grossular \\ + 3\ quartz + 4\ H_2O \quad (7)$$
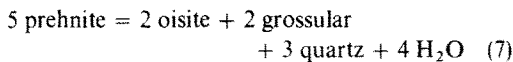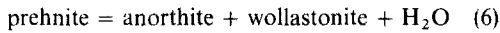
Figure 7 shows the experimentally determined reversals and calculated slopes for both ordered and disordered prehnites. The calculated slope for reaction (6) using the entropy of disordered prehnite fits the reversals of Liou better than that for an ordered phase. Neither curve fits well for reaction (7). The curve for ordered prehnite for reaction (7) was calculated by combining reactions (6), (3), and (8):

$$grossular + quartz = anorthite + 2\ wollastonite \quad (8)$$
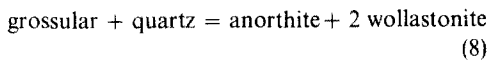
as located by NEWTON (1966), by BOETTCHER (1970) and by HUCKENHOLZ et al. (1975). The curve for disordered prehnite was arbitrarily placed so that the slopes could be compared—a calculated curve falls at significantly greater temperatures and misses all of Liou's reversals by at least 50 K.

The discrepancies between the calculated curves and those located by LIOU (1971) are not readily explained. On the one hand, the results of Liou's experiments on reaction (6) may indicate that he grew a disordered prehnite. On the other hand, the results for reaction (7) are not consistent with a disordered phase. It is possible that the degree of order varied in Liou's experiments, but this problem may not be

completely resolved until more careful experiments are conducted with particular care taken to completely characterize run products. For the rest of the calculations in this paper we assume an ordered prehnite and that the reactions are located as shown by the solid curves in Fig. 7.

Three reactions that limit the stability of margarite have been investigated experimentally:

$$margarite = anorthite + corundum + H_2O \quad (9)$$

$$margarite + quartz = anorthite \\ + kyanite + H_2O \quad (10)$$

$$4\ margarite + 3\ quartz = 2\ zoisite \\ + 5\ kyanite + 3\ H_2O \quad (11)$$
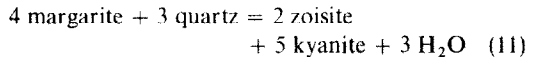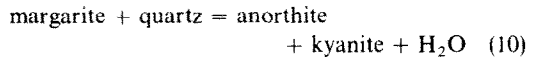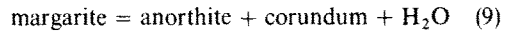
All three reactions were studied by STORRE and NITSCH (1974); and, in addition, reaction (9) was studied by CHATTERJEE (1974). In their studies STORRE and NITSCH used natural margarite and zoisite which contained significant amounts of impurities that may have affected their results. Comparison of their results with those of CHATTERJEE for reaction (9) shows them to be in reasonable agreement at 6 kbar, but to deviate at lower pressures (Fig. 8). A calculated curve for ordered margarite fits well to both sets of experiments.

The limiting experiments for reactions (10) and (11) as determined by STORRE and NITSCH (1974) are shown in Fig. 8. While there is reasonable agreement between the calculated slopes and the experiments for reaction (10), the calculated curve of reaction (11) is in very poor agreement with the experiments. This discrepancy may be explained if the product margarite of Storre and Nitsch was partially disordered, which would extend its stability and steepen the slope of the
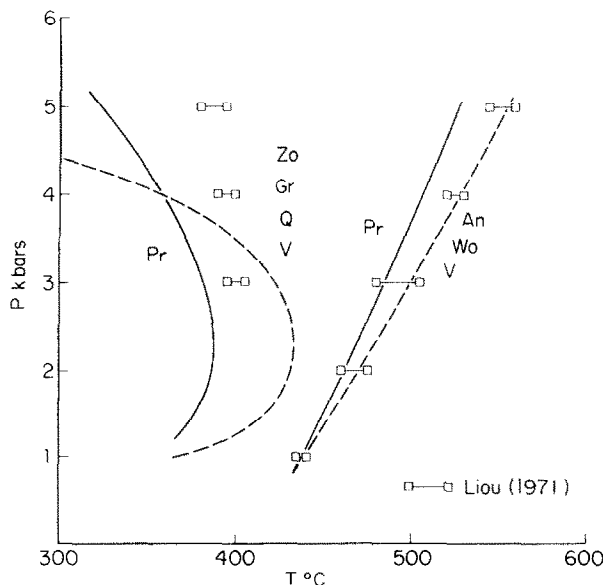

Fig. 7. Comparison of experimental reversals and calculated slopes. The solid lines were calculated for an ordered prehnite while the dashed lines refer to a disordered prehnite. Pr = prehnite. Wo = wollastonite, other abbreviations as before. In this and the next figure, anorthite is assumed to be ordered.
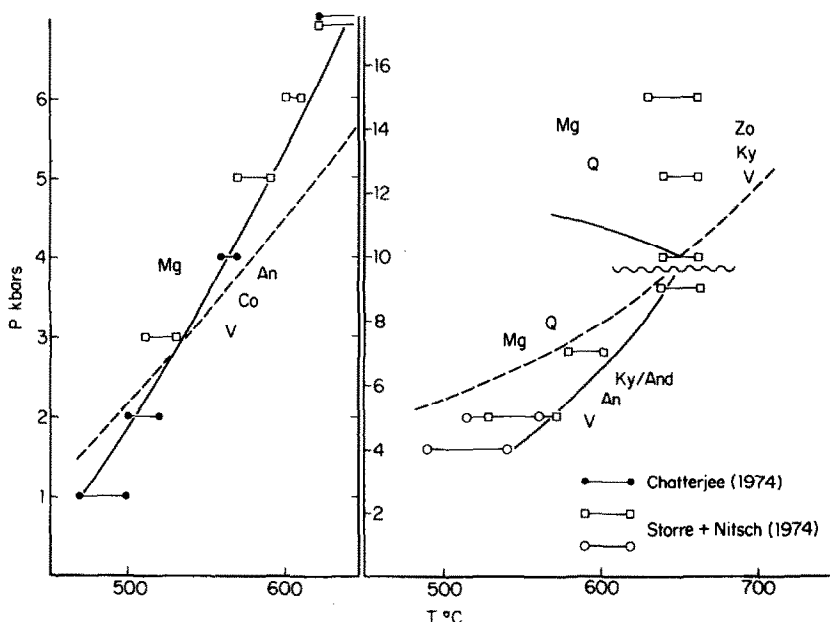
Fig. 8. Experimental reversals and calculated slopes for reactions involving margarite. The solid lines were calculated for an ordered margarite while the dashed lines were calculated for a disordered one. The two lower pressure brackets of Storre and Nitsch for the reaction Mg + Q = Ky/And + An + V were conducted using andalusite; the others used kyanite. Mg = margarite, other abbreviations as before. Note that there are two reactions shown on the right half of this figure.

reaction relative to that for an ordered structure. However, it should be noted that calculated slopes for other margarite reactions at similar temperatures agree well with available experimental data, suggesting reaction of highly ordered margarite. Additional experiments and direct refinement of experimental margarite structures are needed to resolve the questions of the slope and location of reaction (10).

Gibbs energies of formation

Gibbs energies of formation have been measured calorimetrically for some minerals within the CASH system (Table 6). In general, the values have been determined only in a single set of experiments so that there is no data with which to compare them. Of particular interest, however, are the apparent contradictory data for anorthite obtained by HEMINGWAY

Table 6. Calorimetrically determined Gibbs energies of formation (kcal and mol) from the elements at 298.15 K for selected minerals.[a] In this and the following table, values in parentheses are one standard deviation

mineral	$\Delta G^\circ_{f,298}$	mineral	$\Delta G^\circ_{f,298}$
corundum	-378.16 (32)	calcite	-269.80 (33)
quartz	-204.66 (26)	anorthite	-960.15 (75)
water	-54.63 (02)	anorthite[b,c]	-956.62 (89)
CO_2	-94.26 (02)	anorthite[b,d]	-955.83 (84)
kyanite	-583.48 (46)	grossular[b]	-1498.44 (146)
sillimanite	-582.93 (42)	gehlenite	-910.30 (64)
wollastonite	-370.44 (35)	lawsonite	-1081.65 (112)
wollastonite[b]	-370.10 (64)		

[a] All values from ROBIE *et al.* (1978a) unless otherwise specified. Values in parentheses are one standard deviation.

[b] Calculated by combining enthalpy of solution data (CHARLU *et al.*, 1978; CHARLU *et al.*, 1975) with the enthalpies and Gibbs energies of formation of ROBIE *et al.* (1978a).

[c] Natural samples.

[d] Synthetic samples.

Table 7. Gibbs energies of grossular (kcal) at 298.15 K and 1 atm

reaction	source	Robie et al. (1978a)	ordered (this study)	disordered (this study)
Gr + Co = An + Ge	a,b	-1509.09 (104)	-1505.46 (114)	-1505.19 (110)
2Gr = An + Ge + 3Wo	a,b	-1504.68 (214)	-1502.92 (214)	-1502.50 (212)
3An = Gr + 2Ky + Q	c	-1509.06 (148)	-1498.41 (170)	-1500.77 (155)
Gr + Q = An + 2Wo	a,b,d	-1503.49 (166)	-1499.96 (129)	-1499.47 (126)
Cc + An + Wo = Gr + CO₂	e	-1503.94 (089)	-1500.41 (115)	-1500.74 (110)

ᵃ BOETTCHER (1970).
ᵇ HUCKENHOLZ et al. (1975).
ᶜ HARIYA and KENNEDY (1968).
ᵈ NEWTON (1966).
ᵉ GORDON and GREENWOOD (1971); we assumed ideal mixing of H₂O and CO₂ for our calculations.

and ROBIE (1977, from hydrofluoric-acid calorimetry values of BARANY, 1962), and the two values of this study (derived from molten-salt calorimetric data of CHARLU et al., 1978, and thermodynamic values for oxides from ROBIE et al., 1978a). Since all three values are based upon the same enthalpies, entropies, and Gibbs energies of the oxides, the 4 kcal discrepancy must be due to errors in measurement and/or differences in the materials studied. The values derived from CHARLU et al.'s (1978) data for natural and synthetic anorthites suggest that synthetic anorthites are 0.79 kcal less stable than natural ones, perhaps due to disorder or crystallinity effects. This may be important in interpreting experimental results, as most experimentalists have used a synthetic anorthite in their starting materials, and may have grown a (partially) disordered or poorly crystallized one in their products.

The lack of ΔGf° data for margarite, prehnite, and zoisite and the contradictory values for anorthite preclude direct calculation of the location of all reactions in the CASH system. It is possible, however, to derive consistent ΔGf° values for individual minerals from experimental studies if one assumes that the tabulated values for the other phases involved are correct.

As an initial check, the Gibbs energy of formation of grossular was derived (Table 7) from some of the experimentally determined reactions. Three different sets of values were derived, using each of the three values for ΔGf° (anorthite) tabulated in Table 6, and adjusting the entropy of anorthite for order and disorder appropriately. It can be seen from Table 8 that the scatter in values obtained by using Gf° (anorthite) from ROBIE et al. (1978b) is greater than that obtained when using the values derived in our present study. This may be an indication that the latter values are more correct (i.e., more consistent with the experiments). It is also interesting to note that almost all the experimentally derived values are more negative than those obtained by calorimetry.

Values for the Gibbs energies of formation of lawsonite, margarite, prehnite, and zoisite consistent with experiments previously discussed are presented in Table 8. The Gibbs energies in each case were derived by calculating ΔG°ₓₙ,₂₉₈ (using the algorithm of PERKINS et al., 1979) and combining it with values presented in Table 6. Entropy values used in the calculations were taken from this study or from ROBIE et al. (1978b); volume, compressibility, and thermal expansivity values were taken from CLARK (1966) or were

Table 8. Gibbs energies of lawsonite, margarite, prehnite, and zoisite (kcal) derived from experiments

phase	reaction number	source of ΔGf° of anorthite Robie et al. (1978b)	ordered (this study)	disordered (this study)
lawsonite	4	-1075.03 (076)	-1071.50 (090)	-1071.19 (092)
margarite	9	-1399.96 (082)	-1396.43 (090)	-1396.43 (095)
prehnite	6	-1399.61 (170	-1396.08 (167)	-1396.07 (164)
zoisite	3	-1555.06 (225)	-1550.08 (241)	-1550.42 (248)
zoisite	1	-1556.71 (178)	-1549.65 (193)	-1549.22 (185)
zoisite	2	-1554.16 (278)	-1550.63 (300)	-1550.39 (296)

estimated on the basis of similarly structured minerals. Although there may be systematic errors in the values of Table 8, they are internally consistent with each other. The large uncertainties, a result of uncertainties in the Gibbs energies of phases in Table 6, and uncertainties in the exact location of the reactions considered, make direct calculation of a precise phase diagram ambiguous. However, with the exception of expansivity and compressibility values for some phases (which effects are usually small) reliable entropies and volumes of the most important higher-temperature phases in the CASH system are known. Thus, Clapeyron-slope extrapolations and/or addition of experimentally located reactions may be used to construct a phase diagram for the complete system.

The CASH system

Figure 9 represents the stable equilibria in the CASH system excluding reactions involving kaolinite and Ca–Al zeolites. (For a discussion of kaolinite reactions see PERKINS et al., 1979, for zeolites, we do not have the necessary C_p data and accurate third-law entropies for well-characterized materials.) The location of all lawsonite and prehnite reactions are consistent with the specific experiments previously discussed. The location of margarite reactions were calculated from CHATTERJEE's (1974) determined location for reaction (9); pyrophyllite and diaspore reactions are consistent with Model 4 proposed by PERKINS et al. (1979), which was based upon experiments by HAAS and HOLDAWAY (1973) and by REED and HEMLEY (1966). Reactions (1), (2), and (3) are located as previously discussed. All other reactions are based upon the experiments summarized in PERKINS et al. (1977) or were calculated by addition and/or subtraction of the experimentally located ones. Anorthite was assumed to be ordered in all cases. Figure 10, a schematic enlargement, shows a possible chemography for the lawsonite breakdown reactions. The close proximity of the many reactions and the uncertainty in our calculations lead to some ambiguity in this portion of the phase diagram. Indeed, if one compares our extrapolated location of reaction (5) and that of the lawsonite + quartz breakdown with experiments by NITSCH (1972), small errors may be indicated. In general, the scheme of Fig. 9 is the same as that of CHATTERJEE (1976). However, the specific reactions involved and the location of some invariant points are significantly different. In particular, the stability fields of margarite and of margarite + quartz have been
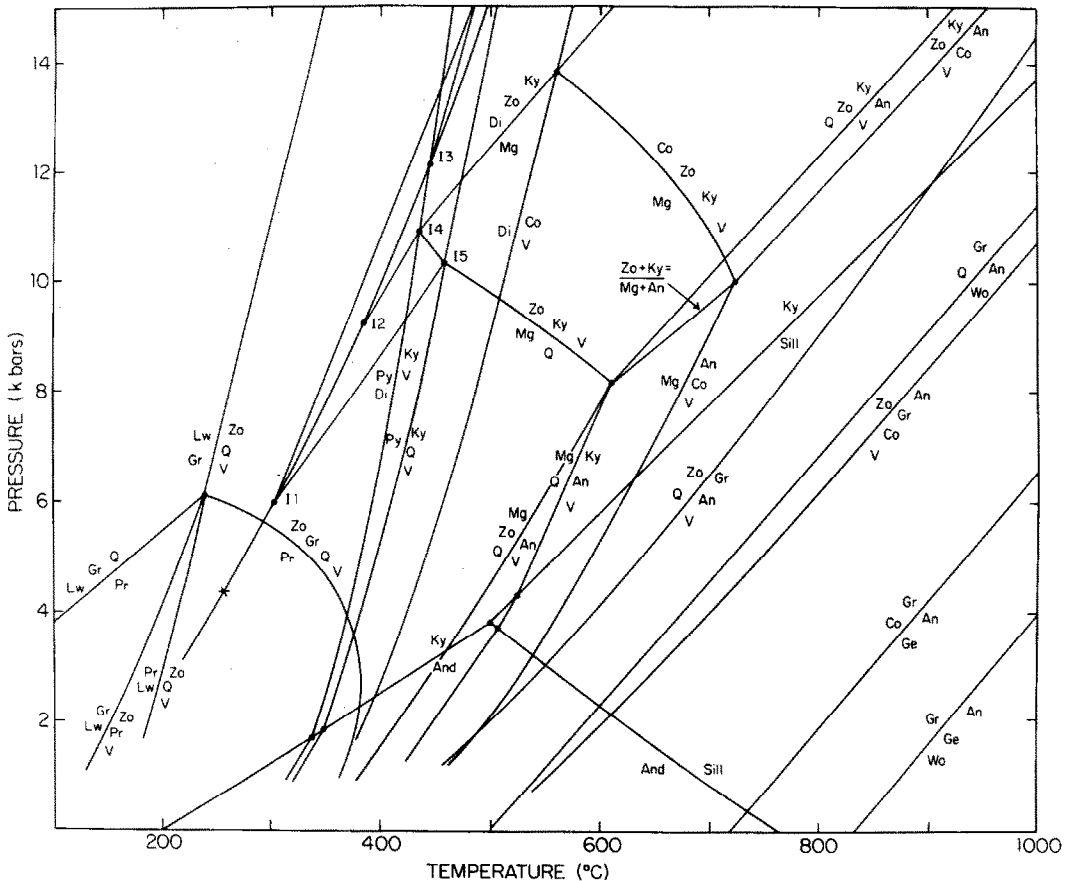

Fig. 9. Phase diagram for the CASH system excluding reactions involving zeolites or kaolinite. Note that the three reactions marked with an x in Fig. 10 have been condensed to one line in this figure. This and Fig. 10, the unlabeled reaction emerging from invariant point 13 is: 2Lw + Di = Ky + Zo + 4H₂O.
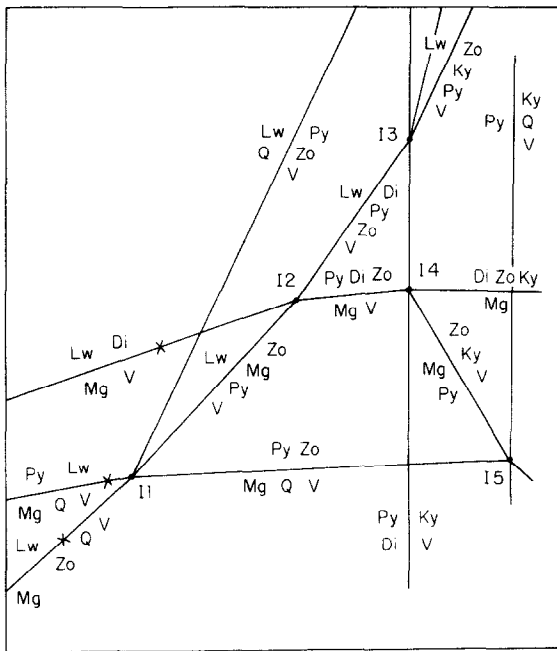
Fig. 10. Schematic enlargement of a portion of Fig. 9.

extended to greater pressure and temperature. Because CHATTERJEE's (1976) phase diagram was based in large part upon estimated or highly uncertain thermodynamic values, Fig. 9 is presumably a better representation of the CASH system.

HELGESON et al. (1978) have also calculated the location of some reactions in the system $CaO-Al_2O_3-SiO_2-H_2O$ based upon estimated values for entropy. Because their estimates of S_T° for margarite and zoisite are close to our measured ones, they have qualitatively similar topologies for reactions involving these phases. However, for reactions involving lawsonite or prehnite their estimated values for the entropies yield results significantly different than ours.

Application of equilibria to metamorphic assemblages

To infer the conditions for formation of metamorphic rocks using univariant assemblages in the CASH system, it is frequently necessary to evaluate the effects of additional components. The phases contained in this system which commonly exibit solid-solutions are plagioclase, garnet, margarite, and zoisite. Fortunately, disagreement involving the activity-composition relations for the first two of these minerals usually does not produce large differences in the thermodynamics of devolatilization equilibria because of the large Gibbs energies associated with such reactions. For margarite and zoisite, little data relating activity to composition are available and an ideal mixing model must be assumed (KERRICK and DARKEN, 1975). Deviations from ideality in silicate mixtures tend to produce activity coefficients greater than one and calculated shifts in reaction equilibria using

an idea model may be in error. While more exact activity-composition data are needed, it is assumed the following calculations represent good first approximations.

The lower stability of zoisite and epidote. Reaction (12):

5 lawsonite + grossular = 4 zoisite
$$+ \text{ quartz } + 8 H_2O \quad (12)$$
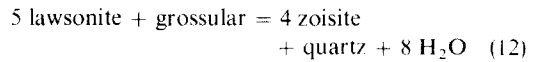
limits the lower stability of zoisite + quartz + H_2O to temperatures greater than 280°C at 10 kbar (Fig. 9). At lower pressures this reaction is replaced by:

prehnite + 2 lawsonite = 2 zoisite
$$+ \text{ quartz } + 4 H_2O \quad (13)$$
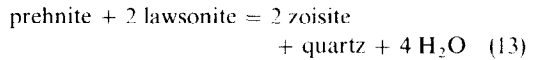
and below 3 kbar, where laumontite becomes stable with respect to lawsonite + quartz + H_2O (LIOU, 1971), the reaction becomes:

2 laumontite + prehnite = 2 zoisite
$$+ 5 \text{ quartz } + 8 H_2O \quad (14)$$
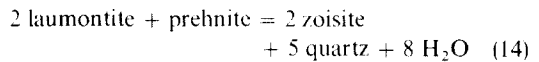
Thermochemical data are not available for laumontite, but reaction (14) will be located at about 210°C for pressures near 3 kbar. These reactions all give lower stability limits for zoisite + quartz + H_2O. If the fugacity of H_2O is reduced (thus generally increasing that of CO_2) the stability of zoisite + quartz is extended to lower temperatures. However, if the fugacity of CO_2 increases significantly, zoisite will decompose to anorthite + calcite, to lawsonite + calcite (or aragonite), or to laumontite + calcite depending upon which is the most stable calcium-aluminum silicate with Ca/Al = 1/2. These equilibria apply to zoisite, but epidote is the most common member of the epidote group at low temperature.

The stability of epidote will depend on its composition, on the fugacity of oxygen, and on the pressure and the temperature (HOLDAWAY, 1966; LIOU, 1974), but no reduction reactions will be considered here. If $Fe^{3+}/(Fe^{3+} + Al) = 1/3 = \text{pistacite}_{33}$ in epidote (Ps_{33}, $Ca_2Al_2FeSi_3O_{12}OH$), the activity of zoisite is zero, provided we assume an ideal mixing model with complete order of Fe^{3+} in the M_0 octahedral site (STRENS, 1968; BURNS and STERNS, 1967; BANCROFT et al., 1968; DOLLASE, 1968). The Gibbs energy difference between the orthorhombic and monoclinic forms of zoisite is also assumed to be negligible. Thus, epidote(Ps_{33}) + quartz + H_2O is stabilized over laumontite, lawsonite, or anorthite + calcite at all pressures and temperatures. Our activity model is only a first-order approximation. Indeed, errors are implied if the reported zoisite-epidote pairs (e.g., HOLDAWAY, 1966; ACKERMAND and RAASE, 1973; NESBITT, 1979) represent an equilibrium assemblage implying a miscibility gap with implied variations in activities from the ideal model.

Reaction (12) has some potential for use as an isograd or in restricting conditions within the blueschist facies. Garnet-lawsonite occurrence are known in the Franciscan formation of California (LEE et al., 1963;

ESSENE, 1967), in the Ouegoa formation of New Caledonia (BLACK, 1973; BLACK and BROTHERS, 1977) and in northeast Corsica (BROUWER and EGGELER, 1948). Some zoisite-quartz blueschists or blueschist-type ecologites have also been reported in California (ESSENE, 1967). WATSON (1960) and ESSENE and WARE (1970) report unusual lawsonite-eclogites from kimberlites at Garnet Ridge, Arizona, with lawsonite partially or completely reacted to a fine-grained zoisite $\pm$ quartz matte. The cores of the garnets are grossular$_{30}$-almandine$_{70}$ and the rims often are as pyropic as grossular$_5$-almandine$_{45}$-pyrope$_{50}$. Many blueschist eclogites contain epidote as an accessory calcium-aluminum silicate. Occasionally assemblages of garnet-epidote-lawsonite-quartz have been found (BLACK, 1973). None of these occurrences have a grossular-rich garnet although all have almandines with 25–35% grossular. If the activities of grossular and zoisite are fixed, reaction (12) is univariant for pressure, water fugacity, and temperature. If we consider the shift in the reaction for a garnet of composition grossular$_{30}$-almandine$_{70}$, the activity of the grossular is 0.03 using PERKINS and ESSENE's (1976) model or 0.5 using GANGULY and KENNEDY's (1974) model. Reaction (12) will shift by -1.5 kbar at 500 K which is equivalent to a shift of $+30°C$ in this temperature range using the first activity model and -0.4 kbar or $+7$ using the second. The effect of Fe^{3+} solid solution in zoisite is to offset much or all of this temperature shift—Ps$_{19}$ will counterbalance the first shift and Ps$_5$ the second. While accurate activity-composition data are obviously needed for these phases for proper evaluation of the shift in equilibria, common solid solutions in garnets and eipdotes tend to have offsetting effects as long as grossular is greater than 10% and pistacite is less than 20%. As a first approximation the solid-solutions may be neglected for garnet-lawsonite-epidote-quartz assemblages and the curve in Fig. 9 may be directly applied.

Garnet-lawsonite eclogites and blueschists may give information on the activity of water if pressure and temperature can be estimated. If we assume a temperature of 250–300°C and a pressure of 6–8 kbar (ESSENE and FYFE, 1967), the activity of water must be high to stabilize lawsonite with garnet. Quite different activities of water were estimated by GHENT and COLEMAN (1973) for blueschist eclogites using other equilibria. While different eclogites need not have formed at the same water activities, part of the disagreement may lie in the pressure and temperature assumed. Neither K_d thermometry, oxygen-isotope thermometry, nor pyroxene barometry are adequately calibrated for low to medium metamorphic temperatures and accurate pressure-temperature estimates are not yet obtainable for blueschists. Reaction (12) may ultimately help in resolving uncertainties in the activity of water for blueschists and low-temperature eclogites.

The lower stability of grossular + quartz. The lower stability of grossular + quartz + H_2O has not been

located experimentally. PISTORIUS and KENNEDY (1960) interpreted synthesis experiments as indicative that hydrogrossular + quartz become more stable than grossular + water at low temperatures and elevated pressures. Recently ELLIS (1978) has published schematic phase diagrams implying that zoisite + wollastonite will break down to grossular + quartz + H_2O at relatively high temperatures. Calculations using our inferred $\Delta G_{f,298}^\circ$ for these phases show that grossular + quartz + H_2O are always significantly more stable than zoisite + wollastonite. At low temperatures zoisite and wollastonite will be replaced by prehnite + xonotolite or laumontite + xonotolite, but our data suggest that grossular + quartz + H_2O will still be more stable than these assemblages.

The upper-pressure limit of prehnite. The reaction:

$$2 \text{ prehnite} = \text{lawsonite} + \text{grossular} + \text{quartz} \quad (16)$$
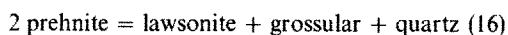
was first proposed by STRENS (1968). It is located by intersection of reactions (7) and (12) and is placed at 6 kbar for temperatures of 240°C although its location is uncertain due to difficulties in interpreting the experimentally calibrated prehnite equilibria. This solid-solid reaction is stable with excess water and may be amenable to direct experimentation. LIOU and SCHIFFMAN (1976) report preliminary experiments on this reaction at somewhat higher temperatures and pressures which are in good agreement with our calculated location. They report hydrogrossular + quartz as decomposition products but these should be less stable than grossular + H_2O. The reaction is important in restricting the pressure limit of prehnite-bearing rocks, particularly the aragonite-prehnite-lawsonite assemblage from the San Juan Islands reported by VANCE (1968) and by GLASSLEY et al. (1976). Comparison of the prehnite stability limit in Fig. 9 with the calcite-aragonite transition as located by CRAWFORD and FYFE (1965b), CRAWFORD and HOERSCH (1972), and BOETTCHER and WYLLIE (1967) shows that the upper stability of prehnite may barely overlap that of aragonite. If our location of reaction (16) is correct, prehnite-aragonite rocks should be rare. It is just possible that the rocks from the San Juan Islands equilibrated at 5–6 kbar and 150–200°C where prehnite, aragonite, and lawsonite may all be stable (see also ESSENE, 1976). However, if the preliminary experiments by Liou and Schiffman have properly delineated the prehnite stability field than either prehnite or aragonite must be metastable. Argonite is the most likely metastable phase due to the inhibition of Mg^{2+} in solution (see FYFE and BISCHOFF, 1968; BISCHOFF and FYFE, 1968). If so, then prehnite and lawsonite could have equilibrated at pressures as low as 3 kbar, closer to the conditions originally estimated by VANCE (1968).

The stability of zoisite-kyanite-quartz and water pressure in eclogites. The assemblage zoisite-kyanite-quartz has long been known in eclogites associated with the amphibolite facies (HAÜY, 1822; BRIERE,

1920; TILLEY, 1936; ESSENE, 1967; MOTTANA et al., 1968). In addition, white micas and/or talc have also been reported and in some cases have been interpreted to be primary (BRYHNI and GRIFFIN, 1971; VELDE, 1966; VRÁNA et al., 1975). Occasionally, margarite has been reported (ESKOLA, 1921; GREEN, 1968, personal communication) although to this date, no analyses of eclogitic margarites have been published. The presence of these hydrous minerals is somewhat surprising in view of the current claim that eclogites represent dry metamorphism (FRY and FYFE, 1969; BRYHNI et al., 1970). If pressure-temperature estimates can be made, limits of water pressures can be obtained from the stabilities of these hydrous phases. In the writers' view, few accurate pressure-temperature data have been obtained for crustal eclogites (pace Velde, Raheim, and Green), due to difficulties in extrapolating experimental equilibria downward from much higher pressures and temperatures, especially for reactions involving omphacite, a phase exhibiting variable cation ordering (CLARK and PAPIKE, 1966). Until the effect of pressure and temperature on ordering in both the natural omphacites and the experimental run products is known, extrapolation of experimental data assuming a straight line is certainly suspect (see NEWTON and SMITH, 1967, for similar effects in other systems). Nevertheless, if we arbitrarily assume that the amphibolite facies eclogites equilibrated at 8 kbar and 600°C we can inspect the range of water activities permitted by the assemblages zoisite + kyanite + quartz and the upper stability of margarite + quartz for fluid pressure equal to load pressure (Fig. 9). Reaction (1), zoisite + kyanite + quartz = anorthite + water is quite insensitive to the activity of H_2O because of a large positive volume change for the solids. However, the breakdown of margarite + quartz (reaction 10) is strongly sensitive to the activity of water and the stability of zoisite + kyanite is rapidly expanded at lower pressures and temperatures with decreased water activity. Margarite-quartz assemblages certainly require high activities of water for a wide range of reasonable pressures and temperatures for these rocks. Unfortunately, margarite is rare and may not even be primary in these rocks. Muscovite, which is more common, requires $a_{H_2O} > 0.2$ at these conditions (KERRICK, 1972). Paragonite, a common accessory mica in eclogites, requires an activity of H_2O greater than 0.8 at these pressures and temperatures and $a_{H_2O} > 0.5$ at 8 kbar and 500°C (see WALL and ESSENE, 1972, and also p. 59 in VERNON, 1976). A higher choice of pressure and temperature will increase inferred a_{H_2O} and a lower one will decrease inferred a_{H_2O}. Quantitative determination of a_{H_2O} must await more accurate barometry and thermometry on these rocks. While we have no certain proof of 'wet' eclogites, the micas require that they were at least 'damp'. Direct experiments, at metamorphic conditions, on basaltic rock compositions for blueschist or amphibolite versus eclogite assemblages are needed, but these will be difficult. Perhaps two-month studies at 10 kbar and 500°C with excess H_2O could be informative.

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APPENDIX 1

Experimental (observed) heat capacities in terms of calories, K and mol and based upon the molecular weight of end-member minerals, but without adjustment for chemical composition[a]

[a] The data of Series III for lawsonite, margarite and zoisite and that of Series IV for prehnite have been obtained by differential—scanning calorimetry; the other data were obtained by (equilibrium) adiabatic-shield calorimetry.

Experimental Heat Capacities of Lawsonite

T	c_p	T	c_p	T	c_p
Series I		279.64	66.56	42.96	3.079
65.95	8.97	290.42	67.28	48.89	4.382
71.82	10.72	300.95	68.50	55.45	6.015
78.45	12.83	311.00	69.80	63.24	8.171
86.04	15.38	320.90	71.08		
94.45	18.23	330.81	70.77	Series III	
103.56	21.41	340.84	72.14	319.6	70.4
112.98	24.81	348.84	73.07	329.6	71.8
122.51	28.09			339.7	72.6
132.26	30.56	Series II		349.7	73.7
142.25	32.94	5.44	0.024	369.7	75.6
152.56	35.82	7.04	0.023	389.8	77.9
162.58	38.63	8.63	0.026	409.9	79.9
172.07	41.21	10.14	0.037	429.9	82.1
181.43	43.61	11.74	0.039	450.0	83.9
190.91	46.00	13.45	0.058	470.0	85.7
200.44	48.32	15.14	0.086	490.1	87.3
210.15	50.68	17.14	0.127	480.1	86.7
219.77	52.89	19.50	0.202	500.2	87.9
229.14	55.54	22.30	0.337	520.2	89.8
238.71	58.00	25.53	0.559	540.3	91.5
248.93	60.53	29.00	0.882	560.4	92.7
259.46	63.43	33.14	1.393	580.4	93.4
269.50	67.50	37.79	2.114	600.5	94.5

Experimental Heat Capacities of Margarite

T	c_p	T	c_p	T	c_p
Series I		6.41	0.037	509.8	105.1
76.53	14.45	8.06	0.047	529.8	106.4
84.05	17.27	9.69	0.065	549.8	107.7
92.25	20.30	11.44	0.078	590.0	109.4
101.15	23.52	13.31	0.108	610.0	110.0
110.93	27.11	15.17	0.152	630.0	111.4
120.33	30.54	17.07	0.214	650.1	112.0
130.42	34.14	19.14	0.302	670.1	112.9
141.07	37.85	21.39	0.430	690.1	113.7
150.95	41.18	23.96	0.622	700.1	114.0
160.74	44.40	26.74	0.887	700.3	114.5
170.74	47.58	29.73	1.251	720.3	114.8
180.80	50.63	33.00	1.747	740.3	115.5
190.74	53.51	36.19	2.327	760.4	116.3
200.61	56.29	39.60	3.026	780.4	117.8
205.71	57.66	43.35	3.903	790.4	117.8
210.56	58.98	47.68	5.031	809.5	119.2
215.15	60.22	52.48	6.393	819.5	119.4
225.27	62.79	57.62	7.992	829.5	119.5
235.24	65.26	63.16	9.813	839.5	119.9
245.18	67.59			849.4	119.6
255.12	69.83	Series III		799.0	118.6
265.09	72.07	319.6	82.5	858.6	120.4
275.08	74.08	329.6	83.8	850.2	120.0
285.01	76.04	339.7	85.5	859.8	120.2
294.38	77.85	349.7	86.8	879.0	121.3
302.97	79.44	369.6	89.5	898.0	121.9
310.73	80.84	389.7	91.8	907.8	122.9
318.95	82.30	409.8	94.0	883.5	121.1
328.15	83.83	429.8	96.5	922.4	122.4
337.73	85.28	449.9	98.5	957.1	124.1
345.79	86.54	469.9	100.7	996.3	124.6
		490.0	102.0	928.2	122.8
Series II		469.8	101.2	947.8	123.4
4.93	0.024	480.8	102.8		

Experimental Heat Capacities of Prehnite

T	C_p	T	C_p	T	C_p
Series I		64.72	12.98	Series IV	
100.77	26.45	71.33	15.37	319.6	82.9
107.76	29.04	79.06	18.29	329.6	84.2
117.14	32.50	87.64	21.60	339.7	85.7
126.37	35.80	96.93	25.51	349.7	87.0
135.78	39.07			369.6	89.7
145.27	42.25	Series III		389.7	91.8
154.73	45.33	5.32	0.012	409.8	94.2
164.29	48.28	6.43	0.017	429.8	96.1
173.95	51.24	7.29	0.023	449.9	97.8
183.72	54.02	8.22	0.030	469.9	99.8
190.60	55.89	9.19	0.038	490.0	101.5
193.69	56.73	10.21	0.052	469.8	99.6
200.17	58.40	11.30	0.066	489.8	101.5
203.77	59.39	12.28	0.087	509.8	103.2
209.82	60.94	13.36	0.115	529.8	104.2
219.51	63.37	14.68	0.165	549.8	106.0
229.42	65.62	16.07	0.232	600.5	108.3
239.61	67.95	17.60	0.329	619.8	109.1
249.96	70.12	19.02	0.444	639.9	110.0
260.35	72.17	20.90	0.631	659.9	111.0
270.60	74.20	23.30	0.932	669.9	111.4
280.67	76.10	25.56	1.284	650.1	110.8
290.61	77.89	28.00	1.720	670.1	112.0
300.54	79.58	30.66	2.273	690.1	112.9
310.44	81.22	33.68	2.979	700.1	113.5
320.24	82.78	37.20	3.897	700.4	133.7
330.05	84.37	40.98	4.965	720.4	133.7
339.97	85.73	44.99	6.184	740.4	114.4
347.89	86.85	49.68	7.699	760.4	114.9
		54.87	9.441	780.4	115.7
Series II		60.21	11.33	790.4	115.9
59.67	11.15	66.17	13.50		

Experimental Heat Capacities of Zoisite

T	C_p	T	C_p	T	C_p
Series I		327.66	89.19	61.62	10.84
58.84	9.840	337.81	90.83	67.76	13.04
64.29	11.79	346.73	92.16		
70.21	13.86			Series III	
76.68	16.32	Series II		344.0	91.5
83.81	19.21	5.25	0.003	364.0	93.5
91.71	22.29	6.33	0.004	384.0	96.0
100.54	25.66	7.45	0.018	404.0	98.5
109.91	29.30	7.95	0.026	419.0	100.3
119.48	33.03	8.85	0.035	424.0	100.8
129.36	36.87	9.90	0.054	439.0	102.4
139.21	40.53	10.88	0.044	459.0	103.7
148.84	44.04	11.90	0.074	479.0	105.8
158.56	47.39	13.02	0.094	499.0	107.3
168.31	50.76	14.28	0.133	499.0	107.5
177.98	53.84	15.66	0.192	519.0	108.4
187.80	56.92	17.16	0.270	519.0	108.4
197.77	59.90	18.82	0.383	539.0	110.1
207.79	62.78	20.36	0.509	559.0	112.0
217.80	65.58	22.08	0.685	579.0	112.9
228.50	68.31	24.22	0.949	579.0	112.8
238.17	70.70	26.58	1.284	599.0	114.3
247.94	73.05	29.26	1.732	599.0	114.7
257.86	75.36	32.18	2.300	619.0	115.6
267.83	77.55	35.33	3.028	639.0	116.5
277.71	79.65	39.21	3.913	649.0	117.0
287.49	81.64	42.44	4.755	659.0	117.0
297.25	83.62	46.04	5.789	669.0	118.1
307.26	85.36	50.78	7.232	689.0	118.7
317.46	87.21	55.94	8.883	709.0	119.3
				729.0	119.6

APPENDIX 2

Smoothed values of the thermodynamic functions below 298.15 K expressed in terms of calories, K and mol based upon the molecular weight of the end-member minerals, but without adjustment for chemical composition

Thermodynamic Functions of Lawsonite

T	C_p	S^o	$H_T^o - H_0^o$	$\dfrac{-(G_T^o - H_0^o)}{T}$
5	0.003	0.001	0.001	0.001
10	0.024	0.008	0.060	0.002
15	0.081	0.027	0.304	0.007
20	0.223	0.067	1.011	0.016
25	0.518	0.145	2.794	0.033
30	0.995	0.279	6.500	0.062
35	1.659	0.480	13.058	0.107
40	2.503	0.754	23.391	0.170
45	3.507	1.106	38.354	0.253
50	4.649	1.533	58.69	0.359
55	5.904	2.034	85.03	0.488
60	7.252	2.605	117.89	0.641
65	8.678	3.242	157.68	0.816
70	10.175	3.939	204.78	1.014
75	11.735	4.694	259.53	1.233
80	13.352	5.503	322.23	1.475
85	15.02	6.362	393.13	1.737
90	16.71	7.268	472.44	2.019
95	18.43	8.218	560.3	2.320
100	20.16	9.207	656.8	2.639
120	27.30	13.515	1131.5	4.085
140	32.37	18.13	1731.1	5.761
160	37.91	22.80	2432.9	7.598
180	43.26	27.58	3245.3	9.552
200	48.24	32.40	4160.8	11.596
220	52.93	37.22	5173	13.706
240	57.25	42.01	6275	15.87
260	60.87	46.75	7459	18.06
280	63.73	51.36	8705	20.27
300	66.64	55.86	10009	22.50
273.15	62.78	49.80	8272	19.51
298.15	66.37	55.45	9885	22.29

Thermodynamic Functions of Margarite

T	C_p	S^o	$H_T^o - H_0^o$	$\dfrac{-(G_T^o - H_0^o)}{T}$
5	0.005	0.002	0.002	0.001
10	0.043	0.014	0.108	0.003
15	0.147	0.051	0.572	0.013
20	0.345	0.117	1.744	0.030
25	0.715	0.230	4.313	0.058
30	1.294	0.408	9.243	0.100
35	2.096	0.665	17.625	0.162
40	3.111	1.009	30.557	0.245
45	4.317	1.443	49.052	0.353
50	5.682	1.968	73.99	0.488
55	7.173	2.578	106.08	0.649
60	8.758	3.270	145.88	0.838
65	10.405	4.035	193.73	1.054
70	12.143	4.869	250.07	1.297
75	13.931	5.768	315.24	1.564
80	15.75	6.725	389.43	1.857
85	17.59	7.735	472.76	2.173
90	19.43	8.792	565.3	2.511
95	21.28	9.892	667.1	2.870
100	23.12	11.030	778.1	3.249
120	30.42	15.89	1313.8	4.945
140	37.47	21.12	1993.2	6.879
160	44.16	26.56	2810.2	8.997
180	50.39	32.13	3756.5	11.257
200	56.13	37.74	4822.4	13.625
220	61.44	43.34	5999	16.07
240	66.38	48.90	7278	18.58
260	70.94	54.40	8651	21.12
280	75.08	59.81	10112	23.69
300	78.88	65.12	11652	26.28
273.15	73.71	57.96	9603	22.81
298.15	78.54	64.63	11507	26.04

Thermodynamic Functions of Prehnite

T	C_p	S°	$H_T^\circ - H_0^\circ$	$\dfrac{-(G_T^\circ - H_0^\circ)}{T}$
5	0.010	0.002	0.007	0.000
10	0.047	0.019	0.138	0.005
15	0.178	0.057	0.633	0.015
20	0.536	0.151	2.302	0.036
25	1.189	0.335	6.489	0.075
30	2.129	0.631	14.673	0.142
35	3.315	1.045	28.197	0.240
40	4.680	1.575	48.119	0.372
45	6.184	2.212	75.23	0.540
50	7.798	2.946	110.1	0.744
55	9.499	3.769	153.4	0.980
60	11.26	4.670	205.21	1.250
65	13.07	5.642	266.01	1.550
70	14.91	6.678	335.94	1.879
75	16.78	7.770	415.15	2.235
80	18.66	8.913	503.7	2.616
85	20.54	10.100	601.7	3.021
90	22.43	11.328	709.1	3.449
95	24.31	12.591	826.0	3.896
100	26.19	13.886	952.3	4.363
120	33.53	19.31	1549.9	6.398
140	40.49	25.01	2290.8	8.648
160	46.98	30.85	3166.4	11.057
180	52.95	36.73	4166.6	13.583
200	58.42	42.60	5281	16.19
220	63.42	48.40	6500	18.86
240	67.98	54.12	7815	21.56
260	72.16	59.73	9217	24.28
280	75.99	65.22	10699	27.01
300	79.52	70.58	12255	29.73
273.15	74.72	63.35	10183	26.07
298.15	79.20	70.09	12108	29.48

Thermodynamic Functions of Zoisite

T	C_p	S^o	$H_T^o - H_0^o$	$\dfrac{-(G_T^o - H_0^o)}{T}$
5	0.006	0.002	0.007	0.001
10	0.044	0.015	0.111	0.004
15	0.158	0.050	0.568	0.012
20	0.477	0.133	2.048	0.031
25	1.057	0.297	5.779	0.066
30	1.875	0.559	13.018	0.125
35	2.899	0.923	24.871	0.212
40	4.107	1.387	42.314	0.329
45	5.478	1.948	66.21	0.477
50	6.983	2.602	97.32	0.656
55	8.591	3.342	136.21	0.866
60	10.272	4.161	183.34	1.106
65	12.014	5.052	239.03	1.374
70	13.819	6.008	303.59	1.671
75	15.70	7.025	377.35	1.994
80	17.66	8.101	460.73	2.341
85	19.64	9.231	554.0	2.713
90	21.58	10.408	657.0	3.108
95	23.54	11.627	769.8	3.524
100	25.50	12.885	892.4	3.960
120	33.27	18.22	1480.4	5.886
140	40.77	23.92	2221.3	8.052
160	47.90	29.83	3108.8	10.404
180	54.53	35.86	4134.0	12.897
200	60.60	41.93	5286	15.50
220	66.12	47.97	6554	18.17
240	71.14	53.94	7928	20.91
260	75.78	59.82	9397	23.67
280	80.12	65.59	10957	26.46
300	84.16	71.26	12600	29.26
273.15	78.66	63.63	10413	25.51
298.15	83.80	70.74	12445	29.00