American Mineralogist, Volume 79, pages 478–484, 1994

Standard thermodynamic properties of meionite, $Ca_4Al_6Si_6O_{24}CO_3$, from experimental phase equilibrium data

JUDY BAKER,* ROBERT C. NEWTON
Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, U.S.A.

ABSTRACT

Reversals of two reactions bounding the stability field of the scapolite meionite,

$$\underset{\text{anorthite}}{3CaAl_2Si_2O_8} + \underset{\text{calcite}}{CaCO_3} = \underset{\text{meionite}}{Ca_4Al_6Si_6O_{24}CO_3} \quad (1)$$

$$\underset{\text{grossular}}{Ca_3Al_2Si_3O_{12}} + \underset{\text{kyanite}}{2Al_2SiO_5} + \underset{\text{quartz}}{SiO_2} + \underset{\text{calcite}}{CaCO_3} = \underset{\text{meionite}}{Ca_4Al_6Si_6O_{24}CO_3} \quad (2)$$

were performed with a variety of experimental conditions and starting materials. Definitive reversals of Reaction 1 were obtained in the presence of an equimolar CO_2-H_2O flux (hydrous oxalic acid) with meionite synthesized at 900 °C and synthetic anorthite and calcite. Reversed brackets obtained in the internally heated gas vessel and higher pressure reversals without a vapor flux in the piston-cylinder apparatus are consistent with the experiments of Goldsmith and Newton (1977) and are higher in temperature by 60–80 °C than the recent experimental results of Huckenholz and Seiberl (1988, 1989). Fluid-absent reversals of Reaction 2 were obtained in the piston-cylinder apparatus for a range 900–1300 °C and 20–32 kbar. The thermal expansion of the scapolite was measured by X-ray diffraction at a series of temperatures between 20 and 800 °C, yielding $\alpha = 1.8164 \pm 0.0148 \times 10^{-5}$/K and $V_{1,298} = 33.985 \pm 0.005$ J/(bar·mol). Best-fit lines through the experimental brackets of Reactions 1 and 2 define $S_{1,298}$ (meionite) as 0.761 kJ/(K·mol). This value requires that meionite has a high degree of disorder.

INTRODUCTION

Scapolite is the general name given to minerals that can be described by solid solutions among a calcium carbonate end-member, meionite, $Ca_4Al_6Si_6O_{24}CO_3$, a sodium chloride end-member, marialite, $Na_4Al_3Si_9O_{24}Cl$ (Ma), a hypothetical end-member $Na_3CaAl_3Si_9O_{24}CO_3$ (Na-Me), and a calcium sulfate end-member, sulfate meionite, $Ca_4Al_6Si_6O_{24}SO_4$. The mineral scapolite is a stable phase in rocks from a wide range of crustal settings. Shaw (1960), Evans et al. (1969), and, more recently, Moecher and Essene (1991) have described many metamorphic occurrences of this mineral, ranging from low-pressure skarn assemblages associated with garnet and vesuvianite (Kerrick et al., 1973) through low- and medium-pressure regional settings (Edwards and Baker, 1953) to high-pressure scapolite-bearing granulites in uplifted deep-crustal blocks (Coolen, 1982; Bradshaw, 1989), scapolite granulite xenoliths in alkalic basalt pipes in southeast Australia (Lovering and White, 1969), and kimberlite pipes of Siberia (Bobrievich and Sobolev, 1957) and Africa (Dawson, 1971). Several occurrences of scapolite as a primary mineral in alkaline igneous rocks have also been recorded (Larsen, 1981; Goff et al., 1982). Accurate thermodynamic data for scapolites are therefore essential to define the conditions of formation of scapolite-bearing rocks in their many settings.

In order to describe the scapolite minerals thermochemically, the activity-composition relations of the solid solutions as well as thermodynamic data pertaining to the end-members are required. Solid-solution relationships along the joins meionite to marialite, meionite to sodian meionite, and meionite to sulfate meionite have been investigated experimentally (Orville, 1975; Goldsmith and Newton, 1977; Ellis, 1978). The P-T stabilities of the end-member with respect to assemblages containing plagioclase (anorthite or albite) and halite, calcite, and anhydrite have been investigated by Newton and Goldsmith (1975, 1976) and Goldsmith and Newton (1977), who showed that scapolites are refractory minerals at elevated pressures, replacing the lower temperature assemblage plagioclase + calcite (+ anhydrite + halite). In particular, Goldsmith and Newton (1977) found that meionite is stable relative to anorthite + calcite at temperatures above 875 °C, almost independent of pressure (Fig. 1). They reported reversals of the meionite-anorthite-calcite reaction, thus defining a set of thermodynamic properties of meionite relative to the well-characterized phases anorthite and calcite.

---

* Present address: Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, U.K.

0003–004X/94/0506–0478$02.00

More recent experimental work by Huckenholz and Seiberl (1988, 1989) has reexamined the *P-T* stability of meionite with respect to the lower temperature assemblages containing anorthite + calcite (i.e., Reaction 1 above). The new determination suggests much lower temperatures for the reaction than those found by Goldsmith and Newton (1977), with meionite stable to temperatures below 800 °C at 10 kbar (Fig. 1). Huckenholz and Seiberl's revised meionite stability field was based on reversed reactions among synthetic minerals in the presence of a vapor phase flux of hydrous oxalic acid, $(COOH)_2 \cdot 2H_2O$. Moecher and Essene (1990) attributed this discrepancy with the earlier work to the possibilities: (1) The meionite used by Goldsmith and Newton (1977), synthesized without flux at 1300–1400 °C and 15 kbar, was considerably more disordered than that used in the study of Huckenholz and Seiberl (1989), which was synthesized at 900–950 °C at low pressures in the presence of a hydrous fluid. (2) The anorthite used by Goldsmith and Newton (1977) was highly disordered. (3) The compositions of the fluids used in the two sets of experiments were different, with Goldsmith and Newton using a variety of compositions, ranging from $X_{CO_2} = 0.5$ to vapor absent conditions, whereas the experiments of Huckenholz and Seiberl (1989) all contained a fluid phase of composition $X_{CO_2} = 0.5$.

The issues raised by Moecher and Essene (1990) indicate the need for further study of meionite stability. The present study is a redetermination of the low-temperature and high-pressure stability limits of meionite in an attempt to resolve the experimental discrepancies and hence to define more precisely the standard thermodynamic properties of meionite.

EXPERIMENTAL METHODS

Pressure-temperature apparatus

A ¾-in. diameter piston-cylinder apparatus and an internally heated Ar pressure vessel (designed after Holloway, 1971) were used in these experiments. Piston-cylinder experiments were carried out in the range 6–30 kbar, the majority of them with a NaCl pressure medium. Before heating, NaCl assemblies were brought to a pressure below that desired and then heated, allowing the large thermal expansion of NaCl to bring the experiment up to the final pressure, thus maintaining a piston-out condition. Generally, a small amount of ram pressure bleeding was required to hold the pressure to the desired value during heating. Some experiments were performed above or close to the melting point of NaCl, requiring the use of a $BaCO_3$ pressure medium. These experiments were brought to the desired pressure before heating, as the thermal expansion of $BaCO_3$ is quite small. Pressure calibration of the $BaCO_3$ assemblies over a pressure range of 3–18 kbar was carried out using the melting point of NaCl. Several overlapping experiments were made at 4–8 kbar with both the piston cylinder and the gas vessel to ensure that the results with the $BaCO_3$ pressure medium were conformable. Temperature was controlled using both W-Re and chromel-alumel thermocouples and, for the setups used, is thought to be accurate to ±5 °C. In fluid-absent experiments and those containing a hydrous oxalic acid flux, the formation of zoisite was minimized by placing the Pt capsule containing the experimental charge within a sealed Au capsule containing deionized H_2O + hematite.

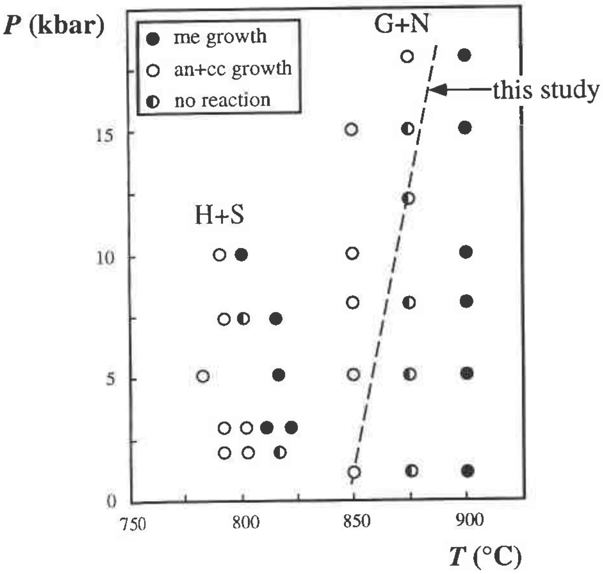

Fig. 1. Experimental reversals of 3 anorthite + calcite = meionite. Lower temperature data set is that of Huckenholz and Seiberl (1989) (H + S), and higher temperature data set is that of Goldsmith and Newton (1977) (G + N). Dashed line labeled this study shows the position of the equilibrium calculated from the experimental reversals of this study (see Discussion and Fig. 2a).

Reversals with the internally heated gas vessel were performed in the range 1–5 kbar. Two chromel-alumel thermocouples, placed 2 mm apart, straddled the Pt sample capsules. The Pt capsules were positioned relative to the thermocouples using a Cu sample holder, which greatly reduced temperature gradients across the samples and ensured that the thermocouples did indeed span the sample position. The temperature difference between the thermocouples did not exceed 4 °C. Hematite was packed around the samples to fix H (a hematite getter), minimizing the presence of reduced gas species. Ar pressure was measured with a 150000 p.s.i. Astra bourdon gauge calibrated against a precise Heise bourdon-tube gauge. Pressure was also measured independently using a manganin cell. Pressure was read and calibrated to ±50 bars.

Starting materials

Starting materials for the reversal experiments consisted of fine-grained mechanical mixtures of synthetic phases, except for quartz, which was a purified natural sample from Lisbon, Maryland, and kyanite, which was a natural sample from Litchfield, Connecticut, with <0.16 wt%

TABLE 1. Microprobe analyses of synthetic starting materials

	Grossular	Meionite	Anorthite
SiO_2	40.98	39.62	43.59
Al_2O_3	23.09	33.07	37.26
FeO	0.00	—	0.00
MgO	0.01	—	—
Na_2O	—	0.048	0.00
CaO	36.55	22.86	20.24
SO_3^{2-}*	—	0.01	—
Cl^-*	—	0.01	—
Total	100.63	95.59	101.09
	Atomic proportions		
Si	3.04	6.14	1.99
Al	2.02	6.05	2.01
Fe^{2+}	0.00	—	0.00
Mg^{2+}	0.00	—	—
Na	—	0.01	0.00
Ca	2.90	3.80	0.99
Total	7.96	16.00	5.00
Cl	—	0.00	—
S	—	0.00	—

* SO_3^{2-} and Cl^- are calculated assuming $25O^{2-}$ equivalents pfu.

Fe_2O_3 as the major impurity. Calcite was a Baker reagent of precipitated $CaCO_3$.

The anorthite used throughout the study was synthesized from a homogeneous stoichiometric glass at 900 °C and 3.5 kbar in the presence of anhydrous oxalic acid for 96 h. The material consisted of equant, mostly untwinned crystals with an average size of 5–15 μm. Meionite was crystallized in a two-step process. Meionite was synthesized from a mix of synthetic anorthite and calcite seeded with synthetic meionite (crystallized at 1350 °C and 15 kbar from a homogeneous 3:1 molar mix of synthetic anorthite and calcite) at 900–950 °C and 3.5 kbar with an anhydrous oxalic acid flux for 48 h. The result was a nearly complete yield of large idiomorphic crystals of meionite (up to 100 μm). The grossular was crystallized from a homogeneous stoichiometric glass at 1300 °C and 25 kbar in graphite containers for 6 h. The unit-cell constant of 11.850 ± 0.001 Å showed that it was pure $Ca_3Al_2Si_3O_{12}$ with no hydrogrossular component.

Experimental mixes for reversals of Reaction 1 were prepared by mixing reaction proportions (3:1:1 molar) of anorthite, calcite, and meionite under acetone in an agate mortar. For experiments to be performed under vapor-absent conditions, mixing was done under distilled H_2O, in order to minimize contamination by organic solutes. The mixes were dried at 110 °C before loading into the Pt capsules. Thirty weight percent of hydrous oxalic acid, which decomposes to an equimolar CO_2-H_2O mixture upon heating, was added to each sample. Higher temperature and pressure experiments were performed without a vapor phase to minimize the production of zoisite.

Experimental mixes for reversals of Reaction 2 were prepared by mixing reaction proportions (1:2:1:1:1 molar) of grossular, kyanite, quartz, calcite, and meionite under distilled H_2O. The mixes were dried at 110 °C and then loaded into Pt capsules, which were subsequently welded.

Analytical techniques

Synthetic minerals and experimental products were examined by X-ray diffraction and electron microprobe analysis. The composition of each sample was determined using the Cameca electron microprobe in the Department of Geophysical Sciences at Chicago. All elements were analyzed using a WD detector, and synthetic anorthite was the principal standard. An accelerating voltage of 15 kV and a beam current of 0.1 μA were used, with acquisition times of 80 s. The compositions of the scapolites are given in Table 1.

Experimental products were examined with the polarizing microscope and by X-ray diffraction. It was sometimes possible to infer the direction of a reaction by overgrowth or dissolution textures of mineral grains. However, the main technique adopted was the relative increase or decrease of X-ray diffraction peak heights. This is a reli-

TABLE 2. Experiments used to delineate the stability of meionite relative to anorthite + calcite

Expt.	P (kbar)*	T (°C)	t (h)	X_{CO_2}**	Results
281	14.5–15.8	923–924	105	no vapor	very strong scapolite growth
280	14.4	908–909	148	no vapor	very strong scapolite growth
305	14.3–14.4	901–903	120	no vapor	strong scapolite growth
306	14.7–14.8	885–886	120	no vapor	strong scapolite growth
311	14.9	879–880	121	no vapor	strong scapolite growth
316	15	865–866	120	no vapor	anorthite + calcite growth
278	7.2	872–873	72	0.60	complete reaction to scapolite
289	6.7	853–854	20	0.59	strong anorthite + calcite growth
315	3.52	880–882	144	no vapor	strong scapolite growth
259	3.27	881–882	81	0.59	strong scapolite growth
277	3.21	865–866	72	0.66	scapolite growth
243	3.58	848–850	180	0.60	strong anorthite + calcite growth
279	1.05	878–882	42	0.68	strong scapolite growth
308	1.36–1.52	858–860	48	0.59	strong scapolite growth
314	1.52	847–851	75	0.65	strong anorthite + calcite growth

* Experiments at 1 and 3.5 kbar were carried out in an internally heated gas vessel, and those at 7 and 15 kbar were performed in a piston-cylinder apparatus using a NaCl pressure cell.

** Individual experiments were carried out either under vapor-absent conditions or in the presence of a hydrous oxalic acid flux. Fluid compositions were determined using the puncture and weigh method.

able qualitative technique for amounts of reaction >20% (Richardson et al., 1969).

Thermal expansion measurements

The thermal expansion of the unit-cell constants of the low-temperature synthetic meionite was determined at a series of temperatures between 20 and 800 °C using a heating stage designed in the Department of Earth Sciences, Cambridge, for the purpose of examining phase transitions in minerals. Details of the design are given in Salje et al. (1993). A small amount of material was crushed, mixed with an internal standard (Si), and spread over a Pt heating strip. A strictly monochromatic (Cu-$K\alpha_1$) focused X-ray beam diffracted from the sample was collected by a 4K-PSD detector. The temperature of the heating strip was monitored with ultrathin Pt-Rd thermocouples welded onto the Pt heating strip. The temperatures were calibrated by measuring the temperature of the α-β quartz transition (585 °C) and applying a linear temperature correction to the data (Baker, in preparation). Unit-cell dimensions were determined by least-squares refinement using 55 peak positions. For each successive temperature measurement, the sample was heated and ½ h allowed for thermal equilibration before 2θ values were collected. A second measurement was made at 20 °C after cooling to ensure that the unit-cell parameters had not changed as a result of heating. Although meionite was metastable relative to anorthite + calcite in this temperature range, it showed no tendency to decompose.

RESULTS OF EXPERIMENTS

Reaction 1: Meionite = 3 anorthite + calcite

Results of experiments on Reaction 1 are listed in Table 2. The gas vessel experiments were very consistent with the vapor-present and vapor-absent piston-cylinder experiments, as shown in Figure 2a. Observations of grain mounts suggest that the growth of meionite in the samples took place through the nucleation and growth of meionite on calcite grains rather than by the growth of original meionite crystals present in the starting material. That was the case for all starting materials.

The vapor-absent experiments all contained small amounts of zoisite (<15%), which must have resulted from infiltration of H through the Pt capsule walls, in spite of the external hematite getter. The amount of zoisite present was not large enough to place in doubt the results shown in Figure 2a, which again is based on a large growth or decline of the starting phases.

Reaction 2: Meionite = grossular + 2 kyanite + quartz + calcite

The experimental charges yielded strong reaction indications for Reaction 2, as shown in Figure 2b and listed in Table 3. Zoisite developed in most of the experiments, occurring as a distinct rind against the capsule wall. It was not present in the core of the samples, and reaction directions were thus not obscured by its development.

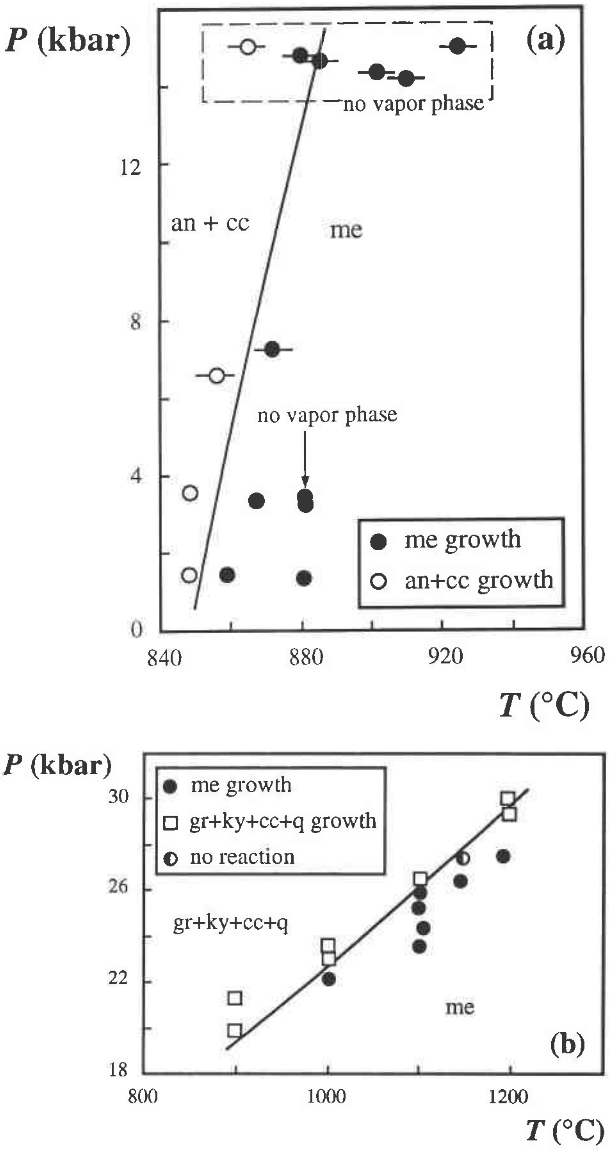

Fig. 2. (**a**) Experimental reversals of 3 anorthite + calcite = meionite (see also Table 2). Experiments above 4 kbar were performed with piston-cylinder apparatus, NaCl pressure medium; experiments below 4 kbar were carried out in a gas pressure apparatus. Experiments performed under vapor-absent conditions (in the presence of an external hematite H getter) are labeled as such. Solid line shows the *P-T* position of the equilibrium calculated by least-squares regression (see text). (**b**) Experimental reversals of grossular + kyanite + quartz + calcite = meionite (see also Table 3), performed in NaCl-medium piston-cylinder apparatus. All experiments were performed under vapor-absent conditions (in the presence of an external hematite getter). Solid line shows the *P-T* position of the equilibrium calculated by least-squares regression (see text).

Thermal expansion of meionite

The unit-cell constants measured for the synthetic meionite are listed in Table 4. Regression of the volume data (Fig. 3) yielded a thermal expansion parameter, α,

TABLE 3. Experiments* used to delineate the stability of meionite relative to grossular + kyanite + quartz + calcite

Expt.	*P* (kbar)	*T* (°C)	*t* (h)	Results
255	19.7–19.8	899–901	65	grossular + kyanite + calcite + quartz growth
246	21.2–21.3	899–900	72	strong grossular + kyanite + calcite + quartz growth
252	22.1–22.2	1001–1002	70	meionite growth
254	23	1000–1002	65	strong grossular + kyanite + calcite + quartz growth
251	23.6	1001–1002	70	strong grossular + kyanite + calcite + quartz growth
238	23.5–23.6	1100–1102	98	very strong meionite growth
268	24.4	1101–1103	96	strong meionite growth
239	25.2–25.3	1098–1100	96	very strong meionite growth
274	26	1100–1101	76	very strong meionite growth
245	26.5	1100–1101	72	very strong grossular + kyanite + calcite + quartz growth
266	26.6	1144–1145	40	strong meionite growth
261	27.4	1150–1151	48	no reaction
258	27.5	1190–1191	2	very strong meionite growth
247	29.3–29.4	1198–1200	36	very strong grossular + kyanite + calcite + quartz growth
248	30–30.5	1198–1199	36	very strong grossular + kyanite + calcite + quartz growth

* All experiments were performed in a piston-cylinder apparatus using a NaCl pressure cell, and no flux was used.

of $1.8164 \pm 0.0148 \times 10^{-5}$/K. This value is substantially greater than that extrapolated by Graziani and Lucchesi (1982) from their measurements of thermal expansion of the scapolite solid-solution series. This is discussed further by Baker (in preparation).

DISCUSSION

Thermodynamic properties of meionite

Thermodynamic properties for meionite were calculated by combining the experimental brackets for Reaction 1 with those for Reaction 2 and regressing them using the least-squares methods outlined in Holland and Powell (1990). The thermodynamic properties of grossular, kyanite, quartz, calcite, and anorthite (see Table 5) were fixed for the purposes of this regression. The thermal expansion, $V_{1,298}$, isothermal compressibility (Hazen and Sharp, 1988), and high-temperature heat capacity of meionite were also held fixed (assuming that the high-temperature heat capacity of meionite is equal to the sum of those of 3 anorthite + calcite). With a maximum pressure and temperature measurement error on each of the experimental determinations of ±5 °C and ±0.5 kbar, best-fit values for $S_{1,298}$ (meionite) of 0.761 kJ/(K·mol) and $\Delta H^0_{f1,298}$ of -13825.85 ± 0.59 kJ/mol were obtained. The *P-T* position of each reaction calculated using these best-fit values is shown in Figure 2.

TABLE 4. Thermal expansion of the lattice parameters of the synthetic meionite used in this study

T (°C)	*V** (Å³)	Molar volume* [J/(bar·mol)]	*a** (Å)	*c** (Å)
20	1128.5(2)	33.985(5)	12.200(1)	7.583(1)
99	1130.6(2)	34.048(5)	12.208(1)	7.586(1)
197	1131.8(2)	34.084(6)	12.217(1)	7.586(1)
295	1134.8(2)	34.174(5)	12.229(1)	7.589(1)
393	1136.8(2)	34.236(5)	12.238(1)	7.590(1)
492	1137.9(3)	34.267(9)	12.246(2)	7.588(2)
590	1139.7(2)	34.323(5)	12.254(1)	7.590(1)
688	1142.2(2)	34.397(4)	12.267(1)	7.591(1)
786	1143.9(2)	34.448(4)	12.275(1)	7.592(1)
20	1128.5(2)	33.982(5)	12.199(1)	7.583(1)

* Figures in parentheses indicate the uncertainty (±1σ) in the last digit.

Implications for order-disorder

The meionite structure comprises two types of four-membered rings containing AlO_4^{5-} and SiO_4^{4-} tetrahedra. Rings of type 1 form columns that are joined laterally by rings of type 2. The resulting structure has large oval-shaped cages, which contain the Ca^{2+} and CO_3^{2-} ions. It is thus expected that the meionite structure can show order-disorder both in the distribution of framework Al/Si and differences in the relative rotation of the CO_3^{2-} groups within the cages. For completely random Al/Si tetrahedral occupancy, the maximum framework disorder would be $12\,R \ln 2 = 0.0692$ kJ/(K·mol) (Goldsmith and Newton, 1977). In order to maintain tetrahedral symmetry, it is necessary that the triangular carbonate groups have rotational disorder, adding another $R \ln 8$, or 0.0173 kJ/(K·mol) (Aitken et al., 1984). Combining these estimates for the entropy contributions due to dis-

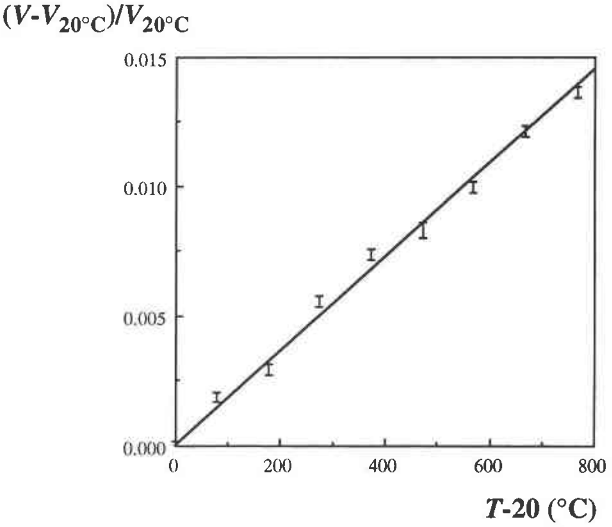

Fig. 3. Relative change in the unit-cell volume, i.e., $(V - V_{20\,°C})/V_{20\,°C}$ of the synthetic meionite used in the experimental reversals of Reactions 1 and 2 with changing temperature ($T - 20$). The best-fit line shown has slope $\alpha = 1.8164 \pm 0.0148 \times 10^{-5}$ K^{-1}.

TABLE 5. Thermodynamic properties* of meionite derived from the experimental reversals of Reactions 1 and 2

	$\Delta H^0_{f1,298}$	$S_{1,298}$ ($\times 10^{-3}$)	$V_{1,298}$	αV ($\times 10^{-5}$)	βV ($\times 10^{-3}$)	a	b ($\times 10^{-5}$)	c	d
Calcite**	−1207.77	91.7	3.689	9.0	5.3	0.1847	−0.1226	513.9	−1.8486
Anorthite**	−4232.74	199.3	10.079	14.3	13.0	0.3914	1.2556	−3036.2	−2.5832
Grossular**	−6638.30	256.0	12.535	30.0	7.9	0.7286	−4.0986	−3128.0	−6.0774
Kyanite**	−2595.33	82.3	4.414	11.2	1.9	0.3039	−1.3390	−895.2	−2.9040
Quartz**	−910.80	41.5	2.269	8.0	5.9	0.0979	−0.3350	−636.2	−0.7740
Meionite	−13825.85 ± 0.59	761.0	33.985	61.7	38.0†	1.3590‡	3.6442‡	−8594.7‡	−9.5982‡

* All data are in units of kilojoules, kilobars, and kelvins and the heat-capacity polynomial is of the form $C_P = a + bT + c/T^2 + d/\sqrt{T}$.

** Thermodynamic data for calcite, anorthite, grossular, kyanite, and quartz from Holland and Powell (1990).

† Compressibility data for meionite from Hazen and Sharp (1988).

‡ It is assumed that the high-temperature heat capacity of meionite is equal to the sum of those of 3 anorthite + calcite.

ordering with an estimate for $S_{1,298}$ for meionite showing complete Al/Si and CO_3-group ordering [$S_{me} = 3S_{an} + S_{cc} = 0.690$ kJ/K·mol)] gives a value of 0.7765 kJ/(K·mol) for $S_{1,298}$ for completely disordered meionite. That implies that the meionite generated in these experiments shows a considerable degree of both Al/Si and CO_3 rotational disorder.

Comparison with previous experiments

The new set of experimental reversals of Reaction 1 does not agree with the reversals of Huckenholz and Seiberl (1988, 1989), although the meionite and anorthite used in these experiments was synthesized under conditions similar to those used in their studies (Huckenholz, personal communication) and the fluid compositions used were, for the most part, the same as theirs. However, the new set of experimental reversals and the *P-T* position of the reaction derived from them is in agreement with all the experimental reversals of Goldsmith and Newton (1977) (Fig. 1), despite the fact that the anorthite and meionite used in their experiments was synthesized at significantly higher temperatures than those of the present study, and the composition of the coexisting fluid phase in their experiments varied from $X_{CO_2} = 0.5–1.0$. This suggests that the temperature difference between the experimental reversals of Huckenholz and Seiberl (1988, 1989) and those of this study or of Goldsmith and Newton (1977) cannot easily be explained by invoking differences in the ordering state of the scapolite or anorthite used in the experiments, nor by invoking differences in the composition of the coexisting fluid phase.

ACKNOWLEDGMENTS

We thank T. Abrahams and A. Graeme-Barber for help in making the thermal expansion measurements, E.K.H. Salje for the use of the X-ray heating stage, H.H. Huckenholz for providing much unpublished experimental data on scapolite, and T.J.B. Holland, for helping to derive the best-fit data for meionite. J.J. Pluth is also thanked for his help with some preliminary high-temperature X-ray diffraction measurements on meionite. This research was supported by a National Science Foundation grant, EAR-9015581 (R.C.N.). Department of Earth Sciences Publication no. 3355.

REFERENCES CITED

Aitken, B.G., Evans, H.T., and Konnert, J.A. (1984) The crystal structure of a synthetic meionite. Neues Jahrbuch für Mineralogie Abhandlungen, 149, 309–324.

Bobrievich, A.P., and Sobolev, V.S. (1957) Eclogitization of the pyroxene crystalline schists of the Archean complex. Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva, 86, 3–17.

Bradshaw, J.Y. (1989) Early Cretaceous vein-related garnet granulite in Fiordland, Southwest New Zealand: A case for infiltration of mantle-derived CO_2-rich fluids. Journal of Geology, 97, 697–718.

Coolen, J.J.M.M.M. (1982) Carbonic fluid inclusions in granulites from Tanzania: A comparison of geobarometric methods based on fluid density and mineral chemistry. Chemical Geology, 37, 59–77.

Dawson, J.B. (1971) Advances in kimberlite geology. Earth Science Reviews, 7, 187–214.

Edwards, A.B., and Baker, G. (1953) Scapolitization in the Cloncurry District of north-western Queensland. Journal of the Geological Society of Australia, 1, 1–33.

Ellis, D.E. (1978) Stability and phase equilibria of chloride- and carbonate-bearing scapolites at 750°C and 4000 bar. Geochimica et Cosmochimica Acta, 42, 1271–1281.

Evans, B.W., Shaw, D.M., and Houghton, D.R. (1969) Scapolite stoichiometry. Contributions to Mineralogy and Petrology, 24, 193–305.

Goff, F., Arney, B.H., and Eddy, A.C. (1982) Scapolite phenocrysts in a latite dome, northwest Arizona, U.S.A. Earth and Planetary Science Letters, 60, 86–92.

Goldsmith, J.R., and Newton, R.C. (1977) Scapolite-plagioclase stability relations at high pressures and temperatures in the system $NaAlSi_3O_8$-$CaAl_2Si_2O_8$-$CaCO_3$-$CaSO_4$. American Mineralogist, 62, 1063–1081.

Graziani, G., and Lucchesi, S. (1982) The thermal behavior of scapolites. American Mineralogist, 67, 1229–1241.

Hazen, R.M., and Sharp, Z.D. (1988) Compressibility of sodalite and scapolite. American Mineralogist, 73, 1120–1122.

Holland, T.J.B., and Powell, R. (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations: The system K_2O-Na_2O-CaO-MgO-MnO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2-C-H_2-O_2. Journal of Metamorphic Geology, 8, 89–124.

Holloway, J.R. (1971) Internally heated pressure vessels. In G.C. Ulmer, Ed., Research techniques for high pressure and high temperature, p. 217–258. Springer-Verlag, New York.

Huckenholz, H.G., and Seiberl, W. (1988) Stability of meionite ($Ca_4Al_6Si_6O_{24}CO_3$) in the presence of a (H_2O-CO_2) fluid. Terra Cognita, 8, 66.

——— (1989) Occurrence of carbonate scapolites and their bearing on geothermometry of rocks of (high-temperature) granulite facies. Abstracts of the 28th International Geological Congress, 2, 79–80.

Kerrick, D.M., Crawford, K.E., and Randazzo, A.F. (1973) Metamorphism of calcareous rocks in three roof pendants in the Sierra Nevadas, California. Journal of Petrology, 14, 303–325.

Larsen, J.G. (1981) Medium pressure crystallization of a monchiquitic magma: Evidence from megacrysts of Drever's block, Ubekendt Ejland, West Greenland. Lithos, 14, 241–262.

Lovering, J.F., and White, A.J.R. (1969) Granulitic and eclogitic inclusions from basic pipes at Delegate, Australia. Contributions to Mineralogy and Petrology, 21, 9–52.

Moecher, D.P., and Essene, E.J. (1990) Phase equilibria for calcic scapolite and implications for variable Al-Si disorder for *P-T*, *T*-X_{CO_2} and *a-X* relations. Journal of Petrology, 31, 997–1024.

——— (1991) Calculation of CO_2 activity using scapolite equilibria: Constraints on the presence and composition of a fluid phase during high grade metamorphism. Contributions to Mineralogy and Petrology, 108, 219–240.

Newton, R.C., and Goldsmith, J.R. (1975) Stability of the scapolite meionite ($3CaAl_2Si_2O_8 \cdot CaCO_3$) at high pressure and storage of CO_2 in the deep crust. Contributions to Mineralogy and Petrology, 49, 49–62.

——— (1976) Stability of the end-member scapolites: $3NaAlSi_3O_8 \cdot NaCl$, $3CaAl_2Si_2O_8 \cdot CaCO_3$, $3CaAl_2Si_2O_8 \cdot CaSO_4$. Zeitschrift für Kristallographie, 43, 333–353.

Orville, P.H. (1975) Stability of scapolite in the system Ab-An-NaCl-$CaCO_3$ at 4 kb and 50°C. Geochimica et Cosmochimica Acta, 39, 1091–1105.

Richardson, S.W., Gilbert, M.C., and Bell, P.M. (1969) Experimental determination of kyanite-andalusite and andalusite-sillimanite equilibria: The aluminum silicate triple point. American Journal of Science, 267, 259–272.

Salje, E.K.H., Graeme-Barber, A., Carpenter, M.A., and Bismayer, U. (1993) Lattice parameter, spontaneous strain and phase transitions in $Pb_3(PO_4)_2$. Acta Crystallographica, B49, 387–392.

Shaw, D.M. (1960) The geochemistry of scapolite. I. Previous work and general mineralogy. Journal of Petrology, 1, 218–260.

Manuscript received May 3, 1993
Manuscript accepted January 5, 1994