

Synthesis and upper thermal stability limit of 2M-Margarite, $\text{CaAl}_2 [\text{Al}_2\text{Si}_2\text{O}_{10}/(\text{OH})_2]$

Autor(en): **Chatterjee, Niranjana D.**

Objektyp: **Article**

Zeitschrift: **Schweizerische mineralogische und petrographische Mitteilungen
= Bulletin suisse de minéralogie et pétrographie**

Band (Jahr): **54 (1974)**

Heft 2-3: **Alpidische Metamorphosen in den Alpen**

PDF erstellt am: **21.07.2024**

Persistenter Link: <https://doi.org/10.5169/seals-42218>

Nutzungsbedingungen

Die ETH-Bibliothek ist Anbieterin der digitalisierten Zeitschriften. Sie besitzt keine Urheberrechte an den Inhalten der Zeitschriften. Die Rechte liegen in der Regel bei den Herausgebern. Die auf der Plattform e-periodica veröffentlichten Dokumente stehen für nicht-kommerzielle Zwecke in Lehre und Forschung sowie für die private Nutzung frei zur Verfügung. Einzelne Dateien oder Ausdrucke aus diesem Angebot können zusammen mit diesen Nutzungsbedingungen und den korrekten Herkunftsbezeichnungen weitergegeben werden. Das Veröffentlichen von Bildern in Print- und Online-Publikationen ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Die systematische Speicherung von Teilen des elektronischen Angebots auf anderen Servern bedarf ebenfalls des schriftlichen Einverständnisses der Rechteinhaber.

Haftungsausschluss

Alle Angaben erfolgen ohne Gewähr für Vollständigkeit oder Richtigkeit. Es wird keine Haftung übernommen für Schäden durch die Verwendung von Informationen aus diesem Online-Angebot oder durch das Fehlen von Informationen. Dies gilt auch für Inhalte Dritter, die über dieses Angebot zugänglich sind.

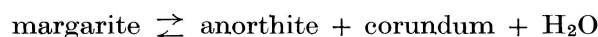
Synthesis and Upper Thermal Stability Limit of 2M-Margarite, $\text{CaAl}_2[\text{Al}_2\text{Si}_2\text{O}_{10}/(\text{OH})_2]$

By *Niranjan D. Chatterjee* (Bochum)*)

With 4 Figures and 5 Tables in the text

Abstract

The univariant $P_{\text{H}_2\text{O}}$ -T curve pertaining to the reaction



has been experimentally determined by the method of reaction reversal, starting with a mixture of synthetically prepared pure phases. The equilibrium constant of the reaction may be expressed as $\log K = \log f_{\text{T, H}_2\text{O}}^P = 8.8978 - 4758/T + 0.0171(P - 1)/T$, P in bars and T in °K.

On the basis of tabulated thermodynamic data of anorthite, corundum and H_2O (ROBIE and WALDBAUM, 1968; BURNHAM et al., 1969), standard thermodynamic parameters of margarite are found to be:

$$\begin{aligned} S_{298.15}^0 &= 63.1 \pm 2.6 \text{ cal deg-gfw}^{-1}, \\ H_{f, 298.15}^0 &= -1490.1 \pm 2.2 \text{ kcal gfw}^{-1}, \\ G_{f, 298.15}^0 &= -1398.3 \pm 3.0 \text{ kcal gfw}^{-1}, \\ V_{298.15}^0 &= 3.0984 \pm 0.0012 \text{ cal bar-gfw}^{-1}. \end{aligned}$$

However, these data will require some modification in future, since the tabulated data for anorthite may not be correct (THOMPSON, 1974). To facilitate recalculation of the thermodynamic data of margarite owing to such change in the suggested thermo-chemical parameters of anorthite and/or corundum, appropriate Gibbs free energy difference functions are given.

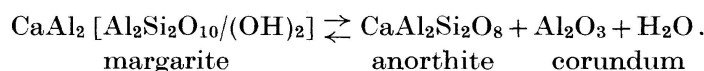
Of the three most important dioctahedral mica endmembers muscovite, paragonite and margarite, the last-named has the lowest thermal stability. This accords well with available petrographic data.

*) Institute of Mineralogy, Ruhr University, D 4630 Bochum, Federal Republic of Germany.

INTRODUCTION

Margarite, $\text{CaAl}_2[\text{Al}_2\text{Si}_2\text{O}_{10}/(\text{OH})_2]$, is commonly regarded as a comparatively rare variety of dioctahedral mica. During the last ten years, however, it has been recognized as a fairly common phase in low- to medium-grade metamorphic rocks of various localities (SAGON, 1967, 1970; JONES, 1971; FREY and NIGGLI, 1972; HÖCK, 1972; FREY and ORVILLE, 1974 and others). Although mineral paragenetic data of margarite-bearing rocks are now available in fair amount (e.g. FREY and NIGGLI, 1972; HÖCK, 1972; FREY and ORVILLE, 1974), data bearing on the chemical composition of margarite in these rocks is still very rare. It seems certain, however, that margarite in these rocks form crystalline solutions with paragonite component (cf. JONES, 1971; ACKERMAN and MORTEANI, 1973), although more complex solution involving ephesite may also be fairly widespread (SCHALLER et al., 1967).

Stability relations of paragonite being fairly well established now (CHATTERJEE, 1970, 1972, 1973a), it seems necessary to study the stability and phase relations of margarite. The present paper deals with the upper thermal stability limit of synthetic 2M-margarite endmember, $\text{CaAl}_2[\text{Al}_2\text{Si}_2\text{O}_{10}/(\text{OH})_2]$. In the system $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$, the thermal stability of margarite is marked by the reaction



From the experimentally determined $P_{\text{H}_2\text{O}}\text{-T}$ data on this univariant four-phase curve, thermodynamic data for margarite have been extracted. Elucidation of common margarite-bearing assemblages with the help of compatibility relations of margarite, presented orally so far (CHATTERJEE, 1973b), will be the subject matter of a forthcoming paper, now in preparation.

PREVIOUS WORK

Early attempts to synthesize margarite include the works of EUGSTER and YODER (1954) and TU (1956). Both prepared margarite, but failed to establish its thermal stability limit due to extremely slow reaction rates. Since that time, VELDE (1971) has synthesized margarite and studied its upper thermal stability limit. Another pertinent work is that by STORRE and NITSCH (1973), who studied the stability relations of the assemblage quartz + margarite, using a natural margarite crystalline solution from Chester, Mass.

Preliminary results of the present work (CHATTERJEE, 1971) included three $P_{\text{H}_2\text{O}}\text{-T}$ reversal brackets of the reaction margarite \rightleftharpoons anorthite + corundum

+ H₂O and unit cell data of synthetic margarite. Since then, better quality margarite could be synthesized; the data presented in this paper will supersede those given earlier.

EXPERIMENTAL METHODS

High Pressure Apparatus

Standard, cold seal, hydrothermal apparatus was used in this study. Approximately 20 mg of starting material along with ~5 mg deionize water was welded shut in thin-walled gold capsules, so that free water vapour was always present during the runs. The uncertainty of temperature measurement is believed to be $\pm 5^\circ\text{C}$, that of pressure measurement ± 100 bars. For further detail, the reader is referred to CHATTERJEE (1970, 1972).

In addition to this, solid-media piston-cylinder apparatus (BOYD and ENGLAND, 1960) was also used for some of the synthesis runs.

Starting Materials

Margarite was prepared on its own composition from a mixture of certified reagent-grade precipitated CaCO₃, synthetically prepared γ -Al₂O₃, SiO₂ and excess H₂O. The product of the first run usually contained fairly well crystallized margarite with some calcite left over. On recycling, the calcite vanished quantitatively and excellently crystallized margarite was obtained.

Nevertheless, synthesis runs on piston-cylinder apparatus did produce single-phase margarite in only one cycle. This is apparently due to (preferential?) loss of CO₂ through the lid of the capsule and consequent decrease of activity of CO₂ in the charge.

The synthetically prepared starting materials included 2M-margarite, anorthite and corundum, which will be briefly characterized in the next section.

Composition Studied

The upper thermal stability limit of margarite is given by the reaction margarite \rightleftharpoons anorthite + corundum + H₂O. To locate the P_{H₂O}-T univariant curve of this reaction, hydrothermal runs were conducted with mixtures of synthetically prepared margarite, synthetic anorthite and synthetic corundum. Two batches of condensed starting materials were synthesized on margarite composition (CaO 2Al₂O₃ : 2SiO₂ + excess H₂O): 1. a 2M-margarite and 2. a mixture of anorthite and corundum. The final mix contained 20% margarite and 80% anorthite + corundum, i.e. both the reactant and the products of the reaction to be studied. By noting the relative increase in the quantities of the products or the reactant, it was always possible to detect the direction of the reaction in a run.

Phase Identification

All run products were routinely investigated under polarizing microscope, followed by X-ray diffraction scanning. Due to the fine-grained nature of the run products, the X-ray diffraction method proved to be more reliable for detecting direction of the reaction.

The cell dimensions of the synthetic materials were obtained from X-ray diffractometer scans, using KI ($a = 7.06516 \pm 0.00010 \text{ \AA}$) as internal standard for margarite and BaF_2 ($a = 6.1971 \pm 0.0002 \text{ \AA}$) as internal standard for anorthite. Both these standards were calibrated beforehand against gem diamond. The techniques of measurement, indexing and data processing have been described in detail elsewhere (CHATTERJEE, 1974).

EXPERIMENTAL RESULTS

Phases Synthesized

Margarite: The synthetically prepared margarite crystallized as very fine-grained flaky material. When viewed with scanning electron microscope, they were found to be euhedral to subhedral platelets, up to 2 microns in size.

The X-ray diffraction pattern compares excellently with that of a natural 2M-margarite of near-endmember composition (Fig. 1). Indexed powder X-ray diffraction pattern has been reproduced in Table 1. A close sympathetic variation between observed and calculated intensities (after BORG and SMITH,

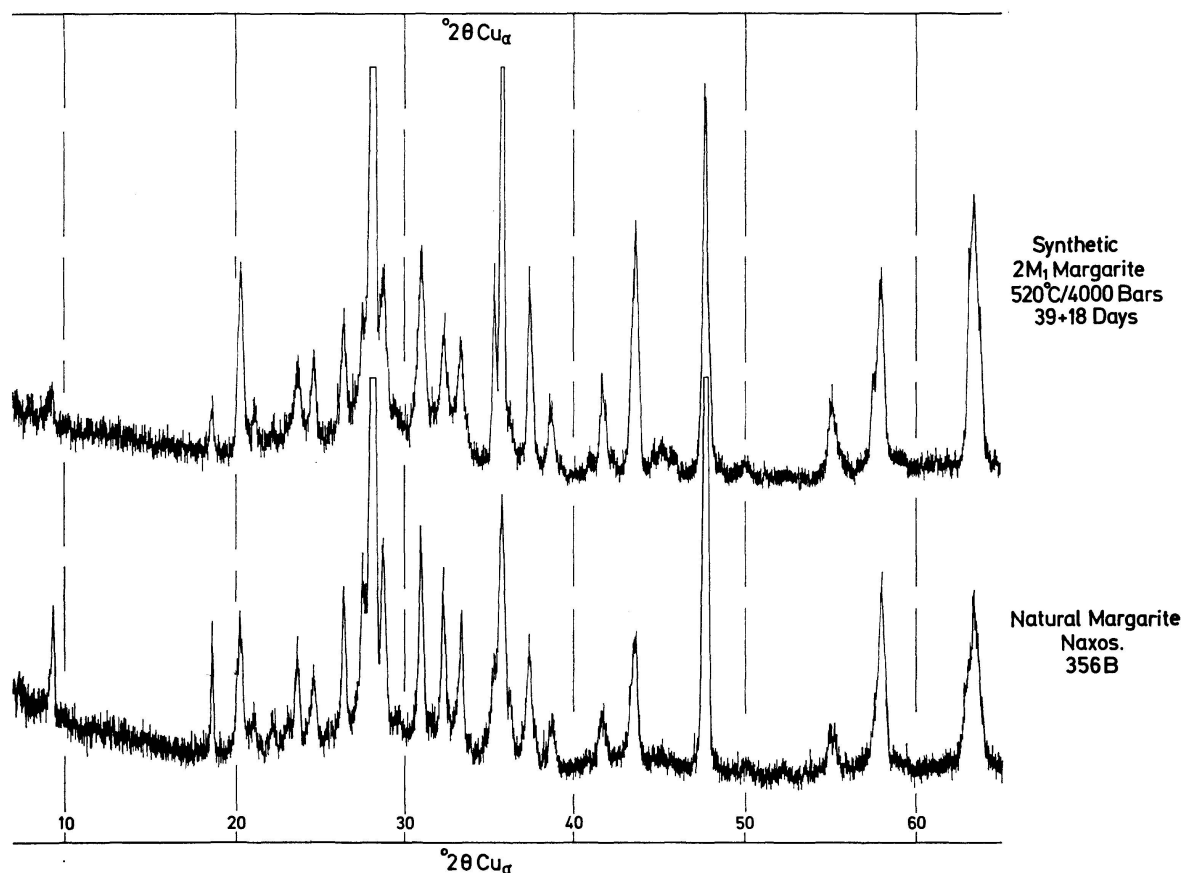


Fig. 1. X-ray diffraction patterns of synthetic and natural 2 M-margarite of near-endmember composition. Stronger non-basal reflections of the synthetic margarite is due to finer grains size (up to 2 microns), as compared to that of natural margarite.

Table 1. Powder X-ray diffraction data for synthetic 2M-margarite prepared at 520°C/4 kb P_{H_2O} /39 + 18 days

h	k	l	$d_{calc.}$ (Å)	$d_{obs.}$ (Å)	I/I ₀ calc. BORG and SMITH (1969)	I/I ₀ obs.
0	0	2	9.539	9.563	8	4
0	0	4	4.769	4.771	1	4
1	1	0	4.406	4.403	19	13
-1	1	1	4.373	4.377	52	15
1	1	1	4.217	4.217	19	4
0	2	2	4.009	4.009	14	3
-1	1	3	3.771	3.774	30	8
0	2	3	3.629	3.629	26	9
-1	1	4	3.379	3.383	35	12
0	2	4	3.241	3.239	38	12
0	0	6	3.180	3.181	52	100
1	1	4	3.110	3.110	42	15
0	2	5	2.888	2.889	40	17
1	1	5	2.773	2.773	27	10
-1	1	6	2.686	2.687	25	10
-1	3	1	2.542	2.542	24	13
1	3	1	2.510	2.511	100	41
2	0	2	2.399	2.401	25	15
1	3	3	2.327	2.328	10	5
-2	2	1	2.209	2.208	2	1
-1	3	5	2.168	2.168	16	7
2	0	4	2.159	2.160	8	6
-2	0	6	2.085	2.085	21	13
1	3	5	2.074	2.075	35	18
0	4	4	2.005	2.005	9	2
-2	2	5	1.9804	1.9815	6	2
0	0	10	1.9077	1.9072	18	30
-1	3	9	1.6696	1.6687	9	6
2	0	8	1.6613	1.6610	6	5
-2	0	10	1.6011	1.6009	11	10
1	3	9	1.5925	1.5922	23	16
-3	3	1)	1.4737}	1.4730}	41	18
0	6	0)	1.4729}	1.4730}		
-1	3	11	1.4670	1.4675	29	21
2	0	10	1.4600	1.4601	14	11

Space group: C 2/c or Cc.

$$a_0 = 5.1061 \pm 0.0010 \text{ \AA}, \quad b_0 = 8.8373 \pm 0.0015 \text{ \AA}, \quad c_0 = 19.1655 \pm 0.0031 \text{ \AA}, \\ \beta = 95^\circ 30.00' \pm 0.79', \quad V_0 = 860.85 \pm 0.18 \text{ \AA}^3.$$

Refinement on the basis of 34 observed diffraction lines. Standard error unit weight observed: $0.018^\circ 2\theta$.

1969) of the margarite diffraction lines is evident. The unit cell dimensions were refined by the method of least squares, using a computer program devised by EVANS et al. (1963).

The unit cell dimensions of two synthetic and two natural margarites are given in Table 2. For the sake of comparison, unit cell data of a natural ephesite of near-endmember composition (SCHALLER et al., 1967) and those of a synthetic 2M-paragonite (CHATTERJEE, 1974) are also reproduced. While the cell sizes of natural margarite from Naxos (NAX 356 B) are virtually identical

Table 2. Refined unit cell dimensions of synthetic and natural margarites and other related micas. Space group: $C2/c$ (or Cc)

Material	a (Å)	b (Å)	c (Å)	β	V (Å ³)	Lines ¹⁾	SEUW ²⁾	Remarks
Synth. Margarite (Ma 1)	5.1061 (0.0010) ³⁾	8.8373 (0.0015)	19.1655 (0.0031)	95° 30.00' (0.79')	860.85 (0.18)	34	0.018	Prepared at 520° C/ 4 kb P _{H₂O} /39 + 18 days
Synth. Margarite (Ma 2)	5.1116 (0.0014)	8.8362 (0.0017)	19.1545 (0.0036)	95° 29.73' (0.87')	861.18 (0.23)	30	0.020	Synthesized at 620° C/ 11 kb P _{H₂O} /11 days
Nat. Margarite Naxos, Greece (NAX 356B)	5.1110 (0.0017)	8.8410 (0.0024)	19.1493 (0.0045)	95° 31.60' (1.31')	861.27 (0.30)	29	0.026	Contain > 95 mole % margarite endmember (CHATTERJEE et al., 1974)
Nat. Margarite Chester, Mass. (Chatt. 1)	5.1219 (0.0024)	8.8603 (0.0033)	19.1607 (0.0067)	95° 20.73' (2.36')	865.75 (0.42)	27	0.034	Chemically inhomogeneous mixed crystal of margarite, paragonite and ephesite (De- tails in CHATTERJEE et al., 1974)
Synth. Paragonite	5.1304 (0.0010)	8.8927 (0.0015)	19.2698 (0.0028)	94° 13.21' (0.98')	876.77 (0.19)	39	0.018	(CHATTERJEE, 1974)
Nat. Ephesite South Africa	5.120	8.853	19.303	95° 5'	871.5			Near-endmember composi- tion. Single crystal data of M. Ross in SCHALLER et al. (1967)

¹⁾ Number of lines used in cell dimension refinements.

²⁾ Standard error unit weight observed, in degrees 2θ .

³⁾ Uncertainty quoted is standard error.

Table 3. *Hydrothermal run data bearing on the upper thermal stability limit of margarite*

Run No.	P _{H₂O} (kb)	Temperature (°C)	Run duration (days)	Condensed phases of run products
All runs conducted on CaO : 2 Al ₂ O ₃ : 2 SiO ₂ composition with excess water with a mix composed of 20% synth. margarite and 80% anorthite + corundum				
56	1	500	181	Trace Ma left, An+C increased ¹⁾
59	1	490	182	No reaction detected
50	1	480	187	No reaction detected
58	1	470	182	Ma increased, An+C decreased
Reaction interval at 1 kb: 470°–500°C				
35	2	550	89	No Ma, all An+C
42	2	530	115	Ma decreased, An+C increased
51	2	520	137	Ma decreased, An+C increased
49	2	510	145	No reaction detected
57	2	500	142	Ma increased, An+C decreased
43	2	490	103	Ma increased, An+C decreased
Reaction interval at 2 kb: 500°–520°C				
39	4	600	70	No Ma, all An+C
34	4	580	81	No Ma, all An+C
54	4	570	103	No Ma, all An+C
36	4	560	95	Ma increased, An+C less
55	4	540	89	Ma increased, An+C decreased
Reaction interval at 4 kb: 560°–570°C				
31	6	640	52	No Ma, An+C only
32	6	620	58	No Ma, all An+C
52	6	610	89	No Ma, all An+C
38	6	600	62	Ma increased, An+C less
41	6	580	59	Ma only
Reaction interval at 6 kb: 600°–610°C				
45	7	660	59	No Ma, only An+C
53	7	650	79	No Ma, only An+C
47	7	640	80	No Ma, all An+C
48	7	630	80	No reaction detected
44	7	620	61	Ma increased, less An+C

¹⁾ Abbreviations used are: Ma: margarite, An: anorthite and C: corundum.

to those of synthetic margarite, the Chester material has a significantly larger cell size, suggesting solid solubility with substantial amounts of paragonite and/or ephesite endmembers. This is corroborated by chemical data (see SCHALLER et al., 1967; and in particular, CHATTERJEE et al., 1974).

Anorthite: The synthetic anorthite, prepared at 700°C/1 kb P_{H₂O}/2 days, showed a powder pattern, which could be indexed on the basis of space group P $\bar{1}$. The cell dimension refinement, based on 41 diffraction lines, gave: $a = 8.1796 \pm 0.0019$ Å, $b = 12.8736 \pm 0.0022$ Å, $c = 14.1720 \pm 0.0025$ Å, $\alpha = 93^\circ 7.09' \pm 1.05'$, $\beta = 115^\circ 52.48' \pm 1.09'$, $\gamma = 91^\circ 14.71' \pm 0.99'$ and $V =$

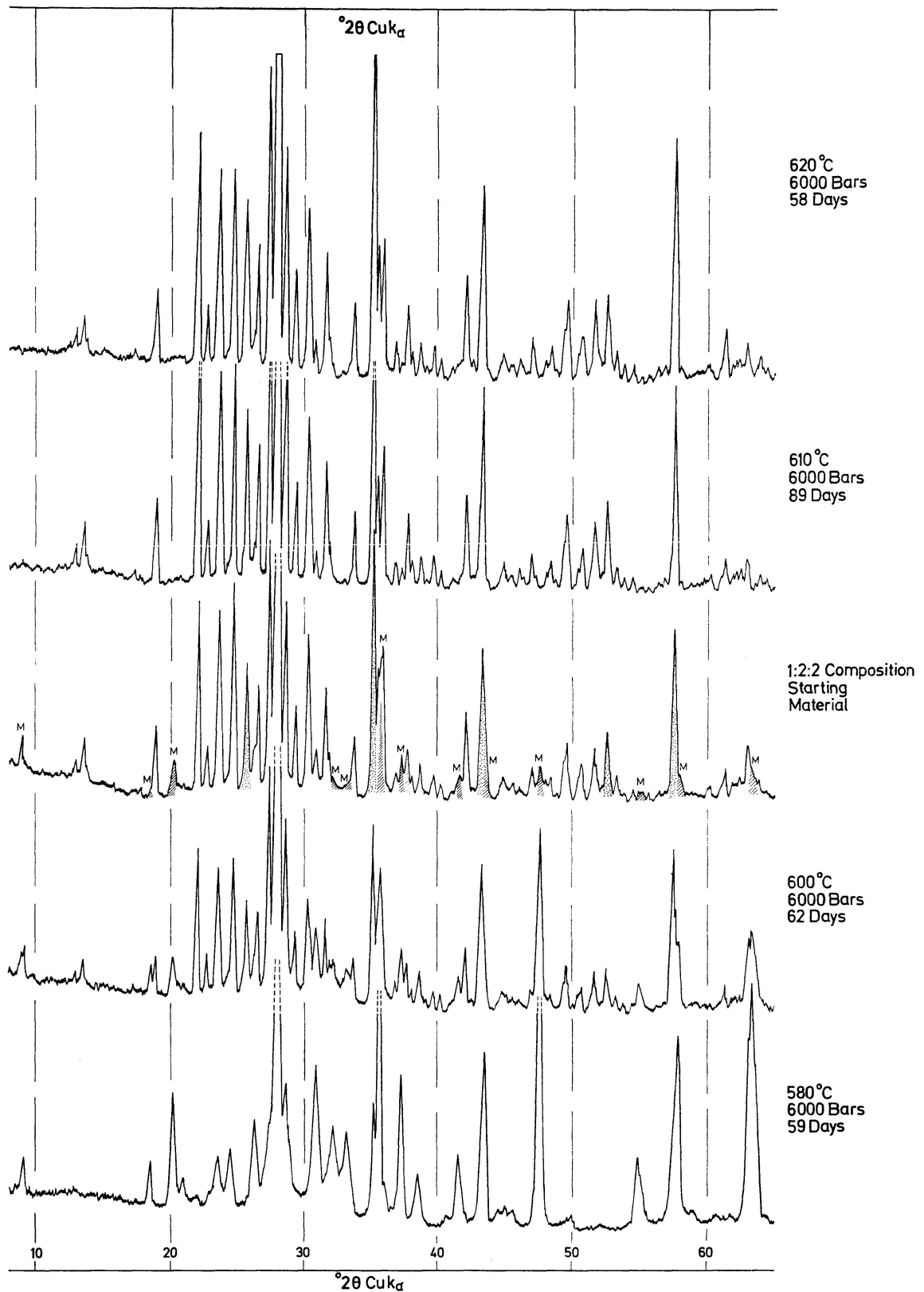


Fig. 2. X-ray diffractograms of condensed $\text{CaO} : 2\text{Al}_2\text{O}_3 : 2\text{SiO}_2$ starting material and run products at 6 kb $P_{\text{H}_2\text{O}}$. The run at 610°C shows complete decomposition of margarite, while that at 600°C a clear growth of the same phase. Note that the interpretation is based on *all* non-interfering margarite reflections. In the X-ray diffractogram of the starting material those margarite peaks (M) were hatched, which could be used in the interpretation of the direction of the reaction. The corundum peaks are stippled.

$1339.0 \pm 0.3 \text{ \AA}^3$. Standard error unit weight observed was $0.012^\circ 2\theta$. These data agree very well with those published for synthetic anorthite by STEWART (1967).

The Reaction: Margarite \rightleftharpoons Anorthite + Corundum + H₂O

The run data bearing on the reversal of this reaction on a condensed CaO: 2Al₂O₃: 2SiO₂ mix, containing both the reactant and the products, are presented in Table 3. Extremely long runs (up to 187 days at 1 kb P_{H₂O}) were necessary for demonstrating reversal of reaction. In all, five reversal brackets could be obtained between 1 and 7 kb P_{H₂O}, including two $\pm 5^\circ \text{C}$ brackets. Fig. 2 shows a series of X-ray diffractograms of run products at 6 kb P_{H₂O}, as an example of interpretation of direction of reaction (cf. Table 3).

The run data have been reproduced on a $\log f_{\text{T,H}_2\text{O}}^{\text{P}}$ vs $1/T^\circ \text{K}$ plot (Fig. 3). The brackets shown in thinner lines are those representing $\log f_{\text{T,H}_2\text{O}}^0$, i.e. after deducting the contribution of the volume change of the solids, ΔV_s , on the Gibbs free energy of the reaction. The thin straight line is a linear regression

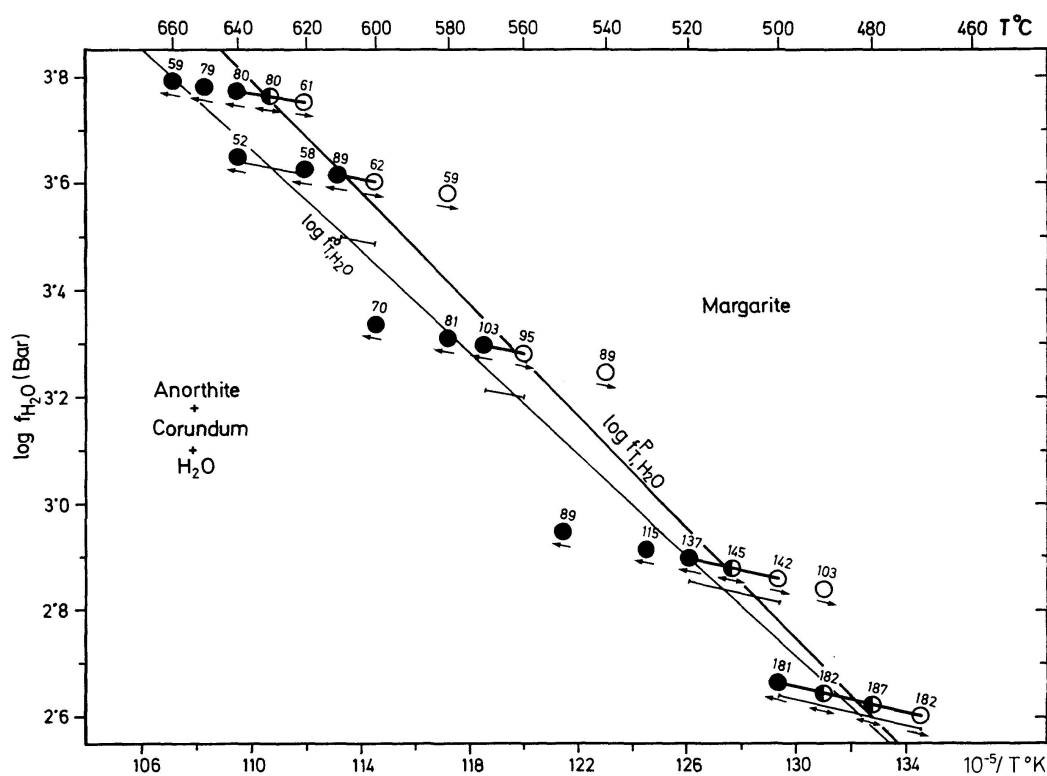


Fig. 3. A $\log f_{\text{H}_2\text{O}}$ vs $1/T^\circ \text{K}$ plot of the univariant margarite-corundum-anorthite-H₂O equilibrium. Filled circles: growth of anorthite + corundum; half-filled circles: no reaction; and open circles: growth of margarite. The arrows also show the direction of the reaction. The figures at the top of each data point represent run durations in days.

Thicker brackets and linear regression fit are for the $\log f_{\text{T,H}_2\text{O}}^{\text{P}}$ vs $1/T^\circ \text{K}$ data; the thinner ones for the $\log f_{\text{T,H}_2\text{O}}^0$ vs $1/T^\circ \text{K}$ set.

fit to the $\log f_{T, H_2O}^0$ vs $1/T^\circ K$ data, which justifies the assumptions (made in the next section) that the heat capacity of the reaction, $\Delta C_{p,r}$, is independent of T at least within the experimentally investigated range.

The P_{H_2O} - T brackets reported here compare favourably with VELDE's (1971) bracket for the same reaction at 2 kb P_{H_2O} , however, the agreement with his 1 kb P_{H_2O} bracket is unsatisfactory.

CALCULATION OF THERMOCHEMICAL PARAMETERS OF MARGARITE

Thermodynamic Data of Margarite

The univariant four-phase equilibrium curve experimentally determined in this study include only one phase, namely margarite, whose thermodynamic data are not yet available from direct calorimetric measurements. Therefore, the experimental P_{H_2O} - T data will be used now to extract thermodynamic data of margarite.

The basic principle underlying these calculations and the method of data reduction has been outlined before (CHATTERJEE, 1970). The format of calculation used tacitly assumes that:

1. All phases involved in the reaction are pure phases of unit activity. This certainly holds true for the solids and possibly also approximately for the vapour present during the runs described above.
2. The volume difference of solids, ΔV_s^0 , is independent of pressure P , so that the $\int_1^P \Delta V_s dP$ term may be set equal to $\Delta V_s^0(P-1)$. This assumption is also tenable (as discussed by FISHER and ZEN, 1971, p. 299) in this case, especially because the ΔV_s term contributes very little to the Gibbs free energy within the range of pressure considered here.
3. $\Delta C_{p,r}$ of the reaction is independent of temperature, T . This has already been demonstrated in the last section on the basis of $\log f_{T, H_2O}^0$ vs $1/T^\circ K$ plot (Fig. 3).

The standard molar entropy S_{298}^0 , the standard molar enthalpy of formation from the elements $H_{f,298}^0$, and the standard molar Gibbs free energy of formation from the elements $G_{f,298}^0$ were calculated for margarite as follows:

$$\begin{aligned} S_{298}^0 &= 63.1 \pm 2.6 \text{ cal deg-gfw}^{-1}, \\ H_{f,298}^0 &= -1490.1 \pm 2.2 \text{ kcal gfw}^{-1}, \\ G_{f,298}^0 &= -1398.3 \pm 3.0 \text{ kcal gfw}^{-1}. \end{aligned}$$

The uncertainties given are two standard errors.

Gibbs Free Energy Difference Functions

It should be noted that the thermodynamic data given above will hold true only if the tabulated data for anorthite, corundum and water are correct. Unfortunately, this does not seem to be so at present. One reason for this is that the reference state for Al in the calorimetric data differ for anorthite and for corundum. Thus, the anorthite data are related to gibbsite (BARANY, 1962, p. 13), which in its turn is tied to $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (BARANY and KELLEY, 1961, p. 4). The latter shows a significant deviation from the corundum state. As such, adjustment of the anorthite data with respect to corundum is necessary (THOMPSON, 1973b). Therefore, the margarite data presented above will also have to be adjusted accordingly. To facilitate such data adjustment, Gibbs free energy difference functions, as suggested by D. R. WALDBAUM and extensively used by THOMPSON (1973a, 1973b), are given below. These were computed from basic thermochemical data of solids reproduced in Table 4 and thermodynamic data of water (BURNHAM et al., 1969) as recast by FISHER and ZEN (1971, Table 1).

Table 4. Basic thermodynamic data of the solid phases, used in computing the Gibbs free energy difference functions X and Y

Phases	S_{298}^0 (cal deg-gfw ⁻¹)	$S_{f,298}^0$ (cal deg-gfw ⁻¹)	$H_{f,298}^0$ (cal gfw ⁻¹)	$G_{f,298}^0$ (cal gfw ⁻¹)	V_{298}^0 (cal bar-gfw ⁻¹)	Source
Margarite	63.11 (2.61) ²⁾	-308.105 (2.61)	-1490136 ¹⁾ (2170)	-1398274 ¹⁾ (2990)	3.0984 ³⁾ (0.0012)	This study
Anorthite	48.45 (0.30)	-180.024 (0.30)	-1009300 (1150)	- 955626 (1160)	2.4089 (0.0012)	ROBIE and WALDBAUM, 1968
Corundum	12.18 (0.03)	-74.854 (0.03)	- 400400 (300)	- 378082 (310)	0.61126 (0.00017)	ROBIE and WALDBAUM, 1968

¹⁾ In order to retain internal consistency, the data have *not* been rounded off on the basis of uncertainty.

²⁾ The uncertainty quoted correspond to *two* standard errors in each case.

³⁾ Averaged from the unit cell data of synthetic margarite, given in Table 2.

The thermodynamic formalism underlying the computation of Gibbs free energy difference functions has been outlined by THOMPSON (1973a, 1973b). Two different Gibbs free energy difference functions X and Y were computed (Table 5), which are defined as follows:

$$X \equiv G_{f,298,\text{An}}^0 - G_{f,298,\text{Ma}}^0 = -G_{f,298,\text{C}}^0 + \Delta S_{f,s}^0 \Delta T - \Delta V_s^0 \Delta P - G_{\text{T},\text{H}_2\text{O}}^{*\text{P}}$$

$$\text{and } Y \equiv G_{f,298,\text{An}}^0 + G_{f,298,\text{C}}^0 - G_{f,298,\text{Ma}}^0 = +\Delta S_{f,s}^0 \Delta T - \Delta V_s^0 \Delta P - G_{\text{T},\text{H}_2\text{O}}^{*\text{P}}.$$

To give an example of the use of these difference functions, we may wish to adjust the $G_{f,298}^0$ of margarite based upon values of $G_{f,298}^0$ of anorthite and corundum, as suggested by THOMPSON (1973b).

Table 5. *Gibbs free energy difference functions X and Y (defined in the text) related to the univariant margarite-anorthite-corundum-H₂O equilibria*

Equilibrium Temperature (°C)	Equilibrium H ₂ O-Pressure (bars)	G _{T, H₂O} ^{*P} (cal gfw ⁻¹) (after FISHER and ZEN, 1971, Table 1)	X (cal)	Y (cal)
485	1000	-40042	+442687	+64605
510	2000	-38543	+442596	+64514
565	4000	-35543	+442680	+64598
605	6000	-33129	+442552	+64470
630	7000	-31764	+442595	+64514
Average			+442622	+64540
			±59	±59

In order to be internally consistent with THOMPSON'S (1973b, Table 5) data set A, $G_{f,298}^0$ of margarite will have to be -1406.246 Kcal gfw⁻¹, while $G_{f,298}^0$ of margarite will be -1402.240 Kcal gfw⁻¹ to be consistent with his data set B.

It should be pointed out, however, that this method of data adjustment based upon Gibbs free energy difference functions is meaningful as long as changes only in $G_{f,298}^0$ of a solid phase is indicated. Should a different value for $S_{f,298}^0$ be found to apply than that used in the computation of the difference function, this method will become vulnerable.

CONCLUSIONS

A P_{H₂O}-T plot of the thermal stability limits of the three important dioctahedral mica endmembers muscovite (CHATTERJEE, 1973, unpublished), paragonite (CHATTERJEE, 1970) and margarite (this study) has been reproduced in Fig. 4. It is seen that muscovite has the highest and margarite the lowest thermal stability limit. In a general way, this agrees with the petrographic data available to date.

However, the thermal stability limits of the mica endmembers have only limited application to natural rocks for two reasons:

1. The micas are almost always found in natural rocks in mineral assemblages, in which they coexist with other minerals. Therefore, not the thermal stability limits but the compatibility relations of the micas would apply to natural rocks.
2. The mica endmembers usually form crystalline solutions with each other in nature. As such, compatibility relations of appropriate mica crystalline solutions will be of interest.

In a forthcoming paper, now in preparation, compatibility relations of margarite as well as their possible geologic applications will be discussed in detail.

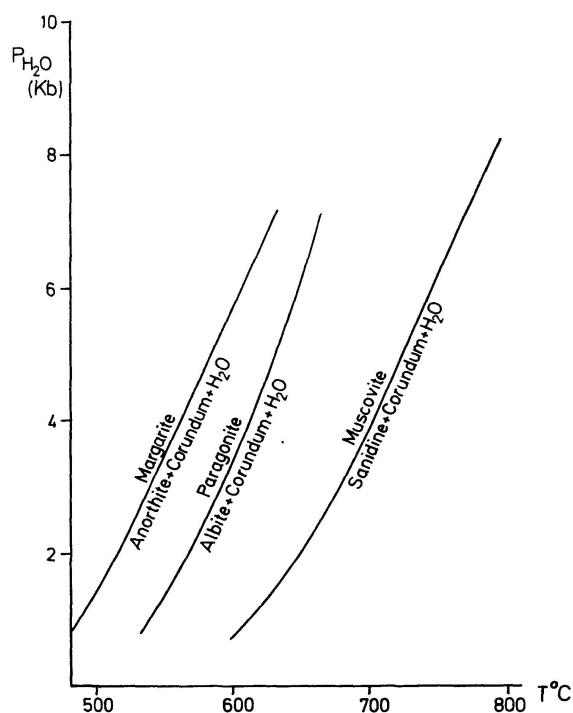


Fig. 4. Comparison of upper thermal stability limits of dioctahedral mica *endmembers* margarite (this study), paragonite (CHATTERJEE, 1970) and muscovite (CHATTERJEE, 1973, unpublished).

Acknowledgements

Experimental high pressure-high temperature set up used in this project was partially financed by grants of the Deutsche Forschungsgemeinschaft, Bad Godesberg, to W. SCHREYER. I am indebted to W. SCHREYER to make the laboratory facilities available to me. All computations were done at the Computing Center of the Ruhr University, Bochum. R. D. SCHULING kindly made available a few samples of margarite from Naxos, Greece, and D. R. WONES donated the BaF₂ internal standard for X-ray work. I would like to express my appreciations to them. A. B. THOMPSON has contributed to this study by providing a preprint of his paper (THOMPSON, 1973b). E-AN ZEN has drawn my attention to the paper by TU (1956) and has made available to me an English excerpt of the Chinese original. In addition, he as well as M. FREY has read an earlier version of the manuscript and made some valuable suggestions to improve its presentation. I extend my sincere thanks to them.

REFERENCES

- BARANY, R. (1962): Heats and free energies of formation of some hydrated and anhydrous sodium- and calcium-aluminum silicates. U.S. Bur. Mines Rept. Inv., 5900, 17 p.
- BARANY, R. and KELLEY, K. K. (1961): Heats and free energies of formation of gibbsite, kaolinite, halloysite and dickite. U.S. Bur. Mines Rept. Inv., 5825, 13 p.
- BORG, I. Y. and SMITH, D. K. (1969): Calculated X-ray powder patterns for silicate minerals. Geol. Soc. Amer., Mem., 122, 896 p.
- BOYD, F. R. and ENGLAND, J. L. (1960): Apparatus for phase equilibrium measurements at pressures up to 50 kb and temperatures up to 1750° C. *J. Geophys. Res.*, 65, 741-748.
- BURNHAM, C. W., HOLLOWAY, J. R., and DAVIS, N. F. (1969): Thermodynamic properties of water to 1000° C and 10,000 bars. Geol. Soc. Amer., Spec. Paper, 132, 96 p.

- CHATTERJEE, N. D. (1970): Synthesis and upper stability of paragonite. *Contr. Mineral. and Petrol.*, *27*, 244–257.
- (1971): Preliminary results on the synthesis and upper stability limit of margarite. *Naturwiss.*, *58*, 147.
- (1972): The upper stability limit of the assemblage paragonite + quartz and its natural occurrences. *Contr. Mineral. and Petrol.*, *34*, 288–303.
- (1973a): Low-temperature compatibility relations of the assemblage quartz-paragonite and the thermodynamic status of the phase rectorite. *Contr. Mineral. and Petrol.*, *42*, 259–271.
- (1973b): Stabilitätsbeziehungen des Margarits, $\text{CaAl}_2[\text{Al}_2\text{Si}_2\text{O}_{10}/(\text{OH})_2]$ (Abstract). *Deutsche Mineralog. Ges., Jahrestagung, Frankfurt*, 8–9.
- (1974): X-ray powder pattern and molar volume of synthetic 2M-paragonite: A refinement. *Contr. Mineral. and Petrol.*, *43*, 25–28.
- CHATTERJEE, N. D., LANGER, K., and ABRAHAM, K. (1974): Infrared studied of some synthetic and natural dioctahedral micas (in Preparation).
- EUGSTER, H. P. and YODER, H. S. (1954): Margarite. *Carnegie Inst. Washington, Year-book*, *53*, 114.
- EVANS, H. T., APPLEMAN, D. E., and HANDWERKER, D. S. (1963): The least squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing method (Abstract). *Amer. Crystallogr. Assoc., Cambridge, Mass., Annual Meeting Program*, 42–43.
- FISHER, J. R., and ZEN, E.-AN (1971): Thermochemical calculations from hydrothermal phase equilibrium data and the free energy of H_2O . *Amer. J. Sci.*, *270*, 297–314.
- FREY, M., and NIGGLI, E. (1972): Margarite, an important rock-forming mineral in regionally metamorphosed low-grade rocks. *Naturwiss.*, *59*, 214–215.
- FREY, M. and ORVILLE, P. M. (1974): Plagioclase in margarite-bearing rocks. *Amer. J. Sci.*, *274*, 31–47.
- HÖCK, V. (1972): Koexistierende Hellglimmer in Metasedimenten der Mittleren Hohen Tauern (Salzburg, Österreich) (Abstr.) *Fortschr. Min.*, *50*, Beiheft I, 39–40.
- JONES, J. W. (1971): Zoned margarite from Badshot formation (Cambrian) near Kaslo, British Columbia. *Canad. J. Earth Sci.*, *8*, 1145–1147.
- ROBIE, R. A., and WALDBAUM, D. R. (1968): Thermodynamic properties of minerals and related substances at 298.15° K (25.0° C) and one atmosphere (1.013 bars) pressure and at higher temperatures. *U.S. Geol. Survey Bull.*, *1259*, 256 p.
- SAGON, J. P. (1967): Le métamorphisme dans le nord-est du bassins de Châteaulin: découverte de chloritoïde et de margarite dans les schistes dévonien. *C.R. Somm. Soc. géol. France*, 206–207.
- (1970): Minéralogie des schistes paléozoïques du bassin de Châteaulin (Massif armoricain): distribution de quelques minéraux phylliteux de métamorphisme. *C.R. Acad. Sci., Paris*, *270*, 1853–1856.
- SCHALLER, W. T., CARRON, M. K., and FLEISCHER, M. (1967): Ephesite, $\text{Na}(\text{LiAl}_2)(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$, a trioctahedral member of the margarite group, and related brittle micas. *Amer. Min.*, *52*, 1689–1696.
- STEWART, D. B. (1967): Four-phase curve in the system $\text{CaAl}_2\text{Si}_2\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$ between 1 and 10 kilobars. *Schweiz. Mineral. Petrogr. Mitt.*, *47*, 35–59.
- STORRE, B., and NITSCH, K. H. (1973): The upper stability of margarite in the presence of quartz. *Naturwiss.*, *60*, 152.
- THOMPSON, A. B. (1973a): Analcime: free energy from hydrothermal data. Implications for phase equilibria and thermodynamic quantities for phases in $\text{NaAlO}_2\text{-SiO}_2\text{-H}_2\text{O}$. *Amer. Min.*, *58*, 277–286.

- (1973b): Calculated Gibbs free energy of formation of Al_2SiO_5 polymorphs and corundum from experimental equilibrium studies: Implications for the tabulated H_f^0 , G_f^0 values for aluminous minerals. *Contr. Mineral. and Petrol.* (in Press).
- TU, KWUANG-CHI (1956): Preliminary results on hydrothermal synthesis of the brittle micas (in Chinese). *Acta Geol. Sinica*, *36*, 229–237.
- VELDE, B. (1971): The stability and natural occurrence of margarite. *Mineralog. Mag.*, *38*, 317–323.

Manuscript received October 26, 1973.