

## The stability and natural occurrence of margarite

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**SUMMARY.** The upper stability of margarite has been determined to be 450 °C at 1 kb and 530 °C at 2 kb total pressure ( $P_{H_2O} = P_{total}$ ). Other experiments delimit in a general way the lower stability of this mineral and its paragenesis in more SiO<sub>2</sub> rich compositions. The presence of the 060 reflection at 1.475 Å can be used to distinguish between margarite and paragonite or muscovite.

MARGARITE is a calcic dioctahedral mica that has been known since the mid nineteenth century but rarely found as a mineral of petrographic interest. The most widely developed occurrences are in regional metamorphic rocks of unusual composition—bauxite carbonate sediments that have been metamorphosed to varying degrees (Önay, 1949) and in contact metamorphism of similar rocks (Williams, 1888). Other types of more isolated occurrences have been reported in association with ore deposits (Aoki and Shimoda, 1965) in metamorphosed anorthositic rocks (Bryhni, 1966) or in vein deposits or metamorphosed vein deposits (Clarke and Chatard, 1884; Niggli, 1955). Identifications in gneissic or pelito-gneissic rocks have been frequently mistaken and can be considered only with great doubt (Niggli, 1955). In sum, it can be remarked that margarite is rare, highly localized in occurrence, and thus probably represents special compositional or physical conditions of formation.

Accepting this brief sketch as a valid summary of the geological importance of margarite, the question can be asked why does it not occur more frequently; is the occurrence of margarite restricted by chemical or physical variables that are rarely realized in nature? The following experimental investigation was designed to answer these questions.

*Experimental methods.* A description of the equipment and starting materials used in this investigation can be found elsewhere (specific details are given by Velde, 1969). Hydrostatic pressure was applied to synthetic glass–water mixtures of appropriate compositions, or synthetic minerals, at various temperatures. Daily readings indicated less than  $\pm 3$  °C fluctuations. The absolute values are believed accurate to  $\pm 2$  °C. Pressures of 1 and 2 kilobars ( $\pm 50$  bars) were used and temperatures between 400 and 550 °C were employed. Table I gives the pertinent experimental results, along with the conditions under which they were realized. Reactions were observed to proceed in two directions at 1 and 2 kb for the upper thermal stability of margarite and indications of this process were observed at 2 kb for the lower stability of mineral. Synthesis of what is thought a stable assemblage from various starting materials was realized at 2 kb for several margarite + Al<sub>2</sub>O<sub>3</sub> + SiO<sub>2</sub> compositions, which enabled

the determination of the stable assemblages more rich in  $\text{SiO}_2$  than margarite (fig. 1). Table II gives X-ray diffraction and optical data for synthetic margarite.

*Identification of phases.* The phases that appear above the thermal stability of margarite are corundum and anorthite. For  $\text{SiO}_2$ -rich compositions sillimanite or pyrophyllite occur with anorthite. The initial appearance of margarite was noted by a weak

TABLE I. *Hydrothermal experiments on the synthesis and breakdown of margarite*

Lower stability of margarite					Margarite = anorthite + corundum			
Reactants	Time days	<i>T</i> °C	<i>P</i> kb	Products	Reactants	Time days	<i>T</i> °C	Products
gel*	61	351	1	boeh. + X	Pressure: 1000 ± 50 bars			
gel*	90	386	1	marg.	syn. marg.	57	476	An + Cor
syn. marg.	90	386	1	marg.	gel	61	464	An + Cor?
syn. An + Cor	90	386	1	marg.	syn. An + Cor	56	460	An + Cor
gel*	64	375	2	boeh. + X	syn. marg.	65	444	marg.
gel*	73	396	2	marg.	gel	65	444	marg.
syn. boeh. + X	73	396	2	marg.	syn. An + Cor	57	433	marg. + An + Cor
syn. marg.	64	360	2	marg.	Interval of reaction reversal 433 to 476 °C, reaction located between 444 and 464 °C			
<i>Compositions containing more SiO<sub>2</sub> than margarite</i>					Pressure: 2000 ± 50 bars			
syn. hydr. + An, Ca 8-Al 55-Si 37	75	498	2	marg. + pyrophyllite + andalusite?	gel	32	540	An + Cor
gel,* Ca 13-Al 52-Si 35	65	600	1	An + sillimanite + Cor?	syn. marg.	32	540	marg. + (An + Cor) tr.
gel,* Ca 12-Al 50-Si 38	57	433	1	An + marg. + pyrophyllite?	gel	55	525	An + Cor + marg.
					syn. An + Cor	62	515	An + Cor
					gel	62	515	marg.
					syn. marg.	62	516	marg.
					syn. marg. + An + Cor	40	507	marg. + (An + Cor) tr.
					Interval of reaction reversal 507 to 540 °C, reaction located between 525 and 540 °C			

Contractions: marg., margarite; boeh., boehmite; hydr., hydralsite; An, anorthite, Cor, corundum; X,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ .

\* A coprecipitated mixture of  $\text{CaO}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$ , which is in a glassy state.

diffraction reflection at 9.6 Å and strong reflections at 4.41, 3.20, and 2.58 Å. This undoubtedly represents a disordered polymorph, similar to *1Md*-muscovite (Yoder and Eugster, 1955). With increased crystallinity a pattern similar to that given in table II, the  $2M_1$  polymorph, was obtained.

Boehmite was found at temperatures below the stability of margarite, characterized by 6.15 and 3.16 Å reflections. A phase corresponding in X-ray diffraction properties to a hexagonal form of  $\text{CaAl}_2\text{Si}_2\text{O}_8$  reported by Davis and Tuttle (1952) was found to be present with boehmite. It is designated as 'X' in the table of run data. The original synthesis of this phase was accomplished with difficulty at 1250 °C, a factor that leads one to think that it represents a metastable reaction product when it appears below 400 °C. Since the temperatures at which this phase occurs are within those

suspected to encompass the stability of zeolites, less than 350 °C, it might be assumed that in fact thomsonite, gismondine, or lawsonite might be stable or that prehnite+boehmite+kaolinite might be stable for a  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$  bulk composition.

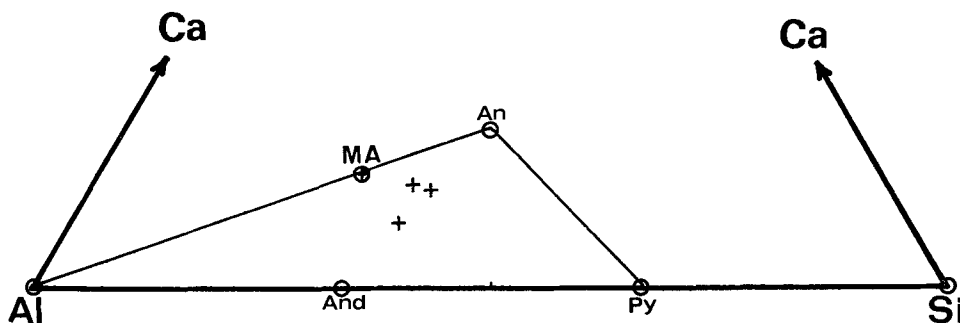


FIG. 1. Compositions investigated are shown as a function of their relative Ca-Al-Si contents. Principal phases encountered are MA, margarite; And, andalusite (or hydralsite or sillimanite); Py, pyrophyllite; An, anorthite, quartz is found at the Si coordinate and boehmite or corundum at the Al coordinate.

TABLE II. *Physical properties of synthetic margarite. Refractive index,  $\beta$  1.629.  $2M_1$  structure, with  $a$  5.104,  $b$  8.836,  $c$  19.117 Å,  $\beta$  95.520°,  $V$  858.09 ± 6.5 Å<sup>3</sup>*

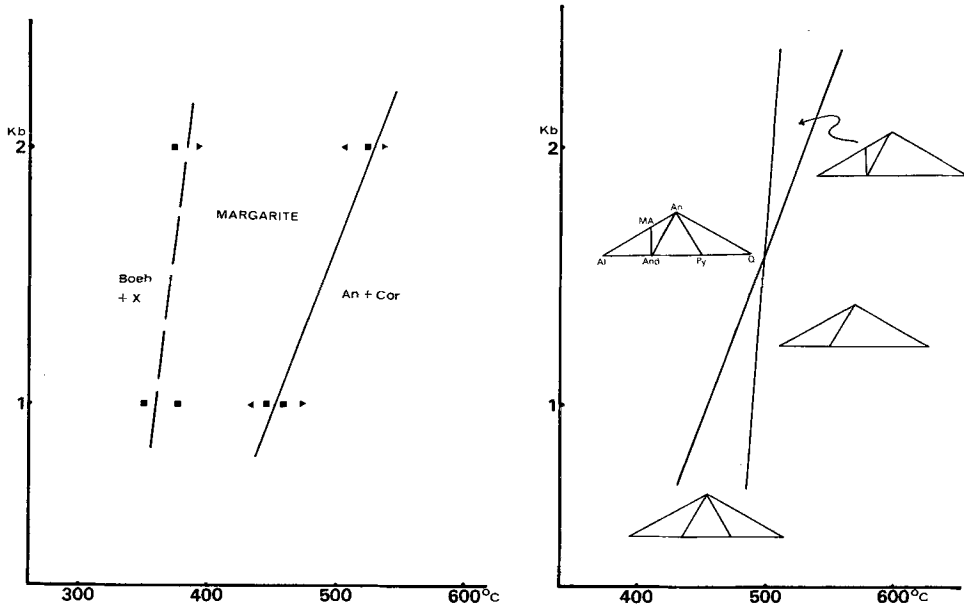
$d$	$I$	$hkl$	$d$	$I$	$hkl$	$d$	$I$	$hkl$	$d$	$I$	$hkl$
9	30	002	3.633	6	023, 104	2.776	15	115	2.127	25	22 $\bar{3}$
4.792	3	004	3.500	4	113	2.690	11	$\bar{1}16$	2.008	6	$\bar{1}41, 044, \bar{1}42$
4.396	16	020	3.384	11	$\bar{1}14$	2.544	19	200, 13 $\bar{1}$ , 130	1.9102	20	045, 143
		110	3.245	19	024, $\bar{1}21$	2.513	65	20 $\bar{2}$	1.6687	8	150, 235, $\bar{1}51, 240$
		$\bar{1}11$	3.179	100	006	2.488	4	13 $\bar{2}$ , 201	1.5940	21	303, $\bar{1}54$
4.212	5	111	3.045	2	$\bar{1}23$	2.407	25	13 $\bar{3}$	1.4749	31	060
4.016	2	022	3.004	6	11 $\bar{5}$	2.330	8	035, 1 $\bar{3}3$	1.4679	22	—
3.790	12	$\bar{1}13$	2.893	15	031, 123	2.184	10	041, 22 $\bar{2}$			

X-ray diffraction data and cell refinement for synthetic margarite, using  $\text{Cu-K}\alpha$  radiation and silicon internal standard. Relative intensities are taken as maximum peak heights. The cell refinement was made using a program by C. Burnham (1962).

The phase 'X' was, however, produced in the present study, along with anorthite at 2 kb and 300 °C, from a glass of anorthite composition, results similar to those of Coombs *et al.* (1959).

*Discussion of results.* One of the most important factors in the hydrothermal study is the very slow rate of reaction observed. This limited quite severely the precision of the equilibrium determinations. At 1000 bars, the interval in which the equilibrium between margarite and anorthite, corundum, and  $\text{H}_2\text{O}$  should exist is 40 °C and it is 35 °C at 2000 bars. Less conclusive determinations permitted a reduction of this interval

to 20 °C at 1 kb and 15 °C at 2 kb (table I). Therefore, the slope of the equilibrium projected in  $P$ - $T$  space must be considered to be approximate, and could be between 3.1 and 0.9 bars/°C. The value of 1.3 given in fig. 2 is based upon an interpretation of experiments that indicate, but do not prove, mineral stability. The determination of the lower stability of margarite is less well defined, and must be considered only as indicative.



FIGS. 2 and 3: FIG. 2 (left). Results of the experiments which determine the stability of margarite (see table I) are shown graphically. Squares represent indicative results and triangles represent observed reactions. Abbreviations as in Table I. FIG. 3 (right). Chemiographic relations of margarite, aluminium silicates and the breakdown products of margarite are shown as they are related to their regions of stability in  $P$ - $T$  space. The two crossed lines represent the limits of stability of margarite and pyrophyllite.

In spite of the imprecision of the results, which would not permit, for example, a thermodynamic calculation or extrapolation based upon them, the general relationships of the phases found to occur on and near the margarite composition can be considered to be valid in a general way and are useful for the interpretation of geologic phenomena. One thing that is apparent from the results of the study is that the range of pressure and temperature conditions under which margarite appears to be stable is quite limited at moderate pressures; it exists only over an interval of 110 to 140 °C at between 1 and 2 kb total pressure. This certainly is an important factor controlling its natural occurrence. Second, the runs for more silica-rich compositions than margarite itself indicate that small changes in chemistry destabilize margarite in favour of other assemblages: anorthite-pyrophyllite or anorthite-andalusite. Thus it would seem that

both physical and chemical factors tend to limit the conditions under which it is stable and thus substantiate its apparent rarity in nature.

Certain aspects of the mutual phase relations involving margarite and more silica-rich bulk compositions are more clearly exposed in graphical form in fig. 3. The phases concerned are margarite, corundum, anorthite, quartz, pyrophyllite, and andalusite. The essential feature displayed is the intersection of the curve of the pyrophyllite stability with that of margarite, which does not modify the slope of the latter curve in  $P$ - $T$  space. The most important relationship shown in the diagrams is the persistent tie-line between plagioclase and an aluminium-silicate phase, which eliminates a quartz-margarite compatibility.

Althaus and Winkler (1962) studied the stability of margarite; however, the bulk compositions used by them were much different from those of the present study. Their exploratory work was done using natural clay mineral assemblages plus 4 to 5 wt. % of a calcium salt. 10 to 15 mg of  $H_2O$  were added to 100 mg of this mixture. The result was a silicate-fluid mixture in which, presumably, the anion in solution was about 3  $N$ , and thus the acidity of the fluid was very high. The stability range thus determined for margarite is between 400 and 580 °C at 2 kb total pressure. An interesting observation made from this work is the destabilization of plagioclase at high hydrogen-ion concentrations. Mineral assemblages thus obtained are reported to contain, among other phases, margarite plus quartz, an association that is only possible if plagioclase becomes unstable, and thus the tie-line plagioclase to aluminium silicate becomes impossible. The stable assemblage under highly acid fluid conditions would then be margarite-quartz- $Ca^{2+}$ . The validity of the conclusions drawn from the work of Althaus and Winkler is put somewhat in doubt by the method of mica identification employed, which was based mainly upon the position of the 060 reflection at  $62.5^\circ 2\theta$ ,  $Cu-K\alpha$ . In the present work the position of this reflection is found to be  $1.475 \text{ \AA}$ , or  $63.0^\circ 2\theta$ ,  $Cu-K\alpha$  radiation, for margarite. The  $62.5^\circ 2\theta$  reflection mentioned by Althaus and Winkler (1962) is, however, characteristic of paragonite (see following section on natural minerals).

The importance of the Althaus and Winkler study is somewhat difficult to assess in terms of natural mineral assemblages, accepting that they did in fact produce a calcic mica. Margarite+quartz-bearing rocks should also, according to their data, contain a calcium salt and be devoid of plagioclase. Such rocks have not yet been reported. It is not impossible that very acid, calcium-bearing solutions do exist in pegmatitic fluids, but it is unlikely. Another possible source of such solutions is the metamorphism or dissolution of sedimentary evaporite deposits. Under such conditions, if temperatures were high enough, rocks of pelitic bulk compositions could become margarite-bearing. However geologic evidence for this is at present lacking.

*Natural margarite compositions.* The chemical composition of natural margarites varies in essentially two ways, one by the addition of Li, which substitutes for octahedrally coordinated ions in the structure, and another through the substitution of sodium for calcium in the interlayer ion position. The first substitution has been studied by Schaller *et al.* (1967). These authors adopted the name ephesite for the

hypothetical lithic end-member of the series,  $\text{Na}(\text{LiAl}_2)(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$ , which is a trioctahedral mica. In general, these lithic micas are pink in hand specimen, and thus easily distinguishable from the non-lithic margarites. The second substitution is somewhat more elusive, and less well known. Ideally, the calcium–sodium substitution involves margarite–paragonite end-members. However, the chemical compositions of the natural micas indicate something more complicated and less well defined. The sodic margarites tend to be silica-poor and water-rich relative to an ideal formula based upon paragonite substitution, a fact that has been noted by Deer *et al.* (1962).

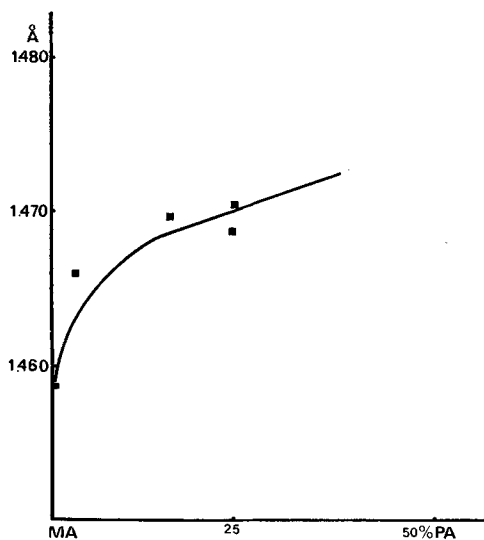


FIG. 4. The *b* cell dimension of calcic lithium-free micas, measured by the position of the 060 reflection, is shown as a function of the ratio  $\text{Ca}/(\text{Ca} + \text{Na} + \text{K})$  of the interlayer ion. The margarite (MA) value is for the synthetic mica, table II; the other four calcium-rich micas are taken from Aoki and Shimoda (1965) and table III.

The 060 spacing or the *b* cell dimensions of natural micas are compared to  $\text{Ca}/(\text{K} + \text{Na} + \text{Ca})$  content in fig. 4. Four non-lithic micas have been used, one analysis taken from the literature, and three new analyses (table III). The shape of the curve deduced from these data appears non-linear, suggesting non-ideal solid solution. The possibility of a solvus relationship between margarite and paragonite is substantiated to a certain extent by the observation of 060 reflections for 6 un-analysed 'margarite' specimens from the collections of the Museum d'Histoire Naturelle de Paris, which showed two phases to be present in 5 of the 6 samples. The minimum  $\text{Ca}/(\text{Na} + \text{K} + \text{Ca})$  observed, using the curve of fig. 4, is about 70 % for the calcic mica. It is not possible at the moment to assess whether or not the solvus is symmetrical, since the sodic end-member can, and probably frequently does contain potassium, and thus the derived cell

spacings become indeterminate. It would appear from chemical analyses of natural minerals that less calcium enters paragonite than sodium enters margarite. Solid solution between margarite and muscovite is probably quite limited (Deer *et al.*, 1962). It is in any event apparent that 060 measurements are quite diagnostic for differentiation of calcic from sodic dioctahedral micas, even though basal spacings are nearly identical. The margarites are characterized by 060 reflections between 1.457 and 1.472 Å, while low-potassium paragonites (Zen *et al.*, 1964; Velde, 1970; Chatterjee, *priv. comm.*) lie between 1.477 and 1.483 Å.

**Conclusions.** The information gathered together in the present study would appear to be self-complementary; natural occurrence of margarite is known to be quite

restricted as are the physical and chemical conditions necessary for its stability. Combination of the experimental results of Althaus and Winkler (1962) and the present study demonstrate the importance of the global chemistry of a geological environment in determining the presence of margarite. If anorthite remains stable, margarite is

TABLE III. *Chemical analyses of three natural margarites (anal. A. Nétillard, Lab. de Pétrographie), with atomic ratios per 12(O,OH).*

	1	2	3		1 (cont.)	2 (cont.)	3 (cont.)		1	2	3
SiO <sub>2</sub>	30.64	29.86	29.84	K <sub>2</sub> O	1.25	0.05	0.48	Si	2.14	1.99	2.01
Al <sub>2</sub> O <sub>3</sub>	50.33	51.06	50.18	TiO <sub>2</sub>	tr	tr	tr	Al <sup>iv</sup>	1.86	2.01	1.99
Fe <sub>2</sub> O <sub>3</sub>	0.09	0.77	1.35	P <sub>2</sub> O <sub>5</sub>	0.03	tr	0.09	Al <sup>vi</sup>	2.00	1.99	1.99
FeO	0.89	0.28	0.66	Li <sub>2</sub> O	tr	tr	0.21	Fe <sup>3+</sup>	—	0.04	0.07
MnO	tr	0.03	tr	H <sub>2</sub> O <sup>+</sup>	4.83	4.52	4.78	Fe <sup>2+</sup>	0.02	0.01	0.01
MgO	0.09	0.14	0.05	H <sub>2</sub> O <sup>-</sup>	0.02	0.01	0.03	Li	—	—	0.06
CaO	11.39	11.79	10.69	Total	100.81	100.26	100.51	Na	0.15	0.23	0.27
Na <sub>2</sub> O	1.25	1.75	2.15					K	0.10	—	—
								Ca	0.74	0.84	0.77
								OH	2.09	2.00	2.12

1. Turkey (AKd2; from P. Ch. de Gracianski).  $d_{060}$  1.470 Å.
2. Grenier, Austria (Lab. de Pétrographie coll.).  $d_{060}$  1.471 Å.
3. Chester, Massachusetts (from V. C. Farmer).  $d_{060}$  1.469 Å.

restricted to silica-poor rock compositions. If the acidity of the total system is high, anorthite becomes unstable and margarite can coexist with quartz. The two limiting conditions (temperature and chemical environment) are probably seldom realized complementarily and thus margarite is a relatively rare mineral. However, should its presence be suspected, a rapid determination of the 060 spacing is diagnostic.

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