

Phengite geobarometry based on the limiting assemblage with K-feldspar, phlogopite, and quartz

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Abstract. Following and extending the early work of Velde (1965) the pressure-temperature dependence of the compositions of potassic white micas coexisting with K-feldspar, quartz, and phlogopite in the model system $K_2O-MgO-Al_2O_3-SiO_2-H_2O$ was investigated up to fluid pressures of 24 kbar by synthesis experiments. There is a strong, almost linear increase of the Si content per formula unit (p.f.u.) of phengite, ideally $KAl_{2-x}Mg_x[Al_{1-x}Si_{3+x}O_{10}](OH)_2$ with pressure, as well as a moderate decrease of Si (or x) with temperature. The most siliceous phengite with Si near 3.8 p.f.u. becomes stable near 20 kbar depending on temperature. However, contrary to Velde's assumption, these phengites coexisting with the limiting assemblage are invariably not of an ideal dioctahedral composition (as given by the above formula) but have total octahedral occupancies as high as about 2.1 p.f.u.

The stability field of the critical assemblage phengite – K-feldspar – phlogopite – quartz ranges, in the presence of excess H_2O , from at least $350^\circ C$ to about $700^\circ C$ but has an upper pressure limit in the range 16–22 kbar, when K-feldspar and phlogopite react to form phengite and a K, Mg-rich siliceous fluid.

For the purpose of using these phase relationships as a new geobarometer for natural rocks, the influence of other components in the phengite (F, Fe, Na) is evaluated on the basis of literature data. Water activities below unity shift the Si isopleths of phengite towards higher pressures and lower temperatures, but the effects are relatively small. Tests of the new geobarometer with published analytical and PT data on natural phengite-bearing rocks are handicapped by the paucity of reliable values, but also by the obvious lack of equilibration of phengite compositions in many rocks that show zonation of their phengites or even more than one generation of potassic white micas with different compositions. From natural phengites that do not coexist with the limiting assemblage studied here but still with a Mg, Fe-silicate, at least minimum pressures can be derived with the use of the data presented.

1 Introduction

Phengites are intermediate members of the muscovite-celadonite, $KAl_2[AlSi_3O_{10}](OH)_2-K(Mg, Fe^{2+})(Fe^{3+},$

$Al)[Si_4O_{10}](OH)_2$, solid solution series. Experimental investigations of their PT stability had been undertaken by Crowley and Roy (1964) as well as by Velde (1965). Crowley and Roy, in a synthesis study, found for the system $K_2O-MgO-Al_2O_3-SiO_2-H_2O$ (KMASH) a miscibility range from ideal muscovite to a phengite which Si = 3.5 per formula unit (p.f.u.) throughout the applied experimental conditions from about 400° to $700^\circ C$ and up to 4 kbar. In contradistinction, Velde (1965, 1967) reported the miscibility from muscovite towards Al-celadonite to increase clearly with rising pressure or decreasing temperature and thus of value for geothermobarometry. The phengites becoming unstable with changing PT conditions were found to decompose to K-feldspar, phlogopite, quartz, water, and a phengite poorer in Si than the decomposing one. Velde (1965) also studied the mica miscibility from muscovite to iron-bearing celadonite end members such as $KMgFe^{3+}[Si_4O_{10}](OH)_2$. However, he found that the micas in the pure KMASH-system exhibited the maximum miscibility for a given PT condition.

Velde's (1965) results are in general agreement with the occurrences of natural phengites that are found mainly in low-temperature metamorphic rocks, whereas muscovites are typical for rocks formed at intermediate to relatively high temperatures (Ernst 1963). Moreover, phengites with contents of celadonite component as high as 70% appear in high-pressure metamorphic rocks, e.g., in rocks of the blueschist facies (Ernst and Dal Piaz 1978; Cimmino and Messiga 1979; Moore and Liou 1979).

The phengite thermobarometer proposed by Velde (1967) and represented by curves of constant maximum Si content of the white micas in a PT plot was applied by several petrologists (e.g., Råheim 1976; Brown et al. 1978; Beccaluva et al. 1979; Saliot and Velde 1982). However, only few of them took into consideration that the maximum Si phengite can only be attained in coexistence with K-feldspar, quartz, and a trioctahedral mica (Fig. 1) or with an alternative assemblage. Although this was already pointed out by Ernst (1963) and by Velde (1965) himself, Velde (1967) contributed to a hazardous or even wrong application of his phengite thermobarometer by the statement "that the Si content of the phengites is independent of the associated mineral phases in the same rock". As a further source of error the maximum Si content of phengites as given by Velde (1967) for pressures above 4.5 kbar was only obtained by extrapolation.

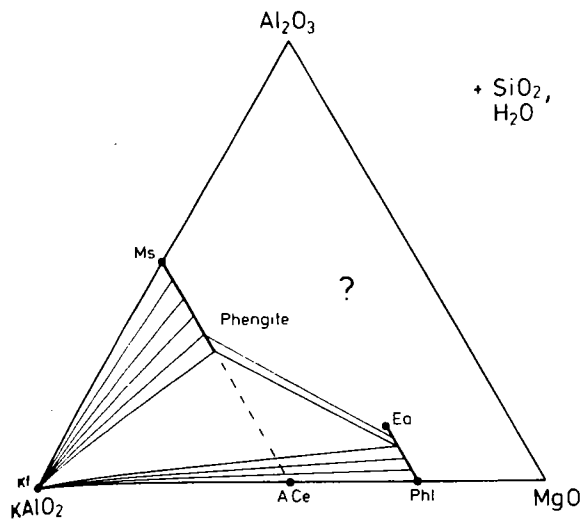


Fig. 1. Modified AKF diagram showing fundamental phase relations in the system $K_2O-MgO-Al_2O_3-SiO_2-H_2O$ relevant to phengite solid solubility. For simplification the two series of mica solid solutions are exhibited here as binary. The truly ternary solid solutions are shown in subsequent figures (5, 7, 9). Abbreviations: *ACe* Al-celadonite, *Ea* eastonite, *Kf* K-feldspar, *Ms* muscovite, *Phl* phlogopite

The aim of the present experimental work was mainly to extend Velde's data towards higher pressure. In addition, the influence of phengite compositions deviating from the ideally dioctahedral muscovite-celadonite solid solution series was to be examined. Synthesis experiments in the KMASH-system showed that binary as well as ternary white mica solid solutions could be obtained and uniquely defined by their lattice parameters (Massonne and Schreyer 1986). In the present paper we discuss the dependence of mica miscibility on the PT conditions of formation and establish a geobarometer that should be useful for petrological work.

2 Experimental techniques

Experiments at pressures up to 7 kbar were conducted in conventional cold-seal hydrothermal bombs. At higher pressures a piston-cylinder apparatus was used with pressure vessels having a WC core and a pressure chamber of 1/2 inch diameter. The NaCl pressure cells employed were described by Massonne and Schreyer (1986), who also discussed the PT corrections applied and the uncertainties of the pressure and temperature determination. The temperature was measured with coated chromel/alumel thermocouples.

Gels and gel mixtures with compositions of ideally dioctahedral micas lying in the KMASH-system were prepared (cf., Massonne and Schreyer 1986) and either crystallized to individual pure phengites or to the mineral assemblages shown in Table 1. Quartz, sanidine, and phlogopite as individual phases were also obtained from gels. Based on 48 reflections of its X-ray powder diffractogram, the phlogopite crystallized on ideal composition, $KMg_3[AlSi_3O_{10}](OH)_2$, shows the following lattice dimensions assuming trigonal metrics: $a_0 = 5.3171 \pm 0.0003 \text{ \AA}$, $c_0 = 30.4516 \pm 0.0016 \text{ \AA}$. If these values are recalculated for an 1M phlogopite, which cannot be distinguished from the 3T polytype in a X-ray powder diffractogram, they are in good agreement with data of previous workers, e.g., Wones (1967).

In order to prepare starting materials containing chlorite, the following procedure was used: mixtures composed of SiO_2 gel (6N, Koch & Light) $\gamma-Al_2O_3$ (cf. Massonne and Schreyer 1986), and $Mg(CH_3CO_2)_2 \cdot 4H_2O$ (>99.5%, Merck) were first heated to 1000°C in order to decompose the acetate and then crystallized under pressure to the assemblage quartz-chlorite \pm corundum (Table 1). After addition of synthetic sanidine, the bulk composition of such mixtures correspond chemically to ideally dioctahedral micas. Other synthetic minerals and mineral associations were also mixed and converted mainly to the assemblage K-feldspar, quartz, phlogopite, and phengite. The same paragenesis was obtained by direct crystallization of gels with compositions of ideally dioctahedral micas as well.

Run products were identified in X-ray powder diffractograms obtained with copper radiation ($K_{\alpha 1} = 1.54050 \text{ \AA}$, $K_{\alpha 2} = 1.54178 \text{ \AA}$). In addition, they were inspected microscopically. The compositions of phengites were determined applying the cell dimension data as reported by Massonne and Schreyer (1986). Barium fluoride and silicon (cf., Massonne and Schreyer 1986) as well as the quartz present in many run products were used as internal X-ray standards. For quartz we used the lattice parameters: $a_0 = 4.9136 \text{ \AA}$, $c_0 = 5.4051 \text{ \AA}$ given by Robie et al. (1967), which were confirmed by some determinations with Si or BaF_2 in our run products.

Table 1. Syntheses of reference and starting materials used in the present study

Run no.	Starting material		Conditions				Product
	Type	Composition	t/d	P/kbar	T/°C	wt.% H ₂ O	
V297	Gel	$KAlO_2 \cdot 3SiO_2$	16	2.0	700	9.5	San
V354	GM	$KAlO_2 \cdot 300SiO_2$	1	2.1	700	5	Qz, San?
V67	Gel	3.000/3.000	2.5	28.0	860	18	Phl
V70	Gel	3.204/2.000	2.5	27.8	862	17	WM(2M ₁ (90))
V272	GM	3.303/2.000	0.5	14.2	555	14	WM(1M(45), Md(45))
V132	Gel	3.399/2.001	3	25.3	834	15	WM(2M ₁ (90))
V274	Gel	3.399/2.001	0.5	20.0	690	7.5	WM(Md(50), 2M ₁ (30))
V280	GM, h	3.501/2.001	2	28.8	844	12	WM(2M ₁ (90))
V294	Gel	3.399/2.001	10	2.1	750	16	Kf, Phl, Co, glass
V300	Gel	3.802/1.999	13	2.0	750	14	Kf, Phl, glass
V165	Gel	3.802/1.999	39	5.0	700	12	Kf, Phl, Qz
V302	OM	$4MgO \cdot Al_2O_3 \cdot 4SiO_2$	40	7.0	650	18	Chl, Qz
V318	OM	$2MgO \cdot 3Al_2O_3 \cdot 2SiO_2$	31	7.0	650	17	Chl, Qz, Co
V332	SM	3.80/2.00	1.5	25.0	645	10	WM(Md(80)), vl. Qz

Abbreviations: *GM* gel mixture, *OM* oxide mixture, *SM* silicate mixture, *h* preheated, *d* days, *Chl* chlorite, *Co* corundum, *Kf* K-feldspar, *Phl* phlogopite, *Qz* quartz, *San* sanidine, *WM* white mica, *vl* very little. Numbers in parentheses indicate percentage of white mica polytype dominating. For explanation of numbers in column "Composition" see section 3. Formula code

Table 2. Syntheses of phengites in assemblage with quartz, K-feldspar, and phlogopite from gels

Run no.	Starting material		Conditions				Phases	Product			
	Type	Composition	<i>t/d</i>	<i>P/kbar</i>	<i>T/°C</i>	wt.% H ₂ O		WM-polytype dominating	WM lattice dimensions		WM composition calculated
									<i>a</i> ₀ /Å	<i>c</i> ₀ /Å	
V155	Gel	3.20/2.00	86	3.0	650	17	WM, l. Kf, vl. Phl, tr. Qz	2M ₁ (60)	5.1998	10.0090	3.053/2.051
V164	Gel	3.40/2.00	39	5.0	700	14	WM, Kf, l. Qz, l. Phl	2M ₁ (50), Md(40)	5.2018	10.0059	3.075/2.056
V160	GM	3.50/2.00	82	7.0	450	19	WM, l. Kf, vl. Qz, tr. Phl	Md(>70)	5.2144	9.9778	3.276/2.078
V102	Gel	3.40/2.00	53	7.0	550	16	WM, l. Kf, tr. Qz, tr. Phl	1M(60)	5.2088	9.9929	3.202/2.065
V103	Gel	3.40/2.00	45	7.0	650	14	WM, l. Kf, vl. Qz, tr. Phl	1M(45), 2M ₁ (45)	5.2073	10.0023	3.156/2.073
V250	Gel	3.60/2.00	6.5	10.6	490	14	WM, l. Kf, vl. Qz, tr. Phl	Md(70)	5.2190	9.9613	3.362/2.082
V269	GM	3.50/2.00	4	10.6	590	13	WM, l. Kf, l. Qz, tr. Phl	1M(60)	5.2161	9.9597	3.371/2.059
V248	GM	3.50/2.00	4	10.9	689	15	WM, l. Kf, l. Qz, vl. Phl	1M(70)	5.2163	9.9663	3.336/2.071
V207	Gel	3.80/2.00	5	15.0	446	14	WM, vl. Qz, tr. Kf	Md(>90)	5.2107	9.9021	3.716/1.985
V198	GM	3.70/2.00	7	15.0	546	14	WM, vl. Kf, vl. Qz, Phl?	Md(70)	5.2168	9.9225	3.584/2.028
V113	Gel	3.60/2.00	8	15.0	649	13	WM, l. Kf, vl. Qz, Phl?	Md(>80)	5.2179	9.9373	3.495/2.042
V258	Gel, h	4.00/2.00	4	19.3	546	5	l. WM, Kf, l. Qz, vl. Phl	Md(>80)	5.2139	9.8923	3.782/2.008
V275	GM, h	3.95/2.00	4	20.0	544	7.5	WM, Kf, l. Qz, vl. Phl	Md(>90)	5.2136	9.9022	3.716/2.006
V237	Gel	3.80/2.00	4	20.0	648	16	WM, l. Qz	Md(>80)	5.2182	9.9073	3.675/2.038
V251	Gel, h	3.80/2.00	3	20.0	642	6.5	WM, Kf, l. Qz, vl. Phl	Md(>90)	5.2148	9.8929	3.776/2.014
V456	Gel, h	4.00/2.00	2.5	20.0	648	16	l. WM, Kf, Qz, Phl	Md(>80)			
V714	Gel, h	4.00/2.00	3	23.55	663	6.5	WM, Kf, Qz, Phl	Md(>70)			

Abbreviations as in Table 1, in addition: *l* little, *tr* trace

3 Formula code

Following Massonne and Schreyer (1986), the ternary composition of mica in the KMASH-system is defined by the two parameters, Si content and octahedral occupancy p.f.u. Thus, in the present paper, ideal muscovite, KAl₂[AlSi₃O₁₀](OH)₂, will be written: 3.00/2.00 and, for example, the ternary mica KMg_{0.51}Al_{1.56}[Al_{0.7}Si_{3.3}O₁₀](OH)₂: 3.30/2.07. Starting from this formula code *x/y* the octahedral occupancies of Mg and Al are derived by the following equations: Mg = *x* + 3*y* - 9, Al = 9 - *x* - 2*y*.

4 Experimental results

4.1 The critical compositions of phengite and phlogopite in the limiting assemblage

The results of synthesis experiments with gels and precrytallized materials, which led to the limiting assemblage of K-feldspar, phlogopite, quartz, and a phengite of critical composition are summarized in Tables 2 and 3. These critical compositions, for a given pressure and temperature, were found to be independent of the nature and composition of the starting material. Based on this behavior, we conclude that these phengites are probably not metastable products of crystallization with respect to their composition. However, these phengites often display the Md polytype instead of an ordered polytype like 2M₁ or 3T, which are the stable ones in nature. Firm evidence for the true stability of particular phengite compositions was expected from reversal experiments starting with both the mineral assemblage phengite + K-feldspar + phlogopite + quartz (Fig. 1) and a single-phase phengite of the same bulk composition. However, all such experiments failed (Table 4). Even, in a run at 7 kbar lasting six months, the amount of newly formed phengite was too small to determine its composition exactly. Never-

theless, despite some overlap of X-ray diffraction peaks, it could be estimated that such newly formed phengites are compositionally at least very close to those phengites that were crystallized directly from gels in coexistence with K-feldspar, phlogopite, and quartz. This extremely sluggish reaction behavior of synthetic phengite is apparently an inherent property of this mica, because even in natural rocks a reequilibration of phengite may fail to occur, as will be discussed in the final section of this paper.

The critical phengite compositions were determined from 22 run products. They show systematic and reproducible compositional trends, which support the assumption that the phengites grown directly from gel in our experiments do indeed exhibit stable compositions. With rising synthesis pressures an increase of the phengite Si content was observed, whereas rising temperatures led to decreasing Si contents (Fig. 2). Only the data point resulting from the experiment at 23.5 kbar (V 714) does not fit the curves of Fig. 2 too well. However, it seems that in this run the maximum miscibility of phengite towards Al-celadonite for any PT condition was reached, namely at an Si content of slightly below 3.8 p.f.u. (Massonne and Schreyer 1986). The deviation, $\sqrt{(\Delta x)^2/n}$, of the remaining 21 data points from the plane correlating water pressure, temperature, and Si contents of phengites coexisting with K-feldspar, quartz, and phlogopite (Fig. 2) amounts to 0.028 Si p.f.u. This value is only slightly higher than the uncertainty given by Massonne and Schreyer (1986) for data correlating the Si content and c-dimension of Md micas synthesized in the KMASH-system. Thus, the method of evaluation employing powder diffractograms influences essentially the accuracy of our measurements. As a further but much less important source of uncertainty, the accuracy of the PT conditions applied in the experiments has to be considered. The standard deviation $\sigma = \sqrt{(\Delta x)^2/n(n-1)}$ for the isothermal curves shown

Table 3. Syntheses of phengites in assemblage with quartz, K-feldspar, and phlogopite from diverse silicate mixtures

Run no.	Starting material Mixture of run products (see Table 1 and 2)	Bulk composition	Conditions				Phases	Product		
			t/d	P/ kbar	T/°C	wt. % H ₂ O		WM lattice dimensions		WM composition calculated
								a ₀ /Å	c ₀ /Å	
V380	V297(62), V318(23), V70(10), V165(5)	3.40/2.00	72	3.5	450	15	WM, Kf, tr. Phl, Qz?	5.2046	10.0031	3.152/2.056
V379	V297(59), V318(16), V274(14), V302(6), V165(5)	3.50/2.00	67	7.0	450	18	WM, Kf, tr. Phl, Qz?	5.2118	9.9818	3.256/2.067
V378	V297(63), V318(24), V102(13)	3.40/2.00	38	7.0	550	18	WM, l. Kf, vl. Qz, tr. Phl	5.2095	10.0015	3.160/2.087
V389	V294(45), V300(45), V280(5), SiO ₂ -Gel(5)	3.60/2.00 + SiO ₂ (5)	4	10.75	493	14	WM, Kf, Qz, vl. Phl	5.2143	9.9560	3.391/2.040
V515	V294(56), V300(33), V269(6), V354(5)	3.55/2.00 + SiO ₂ (5)	6	10.9	593	9	WM, Kf, Qz, l. Phl	5.2146	9.9705	3.314/2.067
V338	V297(60), V302(22), V165(9), V332(9)	3.80/2.00	4	14.6	450	7	WM, Kf, l. Qz, tr. Phl	5.2200	9.9183	3.610/2.051
V381	V297(62), V318(20), V272(11), V165(4), V302(3)	3.45/2.00	68	3.5	350	17	WM, Kf, l. Qz, Qz?	5.2079	10.0009	3.163/2.075
V468	V297(57), V318(14), V274(10), V302(8), V165(8), V354(3)	3.55/2.00 + SiO ₂ (3)	81	7.0	350	16	WM, Kf, l. Qz, tr. Phl	5.2097	9.9675	3.330/2.027
V375	V297(62), V302(17), V165(8), V280(6), V318(6)	3.70/2.00	7	10.7	400	15	l. WM, Kf, tr. Phl, tr. Chl, Qz?	5.2211	9.9489	3.429/2.077

Numbers in parentheses indicate the weight% of the previous run products used as starting materials. The white micas obtained showed the Md polytype dominating. Abbreviations as in Table 1 and 2

Table 4. Experiments to study reaction (11): phengite 1 = phengite 2 + K-feldspar + quartz + phlogopite + vapor

Run no.	Starting material	Run conditions				Product
		t/d	P/kbar	T/°C	wt. % H ₂ O	
V204	3.40/2.00 V164	182	7.0	550	12	2 WM, l. Phl, l. Kf, l. Qz
V224	3.40/2.00 V164	85	7.0	650	16	2 WM, Phl, l. Kf, l. Qz
V201	3.80/2.00 V165	7	15.0	545	12	Phl, Kf, Qz, l. WM
V213	3.60/2.00 V164 + V165	4	15.0	645	12	Phl, Kf, Qz, WM1, l. WM2

Abbreviations as in Table 1 and 2

in Fig. 2 amounts only to 0.0062 Si p.f.u., which can also be related to a pressure uncertainty of about ± 150 bar. Figure 3 presents the same data set in a PT plot with Si isopleths. This plot contains also the 2σ PT uncertainties of our experiments.

It must be emphasized that the X-ray measurements also prove that the octahedral occupancy of the phengites coexisting with K-feldspar, phlogopite, and quartz are generally higher than 2.00 p.f.u. (Fig. 4). Thus, the phengite of critical composition in the four-phase assemblage is usually not that white mica which exhibits the maximum binary miscibility towards celadonite as outlined by Velde (1965). For graphical representation of these relations the reader is referred to Fig. 5. Unfortunately, it was not possible to determine quantitatively the PT dependence of the octahedral occupancy of the critical phengite composition. According to Massonne and Schreyer (1986) the octahedral occupancy of Md micas in the KMASH-system can, in principle, be determined with an uncertainty of less than 0.01 p.f.u. evaluating the X-ray reflections 200 and 300 at about

40° and 62° (2θ , CuK_α-radiation), respectively. However, the Md micas of the present study, especially those in the low-T run products, showed bad CuK_{α1} and CuK_{α2} splitting of 200 and 300. Moreover, the 300 reflection sometimes overlapped with sanidine peaks thus resulting in a higher uncertainty of the white mica octahedral occupancy than in our previous study. The estimated correlation curve (dashed in Fig. 4) may only be representative for phengites coexisting with K-feldspar, phlogopite, and quartz at high temperatures near 600° C.

The phlogopite occurring in the run products could often be easily identified in the X-ray diffractograms by virtue of its 0015 reflection (3T polytype assumed here). However, it is worthy of note that this reflection appeared generally between 44.8 and 44.9° (2θ , CuK_{α1}-radiation), whereas phlogopite of ideal composition, KMg₃[AlSi₃O₁₀](OH)₂, exhibits this particular reflection at 44.595° (for phlogopite lattice dimensions see section on Experimental Procedures). Thus, the critical composition of phlogopite coexisting with K-feldspar, quartz, and phengite is expected to differ signifi-

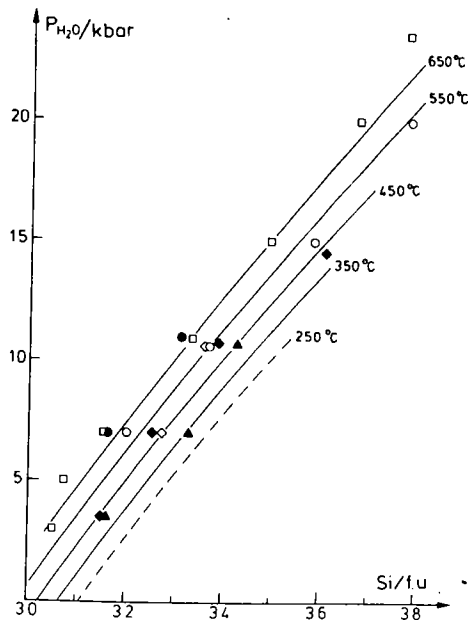


Fig. 2. Pressure-temperature dependence of Si content per formula unit of phengite coexisting with K-feldspar, quartz, and phlogopite. Symbols indicate the starting materials and the specific ranges of run temperatures as listed in Tables 2-3: solid diverse silicate mixtures, open gels; triangle 350-400° C, diamond 445-495° C, circle 540-595° C, square 640-700° C

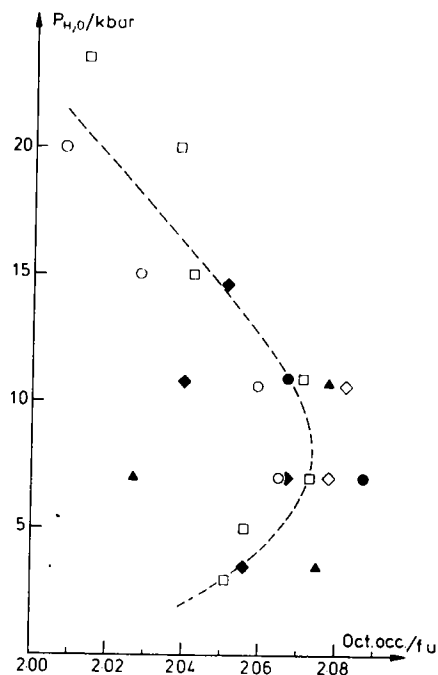


Fig. 4. Variations of octahedral occupancies per formula unit of phengites in the limiting assemblage with K-feldspar, quartz, and phlogopite as a function of water pressure and temperature. Symbols indicate the starting materials and temperature ranges as explained in the legend to Fig. 2. For significance of dashed curve see text

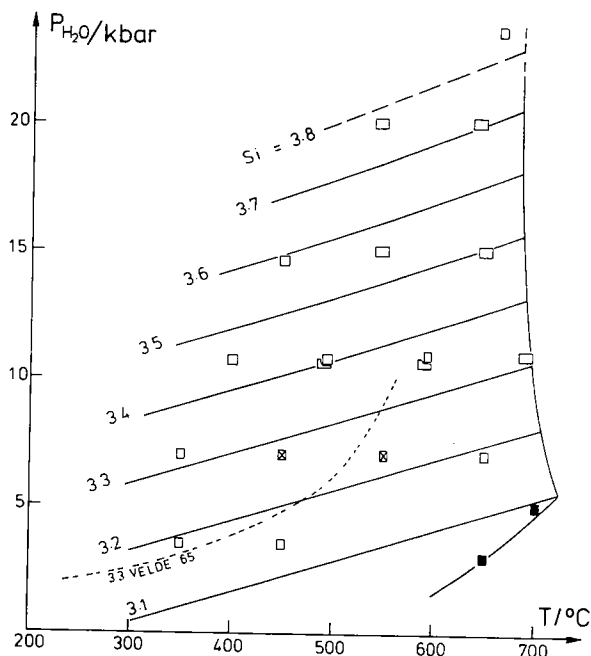


Fig. 3. Pressure-temperature plot with Si isopleths for phengite Si contents per formula unit in the limiting assemblage with K-feldspar, quartz, and phlogopite. Open boxes indicate phengites in which the Md/1M polytypes dominate, closed boxes muscovites with predominantly the 2M₁ polytype. Boxes with crosses represent two runs at these conditions. Size of boxes shows estimated 2σ-uncertainties of run conditions. For comparison, the dashed curve is that of Velde (1965) for 3.3 Si per formula unit. Solid curves at high temperatures mark the border of the stability range of the limiting assemblage as detailed in Fig. 6

cantly from that of ideal phlogopite and to be PT dependent as well. A first clue relating to the latter problem was obtained by comparing run products V 164 and V 165 at 5 kbar, 700° C (Table 1) with those of V 251 and V 456 at 20 kbar, 645° C (Table 2). Considering the compositions of the starting materials for these runs, as shown in Fig. 5, this pressure difference of 15 kbar led to a significant shift of the K-feldspar - phlogopite tie line of the limiting assemblage with phengite, quartz, and H₂O fluid. Thus, in the compatibility triangles of Fig. 5 an eastonitic phlogopite coexists at low pressure, whereas a trioctahedral mica even richer in Si than ideal phlogopite is the stable partner at high pressure. We conclude, therefore, that the inverse Tschermak substitution Mg + Si for 2Al shows a similar pressure dependence in both the dioctahedral and the trioctahedral mica solid solutions. The plot of Fig. 5 suggests octahedral occupancies as low as 2.8 p.f.u. for phlogopite coexisting with K-feldspar, quartz, and phengite. Preliminary experiments in the KMASH-system on the miscibility between dioctahedral and trioctahedral micas as well as the X-ray properties of the phlogopite solid solutions synthesized (Massonne, unpublished work) confirm such low values for the octahedral occupancy. Even stronger deviations from the ideal trioctahedral occupancy were reported by Robert (1976).

4.2 PT stability of the limiting assemblage

The assemblage K-feldspar - quartz - phlogopite - phengite was synthesized in the presence of water within a large PT field ranging from about 3 to 24 kbar and 350 to 700° C (Tables 2 and 3). However, additional experimental data

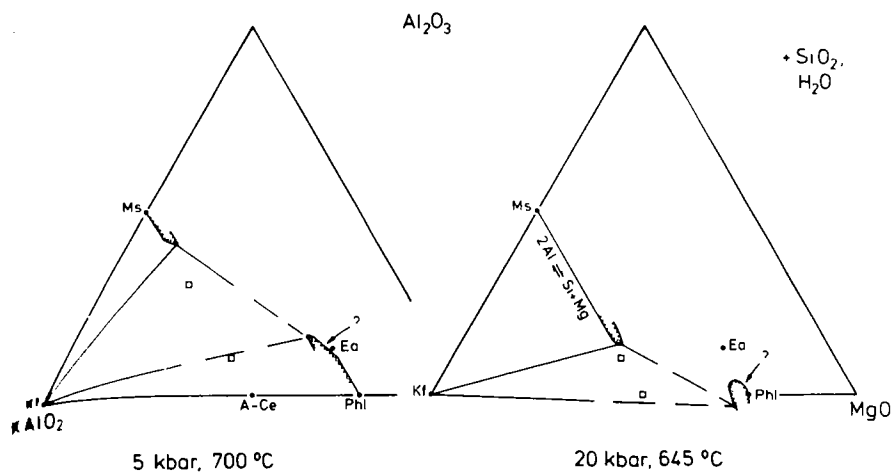


Fig. 5. Modified AKF diagrams as in Fig. 1 to exhibit the changing phase relations of the limiting assemblage phengite – K-feldspar – phlogopite – quartz for two different run conditions. The ternary ranges of the mica solid solutions are indicated. Note that the critical phengites do not lie along the binary solid solution line following $2Al \rightleftharpoons Si + Mg$. *Open boxes* show bulk compositions studied. Abbreviations as in Fig. 1. *Tie lines* given as *solid lines* were determined, the *dashed ones* are estimated

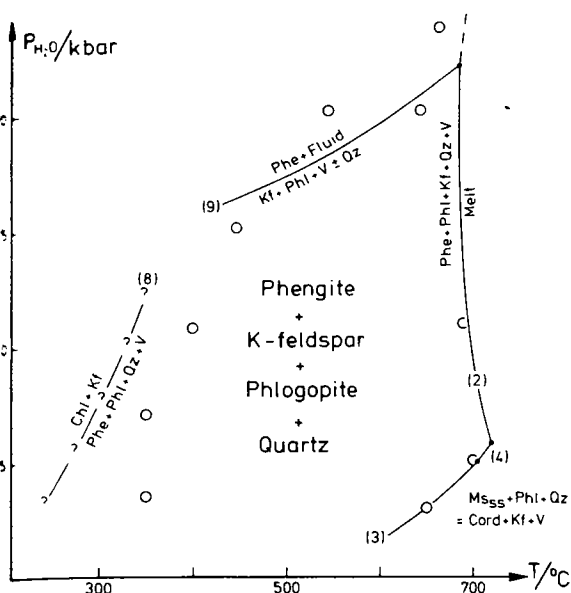


Fig. 6. Pressure-temperature stability field of the limiting assemblage phengite – K-feldspar – phlogopite – quartz in the presence of excess H_2O . *Open circles* show critical experiments. *Solid dots* are invariant points. *Numbers* refer to the reactions identified and further discussed in the text. The phase relations near $700^\circ C$, 5 kbar are shown in detail in Fig. 7. Abbreviations not explained in Fig. 1: *Chl* chlorite, *Cord* cordierite, *Ms_{ss}* phengitic muscovite, *Qz* quartz, *V* H_2O -vapor. For composition of fluid see text

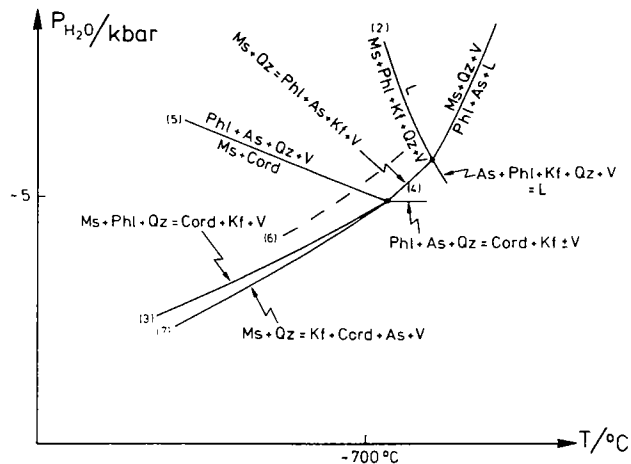
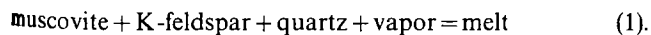


Fig. 7. Phase relations of phengitic muscovite (*Ms*), phlogopite (*Phl*), K-feldspar (*Kf*), quartz (*Qz*), cordierite (*Cord*), Al-silicate (*As*), melt (*L*), and H_2O -vapor (*V*) in the system $K_2O - MgO - Al_2O_3 - SiO_2 - H_2O$ near $700^\circ C$, 5 kbar. For sources of data see text. *Dashed line* applies to a reaction of the limiting system $K_2O - Al_2O_3 - SiO_2 - H_2O$ as identified in the text

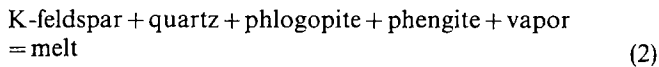
and natural occurrences show that the true stability field for this particular mineral assemblage is actually smaller than the PT range examined. The relevant data and the contribution by our experiments to these stability limits will be discussed in the following (Fig. 6).

An upper thermal stability for K-feldspar + quartz + phlogopite + phengite at high water pressures is very likely to be given by melting of these phases leading to a granite-like eutectic melt, albeit no requisite experimental data are known. However, Storre and Karotke (1972) as well as Huang and Wyllie (1974) discussed the corresponding reaction in the MgO -free KASH-system:



The melting temperatures estimated by these authors depend only slightly on pressure and lie for $P_{H_2O} = 11$ kbar

at about $705^\circ C$. Although the presence of phlogopite caused by the introduction of MgO should reduce the melting temperature, in run V248 (Table 2) at $P_{H_2O} = 10.9$ kbar and $689^\circ C$ no melt could be detected. Hence we conclude that granite-like eutectic melt appears in the KMAsh-system by the reaction



only a few degrees lower than for the KASH-system as reported by the previous authors.

At lower pressures, subsolidus reactions limit the stability of K-feldspar – quartz – phlogopite – phengite towards higher temperatures (Fig. 7). However, neither the reaction phengite + phlogopite + quartz = Mg-cordierite + K-feldspar + vapor

(3)

nula unit of quartz, and nature. Sym-anges as dashed curve

dependent m was ob- l V 165 at d V 456 at positions of 1 in Fig. 5. fificant shift ling assem- bus, in the phlogopite mica even partner at he inverse s a similar d the trioc- 5 suggests phlogopite e. Prelimi- miscibility as well as ations syn- 1 such low ger devia- e reported

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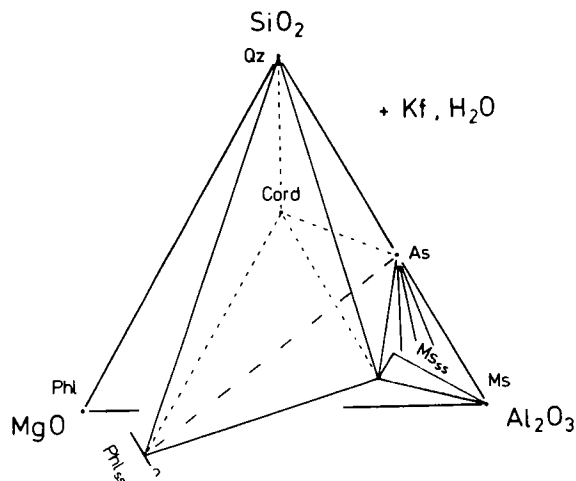
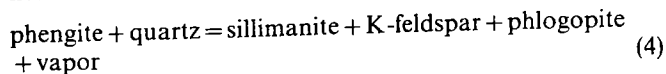
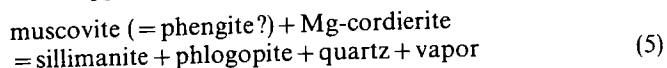


Fig. 8. Phase relations relevant to the breakdown of phengitic muscovite + quartz (cf., Fig. 7) shown in ternary projection from K-feldspar and H₂O. Abbreviation not explained in Fig. 6: *Phl_{ss}*, phlogopite solid solution. The two ranges of mica solid solutions are shaded

nor



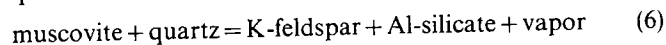
were objects of experimental studies so far. Theoretically the corresponding reaction curves must intersect at an invariant point lying probably near 5 kbar water pressure, if one applies the PT data of Seifert (1970) for the reaction



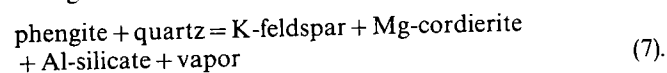
(cf., Fig. 7).

The locations of reaction curves (3) and (4) as shown in Fig. 6 were estimated as follows:

1. Massonne and Schreyer (1980) noted, through an analysis of the phase topology in the KMASH-system, that the stability range of muscovite + quartz is expanded due to the introduction of Mg into ideal muscovite. According to the isopleths of Fig. 3 the phengitic muscovite reacting with quartz to form phlogopite + K-feldspar + Al₂SiO₅ by reaction (4) (see Fig. 7) contains about 3.1 Si per formula unit. If one plots this mica composition together with its coexisting phases Al₂SiO₅, quartz, and phlogopite in a ternary projection from K-feldspar and vapor (Fig. 8) it is clear that the ideal muscovite composition is no longer stable with quartz. The reaction in the pure KASH-system



must have taken place at lower temperatures. As shown in Fig. 8 these relations also hold for the reaction

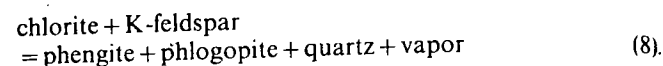


Preliminary experiments indicate that the temperature differences between reaction curve (6) versus (4) and (7) may lie in the order of 5–15° C. Reaction (6) was studied in detail by Chatterjee and Johannes (1974), who employed synthetic minerals of the KASH-system. Their data are probably the most reliable ones available. Previous works by Yoder and Eugster (1955), Evans (1965), Wang and Fuh (1966), Althaus et al. (1970), as well as by Day (1973) showed

non-systematic deviations, for which the natural muscovites of diverse provenance used, non-calibrated hydrothermal bombs, etc. may be responsible.

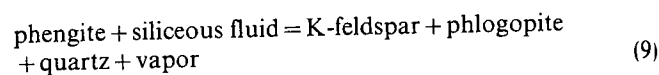
2. In runs starting with gels (V 155 and V 164, Table 1 and 2, respectively) the mineral assemblage K-feldspar – quartz – phlogopite – phengite was obtained at 3.0 kbar/650° C and 5.0 kbar/700° C. Cordierite, which in our experience grows easily from gels and even precrystallized material without seeding, was not observed. Therefore, the cordierite-free assemblage is considered to be stable under these conditions (see Fig. 6).

According to observations on low-grade natural rocks, the low-temperature stability of the assemblage K-feldspar – quartz – phlogopite – phengite should be defined by the reaction



This reaction producing biotite due to the presence of Fe occurs in nature in the PT region of the greenschist facies (Mather 1970; Brown 1975). For water pressure of 5 kbar and Fe/Mg ratios close to 1, Hoschek (1980) expects it to take place at about 440° C. Seeded experiments of the present study in the pure KMASH system on reaction (8) led at 350° C/3.5 kbar, 350° C/7 kbar, and 400° C/10.7 kbar (V 381, V 468, and V 375; Table 3) to clear growth of phengite + phlogopite + quartz relative to chlorite + K-feldspar. These experiments show definitely that, perhaps even in contrast to natural rock systems, K-feldspar + chlorite is not stable in the KMASH system at 350° C. We expect a stability field of K-feldspar + Mg-chlorite to lie at least a few tens of degrees lower because there was complete or almost complete consumption of K-feldspar + Mg-chlorite in our experiments (Fig. 6).

In a more recent experimental study (Massonne 1986) the surprising discovery was made that an upper pressure stability limit exists for the assemblage K-feldspar – quartz – phlogopite – phengite within the PT range studied. It was found to be due to the reaction



in which a K, Mg-rich, but Al-poor siliceous fluid is stable on the low-temperature side of the reaction. The corresponding reaction curve (Fig. 6) shows a flat positive slope of around 25 bar/°C intersecting the curve of reaction (2) at about 22 kbar and 685° C. Reaction (9) is of considerable interest to igneous petrologists, because this strange low-temperature fluid is related to lamproitic types of magmas as they occur in nature (Massonne 1986; Schreyer et al. 1987).

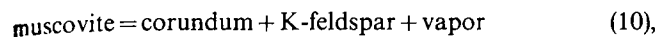
In the present context it should be noted that two data points of Fig. 6 that were used to define the new phengite geobarometer at the highest water pressures in Fig. 3 actually lie outside the field of the limiting assemblage with K-feldspar + phlogopite + quartz + vapor (runs V 275 and V 714 of Table 2). There, K, Mg-rich fluid instead of vapor seems to coexist with the solid phases. With less than 8 wt.% of H₂O added to these run starting materials, excess-H₂O conditions were apparently not attained, so that the solid phases of the limiting assemblage are still in coexistence (see reaction 9). The resulting phengites did show a further increase in their Si contents and thus fit the general trend of Fig. 3, where the final isopleth of Si = 3.8 was dashed.

It may also be of interest to note that, with the use of gels as starting materials, the low-temperature fluid may also be formed metastably at lower pressures than given by curve (9) of Fig. 6 (see runs 207 and 237 of Table 2), because phlogopite and K-feldspar failed to nucleate. However, pretreated starting materials led to the formation of the limiting assemblage (runs V251, Table 2; V338, Table 3).

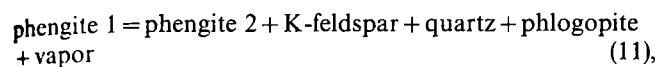
5 Discussion

5.1 Comparison with the phengite thermobarometer of Velde

Although the phengite thermobarometer of Velde (1965, 1967) shows the same tendencies in the variation of the Si content of phengites as outlined here, our data differ significantly from those of Velde (cf. Fig. 3). Since Velde's (1967) Si contour lines for the maximum Si of phengite are based on experiments undertaken solely below 5 kbar, the strong increase in slope of his Si contour lines towards high temperatures is really only assumed, because he believed that they should have slopes similar to the upper thermal stability limit of ideal muscovite (Velde 1966). This latter curve was taken by Velde (1967) to be identical with the contour line for Si=3.0. However, the decomposition of muscovite is due to the reaction



whereas quite a different reaction,



is actually responsible for the change in the Si content of phengite.

Velde's (1967) extrapolation of the phengite Si contour lines are not solely responsible for the discrepancies noted, rather, even Velde's (1965) experimental results seem to be in disagreement with our data, at least at first sight. As an example, the difference in phengite composition at 450°C and 5 kbar is about +0.1 Si per formula unit in the Velde barometer (cf., Fig. 3). However, it is important to note here that the phengite coexisting at these particular conditions with K-feldspar, quartz, and phlogopite has, according to our work, an octahedral occupancy of 2.06 p.f.u. and Si=3.20, while the phengite with the ideally dioctahedral occupancy as determined by Velde (1965) has for these PT conditions the maximum Si content of 3.3 p.f.u. The enlarged part of the AKF plot of Fig. 9 displays these relations, which are simply the result of the shape of the ternary phengite solid solution range. The phase relations as indicated in Fig. 9 also imply that a true dioctahedral phengite cannot actually coexist with the limiting assemblage K-feldspar + quartz + phlogopite, but only with K-feldspar + quartz. Thus, with a rise in temperature or drop in pressure, the true dioctahedral phengite with the maximum Si content (point M in Fig. 9) will react to form K-feldspar + quartz plus a phengite with a higher octahedral occupancy. These relations are actually confirmed by Velde's own experimental data, because he observed phlogopite coexisting with quartz, K-feldspar, and phengite only when the starting material of dioctahedral phengite composition was clearly richer in Si than that of the phengite finally formed. If his starting material was only slightly more siliceous than the dioctahedral phengite with the maximum

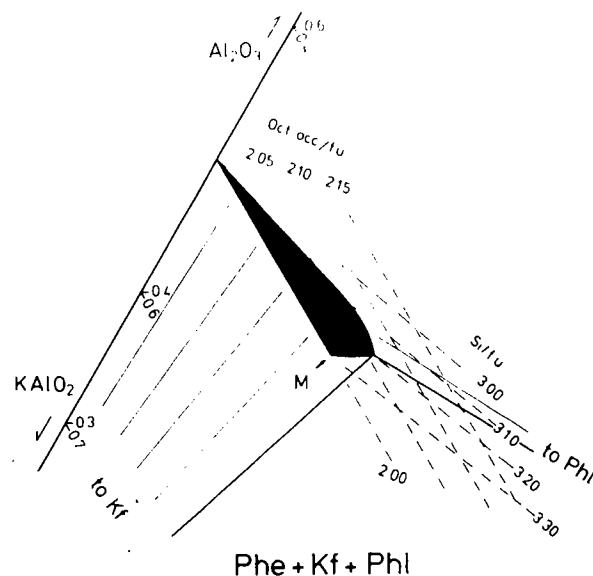


Fig. 9. Expanded portion of an AKF plot such as in Fig. 5 showing the ternary solid solution range of phengite (shaded), the tie lines towards K-feldspar (Kf) and phlogopite (Phl) as solid lines, and (dashed) lines of constant Si and octahedral occupancy per formula unit of phengite (Phe). The phengite with the maximum Si content stable at the PT condition applying to this diagram is indicated by M

Si content (M in Fig. 9) synthesized, solely K-feldspar and quartz appeared as additional phases. Thus, the experimental results of our study and that of Velde (1965) actually seem to be compatible, but the conclusions must differ, simply because of different kinds of phengite investigated. At any rate, it must be clear that only the ternary phengite of the limiting assemblage studied here can be used unequivocally for geobarometry. It is also for this reason that the refinement of Velde's data undertaken by Powell and Evans (1983) on the basis of thermodynamics cannot be applied to natural rocks.

5.2 Influence of fluorine, iron, and sodium in phengite, as well as of reduced water activity on the phengite barometer

A strict application of the present results to natural rocks would require that there is only limited influence of the remaining chemical mica complexity on the Si contents of phengites, or that correction factors for the diverse chemical parameters can be established. Unfortunately, petrological and experimental information bearing on this problem are so far rather limited.

The relationship between the phengite Si content and the fluorine content of the white mica (Fig. 10) can be extracted from a petrological study by Némec (1980) on the F content of phengites from rocks of a limited area in Czechoslovakia showing the assemblage with K-feldspar quartz, and dark mica. The linear correlation curve fitting Némec's data in Fig. 10 indicates increasing phengite Si contents with rising F in phengite by 0.625 Si p.f.u./ x_F . However, natural phengites show x_F values rarely exceeding 0.05. Values close to 0.2 are due to special F-rich environments as for instance in greisen.

Similar deductions for the influence of the more important chemical parameters Fe^{2+} and Fe^{3+} in phengite on the barometer are, unfortunately, impossible due to lack

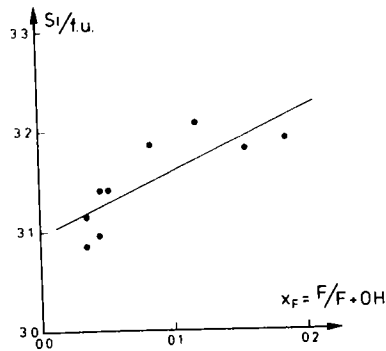


Fig. 10. Relationship between F and Si contents in natural phengites occurring in their limiting assemblage with K-feldspar, dark mica, and quartz as deduced from the data of Němec (1980)

Table 5. Maximum phengite Si contents p.f.u. as obtained experimentally by Velde (1965) at 4.5 kbar and 400° C showing the extent of the binary miscibility from ideal muscovite towards those celadonite end members identified by their cations in octahedral sites

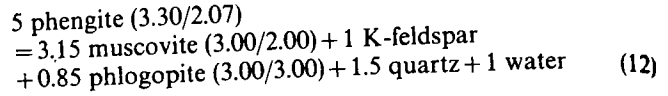
Celadonite end member	Si/p.f.u.
Mg Al	3.361
Mg Fe ³⁺	3.327
Mg Fe _{0.5} ³⁺ Al _{0.5}	3.166
Mg _{0.5} Fe _{0.5} ²⁺ Al	3.295
Mg _{0.5} Fe _{0.5} ²⁺ Fe _{0.5} ³⁺ Al _{0.5}	3.167

of data. However, the experiments of Velde (1965) provide some insight, because this author studied the maximum miscibility of potassic white mica towards end member celadonites including those containing Fe²⁺ and Fe³⁺. Although, as outlined above, the maximum binary Si phengite is not identical to the ternary phengite coexisting with K-feldspar, quartz, and dark mica, a change in maximum Si content by the substitutions Fe²⁺ for Mg and Fe³⁺ for Al in phengite should lead to a similar change of the Si content in phengite of the limiting assemblage. Comparing all of Velde's results for 4.5 kbar and 400° C (Table 5), it can be concluded that Fe in both oxidation states lowers the Si content of phengite in comparison with pure MgAl phengite. A moderate lowering was observed for phengite with a Fe²⁺/Mg ratio of 1, however, some Fe³⁺ may reduce the phengite Si content drastically.

Following the observation that a Si-rich phengite may coexist with a paragonite showing Si contents very close to the ideal value of 3.0 p.f.u. (Cimmino and Messiga 1979; Katagas and Baltatzis 1980), one must conclude that the introduction of Na for K into the white mica interlayer

should clearly reduce the phengite Si content. On the other hand, the paragonite component in natural phengite rarely exceeds values of 10%, so that the influence of Na on the phengite Si content should actually be fairly limited.

To estimate the effect of reduced water activity a_{H_2O} on the Si content of phengite, thermodynamic calculations were conducted. Here, we present an example for the Si = 3.3 isopleth (see Fig. 3). Under the assumption of a constant octahedral occupancy of 2.07 p.f.u. for phengite becoming stable at the PT conditions of that particular isopleth, the underlying reaction equation for this case was formulated as



or

solids (s) = 1 H₂O.

The enthalpy $\Delta H_{T_0}^{P_0}$ and entropy $\Delta S_{T_0}^{P_0}$ for solids were calculated applying the equilibrium relation

$$\Delta G_T^P = 0 = \Delta H_{T_0, H_2O}^{P_0} - \Delta H_{T_0, s}^{P_0} + \int_{T_0}^T c_p dT \\ - T \left(\Delta S_{T_0, H_2O}^{P_0} - \Delta S_{T_0, s}^{P_0} + \int_{T_0}^T c_{p,T} dT \right) \\ + \int_{P_0}^P \Delta V_{T,s}^P dP + RT \ln (f_{T, H_2O}^P \cdot a_{H_2O})$$

with $P_0 = 1$ bar, $T_0 = 298.15$ K, r meaning the reaction, and

$$\int_{P_0}^P \Delta V_{T,s}^P dP = \Delta V_{T_0,s}^{P_0} (P - 1) \text{ for the PT conditions, 7030 bar}$$

673.15 K and 9470 bar/873.15 K, which were taken from the PT diagram of Fig. 3. The activities of the phengite and the hydrous fluid in equation (12) were assumed to be unity. The data sources and the results of this calculation are summarized in Table 6. The water fugacities used are those of Halbach and Chatterjee (1982). The PT data for the curve of the above reaction was subsequently recalculated for different water activities (Fig. 11). Within the T range 350° to 700° C the recalculated curve for $a_{H_2O} = 1.0$ fits the requisite curve of Fig. 3 fairly well; however, towards lower temperatures, the calculated curve develops a steeper slope relative to the Si = 3.3 isopleth of Fig. 3 that was extrapolated linearly. This thermodynamic calculation introduces some uncertainty into the geobarometric potential of the phengite Si contents at low temperatures.

The thermodynamic results of Fig. 11 indicate a shift of the Si isopleths towards higher pressures with reduction of the water activity. In the example shown a reduction

Table 6. Thermodynamic data for water (Robie et al. 1979) and for the solids of the reaction (12) (calculated). The c_p function for solids refers to that of structural bonded water as given by Berman and Brown (1985)

	$\Delta H_{T_0}^{P_0}$ J/Mol	$\Delta S_{T_0}^{P_0}$ J/Mol·K	$\Delta V_{T_0}^{P_0}$ J/Mol·bar	$c_p = a + bT + cT^{-2} + dT^{-0.5} + eT^2 + fT^{-3}$					
				a	b	c	d	e	f
Solids	-282450	67.75	0.700	106.33	0	0	-1243.22	0	90628000
H ₂ O	-241814	188.83		7.368	0.027468	-223160	361.74	-4.8117 E-6	0

The volume of the solids $\Delta V_{T_0}^{P_0}$ was calculated using the molar volume data tabulated by Robie et al. (1979) for quartz and high-sandinite as well as those given by Massonne and Schreyer (1986 and this work) for ideal muscovite, ideal phlogopite, and the particular phengite

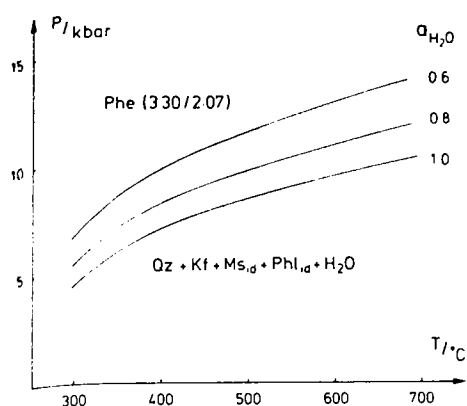


Fig. 11. Pressure temperature plot exhibiting the influence of variable water activity a_{H_2O} on the location of the isopleth of a phengite with 3.3 Si per formula unit and 2.07 octahedral occupancy (compare Fig. 3). Ms_{id} and Phl_{id} indicate the ideal compositions of muscovite and phlogopite used in the calculations. For further details see text

from $a_{H_2O} = 1.0$ down to 0.6 leads to a pressure increase of about 3 kbar.

5.3 The use of phengite b_0 parameters for geobarometry

As pointed out by Guidotti and Sassi (1976) the lattice dimensions of potassic white micas, which are dependent on the phengite Si content (Massonne and Schreyer 1986), can be used as a petrogenetic indicator. In a recent paper Guidotti and Sassi (1986) empirically correlated the b_0 dimension of phengites with metamorphic PT conditions. In order to test the correlation attempted by Guidotti and Sassi (1986, Fig. 1) we have compared the positions of the relevant X-ray powder reflection near $62^\circ 2\theta$ for CuK_α (indexed as 060 by Guidotti and Sassi, but as 300 by Massonne and Schreyer (1986) of their natural phengites with those of the synthetic ones obtained under controlled PT conditions in the present study. For a selected synthesis pressure of 7 kbar strong discrepancies were noted. Using the curves of Guidotti and Sassi, X-ray data on our run products would indicate a pressure of more than 10 kbar at $650^\circ C$, and of about 4 kbar at $350^\circ C$, instead of the true pressure of 7 kbar applied in the experiments.

In the light of the present experience (see also section 6.2), the method of Guidotti and Sassi (1986) seems hazardous unless the phengites measured occur always in the same mineral assemblage which, in addition, must be a limiting one. If the phengite coexists, for example, with one ferromagnesian phase, such as chlorite only, there is not even a constraint on the phengite composition to be a critical one. Thus, the discrepancy between the b_0 curves of Guidotti and Sassi and our data may be at least partly due to phengites of non-critical composition evaluated by Guidotti and Sassi.

6 Petrological applications

6.1 Natural tests of the new geobarometer

As already mentioned in the introduction, the original thermobarometer as proposed by Velde (1967) has often been used by petrologists uncritically, because they ignored the

necessity that the phengite studied in the rock should in fact coexist with its limiting assemblage phlogopite/biotite, K-feldspar, and quartz.

In order to provide a test on the reliability of the new phengite barometer introduced in the present work, the literature was searched for phengite data from this limiting natural assemblage, for which there are also independent estimates available on pressure and temperature based on different, independent geothermometers and barometers. Unfortunately, such ideal circumstances could not be found thus far. Although there are some studies, which present analyses of metamorphic phengites coexisting with K-feldspar, quartz, and dark mica (e.g., Lattard 1974; Frey et al. 1976; Saliot and Velde 1982), metamorphic pressures estimated on the basis of another reliable geobarometer are not given.

Under these circumstances it seems worthwhile to draw attention to the work of McDowell and Elders (1980). These authors determined in borehole samples obtained around $310^\circ C$ and a depth of 950 m the Si contents of potassic white micas coexisting with K-feldspar, quartz, and chlorite, which is the alternative low-temperature limiting mineral assemblage to phengite—K-feldspar—quartz—biotite (cf., Fig. 6). Although the Si-isopleths for phengites of the chlorite-containing assemblage should have a smaller dP/dT slope than those for phengites coexisting with K-feldspar, quartz, and biotite, the difference between both sets of curves should be very small, especially near the curve of reaction (8). With this in mind, the average Si content of 3.11 p.f.u. analyzed by McDowell and Elders (1980) on natural phengitic muscovites formed at $310 \pm 15^\circ C$ and at depths of 955 ± 110 m (giving 0.1 to 0.25 kbar depending on hydrostatic or lithostatic conditions) confirms nicely at least the low-PT portion of the phengite barometer introduced here (see Fig. 3).

Nevertheless, there is a tremendous lack of good data from nature, and it is hoped that the present paper will contribute to the awareness of petrologists studying the requisite phengite-bearing rocks for providing as many comparisons with independent geobarometers as possible.

6.2 The derivation of minimum pressures by means of the new phengite barometer

In the absence of well studied examples from nature, in which phengite coexists with its limiting assemblage K-feldspar—phlogopite/biotite—quartz, but also in view of the fact that there is a fair amount of good analyses of phengites occurring in other than this limiting assemblage but still with a Mg, Fe-silicate, we wish to emphasize here that in such cases the data summarized in Fig. 3 can be used to derive minimum pressures of formation for the enclosing rock. The Si isopleths given in that figure have indeed the function of lower-pressure stability limits for the particular mica just like that of any high-pressure mineral phase such as jadeite, pyrope, or coesite. A few examples will clarify the point.

The phengites analyzed by Smith and Zientek (1979) as well as by Harley and Green (1981) from eclogitic xenoliths within kimberlites of the Colorado Plateau exhibit Si contents between 3.7 and 3.8 p.f.u. Although the coexisting minerals, garnet, omphacite, and phlogopite, are not those of the limiting assemblage, pressures of formation of these micas must at least have been on the order of 17–25 kbar

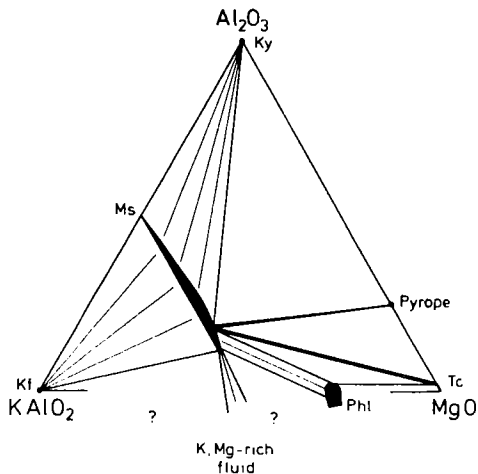


Fig. 12. Modified AKF plot showing compatibility relations of phases for PT conditions near 30 kbar, 700°C as they prevailed during the metamorphism of the pyrope-coesite rock described by Chopin (1984). Additional abbreviations: *Ky* kyanite, *Tc* talc

with temperatures below 700°C. More recently, Sorensen (1986) discovered phengites with similar compositions in Californian blueschists and thus derived minimum pressures around 15 kbar for an assumed temperature of 300°C.

Phengites occurring in the sensational pyrope-coesite rock of the Dora Maira Massif (Chopin 1984) exhibit Si contents near 3.55 p.f.u. According to Fig. 3 this requires minimum pressures of only 12–16 kbar, while the true pressure of formation was, according to other geobarometers, near 30 kbar. However, the minerals coexisting with phengite are kyanite, talc, a nearly pure pyrope, and a SiO₂-phase. The schematic AKF-diagram of Fig. 12 shows that in this assemblage the phengite phase must have a considerably lower Si content than that coexisting with phlogopite and the K, Mg-rich siliceous fluid discussed previously (cf. section 4.2). It must be emphasized, however, that the Dora Maira phengite is clearly of a critical, invariant composition buffered by its mineral assemblage as well. Thus, in order to extend the geobarometric possibilities of phengites, there is obviously a need to study the chemical variations of phengites in additional relevant limiting assemblages. Massonne and Schreyer (1985) have made a first step by determining phengite compositions in coexistence with kyanite, SiO₂, and a Mg-silicate. Using these unpublished data, the Dora Maira phengites are found to yield pressures of about 35 kbar.

6.3 Equilibrium problems of phengite in nature

Petrographic observations indicate that phengites of metamorphic rocks are evidently not always equilibrated with the rest of the minerals of the rock, or not even among themselves: Like most garnets of low to medium grades of metamorphism phengites are frequently chemically zoned and, even more disturbingly, there are numerous examples, in which metamorphic rocks contain several generations of phengite and/or muscovite with appreciably different Si contents.

Zoned phengites with Si ranging from 3.3 to 3.4 are known from high-pressure rocks of the Sesia Zone, Western Alps, where they coexist with jadeite, quartz, and K-feldspar (Stöckhert 1985). These rocks had undergone temperatures

of about 600°C. Råheim (1975) found zoned phengites in Precambrian eclogites and garnet mica schists from Tasmania, which had even experienced a maximum temperature of almost 700°C. These observations indicate, in agreement with our experimental results, that homogenization and reequilibration of phengitic micas are extremely sluggish processes even within geologic times.

However, the lack of equilibration of a mineral to changing PT conditions is obviously not in all respects a disadvantage with regard to its geological interpretation. It may actually be the opposite and could indeed be the key to unravelling the earlier stages of the metamorphic history of the rock. Spear et al. (1984) have set an impressive example in using the varying compositions of zoned garnets to reconstruct the metamorphic PT paths of the enclosing rocks. Although no comparable methods can be offered at this stage for phengite geobarometry, we are citing, in the following, several examples in which the varying chemistry of potassic white micas can be correlated, at least qualitatively, with the complex history of metamorphism of the enclosing rocks.

According to Saliot and Velde (1982) Si-rich phengites from metagranites and related rocks occurring in the Pennine zone of the French Alps are often surrounded by Si-poorer phengites, biotites, and K-feldspar, which is clearly due to reaction (11). This sequence reflects a high-pressure event followed by low-pressure metamorphism as it is typical for this particular zone of the Alps. The latter event was estimated by Saliot and Velde (1982) to have occurred at temperatures between 450 to 500°C. Very similar corona features were reported by Heinrich (1982) from metapelites of the Central Alps, that were remetamorphosed under amphibolite-facies conditions at temperatures near 600°C. Different generations of phengites had also been observed by Lardeaux et al. (1983) in metagranites from the Sesia Zone, Western Alps. The Si content of these phengites could be correlated with different stages of foliation and thus with the stress-time-related development of the rock, which has, during its last metamorphic stage, been subjected to temperatures of about 450°C. A further example coming from the Tauern Window, Eastern Alps, can be extracted from a study of eclogites and related rocks overprinted by retrograde metamorphism at temperatures of about 500°C (Miller 1977a and b). Fresh eclogites show a narrow range of Si contents in phengites around 3.39 p.f.u., whereas the overprinted eclogites contain additional phengites of low-pressure origin with Si contents going down to 3.08 p.f.u. In the Gran Paradiso, Western Alps, Chopin and Maluski (1980) were even able to correlate the petrographically distinct generations of early, coarse, Si-rich phengites followed by finer grained, less siliceous phengites with ⁴⁰Ar–³⁹Ar plateau ages of 60–75 Ma and 38–40 Ma, respectively.

In addition to these occurrences clearly demonstrating the partial survival of Si-rich phengites during retrograde metamorphism even at relatively high temperatures, there are also examples, which show that muscovite of non-metamorphic origin may be preserved during metamorphism. Frey et al. (1976) studied granites from the Monte Rosa Massif, Western Alps, that were metamorphosed at temperatures of around 550°C. Nevertheless, the old coarse grained muscovites yielding Permian ages had survived the Alpine metamorphism, which led to the additional formation of fine grained phengites in the same rock. In a dolomitic quartzite from the Eastern Alps, which had been sub-

ected to temperatures of 450° C, Dietrich (1983) found detrital muscovite to be overgrown by metamorphic phengite. Thus, in conclusion, the sluggishness of reequilibration of potassic white micas, which prevents the establishment of true equilibrium reversals in the experiments as described in this paper, is actually the good fortune of the petrologist, who is interested in reconstructing the complicated history of polymetamorphism in natural rocks.

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