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DIOCTAHEDRAL MICAS IN TRIASSIC METAVOLCANIC ROCKS OF WESTERN GREECE

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ABSTRACT

Chemically the dioctahedral micas from low-grade metamorphosed mafic volcanic rocks (Triassic, western Greece) can be grouped into three distinct types: (1) celadonite, (2) compositions ranging from an aluminous celadonite termed "leucoceladonite" through leucophyllite to phengite and (3) muscovite - paragonite. Celadonite shows substitution of Fe^{3+} for ^{VI}Al beyond the celadonite - leucophyllite - muscovite composition space. There appears to be a natural compositional gap between celadonite and the phengite - leucophyllite - "leucoceladonite" series. Three different structural types correspond to the chemical types. Celadonite shows variable substitution of Fe^{2+} for Mg. In the "leucoceladonite" - leucophyllite - phengite series, the Mg/Fe^{2+} ratio depends on Al content. Muscovite also shows variable substitution of Fe^{2+} for Mg and Na for K. As to genesis, celadonite develops from ferromagnesian minerals in basic rocks in which phlogopite or K-rich groundmass were originally present. At a higher metamorphic grade, rocks in which plagioclase is albitized develop pumpellyite, epidote and "leucoceladonite". Continued substitution of Al for Fe and Mg leads to leucophyllite, phengite and, eventually, muscovite. There is a parallel increase in Al content of epidote. Paragonite forms at higher temperatures, as Na is released from albite.

Keywords: dioctahedral micas, celadonite, leucoceladonite, leucophyllite, phengite, muscovite, paragonite, Triassic metavolcanic rocks, western Greece.

SOMMAIRE

Chimiquement, on peut classer en trois types distincts les micas dioctaédriques des roches volcaniques mafiques triassiques de la Grèce occidentale ayant subi un faible degré de métamorphisme, à savoir: (1) céladonite, (2) compositions allant de la "leucocéladonite" (céladonite à teneur d'aluminium) à leucophyllite et phengite, (3) muscovite - paragonite. Dans la céladonite, on peut substituer Fe^{3+} à ^{VI}Al au delà de l'espace de composition qui s'étend de la céladonite à la muscovite. Une lacune naturelle de composition semble séparer les deux premiers types chimiques. Trois types structurels correspondent aux types chimiques. La céladonite est caractérisée par une substitution variable de Fe^{2+} à Mg. Dans la deuxième série chimique, le rapport Mg/Fe^{2+} est fonction de la teneur en Al. La muscovite montre la substitution variable de Fe^{2+} à Mg, ainsi que celle de Na à K. Quant à la genèse, la céladonite se forme à partir de minéraux ferromagnésiens de roches basiques, dans lesquelles la phlogopite (ou une pâte riche en K) était originellement présente. À un degré plus élevé de métamorphisme, les roches dont le plagioclase a été albitisé produisent pumpellyite, épidote et "leucocéladonite". Comme la substitution de Al à Fe et Mg continue, elle conduit à la formation de leucophyllite, phengite et, finalement, muscovite. L'augmentation de Al s'observe aussi dans l'épidote. La paragonite se forme à température plus élevée, lorsque l'albite se décompose et perd son Na.

(Traduit par la Rédaction)

Mots-clés: micas dioctaédriques, céladonite, leucocéladonite, leucophyllite, phengite, triassique, roches métavolcaniques, Grèce occidentale.

INTRODUCTION

The external Hellenides of western Greece contain a suite of Triassic mafic volcanic rocks (Table 1; Pe-Piper 1982) that have undergone varying degrees of low-grade (principally greenschist) metamorphism. These metavolcanic basic rocks contain several different types of K-bearing mica. The chemical properties and petrographic relationships of these micas are the subject of this paper.

The Triassic volcanic rocks of western Greece have a very limited areal extent (Fig. 1). Outcrops in Lakonia (Pe-Piper & Kotopouli 1981), Kalamae, Zarouhla and Tyros (Pe-Piper 1983b, 1984) are in the Phyllite Series of the Gavrovo–Tripolitsa zone (Panagos *et al.* 1979); the Lakmon Mountain outcrops (Pe-Piper 1983a) are in the tectonically overlying Pindos Nappe, and the volcanic rocks of Melidoni (Pe-Piper *et al.* 1981) and Epidavros are located further east in the Pelagonian zone. All of these areas, except for Epidavros, consist predominantly of mafic rocks.

The metamorphic facies of the mafic volcanic rocks are summarized by Pe-Piper (1982) and in Figure 2. Rocks of the Lakmon Mountains contain fresh primary feldspar and pyroxene. Celadonite and vermiculite are the main metamorphic phases (Pe-Piper 1983a). The Phyllite Series rocks are tectonized and more highly metamorphosed. Neither primary feldspar nor orthopyroxene is preserved, and only rare clinopyroxene relics occur. The predominant metamorphic assemblage from Lakonia is chlorite + epidote ± pumpellyite, together with albite, quartz, hematite, calcite and K-bearing mica. Actinolite is a rare accessory. A similar assemblage

TABLE 1. SUMMARY OF MINERALOGY OF SAMPLES USED IN THIS STUDY

Locality	References	Rock #	Rock Type	Micas	Other Secondary Minerals	Mica Xtallinity (Kübler)(*)
Lakmon	1,2	LK827	B	Cel	Sme	
		LK831	A	Cel	-	
		LK842	A	Cel	Vrm	
		LK847	A	Cel	-	4.4
		LK851	A	Cel,H-Cel	Vrm	
Kalamae	1,3,4	KV1	B	L-Cel,Leuc	Lws,Ep,Chl, Pmp	
		KV4	B	Ph	Chl,Pmp,Ep	
		KV5	B	Leuc	Chl,Ep	
Lakonia	1,5,6	D5	B	Ph,Leuc	Chl,Cal,Kfs	4.0
		D7	B	Leuc	Cal	4.4
		D8	B	Ph	Chl,Pmp,Ep	
		D11	B	Cel	Chl,Ep	3.6
		L7	B	Leuc,Ph	Chl,Ep	4.9
Tyros	1,4	T15	AG	Ms-Pg	Chl,Ep	
		T32	AG	Ms-Pg	Ep,Chl,Tur	
		T38	B	?	Chl,Ep	3.8
Zarouchla	1,4	ZV3	B	Leuc	Chl,Pmp	
Melidoni	1,7	MEL12	A	L-Cel,Ph	Chl,Pmp,Ttn, Cal	
		MEL14	B	L-Cel	Chl,Ep,Pmp, Cal	
Epidavros	1,8	EP19A	R		-	
		EP27	R		Chl	

References: 1 Pe-Piper (1982), 2 Pe-Piper (1983a), 3 Pe-Piper (1984), 4 Fytrolakis (1970), 5 Pe-Piper & Kotopouli (1981), 6 Pe-Piper *et al.* (1982), 7 Pe-Piper *et al.* (1981), 8 Bannert & Bender (1968).
Rock types: B (basalt), $SiO_2 < 53\%$; A (andesite), $53 < SiO_2 < 62\%$; R (rhyodacite), $SiO_2 > 62\%$ (wt.); AG agglomerate. Minerals: Cal calcite, Cel celadonite, Chl chlorite, Ep epidote, H-Cel hydrated celadonite, Kfs K-feldspar, Lws lawsonite, L-Cel "leucoceladonite", Leuc leucophyllite, Na-Ph sodic phengite, Pg paragonite, Ph phengite, Pmp pumpellyite, Sme smectite, Ttn titanite, Tur tourmaline, Vrm vermiculite. Quartz, albite and hematite are almost always present, except in samples from the Lakmon Mountains and Epidavros. * Determined on the < 2 μm fraction of powdered samples, following Kübler (1968).

is present at Zarouhla (except that epidote may be absent), and at Kalamae (where lawsonite is present in some samples). Tyros has chlorite + epidote or chlorite + clinozoisite, with pumpellyite absent, and paragonite in some samples. A chlorite + epidote + pumpellyite assemblage is also found at Melidoni (Pe-Piper *et al.* 1981).

Some of the rocks studied show retrograde metamorphism, represented by local hydration of celadonite and phengite (Pe-Piper & Kotopouli 1981) and alteration of celadonite to vermiculite (Pe-Piper & Kotopouli 1981, Pe-Piper 1983a).

The purpose of this investigation is 1) to define the P–T conditions under which different K-micas occur in low-grade mafic metavolcanic rocks, 2) to evaluate the range of solid solution and the nature of atomic substitutions in the micas, and 3) to establish the metamorphic reactions leading to the development of the micas in low-grade mafic metavolcanic rocks.

METHODS

This study is based principally on electron-microprobe analyses of about 200 grains of K-bearing mica from about 20 different samples. Almost all the crystals analyzed are at least 100 μm across. The analyses were carried out by wavelength-dispersion spectrometry on a Cambridge Microscan 5 electron microprobe. Natural minerals and synthetic standards were used in calibration, and the data were reduced using the EMPADR VII program (Rucklidge & Gasparrini 1969).

Where very similar results were obtained from different crystals in the same sample, data for only one representative sample are reported. This resulted in a set of about 80 compositions. Of these, 25% were rejected as having been altered by retrograde metamorphism, using the criterion that K + Na is less than 1.65, or that the total of the microprobe determinations (sum of SiO_2, TiO_2, Al_2O_3, FeO_t, MnO, MgO, CaO, Na_2O, K_2O) is less than 93% (*i.e.*, >7% volatiles). Twelve representative compositions of this final set of sixty-two are shown in Table 2. The complete data-set is available on request from the author.

Mineral separation for an X-ray investigation was attempted. Unfortunately, only small samples are available for this purpose, and separates were contaminated with groundmass mica. As a result, no useful X-ray patterns could be obtained.

NOMENCLATURE

Compositions of most natural K-bearing dioctahedral micas can be expressed in terms of three components (Fig. 3): celadonite $K_2Fe_2^{3+}Mg_2(Si_8O_{20})(OH)_4$, leucophyllite $K_2Al_2Mg_2(Si_8O_{20})(OH)_4$ and muscovite $K_2Al_4(Si_6Al_2O_{20})(OH)_4$ (Deer *et al.* 1971, Guidotti & Sassi 1976). Velde (1965) used the term *celadonite* for any dioctahedral mica with the general formula $K_2R_2^{3+}R_2^{2+}(Si_8O_{20})(OH)_4$, naming individual species for the R^{3+} and R^{2+} ions. Thus celadonite as listed above is FeMg celadonite, and leucophyllite is AlMg caledonite in Velde's nomenclature. Phengite is intermediate in composition between muscovite and leucophyllite. Na may replace K in the muscovite structure to yield paragonite $Na_2Al_4(Si_6Al_2O_{20})(OH)_4$, but Na-for-K substitution in the other phases is minor.

Many of the samples studied have compositions intermediate between celadonite, leucophyllite and muscovite; the terms celadonite, "leucoceladonite", leucophyllite and phengite have been used to describe the particular compositional ranges shown in Figure 3. The boundaries between these compositional ranges are arbitrary. Samples have been located in Figure 3 on the basis of their Si and Al content, since these are the two elements that show the least replacement by other elements.

Because the oxidation state of iron is not determined by electron microprobe, the partitioning of iron between Fe^{2+} and Fe^{3+} has been estimated from Si content. For an ideal composition within the celadonite - leucophyllite - muscovite composition space, both Al + Fe^{3+} and Mg + Fe^{2+} are fixed for any particular value of Si. Since both Al and Mg are

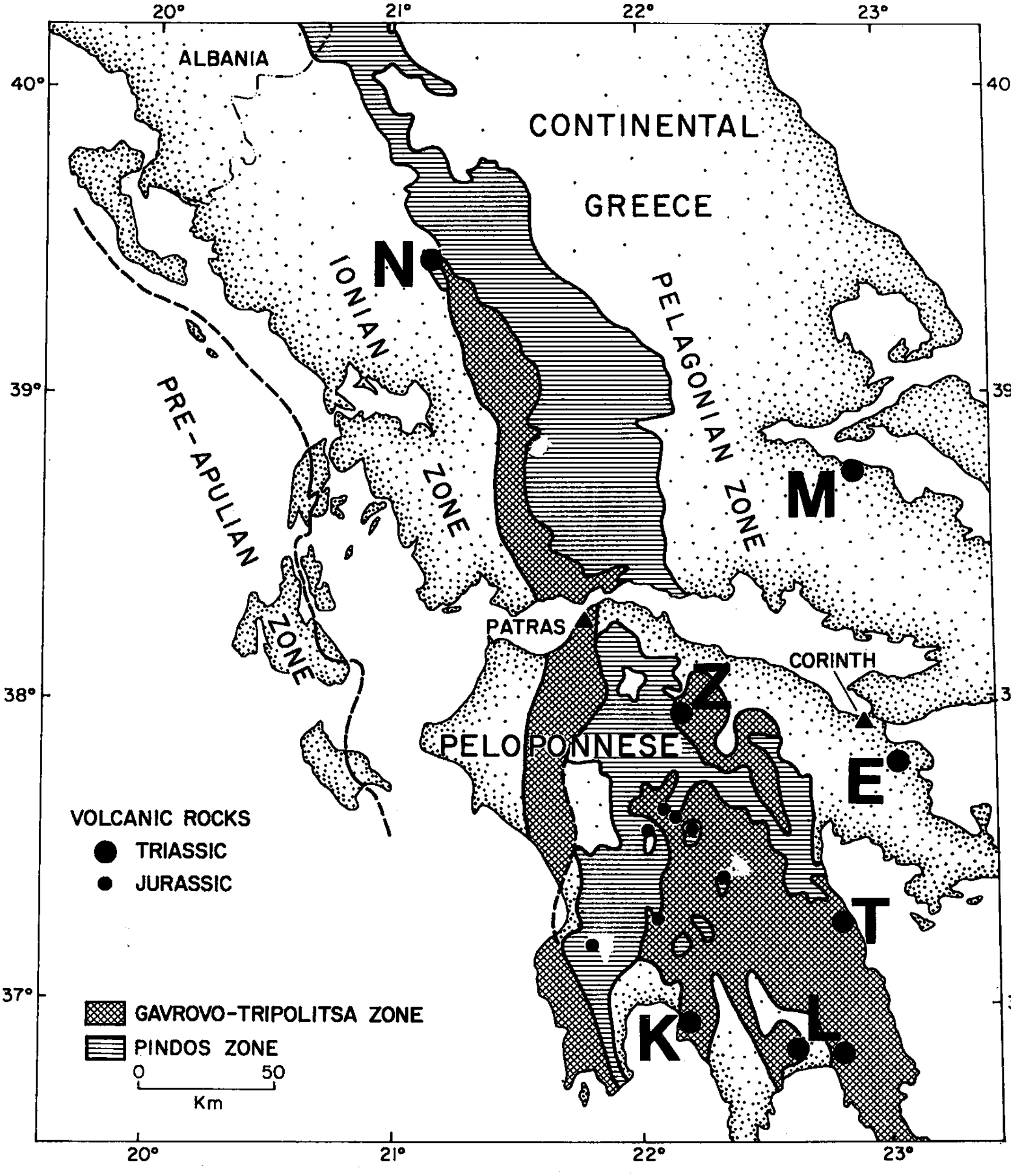

FIG. 1. Generalized geological map of western Greece showing major tectonic zones and sample locations (large dots). E Epidavros, K Kalamae, L Lakonia, N Lakmon Mountains, M Melidoni, T Tyros, Z Zarouhla.

determined, the partitioning of Fe can be estimated, and can be checked against total Fe determined by analysis. In almost all analyses that meet the criteria mentioned above ($K + Na > 1.65$; volatiles $<7\%$), calculated and observed amounts of total Fe lie within the limits set by analytical precision. This suggests that substitutions not within the plane of celadonite – leucophyllite – muscovite (except for muscovite – paragonite) are minor. The few samples where the difference between observed and calculated Fe exceed 0.22 have been omitted.

CHEMICAL VARIATION

Most analyzed samples are chemically similar to K-mica previously analyzed by Wise & Eugster

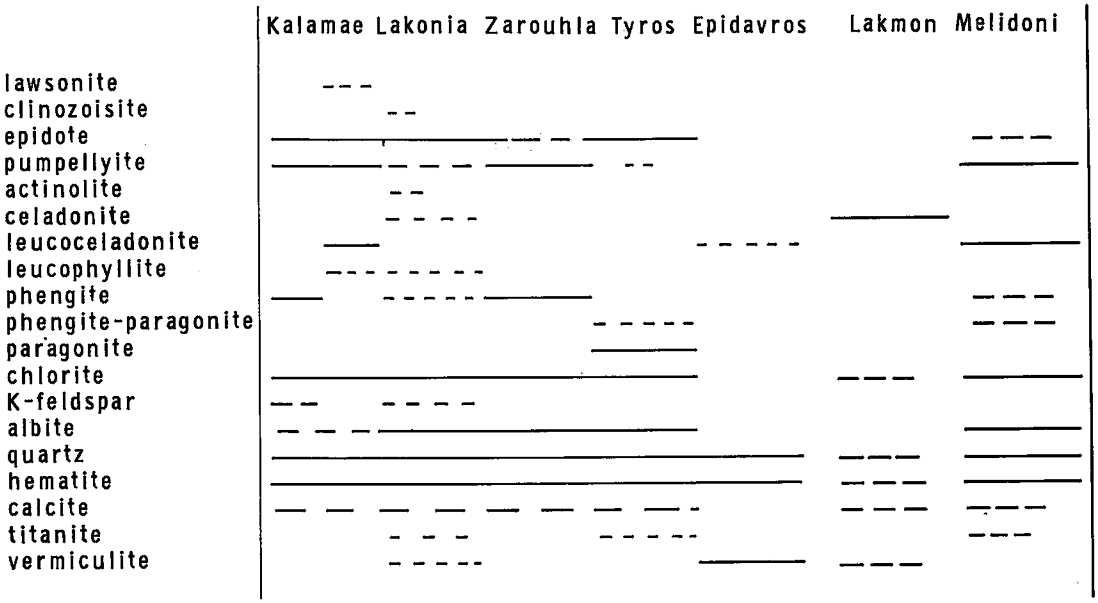

FIG. 2. Mineral assemblages associated with K-bearing micas at the localities studied.

TABLE 2. REPRESENTATIVE COMPOSITIONS OF MICAS, AS DETERMINED BY ELECTRON MICROPROBE

	L-Cel 3	Leuc 8	Ph 16	L-Cel 18	Ph 21	Cel 28	Cel 40	Pg-Ms 44	Pg-Ms 45	Pg-Ms 47	Pg-Ms 49	Leuc 58	Cel 73
SiO_2	55.11	51.92	49.66	53.97	48.07	56.73	57.28	54.19	47.59	46.39	46.26	53.25	53.69
TiO_2	0.00	0.00	0.00	0.00	0.00	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.33
Al_2O_3	14.85	21.10	28.34	14.01	33.41	4.87	2.11	29.33	33.69	35.11	37.63	19.59	2.80
Fe_2O_3	7.66	6.97	3.25	9.80	1.60	17.05	20.33	1.64	3.19	2.02	1.39	5.99	21.28
MnO	0.00	0.00	0.00	0.00	0.26	0.00	0.11	0.00	0.00	0.00	0.00	0.00	0.09
MgO	5.95	4.77	1.91	5.73	0.56	7.24	8.22	0.54	1.05	0.39	0.10	4.63	6.35
CaO	0.08	0.00	0.00	0.07	0.12	0.13	0.04	0.08	0.09	0.08	0.20	0.00	0.50
Na_2O	0.00	0.06	0.12	0.00	0.60	0.00	0.05	5.06	2.26	5.38	6.96	0.24	0.00
K_2O	10.50	10.40	10.43	11.06	10.13	10.00	10.48	6.47	8.24	4.03	2.12	10.01	9.21
Total	94.15	95.22	93.71	94.64	94.75	96.20	98.62	97.31	96.11	93.40	94.66	93.71	94.25
Si	7.541	7.015	6.714	7.446	6.399	7.855	7.858	6.930	6.252	6.163	6.019	7.257	7.730
Ti	0.000	0.000	0.000	0.000	0.000	0.019	0.000	0.000	0.000	0.000	0.000	0.000	0.036
Al	2.396	3.361	4.517	2.279	5.244	0.795	0.341	4.422	5.218	5.499	5.772	3.148	0.475
Fe^{3+}	0.789	0.709	0.330	1.018	0.160	1.776	2.099	0.158	0.315	0.202	0.136	0.614	2.036
Mn	0.000	0.000	0.000	0.000	0.029	0.000	0.013	0.000	0.000	0.000	0.000	0.000	0.011
Mg	1.213	0.961	0.385	1.178	0.111	1.494	1.681	0.103	0.206	0.077	0.019	0.940	1.363
Ca	0.012	0.000	0.000	0.010	0.017	0.019	0.006	0.011	0.013	0.011	0.028	0.000	0.077
Na	0.000	0.016	0.031	0.000	0.155	0.000	0.013	1.255	0.576	1.386	1.756	0.063	0.000
K	1.833	1.793	1.799	1.947	1.721	1.766	1.834	1.056	1.381	0.683	0.352	1.740	1.692
^{IV}Al Calc	0.46	0.98	1.29	0.55	1.60	0.15	0.14	1.07	1.75	1.84	1.98	0.74	0.27
^{VI}Al Calc	1.94	2.38	3.23	1.73	3.64	0.65	0.20	3.35	3.47	3.66	3.79	2.40	0.21
Fe^{3+}calc	0.52	0.61	0.05	0.83	-0.04	1.50	1.94	-0.28	0.28	0.18	0.19	0.34	2.06
Fe^{2+}calc	0.33	0.05	0.33	0.27	0.29	0.36	0.18	0.83	0.05	0.09	-0.00	0.32	0.37
Δ Fe	-0.06	0.05	-0.05	-0.08	-0.09	-0.08	-0.02	-0.39	-0.01	-0.06	-0.05	-0.04	-0.13

Δ Fe is difference between determined and calculated Fe.
Key to samples: 3,8 KV1. 16 KV4. 18 MEL 14. 21 MEL 12. 28 LK 851. 40 LK 842. 44 T38. 45 T15. 47 T32. 49 T32. 58 L7. 73 LK 842.

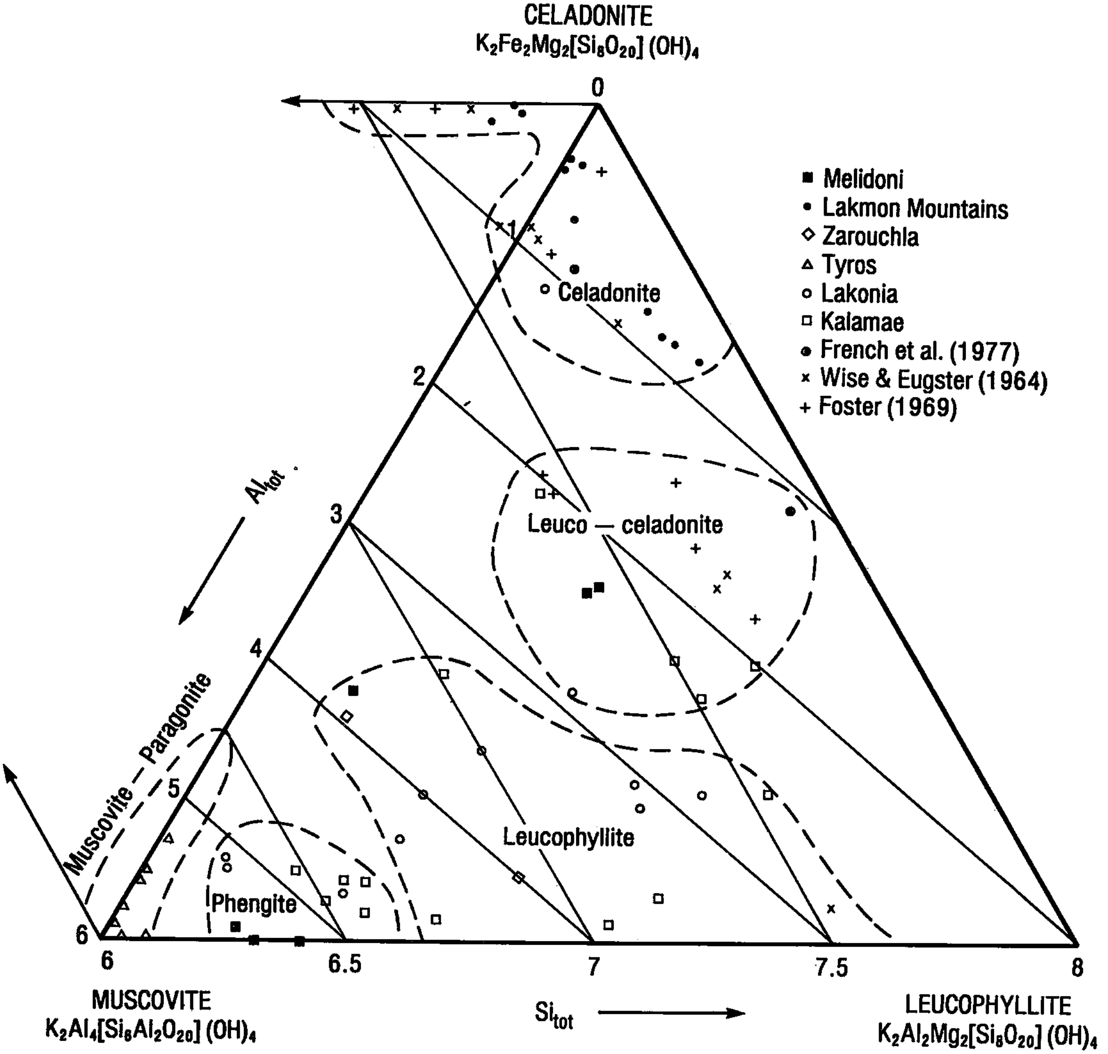

FIG. 3. Celadonite-leucophyllite-muscovite triangular diagram, showing composition of samples from western Greece and samples of celadonite and related minerals reported by French *et al.* (1977), Foster (1969) and Wise & Eugster (1964). Samples plotted on basis of Si and Al composition. Boundaries between groups of compositions that are given different names are located in compositional gaps, but are otherwise arbitrary.

(1964), Foster (1969) and French *et al.* (1977) (Fig. 3). Most of the analyzed grains fall within the celadonite - leucophyllite - muscovite field. Some celadonite compositions (*cf.* Wise & Eugster 1964, Foster 1969) reveal an apparent deficiency in total Al + Si, so that they plot outside the muscovite-celadonite-leucophyllite field in Figure 3 (*e.g.*, composition 40, Table 2). They show up to 15% substitution of a ferrimuscovite component $K_2Fe_4^{3+}Si_6Al_2O_{20}(OH)_4$.

A variety of scatter plots of pairs of elements or groups of elements have been examined in order to assess chemical variability and element substitution. Only a few of these plots are illustrated here. Some plots, such as Si against (^{IV}Al + Na + K), show a reasonable straight-line distribution with little scatter. Plots involving the element Mg, such as (Si + Mg) against total Al, (Mg + Ti) against 2 ^{VI}Al, and ^{VI}Al against Mg, also show a reasonable straight-line distribution for all micas except celadonite and muscovite-paragonite, where there is considerable scatter.

The cause of this scatter is illustrated in Figure 4, which shows total Al against Mg/Fe^{2+}. (The Fe^{2+} is a calculated value, and should therefore be treated with caution). This shows that for muscovite -

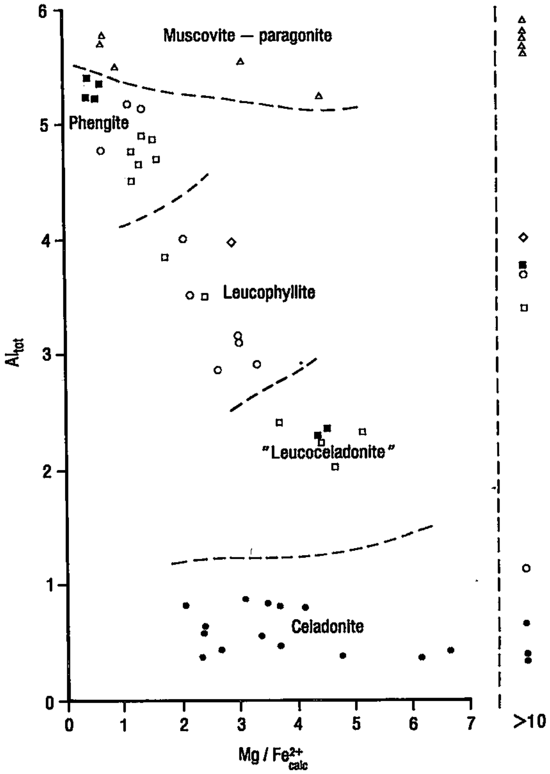

FIG. 4. Plot of Al *versus* Mg/Fe^{2+} for micas from western Greece. Symbols as in Figure 3 (Fe^{2+} is calculated).

paragonite and for celadonite there appears to be random substitution of Fe^{2+} for Mg, whereas in "leucoceladonite", leucophyllite and phengite, the extent of substitution of Fe^{2+} for Mg is dependent on the Al content. The only exception is a small group of phengite compositions (from four different localities) that are essentially lacking in Fe^{2+}.

This separation of muscovite–paragonite and celadonite from the other micas also is illustrated in a plot of total Al against Si + Mg + Mn + Fe^{2+} (Fig. 5). This figure shows muscovite–paragonite compositions lying close to the muscovite–celadonite join. Kanehira & Banno (1960) and Velde (1965) demonstrated that muscovite does not contain more than 25% celadonite substitution; the compositions reported here show no more than 15% substitution, which is shown as the "theoretical limit" by Velde (1965, his Fig. 4). Similarly, celadonite compositions lie close to this join, although they do show rather more scatter. However, phengite, leucophyllite and "leucoceladonite" show increasingly positive deviation from the muscovite–celadonite join, although they do not lie close to the stoichiometric muscovite–leucophyllite join. In all the scatter plots used, there is only one major compositional gap, between celadonite and "leucoceladonite".

Except for samples of phengite and muscovite, the sodium content of the micas is generally too small to determine and never exceeds 0.06% Na_2O. The sodium content of phengite attains 0.6% Na_2O (7.5% paragonite component) (#21, Table 2). The sodium content of the muscovite–paragonite lies between 2.3 and 7.0% Na_2O (between 30% and 75% paragonite component). (No pure K-muscovite has been found.) In some muscovite–paragonite, the total alkalis are substantially in excess of stoichiometric values (from 2.1 to 2.4); many of these alkali-rich compositions show poor agreement between observed and calculated Fe (*e.g.*, #44, Table 2), and thus do not lie in the celadonite–leucophyllite–muscovite composition plane. The paragonite occurs as relatively large, optically clean crystals, so that the excess in alkalis is not likely due to a dispersed microcrystalline phase.

SOLID SOLUTION AND CHEMICAL SUBSTITUTION

In the absence of X-ray data, a definitive discussion of the structure of the various micas is not possible. However, certain conclusions can be drawn from the detailed chemical data presented here.

The celadonite structure may be distinct from that of the other K-rich micas; celadonite compositions show a distinctive behavior on various scatter-plots, and there is a substantial compositional gap between celadonite and "leucoceladonite". Limited substitution into the ideal celadonite structure is possible, of Fe^{3+}Al for MgSi, and of ^{IV}Al ^{VI}Al for Fe^{3+}Si (Fig. 3). There is much greater substitution of Fe^{2+} for Mg^{2+} than in the other K-micas, and this substitution is independent of Al content. The celadonite structure thus appears capable of incorporating the relatively large Fe^{3+} and Fe^{2+} ions.

Mica samples containing phengite, leucophyllite and "leucoceladonite" components appear to have a common composition that allows a systematic substitution of Al for (Mg, Fe^{2+}) Si, possibly forming a solid-solution series. The substitution of Fe^{2+} for Mg is dependent on Al content. The best-fitting linear trend through the compositions shown in Figures 4 and 5 does not pass through any of the muscovite, leucophyllite or celadonite end-member compositions.

With the aluminous species, there is up to 8% substitution of Na for K in phengite, and up to 75% substitution in muscovite, to yield the paragonite–muscovite solid-solution series. Paragonite–muscovite shows slight substitution of Fe^{3+} Mg Si for ^{IV}Al ^{VI}Al (along the muscovite–celadonite join in Figures 3 and 4), but no substitution of Mg in the absence of Fe^{3+} (*i.e.*, no leucophyllite component). Substitution of Fe^{2+} for Mg^{2+} appears to be random, in contrast to the phengite compositions. Thus the muscovite-paragonite structure may be different from that of phengite-leucophyllite-"leucoceladonite".

In his experimental work, Velde (1965) recognized a distinction between muscovite, "$Fe^{2+}Fe^{3+}$ celadonite" and the "$Fe^{2+}Al$ celadonite"-muscovite series, with the latter two showing no solid solution in muscovite. The "$MgFe^{2+}$ celadonite" component (*i.e.*, the celadonite of this paper) shows some solid solution with muscovite, particularly at high pressures.

There is a small group of compositions of phengite and leucophyllite that contain essentially no Fe^{2+} substituting for Mg (*e.g.*, #8, Table 2), and thus form a distinct cluster in Figure 4. The significance of these compositions is uncertain.

Petrography of the Micas

K-bearing micas occur in four main forms: (1) large crystals that are an alteration product of phenocrysts of ferromagnesian minerals (Pe-Piper 1983a) and possibly feldspar, or of glass in the groundmass (Fig. 6), (2) large crystals filling amygdales (Figs. 7, 8), (3) as large neomorphic minerals (Fig. 9), and (4) as fine-grained groundmass. Color varies according to the iron content of the minerals, ranging from green or blue for celadonite to colorless for phengite and muscovite.

In the low-grade metamorphic rocks of the Lakmon Mountains, clinopyroxene and plagioclase phenocrysts are partly replaced by celadonite. Phlogopite in these rocks is also partly altered to celadonite and may thus be the source of potassium for the celadonite. Patches of groundmass in the Lakmon Mountain samples that are altered to celadonite may originally have been glass.

Crystals or crystal aggregates of mica are in places rimmed by retrograde metamorphic products, commonly hydrated phyllosilicates. Hydrated celadonite (Fig. 6) and vermiculite (Pe-Piper 1983a) rim celadonite in the Lakmon Mountain samples. Vermiculite rims celadonite, and hydrated phengite rims phengite in the Lakonia samples (illustrated in Pe-Piper & Kotopouli 1981, Fig. 6). Elsewhere, more sodic or aluminous phases rim the micas. Examples include sodic phengite rimming phengite in the Melidoni samples and phengite rimming leucophyllite from Lakonia (Fig. 9).

More complex relationships between mica phases are also illustrated in Figures 6-9. Mixed leucophyllite and chlorite are rimmed by a zone of chlorite and then an outer rim of pure leucophyllite in a sample from Lakonia (Fig. 8). A sample from Kalamae has euhedral lawsonite and leucophyllite in a mass of "leucoceladonite" crystals (Fig. 7).

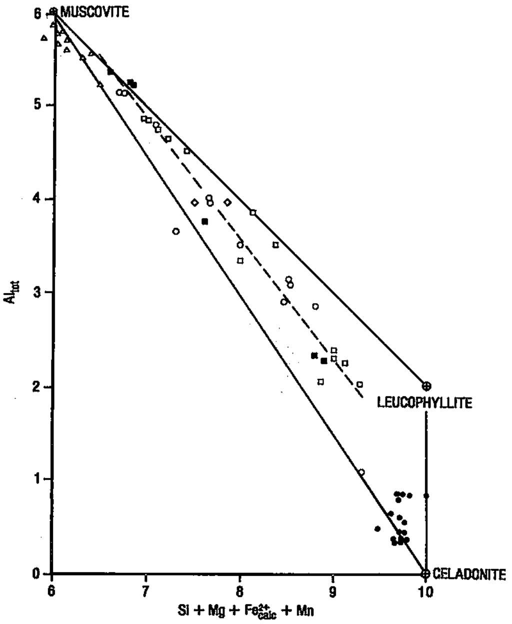

FIG. 5. Plot of Al *versus* $Si + Mg + Mn + Fe^{2+}$ for micas from western Greece. Symbols as in Figure 3. Dashed line is trend of phengite-leucophyllite-"leucoceladonite" compositions. Amount of Fe^{2+} is calculated.

Factors Controlling Mica Composition

Metamorphic grade

Independent estimates of metamorphic grade of host rocks can be made from the mineral assemblages discussed above and summarized in Figure 2. The presence of unaltered pyroxene and feldspar at Lakmon suggests that these rocks are almost unmetamorphosed. The abundance of paragonite and clinozoisite at Tyros indicates higher temperatures than the chlorite-epidote-pumpellyite assemblage of Lakonia, Kalamae, Zarouhla and Melidoni. Degree of crystallinity, estimated from X-ray diffractograms using the method of Kübler (1968), increases from the Lakmon Mountains through Lakonia to Tyros (Table 1).

Celadonite is found in the lowest-grade metamorphosed mafic volcanic rocks at Lakmon. It also occurs in two samples from Lakonia. Pumpellyite is absent in the rocks with celadonite. Muscovite-paragonite is present in the highest-temperature assemblages at Tyros. "Leucoceladonite" is common at Melidoni, and also occurs with lawsonite at Kalamae. It is also common in minerals reported by Foster (1969). Phengite and leucophyllite occur at Lakonia, Zarouhla, Kalamae and Melidoni.

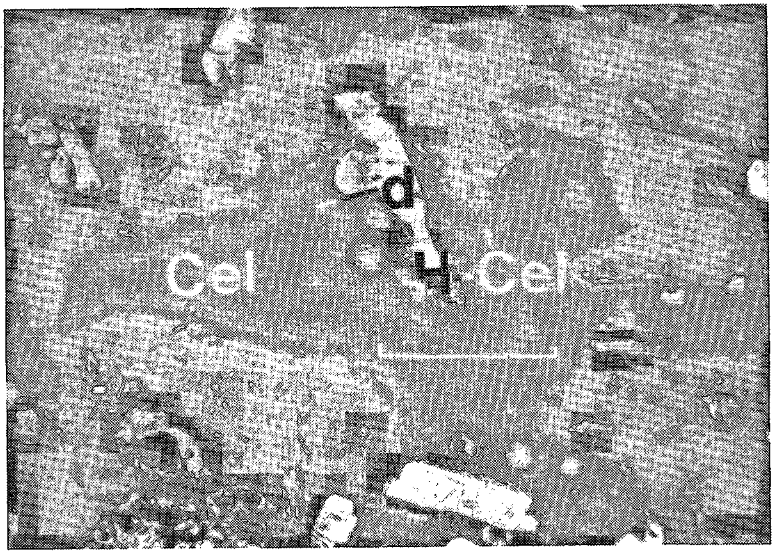

FIG. 6. Blue-green celadonite (Cel) rimmed by a dusty zone (d) of quartz and celadonite and then by light green hydro-celadonite (H-cel) replacing groundmass (possibly originally glass). 851, andesite, Lakmon Mountains. Plane-polarized light. Scale bar 1 mm.

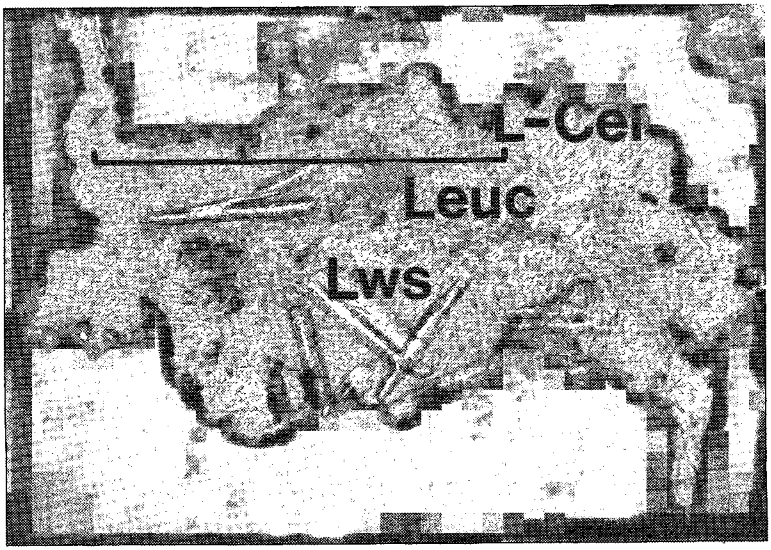

FIG. 7. Amygdale or phenocryst pseudomorph filled with leucoceladonite (L-Cel) with euhedral lawsonite (Lws) and leucophyllite (Leuc). KVI, basalt, Kalamae. Plane-polarized light. Scale bar 1 mm.

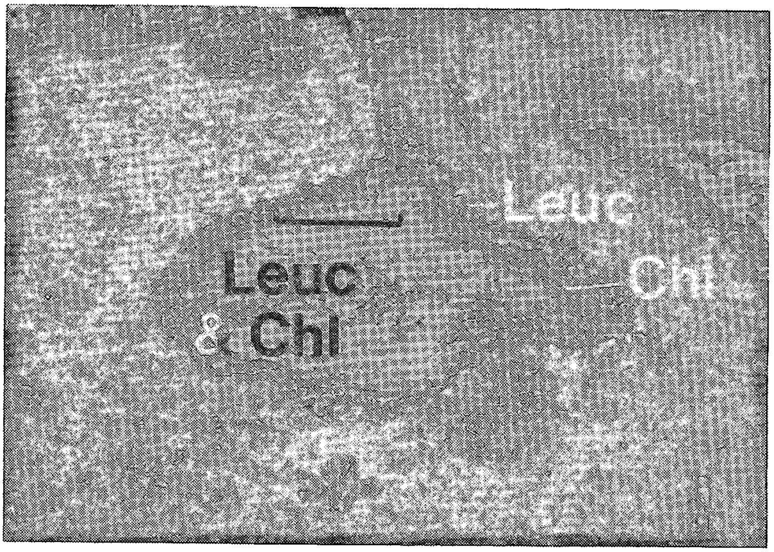

FIG. 8. Leucophyllite (Leuc) and chlorite (Chl) rimmed by a dusty zone of chlorite (Chl) and then leucophyllite (Leuc), apparently filling an amygdale. D5, basalt, Lakonia. Plane-polarized light. Scale bar 1 mm.

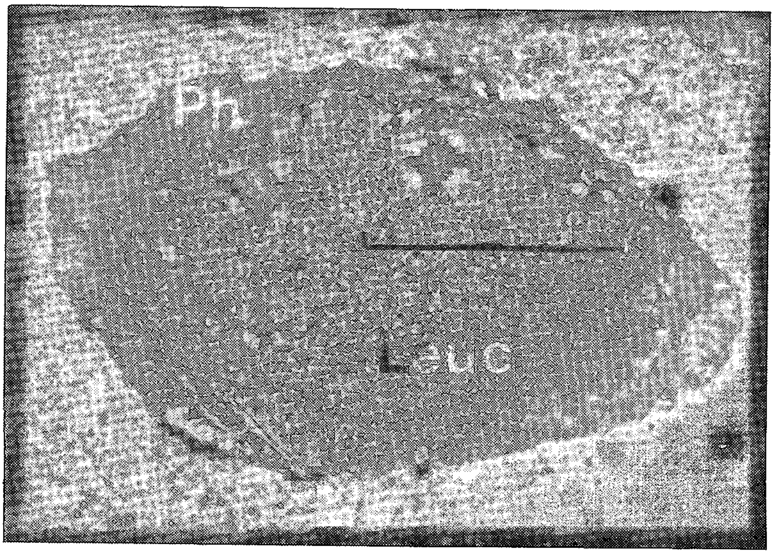

FIG. 9. Leucophyllite (Leuc), in part as spherules, rimmed by phengite (Ph), in places sodium-rich. L7, basalt, Lakonia. Crossed polars. Scale bar 1 mm.

Both the regional variation of mica minerals with metamorphic assemblage and the petrographic relationships described above suggest that there is a prograde metamorphic development of increasingly aluminous micas, from celadonite to the "leucoceladonite" - leucophyllite - phengite series and finally to muscovite - paragonite. Retrograde metamorphism leads to the formation of vermiculite (Pe-Piper 1983a) or hydrated mica (Pe-Piper & Kotopouli 1981).

Host-rock composition

Within individual sample-areas, rocks that are more felsic tend to contain a mica closer to muscovite in composition. Thus, for example, at Melidoni (Pe-Piper *et al.* 1981), basalts and andesites contain "leucoceladonite" with rare phengite, whereas dacites contain phengite zoned outward to sodic phengite. The virtually unmetamorphosed rocks at Epidavros and Lakmon are of similar metamorphic grade. They contain vermiculite and lack epidote. The basalts and andesites at Lakmon contain celadonite; the rhyodacites at Epidavros contain "leucoceladonite".

RELATIONSHIP OF MINERAL CHEMISTRY TO METAMORPHIC GRADE

The petrographic observations and inferred paragenetic sequence of minerals allow inferences on the metamorphic reactions involved in the development of micas in the rocks studied. Celadonite develops from ferromagnesian minerals, particularly pyroxene, with K derived from alteration of a potassium-bearing groundmass or of biotite to chlorite. "Leucoceladonite" develops by substitution of Al for Fe in celadonite. Al is released by the albitization of plagioclase, with Ca and Fe accommodated in pumpellyite and epidote. Continued replacement of Fe and Mg by Al leads to leucophyllite, phengite and, eventually, muscovite. There is a parallel development in epidote (Fig. 10), which shows a progressive buildup in Al and decrease in Fe as the micas become more aluminous. Sodic phengite and paragonite develop at higher temperatures, as Na is released from albite. Representative equations for these reactions are given in Table 3.

CONCLUSIONS

K-bearing dioctahedral micas with a wide range of chemical composition are found in potassium-rich mafic rocks that have undergone greenschist-facies metamorphism. The micas become progressively more aluminous with increasing metamorphic grade. However, the key reactions involve phases of very variable composition, notably mica and epidote. Thus, although representative chemical equations can be written for the inferred reactions (*e.g.*, Pe-Piper & Kotopouli 1981), they neither provide additional insight into the metamorphic reactions nor

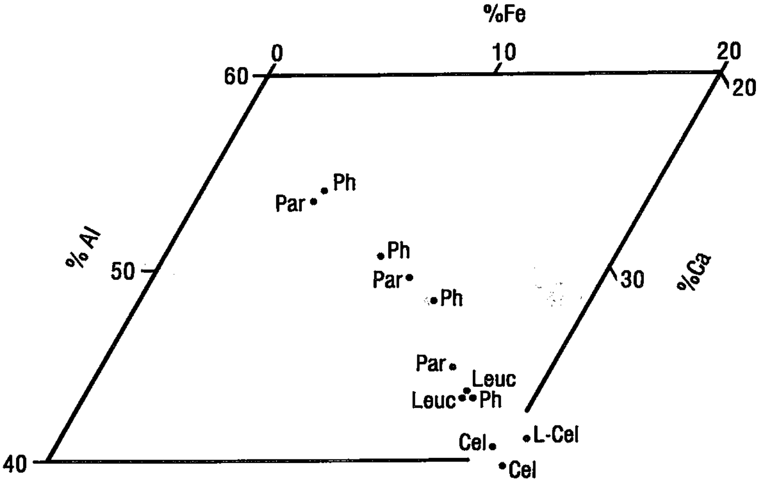

FIG. 10. Epidote compositions plotted on an Al–Ca–Fe triangular diagram, showing compositions associated with each type of mica. Cel celadonite, L-Cel "leucoceladonite", Leuc leucophyllite, Par paragonite, Ph phengite.

TABLE 3. REPRESENTATIVE CHEMICAL COMPOSITION OF MINERALS AND THE INFERRED MASS-BALANCE CHANGES ASSOCIATED WITH INFERRED METAMORPHIC REACTIONS

Mineral Sequence	Representative Formulae	Mass-balance changes	
		Positive	Negative
Pyroxene	$Ca_{3.4}Mg_{3.4}Fe_{1.2}Al_{0.4}(Si_{7.6}O_{24})$		
Celadonite	$K_{1.7}Mg_{1.3}Fe^{2+}_{0.5}Fe^{3+}_{1.8}Al_{0.4}(Si_{7.9}O_{20})(OH)_4$	1.7K 1.1Fe 0.3Si	3.4Ca 2.1Mg
Leuco-celadonite	$K_{1.9}Mg_{1.2}Fe^{2+}_{0.3}Fe^{3+}_{0.8}Al_{2.3}(Si_{7.5}O_{20})(OH)_4$	0.2K 1.9Al	0.1Mg 1.2Fe 0.4Si
Phengite	$K_{1.8}Mg_{0.4}Fe^{2+}_{0.3}Al_{4.5}(Si_{6.5}O_{20})(OH)_4$	2.2Al	0.1K 0.8Mg 0.8Fe 0.8Si
Plagioclase(An_{50})	$CaNaAl_3Si_5O_{16}$		
Albite	$Na_2Al_2Si_6O_{16}$	1.0Na 1.0Si	1.0Ca 1.0Al
Biotite	$K_{1.4}Na_{0.4}Mg_{4.8}Fe_{0.8}Ti_{0.1}(Al_2Si_6O_{20}(OH)_4$		
Chlorite	$Na_{0.1}Mg_{6.8}Fe_{1.9}(Al_{3.3}Si_7O_{20})(OH)_{16}$	2.0Mg 1.1Fe 1.3Al 1.0Si	1.4K 0.3Na 0.1Ti
Pyroxene	$Ca_{3.4}Mg_{3.4}Fe_{1.2}Al_{0.4}(Si_{7.6}O_{24})$		
Fe-epidote	$Ca_4Fe_2Al_4(Si_6O_{11})(OH)$	0.6Ca 0.8Fe 3.6Al	3.4Mg 1.6Si
Al-epidote	$Ca_4Fe_{0.6}Al_5(Si_6O_{11})(OH)$	1.0Al	1.4Fe

allow calibration with experimentally determined phase-equilibria. Many of the micas are pseudomorphs of phenocrysts or fill amygdales, and mica type is dependent on bulk-rock composition at any one metamorphic grade. These observations suggest that local equilibria under the low-grade metamorphic conditions may be important in determining what type of mica is present.

Some indication of the range of temperature and pressure conditions is given by Velde's (1972) determination of 420°C as the temperature of maximum stability for celadonite. Chatterjee (1973) determined that paragonite + quartz is unstable below 335°C at 2 to 7 kbar.

Mineral chemistry suggests that there are three structurally distinct mineral phases. In both celadonite and muscovite, there is a range of substitution of Fe^{2+} for Mg; in contrast, in the leucoceladonite-leucophyllite-phengite series, the Fe^{2+}/Mg ratio is dependent on the Al content. In this series there is probably solid solution with systematic substitution of Al for (Mg, Fe^{2+}) Si. Although there is limited substitution of Na for K in phengite, only in muscovite is there extensive solid-solution with paragonite.

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