

SIGNIFICANCE OF PHENGITIC MICAS FROM
LOW-GRADE SCHISTS

W. G. ERNST, *Department of Geology and Institute of Geophysics
and Planetary Physics, University of California,
Los Angeles 24, California.*

ABSTRACT

Many dioctahedral micas from glaucophane schists and low-grade greenschists are high in silica, low in alumina and contain several percent MgO, FeO and Fe₂O₃. Such micas, representing solid solution between muscovite and celadonite, are appropriately referred to as phengites. Seven new chemical analyses of white micas are presented. Optical and x-ray data have been determined for these and several other analyzed specimens. 2M₁ polymorphs of phengite examined in this study have relatively short interlayer spacings.

The paragenetic relationship of several layer-lattice silicates in blueschist and greenschist facies rocks is thought to be controlled by the reaction: 8 phengite + chlorite = 5 muscovite + 3 biotite + 7 quartz + 4 H₂O. The phengite + chlorite assemblage is favored by high ratios of fluid pressure ($\approx P_{H_2O}$) to total pressure, and by low temperatures. At constant pressure, increased temperature causes diminution of the compositional range of white mica. The phase relations among layer-lattice silicates written above is a multi-variant function of rock bulk composition as well as physical conditions attending the recrystallization. The reaction may represent the biotite isograd of some pelitic schists.

INTRODUCTION AND ACKNOWLEDGMENTS

In the course of a study concerning coexisting minerals in glaucophane schists and related rocks, it became apparent that most of the associated white micas have compositions differing significantly from that of normal muscovite. These micas generally are pale greenish or pinkish in color due to the presence of essential iron (and magnesium); they are characteristically Al-poor and Si-rich. Such micas, essentially high-silica sericites, are generally referred to as phengites by most authors, and will be so designated in this note.

Winchell (1927, 1949) recognized two phengite end members, picrophengite, $KMg_{0.5}Al_{1.5}Si_{3.5}Al_{0.5}O_{10}(OH)_2$, and ferrophengite, $KFe_{0.5}^{2+}Al_{1.5}Si_{3.5}Al_{0.5}O_{10}(OH)_2$. More recently Kanehira and Banno (1960) have defined these micas in terms of four end members:

- muscovite, $KAl_2Si_3AlO_{10}(OH)_2$;
- ferrimuscovite, $KFe_{0.5}^{3+}Al_{1.5}Si_3AlO_{10}(OH)_2$
- phengite, $K(Mg Fe^{2+})_{0.5}Al_{1.5}Si_{3.5}Al_{0.5}O_{10}(OH)_2$; and
- ferriphengite, $K(Mg, Fe^{2+})_{0.5}Fe_{0.5}^{3+}AlSi_{3.5}Al_{0.5}O_{10}(OH)_2$.

Schaller (1950) and Foster (1956) discussed chemical compositions of members of this group and indicated that variation, although incomplete, is between a tetrasilic end member (eg., celadonite, $KFe^{2+}Fe^{3+}Si_4O_{16}(OH)_2$) and a trisilic end member (eg., muscovite). Ferrous iron and magnesium

constitute a diadochic pair (R^{2+}), likewise Fe^{3+} and $Al(R^{3+})$. The generalized substitution relations then, are:



in other words, a divalent cation+one silicon are exchanged for two trivalent cations. Foster (1956, p. 61) stated: "It must be emphasized that in this series, proxying of octahedral trivalent ions by bivalent ions is ion-for-ion with no tendency toward filling the third unoccupied octahedral position." Glauconites may be considered as iron-rich members of the celadonite-muscovite series, but the presence of excess water, exchangeable cations, and low alkali contents suggest glauconites are more appropriately referred to as hydromicas (*e.g.*, see Sabatier, 1949); however, the same observations apply equally as well to celadonites themselves (Hendricks and Ross, 1941; Schüller and Wohlmann, 1951). Yoder and Eugster (1955, p. 257) consider glauconites and celadonites as chemically distinguishable.

Over the past few years, a number of analyses of micas from glaucophane schists and related rocks have been performed. These data indicate a rather widespread occurrence for phengites in the Alps, California Coast Ranges, and Japan (Bearth, 1959, p. 278; van der Plas, 1959, p. 475; Switzer, 1951, p. 63; Ernst, 1963a, p. 15; Iwasaki, 1960, p. 570; Kanehira and Banno, 1960; Miyashiro, 1962). Paragonite is not common, but has been described from an Alpine glaucophane schist terrain (Harder, 1956, p. 231). Biotite is absent from rocks of the blueschist (glaucophane schist) metamorphic facies (*e.g.*, see Turner and Verhoogen, 1960, p. 542); in blueschists of appropriate bulk composition phengite+chlorite apparently take the place of the typical greenschist assemblage muscovite+biotite. It should be noted, however, that phengites are not restricted to blueschist facies rocks, inasmuch as they have been reported from low-grade greenschists (*e.g.*, Lambert, 1959; Foster *et al.*, 1960).

The discovery of unusually short *c*-axis lattice dimensions for phengites from glaucophane schists and associated rocks led the author into further investigation of these micas.

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CHEMICAL DATA

Chemical analyses for members of the celadonite-muscovite series are presented in Table 1. Wherever possible, stably associated minerals are listed. Modes are not tabulated because of the unavailability of several rock specimens; in any case, the significance of this study depends on the presence or absence of phases and their compositions, not on mineral proportions. Nos. 4, 6, 8, 9, 10, 12 and 13 are new analyses; the author wishes to thank J. L. Rosenfeld for permission to publish analysis No. 10, F. R. Boyd for permission to publish analyses Nos. 12 and 13. It is apparent that silica, total iron and magnesia contents decline, alumina increases, proceeding from celadonite-glaucanite→phengite→muscovite. Structural formulas for such complex hydrous silicates can be determined uniquely from the chemical analyses only if the densities as well as cell volumes are known accurately. Lacking high accuracy density information, structural formulas can be calculated on the basis of one of several assumptions, *e.g.*,

(1) on the basis of 12.00 anions, assuming volatile analysis is correct ($O+OH+F=12.00$ per formula); (2) on the assumption that the 12-fold (alkali) position is filled

$$([K + Na + Ba + Ca + H_3O^+]_{12.00}^{XII} + [O + OH + F]_{12.00} = 13.00 \text{ per formula});$$

(3) on the anhydrous basis of 11.00 oxygens,¹ assuming $1.00(H_2O+F_2)$, or assuming that the volatile analysis is correct if the anion sum+ H_3O^+ is greater than 12.00 ($O+OH+F+H_3O^+ \geq 12.00$ per formula).

There appears to be no satisfactory means of deciding among the various methods of calculation.

Structural formulas corresponding to the chemical analyses of Table 1 are presented in Table 2; cation and anion proportions were calculated on the basis of 11.00 oxygens, and assuming analyzed volatile contents, H_2O+ , represent the true values. Ionic proportions were calculated by this method because it seems reasonable that all micas have 12.00 anions per formula. In all but three analyses, small amounts of hydronium ion are computed to be located in the alkali position. In analysis No. 3, and to a negligible extent in analyses Nos. 6 and 9, there is a deficiency of volatiles; therefore these formulas have been adjusted to contain 12.00 anions by calculating cation proportions on the basis of 12.00 ($O+OH+F$). Structural formulas of Table 2 indicate that the investigated micas are dioctahedral and conform closely to the substitution relations proposed by Schaller (1950) and Foster (1956).

Four phengites from low-grade schists and two pegmatite muscovites were analyzed for BaO. Baria contents are negligible except for two of the phengites (1.89 weight per cent in No. 7, and 1.64 weight per cent in No.

¹ *i.e.*, the formula for muscovite may be written $KAl_2Si_3A!O_{11} \cdot H_2O$.

TABLE 1. CHEMICAL ANALYSES OF MEMBERS OF THE CELADONITE-MUSCOVITE SERIES

Oxide in wt. %	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO ₂	52.53	48.66	50.50	51.08	47.28	50.60	48.30	50.18	50.45	46.50	45.25	45.74	45.55	45.87	45.24
Al ₂ O ₃	4.97	8.46	20.57	20.40	24.46	25.19	25.36	24.67	25.77	29.82	31.54	33.52	36.89	38.69	38.41
TiO ₂	0.25	—	0.76	0.95	0.30	0.51	0.20	0.47	0.12	0.18	0.36	0.31	0.26	—	0.00
Fe ₂ O ₃	18.62	18.80	6.95	4.07	8.02	2.06	4.42	3.63	0.99	1.50	1.28	2.65	0.39	—	0.00
FeO	4.58	3.98	0.00	2.75	2.52	0.76	0.20	3.04	1.60	1.86	1.21	1.58	0.86	—	0.00
MnO	0.01	—	0.82	0.06	0.08	tr	0.38	0.07	0.05	0.02	—	0.06	0.02	—	0.00
MgO	5.35	3.56	5.68	4.05	1.86	5.54	3.96	3.27	5.02	3.97	3.48	0.76	0.58	0.10	0.00
Li ₂ O	—	—	—	—	—	—	0.13	—	0.01	0.22	—	0.01	0.01	—	0.00
Cr ₂ O ₃	0.03	—	—	—	—	—	—	—	0.00	0.25	—	—	—	—	0.00
CaO	0.58	0.62	0.26	3.08	0.14	0.07	0.10	0.45	0.29	0.23	0.98	0.08	0.04	—	0.00
BaO	—	—	—	—	—	0.008	1.89	—	0.32	1.64	—	0.00	0.04	—	0.00
Na ₂ O	0.00	0.00	tr	1.16	0.11	0.93	0.50	0.67	0.56	0.37	1.61	0.67	0.80	0.64	0.00
K ₂ O	7.93	8.31	10.95	7.08	10.6	9.36	9.26	8.26	10.11	9.15	9.89	10.44	10.17	10.08	11.83
H ₂ O—	1.15	1.94	—	0.20	—	0.32	0.07	0.10	0.09	—	—	0.12	0.03	—	0.00
H ₂ O+	4.31	4.62	2.74	5.28	4.00	4.42	4.96	4.85	4.29	4.77	4.67	4.54	4.59	4.67	4.52
F	—	—	—	—	—	0.06	—	—	0.00	—	—	0.00	0.04	0.00	0.00
CO ₂	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Minor constituents	—	0.13	0.03	0.07	—	—	0.02	0.06	0.03	0.06	—	0.001	0.001	—	0.00
Total (corr. for F)	100.31	99.08	99.26	100.23	99.45	99.80	99.75	99.72	99.70	100.54	100.27	100.48	100.25	100.05	100.00

1. Celadonite from a vein in metamorphic rocks (Malkova, 1956).

2. Glauconite from dolomite (Gruner, 1935).

3. Ferriphengite from quartz+alkali feldspars+green biotite+calcite+epidote gneiss (Plas, 1959).

4. Phengite from glaucophane+chlorite+epidote+sphene+quartz schist, Kotu district, Shikoku, Japan (new analysis H. Haramura, analyst. Analyzed sample contains 3.2 per cent epidote).

5. Iron-rich muscovite from quartz+K-feldspar+plagioclase+sphene schist (Foster *et al.*, 1960).

6. Phengite from glaucophane schist, Tiburon Peninsula, California (new analysis), H. Asari, analyst.

7. Phengite from glaucophane+garnet+biotite+quartz schist (Iwasaki, 1960).

8. Phengite from chlorite+pyrite+epidote+glaucophane+quartz+calcite schist, Kotu district, Shikoku, Japan (new analysis), H. Haramura, analyst. Analyzed sample contains 4.3 per cent chlorite, 4.0 per cent quartz.

9. Phengite from glaucophane+actinolite+chlorite+aragonite+quartz schist, Tiburon Peninsula, California (new analysis), C. O. Ingamells, analyst.

10. Phengite from glaucophane+chlorite+aragonite+jadeite pyroxene schist, Glauconite Ridge, California (new analysis), J. Ito, analyst.

11. Phengite from glaucophane+eclogite (Beartli, 1959).

12. Muscovite from pegmatite, Ontario (new analysis), H. B. Wiik, analyst.

13. Muscovite from pegmatite, Georgia, U. S. Nat. Museum No. 105100 (new analysis), H. B. Wiik, analyst.

14. Muscovite from pegmatite (Hurlbut, 1956).

15. Composition of pure end member muscovite (for comparison with synthetic muscovite data, Yoder and Eugster, 1955).

TABLE 2. IONIC PROPORTIONS FOR CHEMICALLY ANALYZED MEMBERS OF THE CELADONITE-MUSCOVITE SERIES

Coordination	Ion	1 ¹	2 ²	3	4 ³	5 ⁴	6	7	8 ⁵	9	10	11	12	13	14	15
IV	Si	3.78	3.62	3.53	3.50	3.27	3.38	3.31	3.33	3.39	3.14	3.05	3.07	3.02	3.04	3.00
	Al	0.22	0.38	0.47	0.50	0.73	0.62	0.69	0.67	0.61	0.86	0.95	0.93	0.98	0.96	1.00
VI	Al	0.20	0.36	1.22	1.14	1.27	1.36	1.36	1.40	1.43	1.51	1.55	1.72	1.90	1.98	2.00
	Ti	0.01	—	0.04	0.05	0.00	0.03	0.01	0.03	0.01	0.01	0.02	0.02	0.01	—	0.00
	Fe ³⁺	1.01	1.05	0.36	0.20	0.42	0.10	0.23	0.19	0.05	0.08	0.06	0.13	0.02	—	0.00
	Fe ²⁺	0.28	0.25	0.00	0.16	0.15	0.04	0.01	0.13	0.09	0.10	0.07	0.09	0.05	—	0.00
	Mn	0.00	—	0.05	0.00	0.00	0.00	0.02	0.00	0.00	0.00	—	0.00	0.00	—	0.00
	Mg	0.57	0.39	0.59	0.42	0.19	0.55	0.40	0.29	0.50	0.40	0.35	0.08	0.06	0.01	0.00
	Li	—	—	—	—	—	—	0.04	—	0.00	0.06	—	0.00	0.00	—	0.00
	Cr	—	—	—	—	—	—	—	—	—	0.01	—	—	—	—	0.00
Total	2.07	2.05	2.26	1.97	2.03	2.08	2.07	2.04	2.04	2.17	2.05	2.04	2.04	1.99	2.00	
XII	Ca	0.04	0.04	0.02	0.19	0.00	0.01	0.01	0.03	0.02	0.02	0.07	0.01	0.00	—	0.00
	Ba	—	—	—	—	—	0.00	0.05	—	0.01	0.04	—	0.00	0.00	—	0.00
	Na	0.00	0.00	0.00	0.15	0.02	0.12	0.07	0.09	0.07	0.05	0.21	0.09	0.10	0.08	0.00
	K	0.73	0.79	0.97	0.63	0.94	0.80	0.81	0.78	0.87	0.79	0.85	0.89	0.86	0.85	1.00
	H ₃ O ⁺	0.03	0.10	0.00	0.14	0.00	0.00	0.09	0.06	0.00	0.05	0.03	0.02	0.01	0.03	0.00
	Total	0.80	0.93	0.99	1.11	0.96	0.93	1.03	0.96	0.97	0.95	1.16	1.01	0.97	0.96	1.00
anions	O	10.00	10.00	10.72	10.00	10.00	10.02	10.00	10.00	10.08	10.00	10.00	10.00	10.00	10.00	10.00
	OH	2.00	2.00	1.28	2.00	1.97	1.97	2.00	2.00	1.92	2.00	2.00	2.00	1.99	2.00	2.00
	F	—	—	—	—	0.03	0.01	—	—	0.00	—	—	0.00	0.01	0.00	0.00
Per cent AlVI among 6-fold coordinated cations		9.7	17.5	54.0	57.9	62.5	65.4	65.7	68.6	68.8	69.6	75.5	84.3	93.3	99.5	100.0

¹ Specimen numbers correspond to those of Table 1.² Lime content corrected assuming CO₂ present as calcite.³ Analysis corrected for 3.2 per cent epidote.⁴ SiO₂, TiO₂ and CaO contents corrected for inclusions of sphene and leucoxene.⁵ Analysis corrected for 4.3 per cent chlorite, 4.0 per cent quartz.

10). Nevertheless, because of the high atomic weight, the ionic proportions of Ba in these micas is minor as indicated in Table 2.

X-RAY DATA AND DERIVED LATTICE PARAMETERS

Unit cell parameters for micas of known composition have been published for two muscovites (Yoder and Eugster, 1955; Hurlbut, 1956) iron muscovite (Foster *et al.*, 1960), glauconite (Gruner, 1935) and celadonite (Zviagin, 1957). In addition, Radoslovich and Norrish (1962) presented *b*-axis dimensions for several chemically analyzed celadonites and muscovite; Kanehira and Banno (1960) determined the layer repeat for a sam-

TABLE 3. 2θ VALUES ($\text{CuK}\alpha$) FOR MICAS EXAMINED IN THIS STUDY

hkl	4	6	7	8	9	10	11	12	13
11 $\bar{4}$	25.540 ¹	25.555	25.524	25.483	25.590	25.578	26.577	25.545	25.543
114	27.917	27.910	27.916	27.828	27.940	27.941	27.928	27.916	27.905
025	29.940	29.968	29.936	29.903	30.008	29.991	29.973	29.915	29.921
115	31.312	31.323	31.304	31.253	31.357	31.330	31.340	31.285	31.300
202	34.958	34.947	34.951	34.903	35.001	34.990	35.014	34.937	35.019
008	36.184	36.168	36.204	36.089	36.194	36.222	36.209	39.019	35.998

¹ Specimen numbers correspond to those of Table 1.

ple of chemically analyzed ferriphengite. All micas are of the $2M_1$ structural type (Smith and Yoder, 1956) with the exception of the celadonite and possibly the glauconite.

Chemically analyzed powdered samples of phengitic and muscovitic mica for which lattice parameters were unavailable were investigated employing a Norelco x-ray diffractometer and $\text{CuK}\alpha$ radiation. 2θ values for six reflections were determined using halite (North American Phillips Co. No. 5544, $d_{100} = 5.63937 \text{ \AA}$ at 18° C.) as an internal standard, five complete oscillations being performed on each sample. Peak locations were measured to $0.005^\circ 2\theta$ and averaged (see Table 3). Cell parameters were calculated to four decimal places using a least squares treatment programmed for an IBM 7090 computer (University of California, Los Angeles, Computing Facility) by W. E. Sharp, Department of Geology, University of California, Los Angeles. Lattice parameters for a sample of ferriphengite were computed using the above technique and d-spacings determined by van der Plas (1959, p. 476). Results are presented in Table 4. For comparison with the $2M_1$ micas, the $1M$ celadonite was tabulated with double the *c*-axis repeat. The sample of glauconite is presented as originally determined ($2M_1$) by Gruner (1935); more recent investigations have suggested that many glauconites are single layer-lattice

TABLE 4. LATTICE PARAMETERS FOR CHEMICALLY ANALYZED MEMBERS OF THE CELADONITE-MUSCOVITE SERIES

Specimen number (corresponds to those of Table 1)	<i>a</i> in Å	<i>b</i> in Å	<i>c</i> in Å	β in °	<i>c</i> sin β in Å	Cell vol. in Å ³
1	5.20	9.00	20.50	100.1	20.18	945
2	5.24	9.07	20.03	95.0	19.95	948
3	5.187	9.004	20.221	95.77	20.118	939.5
4	5.201	9.048	19.962	95.73	19.862	934.7
5	5.249	9.064	19.991	95.75	19.882	946.3
6	5.202	9.023	19.969	95.72	19.869	932.6
7	5.203	9.060	19.952	95.72	19.853 ¹	935.7
8	5.210	9.045	20.012	95.69	19.913	938.6
9	5.194	9.005	19.954	95.71	19.855	928.6
10	5.197	9.026	19.940	95.67	19.842	930.7
11	5.193	9.035	19.946	95.68	19.848	931.3
12	5.200	9.006	20.048	95.81	19.945	933.9
13	5.189	9.000	20.060	95.78	19.958	932
14	5.18	8.99	20.01	96.0	19.90	932
15	5.189	8.995	20.097	95.18	20.015	934.2

1. Zviagin (1957), *c* axis of 1*M* celadonite doubled for comparison with 2-layer specimens; values for the *c* axis and β are, of course, not comparable with 2*M*₁ micas.

2. Gruner (1935), as originally indexed (2*M*₁ cell).

3. This study from *d*-values presented by van der Plas (1959).

4. This study.

5. Foster *et al.* (1960).

6-13. This study.

14. Hurlbut (1956).

15. Yoder and Eugster (1955).

¹ Iwasaki (1960) obtained a basal spacing of 9.924 Å ($\times 2 = 19.848$ Å), in good agreement with results of the present study.

silicates (*e.g.*, Burst, 1959, p. 484). Several 3T phengites have been described by Heinrich and Levinson (1955), but none were encountered in this study. It is of interest to note that, among the muscovite polymorphs, the two-layer monoclinic modification is the densest (Yoder and Eugster, 1955, p. 248).

The unit cell dimensions given in Table 4 as well as values determined by Radoslovich and Norrish (1962) and Kanehira and Banno (1960) are shown as a function of composition in Fig. 1. Determinations of cell edges are estimated as accurate to ± 0.01 Å, β values to $\pm 0.1^\circ$ and cell volumes to ± 2.0 Å³. Lattice parameters of members of the celadonite-mus-

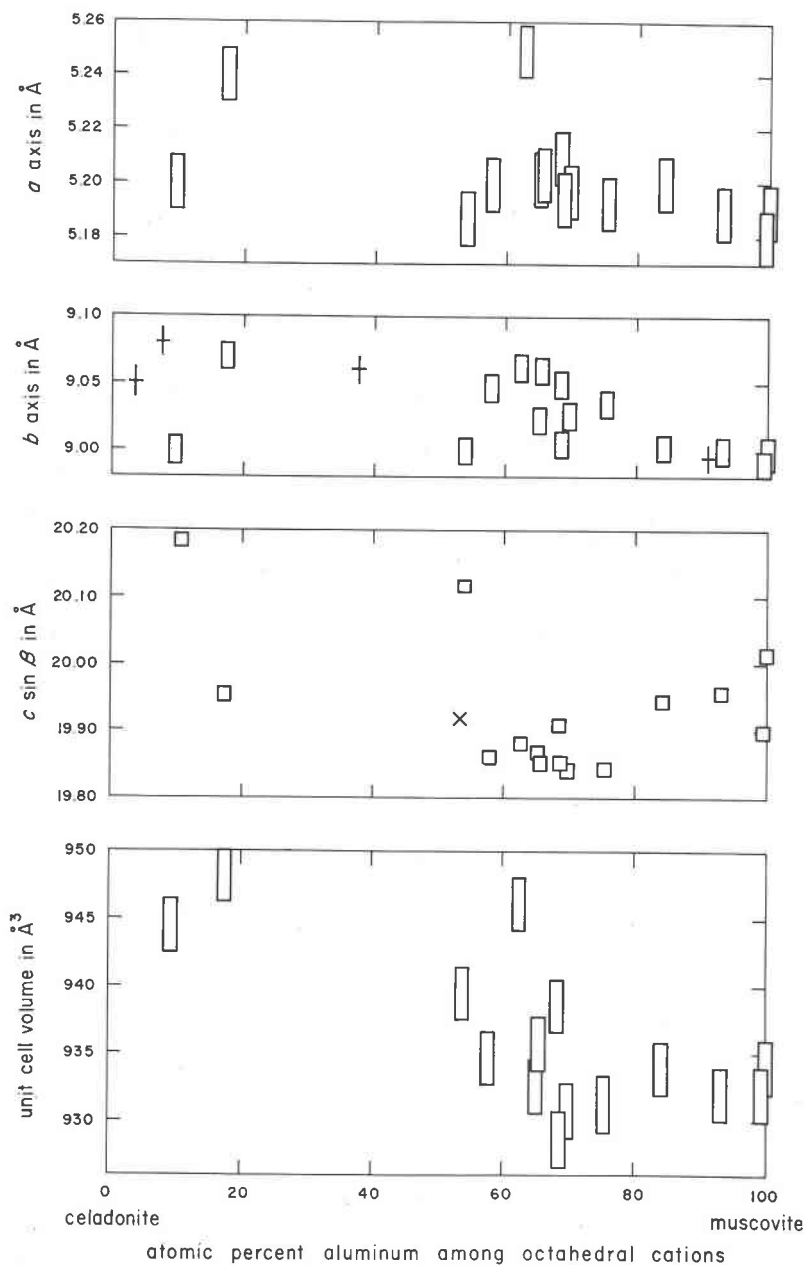


FIG. 1. Variation of lattice parameters of members of the celadonite-muscovite series. Size of symbol indicates estimated uncertainty in sample values. $\times = c \sin \beta$ value determined by Kanehira and Banno (1960); $+$ = b -axis values presented by Radoslovich and Norrish (1962).

covite series are plotted against the ratio $Al^{VI}/(\text{total six-fold coordinated cations})$ because: (1) *tetrahedral* aluminum does not appear to exert an effect on cell dimensions (Radoslovich and Norrish, 1962, p. 603), and (2) the ionic radius of Al^{VI} , 0.51 Å, is considerably less than those of octahedrally coordinated Mg, ferrous and ferric iron, 0.66 Å, 0.74 Å, and 0.64 Å respectively (Green, 1959). Lattice parameters show considerable scatter, probably because these micas contain differing amounts of Al and Fe^{3+} , Mg and Fe^{2+} , as well as many other minor cations such as Ti, Mn, Li, Ca and Ba; to consider them as members of a binary solid solution series is admittedly a rather crude approximation. Nevertheless, it is clear that the phengites, intermediate members of the celadonite-muscovite series, display short interlayer repeats and relatively small cell volumes; with the possible exception of No. 11, Na contents in these micas are too low to account for the observed lattice parameters by solid solution with paragonite (Table 2).

The relatively small $c \sin \beta$ distances for phengites are a function of the "unusual" compositions of these micas. Radoslovich and Norrish (1962, p. 610) have shown that cell dimensions in the micas are controlled principally by compositional variation of the octahedral layers. Replacement of Al^{VI} by Mg and Fe results in b -axis extension, which in turn causes reduced tetrahedral rotation and subsequent decrease in the tetrahedral-tetrahedral layer gap (smaller $c \sin \beta$ values). The greater inter-layer distances observed for the iron-rich minerals glauconite and celadonite probably result from the fact that Fe^{2+} has a considerably larger ionic radius than Mg, thus yielding a relatively expanded octahedral layer compared to phengite and muscovite.

OPTICAL DATA

Optical data for the seven newly analyzed white micas are presented in Table 5. Also tabulated for comparison are optical parameters (quoted from the literature) for the other samples listed in Tables 1 and 2. From the data of Table 5, phengites appear to have higher indices of refraction and slightly lower values of $2V$ than muscovites.

PETROLOGIC SIGNIFICANCE OF PHENGITES

Biotite and muscovite are commonly associated in higher-grade greenschists (corresponding to pelitic schists which recrystallized at grades higher than the biotite isograd), but such compatibility apparently is prohibited in rocks which have recrystallized under conditions of the glaucophane schist (= blueschist) facies and in the lower-grade portion of the greenschist facies. Phengite is commonly associated with chlorite or microcline (but not both), albite, quartz, lawsonite and glaucophane or

jadeitic pyroxene in glaucophane schists. Phengite-bearing assemblages described from the Alps generally contain green biotite and if such assemblages are stable, these rocks may represent either (1) conditions transitional between higher- and lower-grade portions of the greenschist facies or (2), $K_2O + MgO + FeO$ -rich bulk compositions. The apparent incompatibility of muscovite and biotite in glaucophane schist and low-grade greenschist assemblages probably results, not from the lack of stability of biotite itself, but from the *increased compositional range of*

TABLE 5. OPTICAL PROPERTIES OF CHEMICALLY ANALYZED MEMBERS OF THE CELADONITE-MUSCOVITE SERIES

Specimen number (corresponds to those of Table 1)	α	β	γ	$2V_\alpha$	$\gamma - \alpha$
1	1.607		1.640	0°	0.033
2	1.597	1.618	1.619	20°	0.022
3	—	1.60—1.63		32–43°	0.05
4	1.573	1.609	1.611	31°	0.038
5	1.580	1.6195	1.6230	35°	0.043
6	1.564	1.599	1.601	31°	0.037
7	—	1.608	—	36°	—
8	1.571	1.607	1.610	28°	0.039
9	1.563	1.600	1.601	33°	0.038
10	1.563	1.590	1.594	33°	0.031
11	—	1.594	—	40–42°	0.038
12	1.561	1.598	1.601	22°	0.040
13	1.559	1.597	1.600	27°	0.041
14	1.5595	1.5930	1.5991	46.5°	0.0396

1. Malkova (1956).

2. Gruner (1935).

3. van der Plas (1959).

4. This study.

5. Foster, Bryant and Hathaway (1960).

6. This study.

7. Iwasaki (1960).

8–10. This study.

11. Bearth (1939).

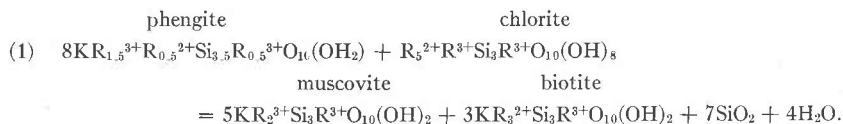
12–13. This study.

14. Hurlbut (1956).

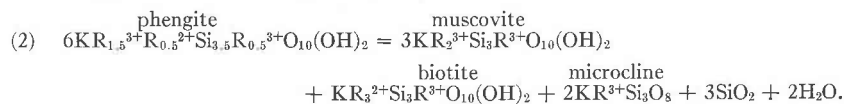
dioctahedral micas. Lambert (1959, p. 560) recognized that, in Moine Series rocks of the greenschist facies, white micas change from phengitic to muscovitic compositions with increasing metamorphic grade.

The reaction involving micas of the blueschist and greenschist facies must be represented in the seven component system, $K_2O-Al_2O_3-Fe_2O_3-FeO-MgO-SiO_2-H_2O$. Because ferric iron and aluminum constitute a

diadochic pair (R^{3+}) for the minerals considered, and Fe^{2+} and Mg likewise are mutually substitutional (R^{2+}), the reaction may be written more simply in terms of five components:



Van der Plas (1959, p. 538) has presented an analogous equation for rocks richer in K_2O to account for Alpine metamorphism of preexisting biotite-bearing granitic rocks to phengite gneisses:



Phase relations are shown diagrammatically in Fig. 2. Enlargement of the compositional range of white mica is thought to be a relatively low-grade phenomenon because of (1) the effect of "contaminants" on coupled reactions, and (2) the association of phengite with low-temperature and commonly high-pressure phases.

Compatibility of microcline and chlorite has not been considered in the construction of Fig. 2. The reaction chlorite + microcline = biotite + white mica + quartz + water conceivably may be realized under some conditions with the chlorite-microcline join replacing that of white mica-biotite, presumably at very low temperatures. This would of course indicate a compositional limit for muscovite-celadonite solid solutions (the data of Table 2 and Fig. 1 indicate that solid solution extends from $Ms_{100}Ce_{00}$ at least as far as $Ms_{54}Ce_{46}$). To the author's knowledge, the stable association of microcline and chlorite has been reported only by Zen (1960),¹ but perhaps could exist unnoticed elsewhere in fine-grained rocks. If so, the absence of biotite in blueschist facies assemblages would be due to the

¹ Zen (1960) has described pelitic schist assemblages containing coexistent chlorite and K-feldspar from west-central Vermont. Values for muscovite layer repeats from this area suggest compositions close to the $KA_2Si_3AlO_{10}(OH)_2$ end member (Zen, 1960, Table 3). The problem of stability of the pair muscovite + biotite versus microcline + chlorite is indicated by crossing tie lines in Zen's Fig. 5, in which FeO and MgO are regarded as a single component. Limited substitution of Fe^{2+} for Mg occurs in minerals of the pelitic schists from west-central Vermont, so Zen (1960, Fig. 6) considers FeO and MgO as independent components; thus the assemblages biotite + microcline + muscovite, and chlorite + microcline + muscovite are stable for rocks of different bulk compositions, but the compatibility of stilpnomelane + microcline + muscovite appears to prohibit the biotite + chlorite association. At best, the question of the compatibility of chlorite + K-feldspar must be considered as unresolved. Ultimately it may prove necessary to distinguish as separate components Fe_2O_3 and Al_2O_3 as well as FeO and MgO.

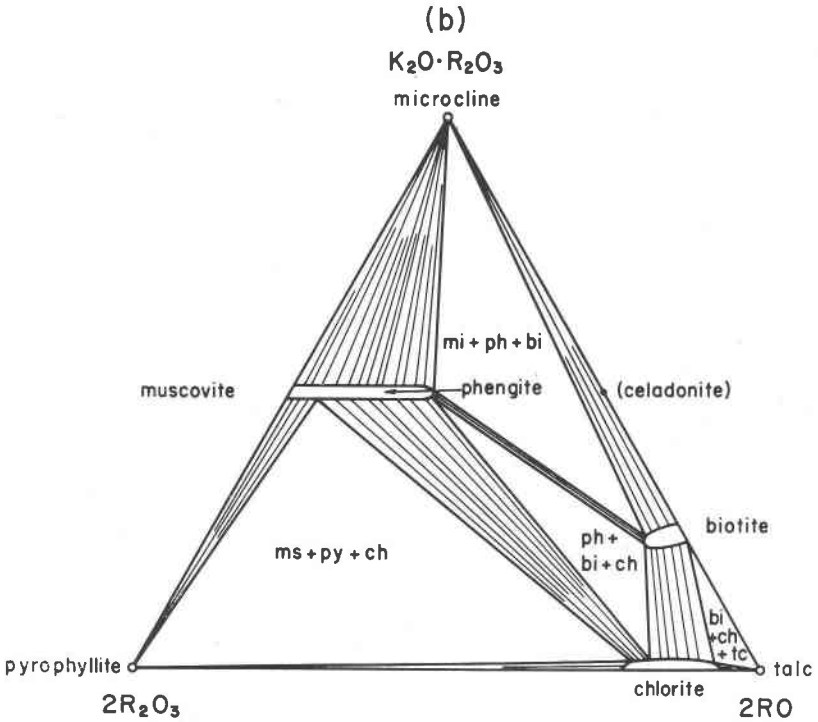
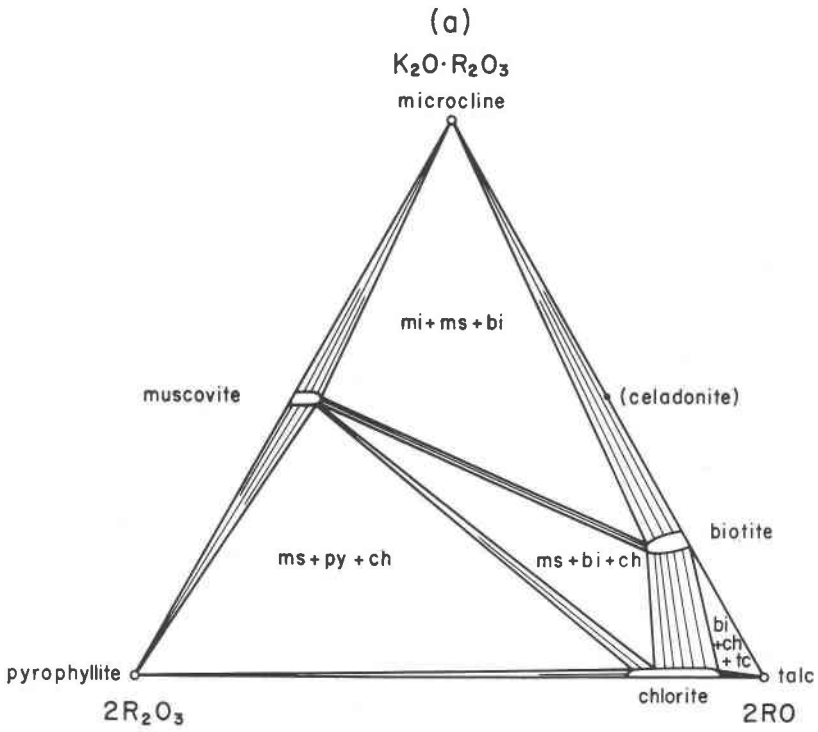
even greater compositional restriction of biotite to $K_2O + MgO + FeO$ -rich rocks than discussed above.

The illustration indicates that, under given physical conditions, the composition of the phengite depends on whether it is associated with chlorite or microcline, but apparently the difference is small judging from the chemical analyses (Tables 1 and 2). In this note, only reaction (1) is considered in detail because white mica coexists with chlorite rather than with microcline in most glaucophane schists and in many low-grade greenschists. However, the practical identity of reactions (1) and (2) is obvious from the chemical data, and is so portrayed in Fig. 2. A somewhat similar diagram has been presented by Yoder (1957, Fig. 12). All assemblages are considered as saturated with respect to SiO_2 and H_2O (with $P_{H_2O} \approx P_{total}$) so the additional phases quartz and fluid may be present. The reaction is divariant only considering R^{3+} and R^{2+} as single components. Actually there will be an unequal partition among ferric iron and aluminum and among ferrous iron and magnesium, not to mention minor elements which have been ignored, so the reaction will take place over a P-T-composition interval. From the observation that the low-temperature, low-entropy, high fluid pressure assemblage is generally more hydrous than the high-temperature, high-entropy and/or low fluid pressure assemblage of equivalent bulk composition, phengite + chlorite constitute the low-temperature, low-entropy, high fluid pressure compatibility. In some rocks of basaltic and pelitic compositions, the reaction relating these phases probably represents the biotite isograd of classic metamorphic terrains. Obviously, a number of chemical variables (*e.g.*, Fe^{2+}/Mg ratio of the parent rock) as well as P_{H_2O} , P_{total} , and T control the mineral paragenesis.



3

FIG. 2. Schematic isobaric, isothermal sections of a portion of the system K_2O-R_2O ($Al_2O_3 + Fe_2O_3$)-RO ($MgO + FeO$) with excess silica + water (all assemblages may contain as additional phases quartz and fluid). The partitioning of ferric iron and aluminum, ferrous iron and magnesium among coexisting phases cannot be represented on such a diagram. Abbreviations are: mi = microcline; ms = muscovite; ph = phengite; bi = biotite; py = pyrophyllite; ch = chlorite; tc = talc. (a) shows typical greenschist assemblages for rocks of metamorphic grade equivalent to the biotite isograd in pelitic schists (*e.g.*, see Turner and Verhoogen, 1960, p. 534 ff.). (b) illustrates an expansion of the compositional field of dioctahedral mica through the following reaction running to the left: 8 phengite + chlorite = 5 muscovite + 3 biotite + 7 quartz + 4 H_2O . Chemographic relations depicted at (b) are thought to replace those of (a) at higher values of P_{H_2O} and/or lower temperatures. Presumably celadonite is stable only in very iron-rich rocks, *i.e.*, where bulk compositions have high $Fe^{3+} + Fe^{2+}/R^{3+} + R^{2+}$ ratios (not considered).



Unit cell volumes of the participating condensed phases are listed in Table 6. Thermal expansions and compressibilities of all crystalline phases are of the same order or magnitude, so $\partial\Delta V_{\text{solids}}$ is assumed to be negligible for the P-T interval considered (Thompson, 1955). If the system is considered open with respect to H_2O at fixed equilibrium pressure

TABLE 6. UNIT CELL VOLUMES OF VARIOUS MINERALS

Phase	Cell Vol. in in \AA^3	Number of Formula Units per Unit Cell	Reference
muscovite	933	4	Yoder and Eugster (1955); Hurlbut (1956)
biotite	1007	4	Yoder and Eugster (1954); Eugster and Wones 1962)
quartz	113	3	Fron del (1962)
liquid water	30	1	
chlorite	1388	4	Winchell and Winchell (1951); Deer <i>et al.</i> (1962)
phengite	935	4	average of 8 samples, this study

of water, the curve slope relating the assemblages is given by the expression:

$$\left(\frac{\partial P_{\text{total}}}{\partial T}\right)_{P_{\text{H}_2\text{O}}} = \frac{\Delta S}{\Delta V_{\text{solids}}} \quad (\text{e.g. Yoder, 1952; Thompson, 1955; Greenwood, 1961}).$$

Under these conditions the reaction as written proceeds to the right with a slight decrease in volume (-1.5 ± 1.0 per cent). Therefore increment in total (lithostatic) pressure at any arbitrary temperature favors the muscovite+biotite assemblage over phengite+chlorite. Where fluid pressure ($\approx P_{\text{H}_2\text{O}}$) approximates total pressure, the system may be considered as closed, even though fluid may pass through the system with time, and the relation between the assemblages is given by the familiar equation:

$$\frac{\partial P_{\text{total}}}{\partial T} = \frac{\Delta S}{\Delta V_{\text{solids+fluid}}}$$

In this case, the volume of water participating in the reaction must be taken into account, and the reaction as written proceeds to the right with a considerable increase in volume (even at temperatures below the critical point of water, ΔV is about $+4.0 \pm 1.0$ per cent). Therefore, high fluid pressures favor production of phengitic mica and chlorite at the ex-

pense of muscovite and biotite; the higher the value of P_{fluid} , the greater will be the compositional extent of solid solution between muscovite and celadonite.

The relatively high-pressure, low-temperature minerals lawsonite, jadeitic pyroxene, metamorphic aragonite, glaucophane II, and the assemblages glaucophane+calcium-aluminum silicate or calcium carbonate, and glaucophane+paragonite indicate that temperature was low, lithostatic pressure was high during blueschist facies metamorphism as discussed by Fyfe *et al.* (1958), Miyashiro and Banno (1958), Coleman and Lee (1962) and Ernst (1963 a, b) among others. The presence of phengite (+chlorite) in rocks of this facies suggests the possibility that fluid pressure was also high during the metamorphism.

The reaction discussed in this paper will not, of course, take place over the same P-T interval as others which involve the relatively dense phases lawsonite, jadeitic pyroxene and metamorphic aragonite or the coupled reactions involving glaucophane and calcium-aluminum silicate, calcium carbonate or paragonite. The presence of phengitic micas in low-grade greenschists as well as in blueschists of similar bulk compositions suggests that this reaction may occur under physical conditions involving slightly lower pressures and/or higher temperatures than those attending production of glaucophane schists. It is pertinent to note that, if fluid ($\approx P_{\text{H}_2\text{O}}$) pressure were significantly less than total pressure in blueschist facies rocks, muscovite+biotite or microcline+chlorite should coexist with anhydrous phases such as jadeitic pyroxene and aragonite in rocks of appropriate bulk composition because the solid-solid phase equilibrium relations of these latter minerals do not depend on P_{fluid} . The lack of such associations and the presence of phengite may be taken as qualitative indication of high fluid pressure during recrystallization of many glaucophane schists.

REFERENCES

- BEARTH, P. (1959) Über Eklogite, Glaukophanschiefer und metamorphe Pillowlaven. *Schweiz. Mineral. Petro. Mitt.* **39**, 267-286.
- BURST, J. F. (1958) Mineral heterogeneity in "glaucinite" pellets. *Am. Mineral.* **43**, 481-497.
- COLEMAN, R. G. AND D. E. LEE (1962) Metamorphic aragonite in the glaucophane schists of Cazadero, California. *Am. Jour. Sci.* **260**, 577-595.
- DEER, W. A., R. A. HOWIE AND J. ZUSSMAN (1955) *Rock-forming Minerals*. V. 3. *Sheet Silicates*: Longmans, Green & Co., London.
- ERNST, W. G. (1963a) Petrogenesis of glaucophane schists. *Jour. Petrol.* **4**, 1-30.
- (1963b) Polymorphism in alkali amphiboles. *Am. Mineral.* **48**, 241-260.
- EUGSTER, H. P. AND D. R. WONES (1962) Stability relations of the ferruginous biotite, annite. *Jour. Petrol.* **3**, 82-125.

- FOSTER, M. D. (1956) Correlation of dioctahedral potassium micas on the basis of their charge relations. *U. S. Geol. Surv. Bull.* **1036-D**, 57-67.
- B. BRYANT, AND J. HATHAWAY (1960) Iron-rich muscovite mica from the Grandfather Mountain area, N. Carolina. *Am. Mineral.* **45**, 839-851.
- FRONDEL, C. (1962) *Dana's System of Mineralogy, III*: John Wiley & Sons, Inc., New York.
- FYFE, W. S., F. J. TURNER AND J. VERHOOGEN (1958) Metamorphic reactions and metamorphic facies. *Geol. Soc. Am. Mem.* **73**.
- GREEN, J. (1959) Geochemical table of the elements for 1959. *Bull. Geol. Soc. Am.* **70**, 1127-1184.
- GREENWOOD, H. J. (1961) The system $\text{NaAlSi}_2\text{O}_6\text{-H}_2\text{O-Argon}$: total pressure and water pressure in metamorphism, *Jour. Geophys. Res.* **66**, 1923-3946.
- GRUNER, J. W. (1935) The structural relationship of glauconite and mica. *Am. Mineral.* **20**, 699-714.
- HARDER, H. (1956) Untersuchungen an Paragoniten und an natriumhaltigen Muskoviten. *Heidelb. Beit. Mineral. Petro.* **5**, 227-271.
- HEINRICH, E. WM. AND A. A. LEVINSON (1955) Studies in the mica group; polymorphism among the high-silica sericites. *Am. Mineral.* **40**, 983-995.
- HENRICKS, S. B. AND C. S. ROSS (1941) Chemical composition and genesis of glauconite and celadonite. *Am. Mineral.* **12**, 683-708.
- HURLBUT, C. S. (1956) Muscovite from Methuen Township, Ontario. *Am. Mineral.* **41**, 892-898.
- IWASAKI, M. (1960) Colorless glaucophane and associated minerals in quartzose schists from eastern Sikoku, Japan. *Jour. Geol. Soc. Japan* **66**, 566-574.
- KANEHIRA, K. AND S. BANNO (1960) Ferriphengite and aegirinjadeite in a crystalline schist of the Iimori District, Kii Peninsula. *Jour. Geol. Soc. Japan* **66**, 654-659.
- LAMBERT, R. S. J. (1959) The mineralogy and metamorphism of the Moine schists of the Morar and Knoydart districts of Inverness-shire. *Trans. Roy. Soc. Edinburgh*, **63** 553-588.
- MALKOVA, K. M. (1956) Celadonite from the Bug region. *Min. Sbornik Lvov Geol. Soc.* **10**, 305-318.
- MIVASHIRO, A. (1962) Notes on rock-forming minerals (22). Common occurrence of muscovite-rich in iron and magnesium in glaucophanitic metamorphic terrains. *Jour. Geol. Soc. Japan* **68**, 234-235.
- AND S. BANNO (1958) Nature of glaucophanitic metamorphism. *Am. Jour. Sci.* **256**, 97-110.
- PLAS, L. VAN DER (1959) Petrology of the northern Adula region, Switzerland. *Leid. Geol. Med.* **24**, 418-598.
- RADCSLOVICH, E. W. AND K. NORRISH (1962) The cell dimensions and symmetry of layer-lattic silicates I. Some structural considerations. *Am. Mineral.* **47**, 599-616.
- SABATIER, M. (1949) Recherches sur la glauconie. *Bull. Soc. Franç. Mineral. Crist.* **72**, 474-542.
- SCHALLER, W. T. (1950) An interpretation of the composition of high silica sericites. *Mineral. Mag.* **29**, 407-415.
- SCHÜLLER, A. AND E. WOHLMANN (1951) Über Seladonit und seine systematische Stellung. *Neues Jahrb. Mineral., Abh.* **82**, 111-120.
- SMITH, J. V. AND H. S. YODER (1956) Experimental and theoretical studies of the mica polymorphs. *Mineral. Mag.* **31**, 209-235.
- SWITZER, G. (1951) Mineralogy of the California glaucophane schists. *Calif. Dept. Nat. Res., Div. Mines Bull.* **161**, 51-70.

- THOMPSON, J. B. (1955) The thermodynamic basis for the mineral facies concept. *Am. Jour. Sci.* **253**, 65-103.
- TURNER, F. J. AND J. VERHOOGEN (1960) *Igneous and Metamorphic Petrology*. McGraw-Hill Book Co., New York.
- WINCHELL, A. N. (1927) Further studies in the mica group. *Am. Mineral.* **12**, 267-279.
- (1949) What is a mineral? *Am. Mineral.* **34**, 220-225.
- AND H. WINCHELL (1951) *Elements of Optical Mineralogy. Part II. Descriptions of minerals*. John Wiley & Sons, Inc., New York.
- YODER, H. S. (1952) The MgO-Al₂O₃-SiO₂-H₂O system and the related metamorphic facies. *Am. Jour. Sci., Bowen Vol.*, 569-627.
- (1957) Experimental studies on micas: a synthesis. *Proc. Sixth Nat. Conf. Clay, Clay Minerals*, 42-60.
- AND H. P. EUGSTER (1954) Phlogopite synthesis and stability range. *Geochim. Cosmochim. Acta*, **6**, 157-185.
- AND H. P. EUGSTER (1955) Synthetic and natural muscovites. *Geochim. Cosmochim. Acta*, **8**, 225-280.
- ZEN, E-AN (1960) Metamorphism of lower Paleozoic rocks in the vicinity of the Taconic Range in west-central Vermont. *Am. Mineral.* **45**, 129-175.
- ZVIAGIN, B. B. (1957) Determination of the structure of celadonite by electron diffraction. *Soviet Physics, Cryst.* **2**, 388-393.
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