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NOTES

Compositional and structural relationships between phengites and illites*

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INTRODUCTION

THE NATURE of illite as a monomineral phase has been recently discussed by Gaudette, Eades and Grim (1966) and by Hower and Mowatt (1966). Illites are nonexpandable and generally dioctahedral mica-type 10Å clay minerals whose chemical composition shows a closer relationship to phengites than to muscovites. Warshaw (1960) was not able to hydrothermally synthesize illites or any other mica from gels with the same composition as muscovite but with less K; however, when K deficiency was compensated by Si for Al substitutions in the gel compositions Warshaw was able to synthesize mica-type layer silicates similar to natural illites.

Recent studies on natural and synthetic micas have shown that muscovites occur in igneous and high grade metamorphic rocks whereas phengites occur in low grade metamorphic rocks formed under high pressures. Illites occur in sedimentary rocks as diagenetic or detrital products and are sometimes subjected to deep burial with the resulting greater pressure increase relative to temperature. Illites are therefore environmentally closer to phengites than to muscovites. With regard to polymorphism, illites as well as phengites show 2M, 3T, 1M and 1Md forms (Levinson, 1955; Velde and Hower, 1963; Hower and Mowatt, 1966) whereas muscovite almost invariably occurs in the $2M_1$ form. In clay mineralogy, however, structural information concerning illites has been so far inferred from the available data of the $2M_1$ muscovite structure for it has not been possible to carry out a single crystal structure determination of illites because of their fine grain size. Recent crystal structure analyses of $2M_1$ phengite and $2M_1$ muscovite (Güven, 1970) with counter-obtained intensity data and using three dimensional least squares methods showed significant differences between these dioctahedral micas, which may have bearing on dioctahedral mica-type clay minerals. The crystal structure of $2M_1$ phengite from Tiburon Peninsula, California will probably give a better insight into the structure of illites.

COMPOSITIONAL RELATIONSHIPS BETWEEN THE TIBURON PHENGITE AND ILLITES

Cation distributions in muscovite, phengite and illites are given in Table 1 as well as stacking sequences. Illites are well-analyzed and almost free of mixed layering with expandable layers, the amount of which is less than 10 per cent in each illite sample. Compositional variations between muscovite and phengite involve $^{VI}R^{2}Si$ for $^{VI}Al^{IV}Al$ type substitutions, where $^{VI}R^{2+}$ is mainly Mg and Fe^{2+}. (Roman numerals indicate coordination of the cation).

The distribution of cations in illite is similar to that in phengite except for additional Si for ^{IV}Al K and/or R^{3+} for $^{VI}R^{2+}K$ type substitutions ($R^{3+} = Fe^{3+}$, Al) which result in the characteristic K-deficiency in illites.

STRUCTURAL EFFECTS OF ISOMORPHIC SUBSTITUTIONS IN THE MUSCOVITE-PHENGITE JOIN

The important results of the crystal structure analyses of $2M_1$ muscovite and $2M_1$ phengite are listed in Table 2, and a comparison of these two mica structures shows the structural changes caused by $^{IV}R^{2+}Si$ for $^{VI}Al^{IV}Al$ substitutions on the muscovite–phengite join. The configuration of the tetrahedral and octahedral sheets in the illite structure is expected to be similar to those of phengite. The following conclusions, drawn from the comparison of the $2M_1$ phengite and muscovite structures, may give an insight into the structural features of illites.

(a) Tetrahedral cation–oxygen distances indicate a slight tendency in phengite for ordering of tetrahedral cations, whereas there is a complete disorder of tetrahedral silicon and aluminum in the $2M_1$ muscovite structure. Increased silica content in the tetrahedra of $2M_1$ phengite, as shown by the smaller T–O distances in Table 2, decreases the electrostatic unsatisfied charges on basal oxygens. A similar situation will probably exist for illites and hence interlayer cation-basal oxygen bonds will be weaker in phengites and illites than in muscovites.

(b) Increased R^{2+} content of the octahedral layer in phengite results in larger metal–oxygen distances. The major octahedral cations Mg, Fe^{2+} have an opposite distortion effect on the framework of anions in octahedral layers than a smaller cation like Al. The R^{2+} replacements in octahedral sites cause "polyhedral misfit" and create strains in the octahedral sheets. This may be the structural factor limiting the $R^{2+} \rightarrow Al$ substitutions in octahedral sheets and also favoring the breakdown of the phengite into two mica phases with increasing temperature (Velde, 1965) each having a uniform octahedral population. Illites also exhibit this type of octahedral substitution which may cause similar effects.

(c) The $R^{2+}Si$ for $^{VI}Al^{IV}Al$ substitutions on the other hand decrease the "dimensional misfit" between octahedral and tetrahedral sheets in the mica structure. The tetrahedral rotations (2α) and tetrahedral tilt in phengite are therefore

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Table 1. Distribution of cations in dioctahedral micas and illites on the basis of $O_{10}(OH)_2$ anions per unit structural formula

	Georgia muscovite*	Tiburon phengite*	Marblehead illite†	Beavers Bend illite†	Rock Island illite†	Interlake† (< 0·5 μ fraction)	Silver† Hill (< 0·5 μ fraction)	Morrison‡ (< 2μ fraction)	Burnt, Bluff‡ (< 2 μ fraction)
Octahedral population									
Al	1·90	1·43	1·50	1·29	1·61	1·66	1·38	0·98	1·56
Fe^{3+}	0·02	0·05	0·04	0·41	0·07	0·03	0·26	0·70	0·04
Fe^{2+}	0·05	0·09	0·07	0·19	0·08	0·05	0·07	0·08	0·07
Mg	0·06	0·50	0·36	0·18	0·20	0·30	0·28	0·29	0·36
Ti	0·01	0·01	0·05	0·04	0·03				
Tetrahedral population									
Si	3·02	3·39	3·54	3·34	3·57	3·43	3·66	3·48	3·58
Al	0·98	0·61	0·46	0·66	0·43	0·57	0·34	0·52	0·42
Interlayer population									
K	0·86	0·87	0·68	0·61	0·58	0·77	0·68	0·71	0·69
Na	0·10	0·07	0·03	0·02	0·03	0·01	0·01	0·01	0·03
Ca		0·02	0·05	0·01	0·03				
Ba		0·01							
H_3O+	0·01								
% expandable layer			5		5	< 10	< 10	< 10	< 10
stacking sequence	$2M_1$	$2M_1$	$2M_1$	$2M_1$	$2M_1$	1Md	1Md	1Md	1Md

*Ernst (1963).
†Gaudette, Eades and Grim (1966).
‡Hower and Mowatt, (1966).

Table 2. Average values of interatomic distances (in Å) in $2M_1$ phengite and $2M_1$ muscovite

Tetrahedral cation–O	$2M_1$ phengite	$2M_1$ muscovite
T_1–O	1·622 ± 0·003	1·643 ± 0·002
T_2–O	1·633 ± 0·003	1·643 ± 0·002
Octahedral cation–O	1·956 ± 0·002	1·932 ± 0·002
$K–O_{inner}$	2·970 ± 0·003	2·855 ± 0·002
$K–O_{outer}$	3·237 ± 0·003	3·362 ± 0·002
Tetrahedral tilt	0·16 ± 0·01	0·22 ± 0·01
Tetrahedral rotation (2α) in degrees		
Between basal oxygens	12·1 ± 0·1	22·7 ± 0·1
Between apical oxygens	9·1 ± 0·1	10·8 ± 0·1
Between tetrahedral cations	1·6 ± 0·1	1·9 ± 0·1

much less than in muscovite (Table 2), and is also expected to be the case in the illite structure. As a result of less tetrahedral rotation the distance from the interlayer cation to the oxygens in its primary coordination is increased. The larger K–O bond lengths and the smaller amount of unsatisfied charges on oxygens due to Si for Al replacements indicate that interlayer cation–oxygen bonds are likely to be considerably weaker in phengite and illites than in muscovite.

(d) As discussed in detail by Güven (1970) the $^{VI}R^{2+}Si$ for $^{VI}Al^{IV}Al$ substitutions decrease the structural control over stacking sequences in phengite, thus allowing a larger polymorphic variety involving 0°, ± 120° rotations (1M, 3T, 2M, 1Md forms) between the single mica layers. There will be even less structural control over stacking sequences in illites since in addition the role of interlayer cations will be less effective.

SUMMARY

Dioctahedral mica-type 10 Å clay minerals are more closely related in their composition and environment to phengites than to muscovites. Structural effects of the $^{VI}R^{2+}Si$ for $^{VI}Al^{IV}Al$ isomorphic substitutions (R = Mg, Fe^{2+}) along the muscovite–phengite join, as assessed from the recent crystal structure refinements of these micas, allow inferences to be made concerning the structural features in illite and its polymorphism.

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REFERENCES

Ernst, W. G. (1963) Significance of phengitic micas from low-grade schists: *Am. Mineralogist* **48**, 1357–1373.

Gaudette, H. E., Eades J. L. and R. E. Grim (1966) The nature of illite: *Clays and Clay Minerals* **13**, 33–48.

Güven, N. (1970) The crystal structures of $2M_1$ phengite and $2M_1$ muscovite, and structural factors controlling stacking sequences in dioctahedral Micas: in preparation.

Hower, J. and Mowatt T. C. (1966) The mineralogy of illites and mixed-layer illite/montmorillonites: *Am. Mineralogist* **51**, 825–854.

Levinson, A. A. (1955) Studies in the mica group: Polymorphism among illites and hydrous micas: *Am. Mineralogist* **40**, 41–49.

Velde, B. and Hower J. (1963) Petrological significance of illite polymorphism in Paleozoic sedimentary rocks. *Am. Mineralogist* **48**, 1239–1254.

Velde, B. (1965) Phengite micas: Synthesis, stability and natural occurrence. *Am. J. Sci.* **263**, 886–913.

Warshaw, C. M. (1960) Experimental studies of illite. *Clays and Clay Minerals* **7**, 303–316.

Department of Geology
University of Illinois
Urbana, Illinois 61801
U.S.A.

NECIP GÜVEN

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