

Hydrous micas.

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HYDROUS micas differ from normal micas in that they contain less potassium and more water. In the calculation of structural formulae from their chemical analyses, two methods have been used which rely on the following different assumptions:

1. As these minerals are often fine-grained and may contain adsorbed water, no reliance is placed on the value of H_2O+ (water lost above $105^\circ C.$) as a measure of structural water. The water content is ignored and the structural formula is calculated on the basis of 20 oxygens plus 4 hydroxyls per structural unit.² This method has been used by Hendricks and Ross³ and by Grim and Bradley.⁴

2. The water which is recorded as H_2O+ in the chemical analysis is assumed to represent hydroxyl groups in the aluminosilicate layers of the minerals. Thus, instead of having 20 oxygens and 4 hydroxyl ions per structural unit as in normal micas, formulae are derived which show less than 20 oxygens and more than 4 hydroxyls, the total oxygen plus hydroxyl remaining 24. This method has been used by Brammall, Leech, and Bannister.⁵

The above treatments generally result in structural formulae which depart considerably from those of ideal micas. In particular, the inter-layer positions are little more than half-filled and the number of ions in octahedral co-ordination, in the dioctahedral type of mica, is somewhat removed from 4.

Recently N. V. Shishkin⁶ has established the existence of oxonium

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² We take as the structural unit a cell of volume $abc \sin \beta/m$, where a , b , c , and β are the unit-cell parameters, and m is the number of layers per unit cell. This structural unit is chosen as it is independent of polymorphism of micas (S. B. Hendricks and M. E. Jefferson, *Amer. Min.*, 1939, vol. 24, p. 729 [M.A. 7-496]).

³ S. B. Hendricks and C. S. Ross, *Amer. Min.*, 1941, vol. 26, p. 683. [M.A. 8-275.]

⁴ R. E. Grim and W. F. Bradley, Chapter V in *X-ray identification and crystal structures of clay minerals*. *Min. Soc.*, London, 1951. [M.A. 11-253.]

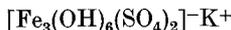
⁵ A. Brammall, J. G. C. Leech, and F. A. Bannister, *Min. Mag.*, 1937, vol. 24, p. 507.

⁶ N. V. Shishkin, *Zhurn. Obschei Khim.* (*Acad. Sci. U.S.S.R.*), 1951, vol. 21, p. 456.

ions $(\text{H}_3\text{O})^+$ in the system $\text{H}_2\text{O}-\text{SO}_3-\text{Fe}_2\text{O}_3-(\text{NH}_4)_2\text{O}$. He believes that



and



are isostructural, the potassium, ammonium, and oxonium ions replacing one another isomorphously.

In view of the above evidence for the replacement of potassium ions by oxonium ions and as these ions are approximately the same size, it seems probable that the high water and low potassium content of hydrous mica is due to the replacement of potassium by oxonium ions. To test this hypothesis we have calculated the structural formulae of some hydrous micas. The analyses used are those given by Brammall, Leech, and Bannister (*loc. cit.*) for hydromuscovites A and B, and those of Grim, Bray, and Bradley¹ for illites 1 and 2. These analyses were selected because the minerals were well characterized and pure. We have confined our attention to dioctahedral micas as hydrobiotites are usually vermiculitic.²

TABLE I. Chemical analysis of illite with calculation of structural formula.

	Atomic proportions		Atoms per structural unit.		
	Oxygen.	Cations.			
SiO_2 ... 51.22	1.7056	0.8528	Si	6.7495	8.0000
Al_2O_3 ... 25.91	0.7626	0.5084	Al	$\left. \begin{array}{l} 1.2505 \\ 2.7732 \end{array} \right\}$	
TiO_2 ... 0.53	0.0132	0.0066	Ti	0.0522	4.02
Fe_2O_3 ... 4.59	0.0861	0.0574	Fe^{3+}	0.4543	
FeO ... 1.70	0.0237	0.0237	Fe^{2+}	0.1876	
MgO ... 2.84	0.0704	0.0704	Mg	0.5572	
CaO ... 0.16	0.0029	0.0029	Ca	0.0230	1.85
Na_2O ... 0.17	0.0027	0.0054	Na	0.0427	
K_2O ... 6.09	0.0646	0.1292	K	1.0226	
H_2O^+ ... 7.14	0.3692	0.7924	H	$\left. \begin{array}{l} 2.2714 = 0.7572(\text{H}_3\text{O}^+) \\ 4.0000 = 4.0000(\text{OH}) \end{array} \right\}$	
ΣO ... —	3.1280	—	O 24.7566 — $(\text{H}_3\text{O}^+ + \text{OH}) = 20$	20(OH)	

Table I shows the calculation of the structural formula of illite 2 assuming that the excess water is present as oxonium ions occupying interlayer positions. Columns 1, 2, and 3 are self-explanatory. To obtain the number of ions per structural unit, shown in column 4, column 3 must be multiplied by a factor n . To determine n we make the following assumptions.

(a) There are 20 oxygens and 4 hydroxyl ions per structural unit, i.e. that the oxygen-hydroxyl framework is identical with that of a normal mica.

¹ R. E. Grim, R. H. Bray, and W. F. Bradley, *Amer. Min.*, 1937, vol. 22, p. 813. [M.A. 7-12.]

² J. W. Gruner, *Amer. Min.*, 1934, vol. 19, p. 557. [M.A. 6-181.]

(b) The excess water over that required for 4 hydroxyl ions is present as interlayer oxonium ions, ny per structural unit. We then have the following equations:

$$4/n + 3y = (\text{atomic proportion of hydrogen}),$$

and

$$24 + ny = (\text{atomic proportion of oxygen}),$$

and a solution of these gives n .

Column 5 gives the number of ions occupying the various positions in the structure. The number in tetrahedral co-ordination is made equal to 8 per structural unit by putting all the silicon and the necessary amount of aluminium in this position. The remaining aluminium together with the iron, titanium, and magnesium is put into positions of octahedral co-ordination, while the large ions, calcium, sodium, potassium, and oxonium are given interlayer positions.

TABLE II. Atomic cell contents of hydromuscovite and illite.

	Hydro- muscovite A.		Hydro- muscovite B.		Illite 1.		Illite 2.	
Si ...	6.1183	8.00	6.3629	8.00	6.6325	8.00	6.7495	8.00
Al ...	5.6467	—	5.3670	—	3.9181	—	4.0237	—
Ti ...	—	—	—	—	0.0501	—	0.0522	—
Fe ³⁺ ...	0.0712	3.97	0.1122	3.96	0.5105	4.04	0.4543	4.02
Fe ²⁺ ...	0.0396	—	0.0300	—	0.1685	—	0.1876	—
Mg ...	0.0981	—	0.0861	—	0.7752	—	0.5572	—
Ca ...	0.0309	—	0.0364	—	0.0636	—	0.0230	—
Na ...	0.1171	1.99	0.0553	1.84	0.0127	2.02	0.0427	1.85
K ...	1.3547	—	1.3110	—	1.1704	—	1.0226	—
H ...	5.5423	4 OH	5.3197	4 OH	6.3351	4 OH	6.2714	4 OH
O ...	24.5159	20 O	24.4400	20 O	24.7744	20 O	24.7566	20 O

This method has been applied to the four hydrous micas and Table II shows the complete structural formulae obtained. It will be seen that the formulae derived by these calculations show good agreement with those of normal dioctahedral micas in having the total of interlayer cations close to 2 and octahedral cations to 4 per structural unit. An ideal general formula for hydrous micas would be

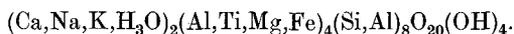


Table III shows a comparison of the structural formulae obtained by calculation from the various sets of assumptions noted above. It will be seen that better agreement with the ideal mica formula is obtained by using our assumptions than by either of the others.

In addition to the above we have considered other analyses of hydrous micas, including glauconites, given in the literature. Generally the formulae obtained are in better agreement with that of an ideal mica

than those derived by other methods of calculation. However, no definite conclusion can be drawn from studying these structural formulae in detail as in most cases the purity of the samples was not satisfactorily established.

TABLE III. Comparison of interpretations of structural formulae.

	Method of calculation.	Tetrahedral ions.	Octahedral ions.	Interlayer ions.
Ideal mica	—	8.00	4.00	2.00
Hydromuscovite A ...	{ a	8.00	3.97	1.99
	{ b	8.00	3.76	1.44
	{ c	8.00	3.03	1.38
Hydromuscovite B ...	{ a	8.00	3.96	1.84
	{ b	8.00	3.77	1.34
	{ c	8.00	2.98	1.29
Illite 1	{ a	8.00	4.04	2.02
	{ b	8.00	3.68	1.21
	{ c	8.00	3.94	1.27
Illite 2	{ a	8.00	4.02	1.85
	{ b	8.00	3.64	1.06
	{ c	8.00	4.26	1.11

Methods of calculation:

- Calculated assuming presence of H_3O^+ ions in addition to 20 oxygen and 4 hydroxyl ions per structural unit.
- Calculated assuming that oxygen+hydroxyl= 24 per structural unit.
- Calculated assuming presence of 20 oxygen and 4 hydroxyl ions per structural unit.

During the preparation of this paper our attention was directed to evidence presented by Ganguly¹ for the existence of oxonium ions as the exchangeable cations in hydrogen-saturated kaolinite, muscovite, and montmorillonite.

Conclusion.—It is our opinion that the excess of water and deficiency of potassium in the hydrous micas compared with the normal micas can be explained by the presence of oxonium ions in the interlayer positions. The consistency of the formulae derived above is adduced to evidence in support of this hypothesis.

¹ A. K. Ganguly, *Soil Sci.*, 1951, vol. 71, p. 239. [M.A. 11-450.]