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HARDNESS OF SYNTHETIC AND NATURAL MICAS[1]

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Abstract

The hardness of synthetic fluorphlogopite and of two natural muscovites, as measured on (001) by the Knoop indentation method, is definitely anisotropic. In both types of mica, maximum hardness is observed when the long axis of the indentation parallels the *b*-axis, minimum hardness when it parallels the *a*-axis. The pattern of the anisotropy shows, within the limits of measurement, a bilateral symmetry with respect to the (010) plane. Additional minima also occur on either side of the *a*-axis at an angle of 60° thereto for muscovite but at 75° thereto for fluorphlogopite. Additional maxima for hardness were observed at about 45° to the *b*-axis, not at 60° as had been expected. The anisotropy is interpreted in terms of the ionic structure of the micas involved.

Knoop hardnesses were measured parallel to the *a* and *b* axes for synthetic fluorphlogopites in which the following substitutions had been effected: (1) ferric and boron ions respectively into the tetrahedral aluminum positions, (2) manganese and cobalt respectively into the octahedral magnesium positions and (3) barium and strontium into the potassium positions. The boron mica was slightly softer, and the barium mica was much harder than the normal fluorphlogopite. The Knoop hardnesses of natural phlogopite, muscovite, margarite, and biotite were compared with those of the synthetics. The lesser hardness of these natural micas (excluding margarite) in comparison with the synthetic fluormicas is postulated to result, at least in part, from the greater polarizability of (OH) ion than of F ion.

Introduction

The synthetic fluorphlogopites are generally said to be harder than the comparable natural micas. However, as pointed out by Noda (1956, p. 12) "it is not known whether this hardness is its own property or only an apparent one caused by glassy material which exists between cleavage planes of mica crystals." This paper furnishes sufficient data on the relative hardness of synthetic and natural micas to answer these questions. Answers to several other questions that arose during the investigation, particularly regarding the anisotropy of hardness on (001) in mica, also have been suggested tentatively.

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[1] Synthetic Mica Investigations, I–VIII, are listed on pages 78 and 79 of Bureau of Mines Report of Investigations 5337, Synthetic Mica Investigations IX, Review of Progress from 1947 to 1955, by R. A. Hatch, R. A. Humphrey, W. Eitel, and J. E. Comeforo.

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ANISOTROPY OF HARDNESS ON (001) IN MICA

Any comparison of hardness between two minerals must be prefaced with a determination of possible anisotropy of hardness with respect to crystallographic direction. Considerable anisotropy of hardness in micas was shown to exist by Switzer (1941, p. 316) who noted the Mohs hardness to be 2.5 parallel to (001) and 4.0 perpendicular to (001) for both muscovite and biotite. Consequently even though the hardness of all the micas studied was to be measured on the (001) plane, a preliminary investigation of possible directional variations of hardness on (001) in mica was deemed advisable.

For the study of the possible anisotropy, smooth, relatively flawless, single crystals of three specimens of mica were selected with compositions and identities as noted in Table 1. A reference line was drawn perpendicular to the optic plane for the phlogopites and parallel to it for the muscovites, thus locating the *b*-crystallographic axis for each. The crystals studied, two of the synthetic fluorphlogopite and one each of the muscovites, were next carefully cemented with Canada balsam or similar material upon the plastic cylinders in which specimens are ordinarily embedded,[5] care being taken to eliminate air bubbles from beneath the mica. The indentation hardness of choice areas of these flakes was next measured with a fully automatic Tukon hardness tester equipped with a Knoop indenter under a load of 100 grams. At each of eight different

TABLE 1. COMPOSITION OF MICAS SELECTED FOR THE STUDY OF HARDNESS ANISOTROPY ON (001)

Identity	Composition	Analyst
Synthetic fluorphlogopite (Electrotech. Lab)	$K_{0.98}Na_{0.01}Mg_3Al_{1.01}Si_{3.01}O_{10}F_{2.03}$	Shell and Craig
Natural muscovite (Brazil)	$K_{0.88}Na_{0.09}Al_{1.78}Fe_{0.10}^{+++}Fe_{0.04}^{++}Mg_{0.04}Li_{0.04}Al_{0.96}$ $Si_{3.03}O_{9.8}(OH)_{2.03}F_{0.09}$	Craig
Natural muscovite (India)	$K_{0.85}Na_{0.19}Al_{1.88}Fe_{0.05}^{+++}Fe_{0.02}^{++}Mg_{0.02}Al_{0.97}Si_{3.02}$ $O_{10.02}(OH)_{1.81}F_{0.16}$	Craig

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[5] The ordinary method of embedding had been previously found unsuitable for this work, primarily because the unequal thermal expansions between mica and plastic caused a bowing up of the embedded mica flakes during cooling of the mount. The resultant free space below the center of the mica flake was found to seriously affect accuracy.

choice locales on the flakes studied, a series of 13 hardness measurements was made, the long axis of the indentation being successively oriented at angles of 0°, 15°, 30° . . . 165°, and 180° to the *b*-axis. Results for the four flakes thus studied are shown in Fig. 1, each point representing the average of eight hardness determinations. The spread of the hardness determinations was statistically distributed about an average deviation of 1.0 to 1.5 Knoop_{100} hardness values.

As may be seen in Fig. 1, a definite anisotropy of hardness on (001) exists for both synthetic fluorphlogopite and the two natural muscovites.

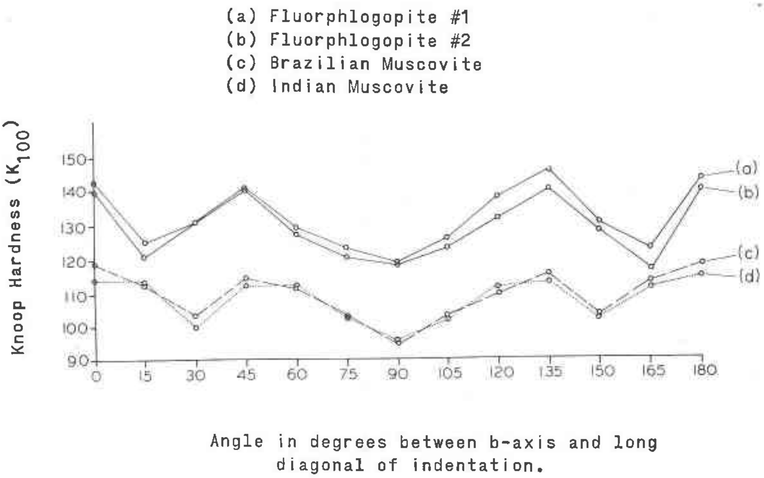

FIG. 1. The anisotropy of Knoop hardness on (001) for two flakes of synthetic fluorphlogopite and for two different muscovites. The bilateral symmetry of the curves around the 90° orientation reflects the plane of symmetry in mica.

The plane of symmetry of mica is clearly reflected in the bilateral symmetry of all curves with respect to the 90° orientation. The two muscovites show remarkable agreement, better in fact than that between the two flakes of fluorphlogopite. For both muscovite and phlogopite minimum hardness is observed parallel to the *a*-axis (i.e. at 90° to *b*). This minimum appears to be slightly less than the other two minima, which for muscovite are at 30° angles to the *b*-axis, whereas for phlogopite they are at only 15° angles to the *b*-axis. Maximum hardness on (001) in mica occurs parallel to the *b*-axis and at 45° thereto for fluorphlogopite; for muscovite the location of the maxima at 45° is less definite, since the hardness at 60° to the *b*-axis is nearly as great.

This observed anisotropy of hardness undoubtedly results from the interplay between (1) the shape of the diamond pyramid of the Knoop indenter and (2) the atomic structure of the mica investigated. The indenter's shape is important because it produces a diamond-shaped identation, one diagonal of which is much longer than the other. Its penetration, therefore, resembles that of a wedge rather than of a needle. The atomic structure is important since particular directions in the sheet structure may represent lines of weakness by virtue of representing an alignment of weaker bonds or of fewer bonds. The stacking of the mica sheet structures according to the theories elucidated by Smith and Yoder (1956) would distribute these lines of weakness along particular planes parallel to which the wedge action of the Knoop indenter could penetrate more easily.

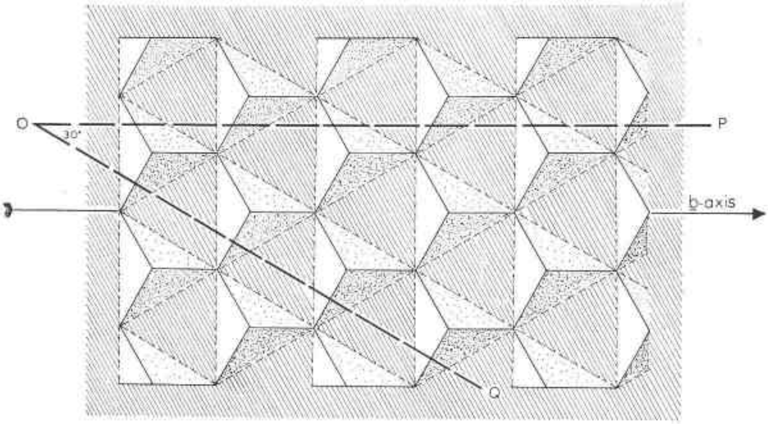

FIG. 2. Schematic drawing of the SiO_4 or AlO_4 tetrahedra in the mica sheet structure. The light, dashed lines represent the bases of the tetrahedra. The heavier solid lines represent the direction of the Si—O (or Al—O) bonds as well as the other three edges of the tetrahedra. A line along OQ cuts the minimum number of bonds per unit length whereas OP cuts 15.5% more per unit length and is one of the directions of maximum density of bonding in the sheet.

Any indentation of the (001) plane of mica is accompanied by (1) breakage of the Si—O or Al—O bonds of the $AlSi_3O_{10}$ sheets, (2) breakage of the K—O bonds linking these sheets, and (3) breakage of the bonds octahedrally coordinating Mg or Al to the surrounding O, OH, or F ions. Considering the $AlSi_3O_{10}$ sheets alone (Fig. 2), the insertion of a wedge along direction OP (or 60° thereto) would involve breakage of 15.5% more Si—O or Al—O bonds than along OQ (or 60° thereto). A similar situation exists for the K—O bonds (Fig. 3), bond breakage along OP again exceeding that along OQ by 15.5%. The octahedral ions have a somewhat different arrangement in phlogopite than in muscovite. In

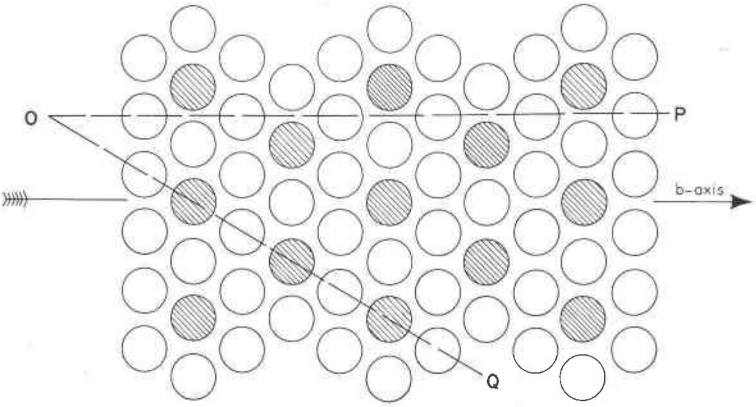

FIG. 3. Location of potassium ions (shaded) with respect to the oxygen ions in the planes above and below them. OQ, and directions at 60° thereto, represent the direction of minimum bond breakage; OP and directions at 60° to it, represent the direction of maximum bond breakage.

phlogopite (Fig. 4), OP represents a minimum for Mg—O or Mg—F, OH bond breakage, OQ exceeding it in this respect by 15.5%. On the other hand in muscovite (Fig. 5), two directions of weakness, OQ and RS,

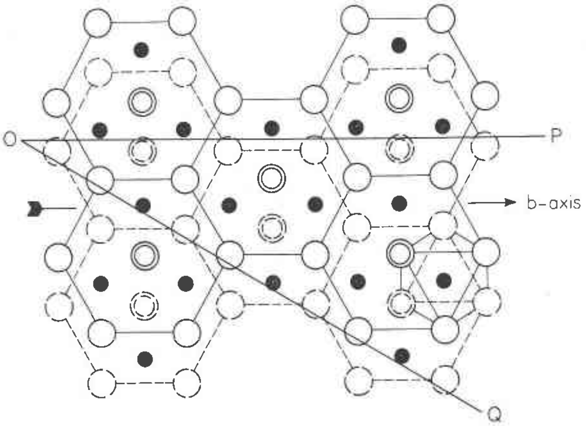

FIG. 4. Projection on (001) of a portion of a phlogopite layer after Hendricks and Jefferson (1939, p. 731). The distribution of the oxygen ions (hollow circles) and the fluorine or hydroxyl ions (double circles) are shown with respect to the magnesium ions (solid black circles). Dashed lines signify the anions to be in a plane slightly below the cations; solid lines signify them to be slightly above. Line OP and directions at 60° thereto here represent the directions of minimum bond density; OQ and associated 60° directions represent lines of maximum bond density.

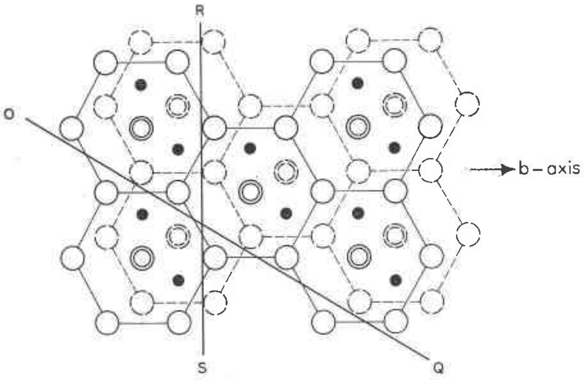

FIG. 5. Projection of a portion of a muscovite layer after Hendricks and Jefferson (1939, p. 731). Ion symbolism as before except solid black circles now represent aluminum ions. Line OQ, in contrast to Fig. 4, now represents a direction of minimum bond density as does RS. The direction at 60° to each of them, however, is not so favored.

are created by the systematic non-filling of one third of the octahedral positions.

By using the terminology of Smith and Yoder (1956), as well as their data and method for identifying the various mica polymorphs, the fluorphlogopite was determined from x-ray data to be a 1M type whereas the two muscovites were $2M_1$ types. The manner of alignment of the previously discussed lines of weakness by the 1M and $2M_1$ types of stacking thus becomes of interest in interpreting the observed anisotropy of hardness. To illustrate the relationships more simply, the Smith and Yoder (1956) device of depicting the sheet structure of the mica as hexagons has been adopted (Fig. 6).

The dashed lines in Fig. 6a represent the lines of weakness for both the

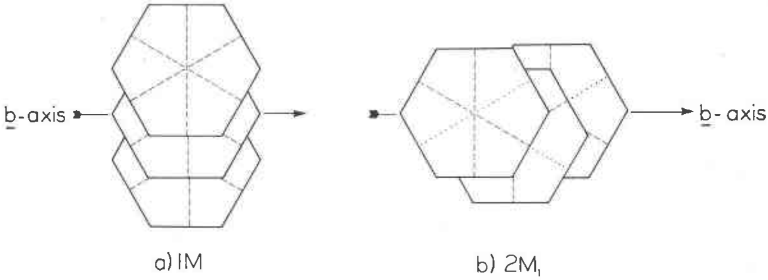

FIG. 6. The relationship of the method of stacking to the directions of presumed weakness (dashed or dotted lines) in the sheet structure of mica for (a) phlogopite and (b) muscovite. In (b) the dotted line is not as favored a direction of weakness as are the dashed lines since it is not as favorably disposed with respect to the distribution of the AlO_6 octahedra.

$AlSi_3O_{10}$ sheets and the K—O arrays; with respect to the Mg—O, F bonds they represent lines of strength. The over-all effect, however, appears to be that they are truly lines of weakness, the identation hardness parallel to the *a*-axis being significantly less than that observed parallel to the *b*-axis. From Fig. 6*a* one would expect Knoop hardness on fluorphlogopite to repeat cyclically every 60°, with minima at 30° and 90° to the *b*-axis. Actually, however, in Fig. 1 the minima are at 15° and 90° to the *b*-axis. Similarly the maxima would be expected (from Fig. 6*a*) to be parallel to and at 60° to the *b*-axis; actually they were observed parallel to and at 45° to the *b*-axis. The explanation thus far found most attractive is that one of the planar arrays of ions composing an individual sheet in the mica structure is not truly hexagonal; the suspicion therefore arises that there is an ordering of the Al ions in the $AlSi_3O_{10}$ sheets.

In muscovite, it may be recalled, two of the three theoretical directions of weakness in the $AlSi_3O_{10}$ and K—O arrays actually coincided with the two rather significant directions of weakness produced by the systematic absences in one third of the octahedral positions. In Fig. 6*b* these two weakest directions are shown on the hexagons as dashed lines; the dotted line represents that direction of weakness in the $AlSi_3O_{10}$ and K—O arrays which was not reinforced by the systematic absence of the octahedrally coordinated ions.

The $2M_1$ stacking (Fig. 6*b*) may be seen to maintain a parallelism of the dashed lines in a direction perpendicular to the *b*-axis between the different layers; at 30° to the *b*-axis, however, the dashed and dotted lines are alternately parallel to each other between neighboring layers. This may possibly account for the slightly lesser hardness at 90° than at 30° to the *b*-axis (Fig. 1).

EFFECT OF IONIC SUBSTITUTION ON HARDNESS

General

Indentation hardness on (001) was measured parallel to the *a*-axis and the *b*-axis, the directions of demonstrated minimum and maximum hardness, for several synthetic and natural micas. The effect of hardness of various ionic substitutions is discussed in the succeeding sections.

Substitution in the tetrahedral positions

Table 2 compares the observed Knoop hardness values for the normal synthetic fluorphlogopite with some substituted analogs. The replacements involve the ferric and boron ions substituting for aluminum in the tetrahedral positions. Each value in this (and succeeding tables) is based on an average of 8 Knoop hardness determinations. "Normal" fluorphlogopite is theoretically $KMg_3AlSi_3O_{10}F_2$. The compositions given in this and the following tables were determined by calculation from the actual chemical analysis of selected clear single crystals.

Substitution of Fe^{+++} for Al^{+++} in the tetrahedral positions of the $AlSi_3O_{10}$ sheets causes little, if any, increase in hardness. On the other hand, the analogous substitution of B^{+++} for Al^{+++} effects a definite decrease in hardness. The radii given by Pauling (1940, p. 346) for these ions (i.e. Fe^{+++}, 0.60 Å; Al^{+++}, 0.50 Å; and B^{+++}, 0.20 Å) indicate Fe^{+++} to be larger than B^{+++} as well as closer in size to Al^{+++}. The increased softness of the boron mica may perhaps be due to B^{+++} being rather small for the position it occupies; Fe^{+++}, however, evidently fills it more adequately. If one considers that the radius of Si^{++++} is 0.41 Å, i.e. midway between Fe^{+++} and B^{+++} in size, the interesting conjecture arises that the Al positions in the sheets may differ in size from the Si^{++++} positions.

TABLE 2. EFFECT OF TETRAHEDRAL SUBSTITUTIONS ON HARDNESS OF SYNTHETIC MICAS

Mica Type	Composition	Observed Knoop Hardness values for 100 gram indenter load		
		Trial	Orientation of long axis of indentation	
			Parallel to *a*-axis	Parallel to *b*-axis
"Normal" fluorphlogopite	$K_{0.98}Na_{0.01}Mg_3Al_{1.01}Si_{3.01}O_{10}F_{2.03}$	(1)	119	143
		(2)	118	140
Ferric fluorphlogopite, No. 18-47	$K_{0.99}\cdot Fe_{0.29}^{+++}Mg_{2.70}\cdot Fe_{1.08}^{+++}Si_{2.93}O_{10.18}F_{1.82}$	(1)	128	150
		(2)	119	145
Fe-Al fluorphlogopite No. 25-55	$K\cdot Mg_3\cdot Al_{0.5}Fe_{0.5}^{+++}Si_3\cdot O_{10}F_2$		129	140
Boron fluorphlogopite No. 25-23	$K_{0.87}\cdot Mg_{2.71}\cdot B_{.34}\cdot Al_{.04}Si_{3.65}\cdot O_{10}F_{2.00}$	(1)	100	125
		(2)	95	122
Boron fluorphlogopite, No. 25-58	$K_{1.00}\cdot Mg_{3.00}\cdot B_{.15}Al_{.83}Si_{3.01}\cdot O_{9.97}F_{4.03}$		114	126
Boron fluorphlogopite No. 25-59	$K_{0.97}\cdot Mg_{2.91}\cdot B_{0.27}Al_{0.61}Si_{3.14}\cdot O_{10}F_{2.01}$		111	120

Substitution in octahedral positions

Table 3 compares the observed Knoop hardness values for the normal synthetic fluorphlogopite with two modifications in which Mn^{++} and Co^{++} respectively are substituted into some of the Mg^{++} positions. The differences appear rather minimal, being within the range of experimental error.

TABLE 3. EFFECT OF OCTAHEDRAL SUBSTITUTIONS ON HARDNESS OF SYNTHETIC MICAS

Mica Type	Composition	Observed Knoop hardness values for 100 gram indenter load		
		Trial	Orientation of long axis of indentation	
			Parallel to *a*-axis	Parallel to *b*-axis
Normal fluorphlogopite	$K_{0.98}Na_{0.01}Mg_3Al_{1.01}Si_{3.01}O_{10}F_{2.03}$	(1) (2)	119 118	143 140
Manganese fluorphlogopite No. 18-13	$K_{1.07}\cdot Mg_{2.94}Mn_{0.08}\cdot Mn_{0.11}Al_{0.88}Si_{3.01}O_{10.03}F_{1.97}$	(1) (2)	116 119	141 141
Cobalt fluorphlogopite No. 18-24	$K\cdot Mg_{2.03}Co_{0.88}{}^{++}\cdot Al_{0.12}\cdot Al_{0.96}Si_{3.04}O_{10.15}F_{1.95}$	(1) (2)	103 114	128 132

Substitution in the twelve-fold position

Table 4 compares the Knoop hardness on (001) for several micas which differ chiefly as to the ion occupying the twelve-fold coordinated positions. As may be seen from two of the examples, increased substitution of Ba^{++} for K^+ resulted in a significant increase in hardness. Complete substitution of Ba^{++} for K^+ resulted in the hardest of all synthetic micas. Sr^{++} in small amounts increased hardness. Synthetic micas containing all Sr^{++} or Ca^{++} in the twelve-fold position could not be made large enough for testing by the methods described. In fact, complete Ca^{++} substitution would yield a fluoramphibole, not a fluormica. Occupancy by Ca^{++} of the twelve-fold positions greatly increases hardness, as shown by the measurements on a natural margarite from Chester, Massachusetts. Results thus bear out the well known hypothesis that the hardness of mica is strongly affected by the bond strength of the twelve-fold coordination ions.

Samples of otherwise normal fluorphlogopite containing small amounts of Na^+, Li^+, or even Ca^{++} in the twelve-fold position, were apparently slightly softer than an all K^+ fluorphlogopite. Amounts involved were $Na^+_{0.1}$ to $_{0.04}$, $Li^+_{0.03}$, and $Ca^{++}_{0.02}$ per unit formula of $KMg_3AlSi_3O_{10}F_2$, and were determined on selected clear crystals by chemical analysis. It was also noted that synthetic fluorphlogopite synthesized from a batch containing feldspar averaged slightly softer than one from a batch containing potassium carbonate. Potassium feldspar of commerce always contains 2 to 3% Na_2O.

TABLE 4. EFFECT OF TWELVEFOLD COORDINATION SUBSTITUTIONS ON HARDNESS OF MICAS

Mica Type	Composition	Observed Knoop hardness values for 100 gram indenter load		
		Trial	Orientation of long axis of indentation	
			Parallel to *a*-axis	Parallel to *b*-axis
"Normal" fluorphlogoopite	$K_{0.98}Na_{0.01}Mg_3Al_{1.01}Si_{3.01}O_{10}F_{2.03}$	(1)	119	143
		(2)	118	140
Barium fluorphlogopite I 25-28	$K_{0.77}Ba_{0.11}\cdot Mg_3\cdot AlSi_3\cdot O_{10}F_2$	(1)	144	176
		(2)	140	172
Barium fluorphlogopite II 25-29	$K_{0.50}Ba_{0.25}\cdot Mg_3\cdot AlSi_3\cdot O_{10}F_2$	(1)	173	206
Barium fluormica 18–26X	$Ba\cdot Mg_{2.5}\cdot AlSi_3\cdot O_{10}F_2$	(1)	241	252
		(2)	232	259
Barium lithium mica 18–34X	$Ba_{0.97}\cdot Mg_{2.23}Li_{0.77}\cdot Al_{1.1}Si_{2.84}\cdot O_{9.90}F_{2.08}$	(1)	235	260
		(2)	225	246
Strontium fluormica 25–33	$K_{0.84}Sr_{0.08}\cdot Mg_3\cdot AlSi_3\cdot O_{10}F_2$		122	148
Natural margarite from Chester, Mass.	$Ca_{0.5}\cdot Al_2\cdot AlSi_3\cdot O_{10}(OH)_2$	(1)	238	402
		(2)	247	375

Very low hardness values were obtained on some small samples of natural phlogopite which had previously been flexed or bent. Although these apparently were clear and free of air inclusions, Knoop hardness values of 30 to 50 were obtained on the (001) face.

Substitution of F^- for $(OH)^-$

Micas representing various degrees of substitution of F^- for $(OH)^-$ were unavailable at the time of the study. Since this substitution is a chief difference between the natural and synthetic micas, a comparison of their observed hardness (Table 5) should indicate the effect on hardness of substituting fluorine for hydroxyl in the mica structure. (Each value in Table 5 is again the average of eight determinations on a particular flake.) Judged from these results, the synthetic micas apparently are slightly harder than the nearest comparable natural micas. Absolute comparisons, ion for ion, were not obtained, but the trend was definitely for slightly greater hardness in the synthetic than in natural micas. The difference was not sufficiently great, however, to affect the useful properties of the synthetic, nor its substitution for natural when large enough sheets are synthesized. Microscopic examination demonstrated that all flakes tested were free of interlayered glass as well as, in the case of the natural micas, alteration products.

It is here suggested that the substitution of F^- for $(OH)^-$ in the mica structure in general (and in the phlogopite structure in particular) produces increased hardness because of the lesser polarizability of F^- as compared with $(OH)^-$. As may be seen in Fig. 7*a*, an $(OH)^-$ ion would be so polarized (by the three Mg^{++} ions underlying it and by the six

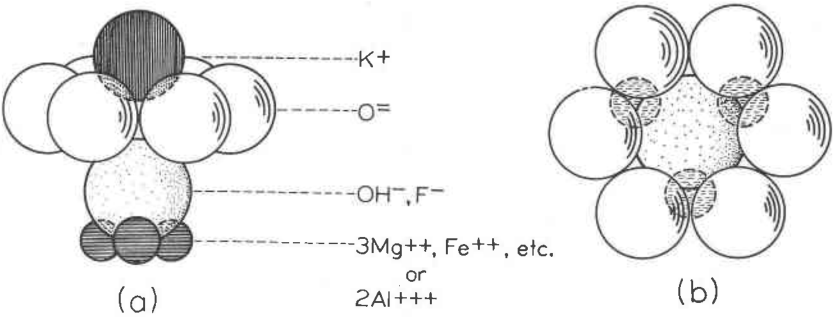

FIG. 7. Structural relationship between the potassium and hydroxyl (or fluorine) ions in mica. (*a*) Side view looking almost edgewise onto (001), (*b*) view looking directly down on (001) with the potassium ion which directly overlies the hydroxyl removed for illustrative purposes. The positive pole of the hydroxyl ions is probably on the side directly underlying the potassium ion.

TABLE 5. HARDNESS OF SOME SYNTHETIC FLUORMICAS AND NATURAL HYDROXY-MICAS FOR COMPARISON OF F^- VS. OH

Mica Type	Composition	Observed Knoop hardness for 100 gram indenter load		
		Trial	Orientation of long axis of indentation	
			Parallel to *a*-axis	Parallel to *b*-axis
	Synthetic Fluormicas			
"Normal" fluorphlogopite	$K_{0.98}Na_{0.01}Mg_3Al_{1.01}Si_{3.01}O_{10}F_{2.03}$	(1) (2)	119 118	143 143
Manganese fluorphlogopite 18–13	$K_{1.07}\cdot Mg_{2.94}Mn_{0.08}\cdot Mn_{0.11}Al_{0.88}Si_{3.01}$ $\cdot O_{10.13}F_{1.97}$	(1) (2)	116 119	141 141
Cobalt fluorphlogopite 18–24	$K\cdot Mg_{2.03}Co_{0.88}^{++}Al_{0.12}\cdot Al_{0.96}\cdot Si_{30.4}$ $\cdot O_{10.15}F_{1.95}$	(1) (2)	103 114	128 132
Ferric fluorphlogopite 18–47	$K_{0.99}\cdot Fe_{0.29}^{+++}Mg_{2.70}\cdot Fe_{1.08}^{+++}Si_{2.93}$ $\cdot O_{10.18}F_{1.82}$	(1) (2)	128 119	150 146
	Natural Micas			
Phlogopite, Canada	—	(1) (2)	98 84	114 101
Biotite, Mitchell Co., N. C.	—	(1)	66	69
Lepidomelane, Faraday Twp., Can.	—	(1)	71	84
Muscovite, Brazil	$K_{.88}Na_{.09}Ca_{.005}Al_{1.78}Fe_{.10}^{+++}Fe_{.04}^{++}$ $Mg_{.04}Li_{.04}Al_{.96}Si_{3.03}O_{9.8}(OH)_{2.03}F_{.09}$	(1) (2)	97 99	116 126
Muscovite, S. Dakota	$K_{.85}Na_{.19}Ca_{.005}Al_{1.88}Fe_{.05}^{+++}Fe_{.02}^{++}$ $Mg_{.02}Al_{.97}Si_{3.02}O_{10.02}(OH)_{1.81}F_{.16}$	(1) (2)	93 95	123 126
Muscovite, India	$(K_{.87}Na_{.10}Ca_{.005})Al_{1.80}Fe_{.06}^{+++}Fe_{.06}^{++}$ $Mg_{.06}Al_{.97}Si_{3.03}O_{9.85}(OH)_{2.09}F_{.05}$	(1) (2)	102 96	115 115

oxygen ions overlying it) as to develop a positive pole on its side nearest the potassium. Figure *7b*, wherein the potassium ion lying directly over the $(OH)^-$ ion has been removed for illustrative purposes, shows this presumed positive region on the hydroxyl to be unscreened by the oxygen ions with respect to the overlying potassium. The resultant mutual repulsion would thereby weaken the K—O bonding and consequently cause a decrease in hardness. Substitution of F^- for $(OH)^-$, since fluorine is less polarizable, would reduce this effect and result in increased hardness.

The above hypothesis may also explain, in part, the increased thermal stability and decreased basal spacing (001) of fluorphlogopites as compared to their hydroxyl analogs. As noted by Yoder and Eugster (1954, p. 176), "The substitution of F^- for $(OH)^-$ appears to result in a rise of 575° C. in the upper stability limit at one atmosphere pressure!" A more important factor regulating this increased thermal stability may be the lesser ability of the fluorine ion to escape from the mica structure as an electrically neutral phase. Whereas F^- requires a cation in order to escape, the $(OH)^-$ ion may escape as H_2O simply by combining with an H^+ ion from a second, nearby $(OH)^-$ ion. The resultant $O^=$ remains in the structure, thereby preserving electrical neutrality.

The basal spacing (001) of fluorphlogopite is reported by Noda and Roy (1956, p. 931) to be 0.17 ± 0.02 Å less than for the comparable OH^- phlogopite. Under the hypothesis of increased polarization of the hydroxyl ion, this would be expected.

EFFECT OF MECHANICAL PRESSURE ON HARDNESS OF SYNTHETIC FLUORPHLOGOPITE

Specimens of the "normal" fluorphlogopite were subjected to high pressure at room temperature and at 1250° C. prior to testing their hardness. Such treatment had no striking effect on hardness.

CONVERSION FROM KNOOP TO MOHS

The conversion of Knoop hardness to Mohs hardness is subject to considerable uncertainty, primarily because, as shown by Winchell (1945), the Knoop hardness of some minerals of Mohs' scale depends upon crystallographic orientation. Roughly converted, however, the micas studied possessed Mohs hardnesses as indicated in Table 6.

CONCLUSIONS

1. The hardness of synthetic fluorphlogopite and of two natural muscovites, as measured on (001) by the Knoop indentation method, is definitely anisotropic, the pattern possessing a bilateral symmetry with respect to (010).

TABLE 6. KNOOP HARDNESS ROUGHLY TRANSLATED INTO MOHS HARDNESS

Mica	Mohs Hardness		
	Trial	Parallel to *a*-axis	Parallel to *b*-axis
	Synthetic Fluormicas		
"Normal" fluorphlogopite	(1) (2)	3− 3−	3½ 3½
Manganese fluorphlogopite No. 18-13	(1) (2)	3− 3−	3½ 3½
Cobalt fluorphlogopite No. 18-24	(1) (2)	3− 3−	3 3
Ferric fluorphlogopite No. 18-47	(1) (2)	3− 3−	4− 4−
Boron fluorphlogopite No. 25-23	(1) (2)	3− 3−	3 3
Barium fluorphlogopite I No. 25-28	(1)	4	4+
Barium fluorphlogopite II No. 25-29	(1)	4+	4+
	Natural Micas		
Phlogopite (Canadian)	(1) (2)	3− 3−	3− 3−
Biotite (Mitchell Co., N. C.)		2½	2½
Lepidomelane (Faraday Twp., Canada)		2½	2½
Muscovite (Brazil)	(1) (2)	3− 3−	3− 3
Muscovite (S. Dakota)	(1) (2)	3− 3−	3 3
Muscovite (India)	(1) (2)	3− 3−	3 3
Margarite	(1) (2)	4+ 4+	5 5

2. Maximum hardness on (001) in mica is observed when the long axis of the indentation is parallel to the *b*-axis.
3. For synthetic fluorphlogopite the two other directions for minimum hardness are at 15° on either side of the *b*-axis; for muscovite at 30° on either side.
4. For both fluorphlogopite and muscovite, two other maxima exist at 45° to the *b*-axis.
5. Substitution of boron ions into the aluminum positions of fluorphlogopite produced a softer mica; however, substitution of ferric ion for aluminum produced little change.
6. Substitution of Mn for Mg in fluorphlogopite effected little change in hardness; substitution of Co for Mg decreased hardness slightly.
7. Substitution of Ba for K produced a marked increase in the hardness of fluorphlogopite.
8. Except for margarite, the natural micas are softer than the synthetic micas.
9. The natural phlogopite and biotites examined proved softer than the natural muscovites.
10. The increased softness of natural phlogopite and of natural micas in general, as compared to the synthetic fluormicas, is believed partly due to the greater polarizability of the hydroxyl ion as compared to the fluorine ion.

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