

Changes in *b*-dimension in relation to potassium exchange and to oxidation of phlogopite and biotite

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EXPANSION and hydration of micas resulting from the exchange of K with a hydrated cation generally cause an increase in the *b*-dimension of the vermiculitic products (Leonard and Weed, 1967 and 1970b). The explanation for this increase (Leonard and Weed, 1970b) has been based on Radoslovich's (1963) interpretation of the *b*-dimension of vermiculite. Briefly, the replacement of interlayer K by hydrated cations, which are displaced from the mineral surface by that water of hydration, imparts an increased charge density to the surface oxygens of the silica sheet. The resulting increased repulsion between these oxygens tends to untwist the surface ditrigonal network and these to increase the *b*-dimension.

Oxidation may cause a decrease in the *b*-dimension of high-iron vermiculites and biotites (Wones, 1963; Rimsaite, 1967; Farmer *et al.*, 1971). This decrease has been attributed, at least in part, to the oxidation of octahedral Fe²⁺ ions, followed by an irreversible loss of Fe³⁺ ions from the octahedral sheet. The resulting increased number of dioctahedral sites decreases the *b*-dimension.

In most of the experiments reported in the literature, the *b*-dimensions were computed from 060 reflections obtained by X-ray diffraction from randomly oriented powder specimens. Partly owing to the difficulty of achieving complete random orientation, the reflections are generally weak and difficult to measure accurately (e.g. Leonard and Weed, 1970b). Preliminary experiments indicated that strong and symmetrical 060 reflections could be obtained from micas and vermiculites if specimens consisting of basally oriented, relatively large particles were mounted perpendicular to the X-ray beam according to the method of Rich (1957). Hence, using this method, experiments were done to (a) determine the relation between change in *b*-dimension with progressive exchange of potassium for calcium, (b) measure changes

in *b*-dimension upon oxidation of the vermiculized products, (c) calculate *b*-dimensions and tetrahedral rotations to estimate the degree of untwisting of the ditrigonal surface-oxygen configuration of the vermiculized products.

EXPERIMENTAL PROCEDURE

The micas used were a phlogopite from Loughborough County, Ontario and a biotite from Amelia, Virginia. The chemical formulas of these micas are shown in Table 2, Nos. 1 and 6. Most samples had a particle-size range of 54–75 μm which was obtained by wet-grinding and sieving. The K was extracted with 0.2 N CaCl₂ at 80°C in an incubator. The sample to solution ratio was generally 40 mg–200 ml. After reaction periods of 2 days (shorter initially) the solutions were replaced with fresh solutions, and the K in the replaced solutions was determined by atomic absorption spectrophotometry. The K content remaining in the samples was computed by subtracting the released K from the total K in the original samples. Samples of increasing interlayer Ca to K contents were obtained by increasing the number of reaction periods. About 5 reaction periods were needed for complete exchange. Some of the K-depleted samples were oxidized by placing them in 100 ml of water which contained approximately 5 ml H₂O₂, and then heating for about 2 hr on a steambath.

The X-ray diffraction measurements were made using the procedure and equipment described by Rich (1957). The instrument was a General Electric XRD-3 with CuKα radiation. The slit system consisted of a 1° divergence slit, a MR soller slit and a 0.2° detector slit. The sample holder and the sedimentation technique were also similar to those described by Rich (1957). The 060 reflections of the untreated micas were obtained from disks 2.5 cm in dia. which were cut from thin sheets of the

Table 1. *b*-dimensions (Å) and tetrahedral rotations* for phlogopite and biotite and their K-depleted, Ca-saturated products and some comparisons of these dimensions and rotations obtained and calculated from data in the literature for corresponding minerals

No.	Mineral	<i>b</i> _{obs}	<i>b</i> _{calc}	<i>b</i> _{obs} – <i>b</i> _{calc}	<i>b</i> _{tetr}	α ^o _{calc}
1	Phlogopite Po	9.213	9.204	+0.011	9.407	11°39'
2	Phlogopite PI	9.200	9.187	+0.013	9.417	12°18'
3	Phlogopite (–K, +Ca) P100	9.279	9.268	+0.011	9.407	9°27'
4	Phlogopite (–K, +Ca) VP1	9.250	9.203	+0.047	9.417	10°48'
5	Vermiculite (Kenya)	9.262	9.264	–0.002	9.373	8°42'
6	Biotite Bo	9.246	9.232	+0.014	9.343	8°16'
7	Biotite J-56-21	9.246	9.253	–0.007	9.371	9°22'
8	Biotite (–K, +Ca) B96	9.312	9.063	+0.249	9.343	4°41'
9	Biotite (–K, +Ca, oxidized) B96 ox.	9.042	9.149	–0.107	9.343	14°34'

**b*-dimensions and tetrahedral rotations for Nos. 1, 3, 6, 8 and 9 obtained and calculated in this experiment, for Nos. 2 and 4 obtained and calculated from data in Leonard and Weed (1970a, b) and for Nos. 5 and 7 obtained from data in Radoslovich (1962) and Radoslovich and Norrish (1962) respectively.

Table 2. Structural formulas* of, and references† to, the minerals in Table 1

No.	Reference	K	Na	Ca	Mg	Fe ²⁺	Fe ³⁺	Ti	Al ^{VI}	Al ^{IV}	Si	OH	F	O
1	Ross and Rich (1973)	0.97	0.06	0.04	2.77	0.04	0.07		0.16	1.40	2.60	2		10
2	Leonard and Weed (1970a)	0.81	0.06	0.01	2.02	0.24	0.12	0.07	0.47	1.44	2.56	2		10
5	Mathieson and Walker (1954)				2.36		0.48		0.16	1.27	2.73			
6	Le Roux <i>et al.</i> (1970)	0.84	0.05	0.07	0.65	1.34	0.15	0.11	0.42	1.15	2.85	2		10
7	Jones (1958)	0.92	0.03	0.01	0.88	1.27	0.16	0.12	0.38	1.26	2.74	1.80	0.09	10.11
9	This experiment				0.65		1.04	0.11	0.42	1.15	2.85			

* Anions and interlayer cations for No. 5 and 9 not included

† Data for Nos. 5 and 7 also in Radoslovich (1962) and Radoslovich and Norrish (1962) respectively.

original phlogopite and biotite. These disks were also mounted at 90° from the usual position but with the regular sample holder. In this procedure, however, no 060 reflection is obtained at the correct 2θ angle unless at this angle the disk is rotated around its center to the point where the 060 planes are in the diffraction position.

This rotation is not necessary for a sample consisting of many basally oriented particles because a sufficient number of them will be in the required diffraction position. The 060 reflection of a randomly-oriented powder specimen of the K-depleted, oxidized biotite was also measured using a Philips diffractometer unit with CoKα radiation. Powdered CaF₂ was used as an internal standard.

RESULTS AND DISCUSSION

Figure 1 shows sharp and symmetrical 060 reflections of phlogopite and biotite for several stages of K for Ca exchange. The *b*-dimensions were computed from the spacings measured at the centers of the peaks at half their heights.

Figure 2 demonstrates that, except for phlogopite at 36% K depletion, the *b*-dimensions of phlogopite and biotite increased linearly with exchange of K for Ca. The slopes of the lines for the two micas are the same and show that the replacement of K by Ca was accompanied by an increase in *b* of 0.066 Å. Kodama and Ross (1972) found for exchange of K for Ba in muscovite a linear increase in *b* about half that obtained for the micas in this experiment. Although the rate and extent of increase in *b* were the same for the two micas used in this experiment, it is likely that this increase depends on the hydrated cation replacing K and perhaps also on the type of mica (Leonard and Weed, 1967 and 1970a, b).

The *b*-dimensions of the micas and their vermiculized products were calculated using the equations of Radoslovich (1962) for micas and montmorillonites. For micas the equation is:

$$b = (8.925 + 0.099 K - 0.069 Ca + 0.062 Mg + 0.116 Fe^{2+} + 0.098 Fe^{3+} + 0.166 Ti) \mp 0.03 \text{ \AA}. \quad (1)$$

For montmorillonites, which included some vermiculites,

$$b = (8.944 + 0.096 Mg + 0.096 Fe^{3+} + 0.037 Al_{\text{tet}}) \pm 0.012 \text{ \AA}. \quad (2)$$

The value of *b* for the "free" tetrahedral layer, i.e. the tetrahedral layer with zero rotations, is given (Radoslovich and Norrish, 1962) by:

$$b_{\text{tet}} = (9.051 + 0.254x) \quad (3)$$

where *x* is the number of Al atoms in four tetrahedral sites. The tetrahedral rotation (α) may then be calculated (Radoslovich and Norrish, 1962) by:

$$\alpha = \arccos (b_{\text{obs}}/b_{\text{tet}}) \quad (4)$$

The data in Table 1 show that the differences between *b*_{obs} and *b*_{calc} for the micas are well within the error given with equation (1) above. The (*b*_{obs} - *b*_{calc}) for vermiculized phlogopite No. 3 is also within the error given with equation (2). However, this difference is considerably larger for vermiculized phlogopite No. 4 and much too large for vermiculized biotite No. 8. The increased differences are due to the absence of Fe²⁺ in equation (2). This omission is a result of the restricted range of montmorillonite compositions which could be included in the regression analysis from which equation (2) was derived (Radoslovich, 1962). Consequently, this equation does not apply to montmorillonites and vermiculites, such as Nos. 4 and 8, which contain considerable amounts of Fe²⁺. The values of *b*_{obs} and α_{calc} for the vermiculized phlogopites (Nos. 3 and 4) are fairly close to those for Kenya vermiculite (No. 5). For the vermiculized biotite α_{calc} is about half that for Kenya vermiculite. The decrease in tetrahedral rotation or untwisting upon exchange of K with Ca was calculated to be 2°12' and 3°30' for phlogopites No. 1 and 3°35' for biotite No. 6.

The 060 reflections for B96 in Fig. 1 show that oxidation of the K-depleted biotite shifted the peak from the trioctahedral 060 spacing of 1.552 Å to the dioctahedral spacing of 1.508 Å. As expected from the low Fe²⁺ content in phlogopite, oxidation did not change significantly the 060 spacing of the K-depleted phlogopite. The decrease in *b* upon oxidation, for K-depleted biotite, is larger than hitherto reported for similarly-treated high-iron biotites and vermiculites (Farmer *et al.*, 1971). The chemical formula for the oxidized vermiculized biotite (Table 2, No. 9) was calculated with the assumption, not yet substantiated by additional analyses, that all Fe²⁺ was oxidized to Fe³⁺ and that one-third of the original Fe²⁺ was ejected from the octahedral layer to maintain

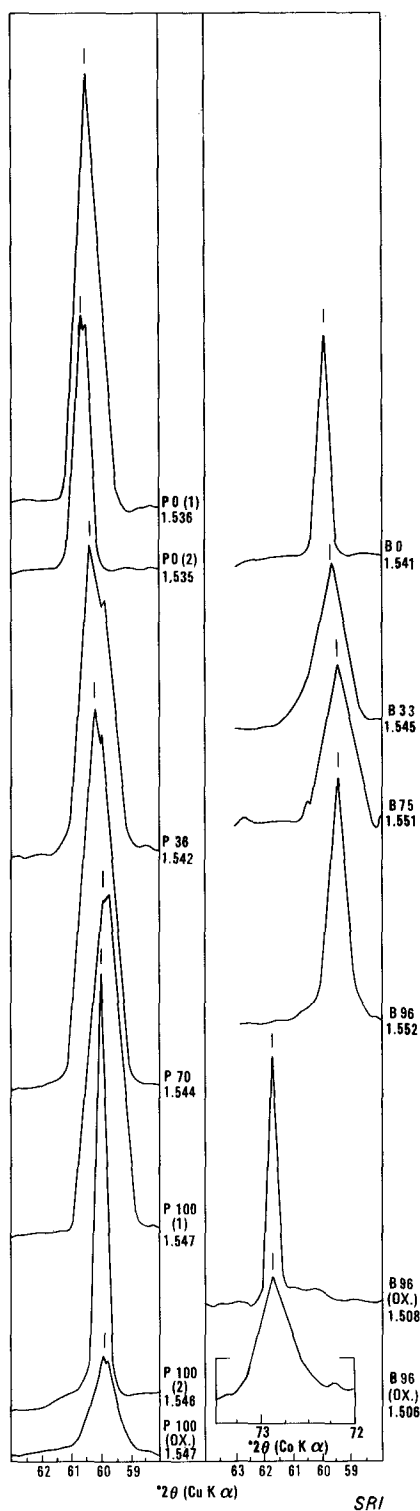


Fig. 1. 060 X-ray diffraction peaks of basally oriented phlogopite (P) and biotite (B). Per cent K exchanged for

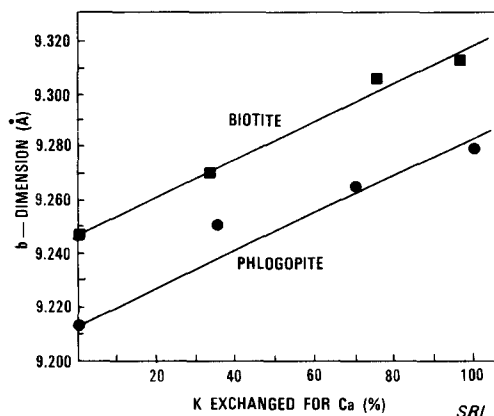


Fig. 2. Relationships between K for Ca exchange and b -dimension for phlogopite and biotite.

charge balance. Table 1 (No. 9) shows that b_{calc} obtained by equation (2) is considerably larger than b_{obs} . Again, the equation may not apply to oxidized high-iron vermiculites. Oxidation of the vermiculized biotite increased α_{calc} from $4^{\circ}41'$ to $14^{\circ}34'$. This increase is expected since ejection of octahedral Fe would contract the octahedral sheet and increase the misfit between the octahedral and tetrahedral sheets. The increased strain is relieved, at least partly, by a contraction of the tetrahedral layer brought about by an increased tetrahedral rotation.

In summary, the X-ray diffraction method used in this investigation is well suited to measure 060 spacings of micas and vermiculites. The measurements so obtained on a phlogopite and a biotite gave a regular increase in b -dimension with progressive replacement of K by Ca. The measured b -dimension (b_{obs}) and the calculated tetrahedral rotation (α_{calc}) for the vermiculized phlogopite were close to these for a vermiculite of similar composition. The replacement of K with Ca was accompanied by a decrease of $2^{\circ}12'$ in the calculated tetrahedral rotation for the phlogopite and $3^{\circ}35'$ for the biotite. Oxidation of the K-depleted biotite decreased the trioctahedral 060 spacing of 1.552 Å to the dioctahedral spacing of 1.508 Å. Additional analyses, including sodium dithionite extraction, are necessary to estimate the loss of octahedral cations and to confirm the dioctahedral nature of this oxidized vermiculized biotite.

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Ca and 060 spacing (Å) are shown at the base line of each reflection. Reflections for Po (1) and Bo from 2.5 cm disks, for Po (2) and P100 (2) from numerous 1 mm disks, and for the other samples from the 54–75 μm fraction. P100 (ox.) and B96 (ox.) refer to oxidized samples.

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REFERENCES

- Farmer, V. C., Russell, J. D., McHardy, W. J., Newman, A. C. D., Ahlrichs, J. L. and Rimsaite, J. Y. H. (1971) Evidence for loss of protons and octahedral iron from oxidized biotites and vermiculites: *Miner. Mag.* **38**, 121-137.
- Jones, J. B. (1958) Dispersion in trioctahedral micas: Ph.D. thesis, Univ. Wisconsin.
- Kodama, H. and Ross, G. J. (1972) Structural changes accompanying potassium exchange in a clay-size muscovite. *Proc. Intern. Clay Conf.*, Madrid, 1972 Preprints **2**, 159-171.
- Leonard, R. A. and Weed, S. B. (1967) Influence of exchange ions on the *b*-dimensions of dioctahedral vermiculite: *Clays and Clay Minerals* **15**, 149-161.
- Leonard, R. A. and Weed, S. B. (1970a) Mica weathering rates as related to mica type and composition: *Clays and Clay Minerals* **18**, 187-195.
- Leonard, R. A. and Weed, S. B. (1970b) Effects of potassium removal on the *b*-dimension of phlogopite: *Clays and Clay Minerals* **18**, 197-202.
- Le Roux, J., Rich, C. I. and Ribbe, P. H. (1970) Ion selectivity by weathered micas as determined by electron microprobe analysis: *Clays and Clay Minerals* **18**, 333-338.
- Mathieson, A. M. and Walker, G. F. (1954) Crystal structure of Mg-vermiculite: *Am. Mineralogist* **39**, 231-255.
- Radoslovich, E. W. and Norrish, K. (1962) The cell dimensions and symmetry of layer-lattice silicates—I. Some structural considerations: *Am. Mineralogist* **47**, 599-616.
- Radoslovich, E. W. (1962) The cell dimensions and symmetry of layer-lattice silicates—II. Regression relations: *Am. Mineralogist* **47**, 617-636.
- Radoslovich, E. W. (1963) The cell dimensions of layer silicates—IV. Interatomic forces: *Am. Mineralogist* **48**, 76-99.
- Rich, C. I. (1957) Determination of (060) reflections of clay minerals by means of counter type X-ray diffraction instruments. *Am. Mineralogist* **42**, 569-570.
- Rimsaite, J. (1967) Biotites intermediate between dioctahedral and trioctahedral micas: *Clays and Clay Minerals* **15**, 375-393.
- Ross, G. J. and Rich, C. I. (1973) Effect of particle thickness on potassium exchange from phlogopite: *Clays and Clay Minerals*, **21**, (In press).
- Wones, D. R. (1963) Physical properties of synthetic biotites on the join phlogopite-annite: *Am. Mineralogist* **48**, 1300-1321.