Reports

Potassium Content of Illite

Abstract. *The average potassium oxide content of 18 Paleozoic two-layer monoclinic illites is 8.75 percent. There is an excellent linear relation between the ratio of the intensities of the reflections at 10 angstroms and 5 angstroms (10 Å/5 Å) and the potassium oxide content. The frequency distribution curve of the 10 Å/5 Å intensity ratio of 249 Paleozoic illite-rich shales is approximately normal. The modal value is 2.0, equivalent to 9.3 percent potassium oxide, and the average ratio is 2.47, equivalent to approximately 8.5 percent potassium oxide. The illite layers of many of the mixed layer illites-montmorillonites have from 8 to 10 percent potassium oxide. With a minimum number of assumptions realistic structural formulas for the two members of a mixed-layer illite-montmorillonite can be calculated.*

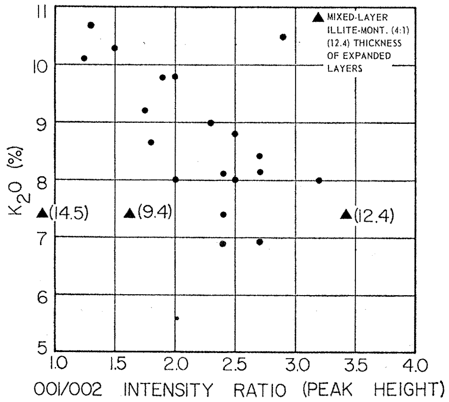
Many of the illites described in the literature contain 5 to 6 percent of K_2O. These values were once thought to represent the pure end member illite. Mehra and Jackson (*1*), by assuming a value of 10 percent K_2O for the 10-Å illite layers and a planar sorption surface of 760 to 808 m^2/g for the expandable layers, obtained a constant sum for the interlayer sorption surface and equivalent K_2O (mica) surface for a number of illites and mixed-layer minerals. Their data suggest that any illite with less than 10 percent K_2O should contain some expanded layers and that all the K_2O present is concentrated entirely between the contracted layers.

My data indicate that whereas a value of 10 percent may be high, the true value is closer to 10 percent than to 5 to 6 percent K_2O. Table 1 lists the K_2O for 16 Paleozoic and two Precambrian (two-layer monoclinic) illites. The analyses were made by using the "less-than-2-micron" fraction of the shales (one bulk sample is included). Most of these samples contain minerals other than illite, commonly less than 25 percent of the total. None of the contaminant minerals (quartz, dolomite, calcite, and chlorite) contained K_2O. The percentage of contaminant was calculated by the x-ray method of Shaw and Weaver (*2*) which has an accuracy of better than ± 10 percent of the amount present. The corrected average K_2O content is 8.75 percent. Twenty-four illite analyses taken from the literature have an average K_2O content of 7.02 percent. Many of these illites are poorly crystallized and contain some expanded layers. The range of values reported for Fithian illite is 4.6 to 6.13 percent K_2O.

Brown (*3*) and White (*4*) have calculated the effect of various isomorphous substitutions on the intensities of the (00*l*) reflections from mica. Calculations indicate that with increased K_2O content the intensity of the (00*l*) reflections decreased but the 001 reflection decreased more rapidly than the 002. Thus the ratio of the intensities at 10 and 5 Å, respectively, should be partially dependent on the K_2O content. The composition of the octahedral layer also affects the relative intensity of the (00*l*) reflections. Iron is the element most likely to cause variations in the (00*l*) intensities, but the calculations of Brown (*3*) indicate that the small amount of iron in the illite lattice (less than 5 percent) will cause only minor differences in the relative intensity of the 001 and 002 reflections.

White (*4*) systematically removed the interlayer potassium from a muscovite and showed how the 001/002 (10 Å/5 Å) intensity ratio of both the peak area and the peak height increased as the percentage of potassium decreased. In Figs. 1 and 2 the 001/002 intensity ratios, based on peak height and peak area, respectively, are plotted against the K_2O content of 19 illites. With one exception, the data show a good linear relation considering all the variations that are possible in such measurements. The sample with the abnormally high 001/002 ratio probably has a high iron content which preferentially weakens the 002 reflection. The triangles in Fig. 1 show the various intensity ratios that can be obtained by varying the nature of the interlayer material in the expandable layers of a mixed layer illite-montmorillonite (4 : 1). If the expanded layers contain Ca^{++}, H^+, or Mg^{++} and contain two layers of water, a thickness of approximately 15 Å will be attained. The third-order reflection from these layers will enhance the 5-Å reflection obtained from the illite layers, whereas the first and second orders are sufficiently different from the 10-Å reflection that they contribute little to the peak height. Thus the 10 Å/5 Å ratio is smaller than would be expected. When the same sample is treated with sodium and the expanded layers are reduced to 12 Å, the 10-Å reflection is enhanced more than the 5-Å reflection, and the value of the ratio increases.

Obviously the relation on the graphs can be used only for nonexpanded material. It is likely that a relation between K_2O content and 10 Å/5 Å ratio can be established for mixed-layer clay, but it will be necessary to standardize the nature of the interlayer material. This is essentially what White (*4*) did when he removed varying amounts of



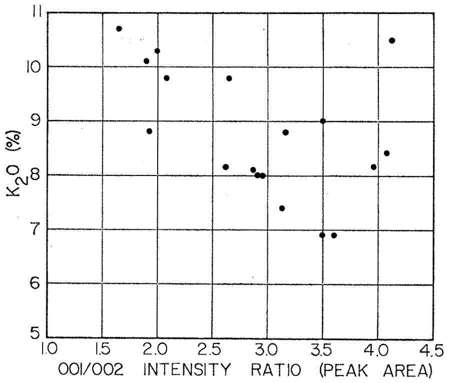


Fig. 1 (left). Variation in (001)/(002) intensity ratio (peak height) with percentage of K_2O for 19 illites; K_2O ± 1 percent, (001)/(002) ± 5 percent. The solid triangles indicate the intensity ratios for a mixed layer illite-montmorillonite (4 : 1) where the thickness of the expandable layers is varied. Fig. 2 (right). Variation in (001)/(002) intensity ratio (peak area) with percentage of K_2O for 18 illites.

Table 1. Composition of illites from various sources.

Illites (< 2 μ)	Nonillite (%)	K_2O	
		Bulk sample (%)	Illite (%)
O–120 Tuff, Stanley, M. Miss	32	6.64	9.8
O–100 Collier Sh., L. Ord.	25	5.96	8.0
PA–73 Rable Run Red Bed, Sil.	17	7.47	9.0
PA–64 Bellefonte Dol., Ord.	13	6.93	8.0
Cabin Creek 21–34. Sil.	15	5.87	6.9
PA–69 Rose Hill Sh., Sil.	31	5.59	8.1
PA–75 Bloomsburg Red Bed, Sil.	21	6.59	8.35
PA–84 Tonoloway Ls., Sil.	10	7.17	8.0
O–113 Lukfata Sh., Cambrian	28	6.32	8.8
T–8–5 Shady Dol., L. Cambrian	52	5.1	9.8
T–2–lb Sequach Sh., U. Ord.	23	5.31	6.9
PA–74 McKenzie Sh., Sil.	11	6.44	7.45
O–119 Ark. Novaculite, Dev.	22	6.73	8.65
PA–11 Chemung Sh., Dev.	23	6.26	8.15
O–117A Missouri Mt. Sh., Sil.	25	8.07	10.7
T–19–5 Juniata Sh., U. Ord.	20	8.43	10.5
Belt Series, U. Precambrian	0	10.29	10.29
Belt Series, Bulk, U. Precambrian	5	9.65	10.1
			Av. 8.75

K_2O from muscovite. The values in Figs. 1 and 2 are much closer to White's calculated values than are his experimental values.

The 10 Å/5 Å ratio based on peak area increases at a faster rate than the ratio based on peak heights (Fig. 1). This means that the peak widths are also changing. Graphs of the peak widths at half-height plotted against K_2O content indicate that the peak at 10 Å broadens at a greater rate than does the peak at 5 Å as the K_2O content decreases. Though both area and width change, the area changes more. This suggests that the change in structure factor due to the variation in potassium content is the major factor influencing the peak height of the ratios of the intensities at 10 and 5 Å.

A decrease in K_2O would affect the structure factor, the peak area, and the peak height, but should have no effect on the peak width at half-height. Thus this peak broadening could result from a decrease in crystallite size as the K_2O content decreases; however, the equations for broadening, whether due to size or strain, indicate the peak at 5 Å would broaden at a greater rate than the peak at 10 Å. Although it is likely that there is some broadening due to size and strain, it is overshadowed by some other effect.

The peaks at 10 Å of the high-potassium illites are symmetric, and there is a relatively systematic departure from symmetry with decrease in K_2O content (Fig. 3). The asymmetry is manifested as a decrease of the slope of the low-angle side of the peak at 10 Å. The asymmetry of the peak at 5 Å is less than that of the peak at 10 Å; this is indicated by a lessening of the slope on the high-angle side of the peak.

Thus the asymmetry and the differential peak broadening are likely due to some layers with a thickness greater than 10 Å. In order for the peak at 10 Å to broaden more than the peak at 5 Å and for the asymmetry to occur on opposite sides of these two peaks, the thicker layers would have to be on the order of 14 to 15 Å. Since there is no variation in the position of the peak maximum, the thicker layers probably comprise less than 10 percent of the clay. When the low K_2O (7 to 8 percent) illites are treated with ethylene glycol there is no shift in peak position or change in area but, in some, the 001 peak is sharpened and the 10 Å/5 Å ratio slightly increased.

The presence of some expanded layers in these relatively well "crystallized" illites would indicate that the potassium content of the contracted layers is even higher than indicated. If the "illite" layers contain as much as 10 percent K_2O there are more "nonillite" layers than suggested by the ethylene glycol treatment. These layers may contain other cations, such as Na^+ and H_3O^+, or they may be neutral.

The frequency distribution of the 10 Å/5 Å ratio of 249 Paleozoic two-layer monoclinic illite samples is shown in Fig. 4. Also shown are the data for 143 soil illites reported by White (*4*). The values are quite similar. Arnold (*5*) has suggested that approximately 5 percent K_2O [or 1.1 K per unit layer of $O_{20}(OH)_4$] is the minimum amount necessary to prevent expansion of the illite lattice. On the basis of the data in Fig. 1 an illite with 5 percent K_2O should have a 10 Å/5 Å ratio of approximately 4. Both frequency distributions (Fig. 4) show few values higher than 4.

The frequency distribution graph of the 10 Å/5 Å intensity ratio for the shales has a modal value of 2.0, which would be equivalent to approximately 9.3 percent K_2O. The average ratio is 2.47, equivalent to approximately 8.5 percent K_2O. Both histograms are skewed toward the larger ratio values, and the shale histogram in particular may be slightly bimodal. The possible secondary mode has a ratio value of approximately 3.4, which is equivalent to approximately 6 percent K_2O—a common value for many of the more poorly organized illites.

Strongly bonded illite-like layers commonly have 9 to 10 percent K_2O, and any significant smaller values indicate the presence of expanded layers or weakly bonded lMd (one-layer mon-

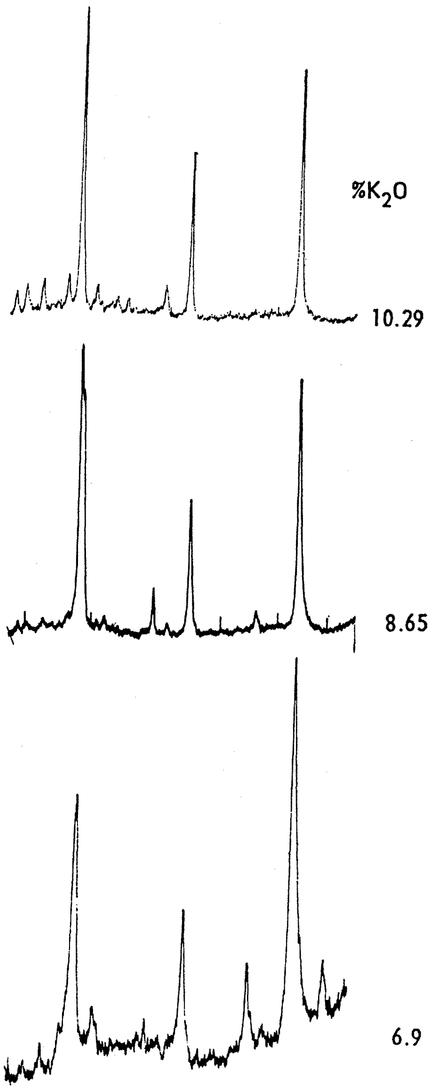


Fig. 3. X-ray diffraction patterns of three illites with varying K_2O content and (001)/(002) intensity ratios. Note slight change in symmetry of the 10-Å peak.

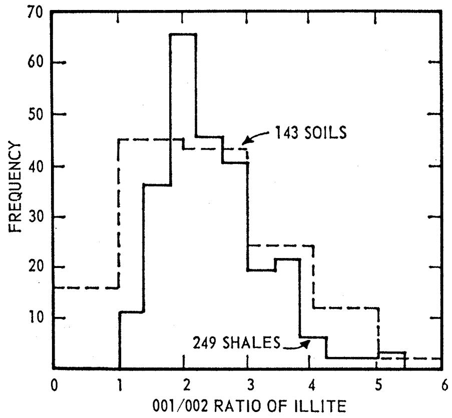


Fig. 4. Frequency distributions of (001)/(002) intensity ratio of illites for 249 shale and 143 soil clay fractions.

oclinic disordered structure) contracted layers. In mixed-layer illite-montmorillonites the potassium commonly occurs in the contracted layers and the K_2O content of these layers usually is in the ranges of 8 to 10 percent.

An excellent example of this is the mixed-layer illite-montmorillonite (4 : 1 to 3 : 1) (*6*) containing 7.39 percent K_2O. If all of it is in the contracted 10-Å layers (75 percent), as leaching tests indicate, these layers would contain 9.85 percent K_2O. The structural formula for this mixed-layer clay is:

$$\begin{gathered} K_{0.64}\ Ca/2_{0.10}\ Na_{0.02} \\ (Al_{1.64}Mg_{0.36})\ (Al_{0.45}Si_{3.55})\ O_{10}(OH)_2 \end{gathered}$$

If (i) the 75 percent 10-Å layers are illite-like and contain all the tetrahedral aluminum and the potassium and (ii) 25 percent of the layers are montmorillonites, have no tetrahedral aluminum, and contain all the calcium and sodium in the exchange position, the following two formulas can be calculated from the chemical analysis.

$$\begin{gathered} K_{0.84} \\ (Al_{1.67}Mg_{0.32})\ (Al_{0.60}Si_{3.40})\ O_{10}(OH)_2 \\ \text{Illite} \end{gathered}$$

$$\begin{gathered} Ca/2_{0.38}\ Na_{0.09} \\ (Al_{1.54}Mg_{0.46})\ (Si_{4.00})\ O_{10}(OH)_2 \\ \text{Montmorillonite} \end{gathered}$$

These structural formulas are almost perfect end members for high caliber illite and montmorillonite. If the entire base exchange capacity of 27 meq/100 g is assigned to the montmorillonite layers a value of 108 is obtained for these layers. These structural formulas must be reasonably close to the actual situation as a tetrahedral charge of this magnitude is almost essential for so much potassium to be strongly bonded. Likewise the expanded layers are not likely to have much of a tetrahedral charge as they will not contract when treated with potassium, and they will readily adsorb two layers of ethylene glycol.

Another interesting calculation of this type can be made. A structural formula for Wyoming bentonite is:

$$(Al_{1.64}\overset{3+}{Fe}_{0.15}\overset{2+}{Fe}_{0.02}Mg_{0.19})\ (Al_{0.10}Si_{3.90})\ O_{10}(OH)_2$$

If all the tetrahedral aluminum is assumed to be concentrated in a few layers and if the tetrahedral portion of these layers are assumed to have the composition $(Al_{0.60}Si_{3.40})$ then it can be calculated that the material contains 16.7 percent of these highly charged layers. Weaver (*7*) has reported that approximately 20 percent of the layers in this material have high enough charge to bond potassium and contract to 10 Å.

CHARLES E. WEAVER
Georgia Institute of Technology,
Atlanta

References

1. O. P. Mehra and M. L. Jackson, *Soil Sci. Soc. Am. Proc.* **23**, 101 (1959).
2. D. B. Shaw and C. E. Weaver, *J. Sediment. Petrol.*, in press.
3. G. Brown, *Mineral. Mag.* **30**, 657 (1955).
4. J. L. White, *Soil Sci.* **93**, 16 (1961).
5. P. W. Arnold, *J. Sci. Food Agr.* **11**, 285 (1960).
6. C. E. Weaver, *Geol. Soc. Am. Bull.* **64**, 921 (1953).
7. ———, *Am. Mineralogist* **43**, 839 (1958).

28 October 1964

Crystal Packing of Molecules

Abstract. *The packing position of a molecule of known or assumed dimensions in a crystal can be found by minimizing the energy of the crystal with respect to molecular position by the method of steepest descent. Molecular flexibility can be introduced by allowing internal rotation about selected bonds. The method can be used to solve the diffraction phase problem in appropriate cases.*

If the shape of a molecule is known, or can be postulated from expected intramolecular distances and angles, the position of the molecule in a crystal unit cell of known dimensions and symmetry should be calculable. The molecule will position itself so as to minimize the free energy of the crystal. For practical calculations at constant entropy and volume, the potential energy of the crystal, E, may be minimized by positioning the molecule, subject to the constraints of the known lattice constants and cell symmetry, so that the sum of all nonbonded potential energies is a minimum. If an individual interatomic potential energy between atom j and atom k is E_{jk} then

$$E = \tfrac{1}{2} \sum E_{jk}$$

where the sum includes all the neighbors of a given molecule. Simple additivity of isotropic atom-pair interactions in the crystal is assumed. Temperature effects and zero-point quantum effects are neglected.

A computer program (*1*) has been written which minimizes E by a "steepest descent" procedure. The adjustable parameters are three translational parameters specifying the coordinates of the center of the molecule, three rotational parameters specifying the angular orientation of the molecule, and the six or less lattice constants. In addition, the program provides for flexibility of the molecule by allowing intramolecular rotations (subrotations) about selected bonds within the molecule. The program obtains the derivatives of E, with respect to the parameters, numerically. The derivative of E with respect to a particular parameter is obtained by increasing that parameter and reevaluating E; the derivative is the difference in E divided by the increment to the parameter. The gradient of E is thus obtained, and shifts are made along the gradient to minimize E.

Before any reliable calculations of positions of molecular packing could be made, it was necessary to have reasonably accurate interatomic potential functions (*2*); the Buckingham potential function was used:

$$E_{jk} = -Ad_{jk}^{-6} + B\exp(-d_{jk}/\rho)$$

Considerable range for the parameters A, B, and ρ has been reported for the needed C—C, C—H, and H—H potential functions (*3*).

The potential parameters given by Kitaigorodskii (*4*) were tried first, having been developed for a similar purpose, but Bartell's potential parameters (*5*), developed primarily for intramolecular use, proved more satisfactory. Bartell's functions (approximated in Buckingham form) were used in our numerical work. There is considerable need for more accurate interatomic nonbonded potential functions. The packing program itself can be used to select the most appropriate potential functions, which are such that, when they are used in the program, known crystal structures are accurately reproduced; in other words, the calculated