American Mineralogist, Volume 59, pages 491–495, 1974

Effect of Layer Charge Location on Potassium Exchange and Hydration of Micas[1]

HIDEOMI KODAMA, G. JOHN ROSS,

Soil Research Institute, Research Branch, Agriculture Canada,
Ottawa, Ontario K1A OC6

J. TOSHIMICHI IIYAMA, AND JEAN–LOUIS ROBERT

Centre de Synthèse et Chimie des Minéraux, C.N.R.S.,
Rue de la Férollerie 45045 Orléans, France

Abstract

The rate of K exchange by Ca of Al-free phlogopite (no tetrahedral ionic substitution but with octahedral vacancies) was much lower than that of phlogopite. Since some of the hydroxyls in the Al-free phlogopite are inclined like those in muscovite, it was suggested that for the rate of K exchange hydroxyl orientation is a more determinant factor than layer charge location. However, after K exchange, the hydrated layers in the former sample under moist conditions expanded to 18.6Å whereas the hydrated layers in phlogopite expanded to 14.8Å. This implied that layer charge location has a greater effect on hydration behavior than on the rate of K exchange.

Introduction

Studies in the artificial weathering of micas have suggested that important factors governing the rate of potassium replacement by a hydrated cation are (1) hydroxyl orientation and degree of F^- substitution for OH^- in the octahedral sheets, (2) total layer charge, (3) layer charge location, and (4) particle size. The effect of the hydroxyl orientation on K-exchange is illustrated by observations that the rate of K release is much slower in dioctahedral micas than in trioctahedral micas where the OH dipole is nearly normal to the octahedral sheets and the proton is directed toward the K. Consequently a repulsion force between proton and K^+ reduces the stability of K (Reed and Scott, 1962; Rausell-Colom *et al*, 1965; Leonard and Weed, 1970). The presence of F^-, on the contrary, increases the stability of K, since F^- has no such dipole. Variations in K-O bond lengths due to the ditrigonality of basal oxygens of tetrahedral sheets may also be considered as a factor in K release (Leonard and Weed, 1970). Since this aspect is closely related to the hydroxyl orientation (Drits, 1969), the effect of K-O bond lengths is regarded as a part of hydroxyl orientation effects.

Several investigations have shown that completeness of K exchange from micas decreases with decrease in particle size, and a number of hypotheses have been proposed to explain this effect (Mortland and Lawton, 1961; Scott, 1968; Ross and Rich, 1973). Isomorphic substitutions in micas are rather complex and often accompanied by other structural changes. This situation perplexes the charge relationship in micas so that it is difficult to establish the sole importance of charge location. Ross and Kodama (1970) and M. Robert (1973) related a lower rate of K exchange and mica alteration to an increase in tetrahedral charge as a result of a higher Al for Si substitution. Although many studies have dealt with the degree of hydration or the swelling behavior of vermiculite and smectite minerals in terms of their total layer charge and charge location (Barshad, 1952; Harward, Carstea, and Sayegh, 1969; Doner and Mortland, 1971; Weir, 1965), interpretations from those observations are not necessarily correctly applied to the case of micas, since the total layer charge is smaller than that of the micas. An attempt has been made to identify and evaluate the effect of charge location on K exchange and hydration of micas. Results are reported herein.

Experimental

To avoid the complexities due to ionic substitutions in naturally occurring micas, two synthetic Mg micas, each having the same total layer charge, were used

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[1] Contribution No. 472.

for a comparative K exchange study: phlogopite, K $Mg_3(Si_3Al)O_{10}(OH)_2$, with the total layer charge originating in the tetrahedral sheet; and Al-free phlogopite, $K(Mg_{2.5}\square_{0.5})$ $Si_4O_{10}(OH)_2$, with its total layer charge due to vacancies of sites for Mg in the octahedral sheet (Seifert and Schreyer, 1971). The synthetic phlogopites were prepared in the French laboratory and examined by various methods to confirm their identification (J-L. Robert, 1973). X-ray diffraction data indicated them to be a 1*M* or 3*T* polytype and gave values along *b* of 9.209 ± 0.001 and 9.116 ± 0.003 Å for the phlogopite and the Al-free phlogopite, respectively. These and other X-ray data were consistent with those reported by Yoder and Eugster (1954) for phlogopite and by Seifert and Schreyer (1971) for Al-free phlogopite. The phlogopite showed a single infrared absorption band at 3725 cm^{-1} in the OH region, and its absorbance was dependent upon the angle of incidence as reported by Serratosa and Bradley (1958), whereas the Al-free phlogopite exhibited four distinct absorption bands at 3595, 3625, 3695, and 3735 cm^{-1} in the region (Fig. 1). A comparison between the absorption spectra of an oriented aggregate at two different angles of incidence (Figs. 1, B and C) showed that the 'relative' pleochroism of the major OH band at 3595 cm^{-1} was very small. This indicated the presence of inclined OH bonds as in muscovite in which the OH dipoles are tilted out of the basal plane by about 16° (Vedder and McDonald, 1963). In this Al-free phlogopite, the absorbance of the second major band at 3735 cm^{-1}, which was increased by approximately 40 percent on tilting the preferred oriented aggregate 45°, corresponded to that obtained with the phlogopite under similar conditions. This band thus matches the normal band (so called N-band) in trioctahedral micas arising from normal octahedral surroundings, namely in the present case, $Mg^{2+}Mg^{2+}Mg^{2+}$ (Vedder, 1964). Similarly the band at 3595 cm^{-1} may be comparable to the vacancy band (V-band) due to hydroxyls in octahedral surroundings where vacancies are present. Obviously various manners of distribution of the vacancies will add more complexity to the absorption in the OH region. This may be the reason that the OH absorption of the Al-free phlogopite consists of four bands. Since the data available for polycrystalline Al-free phlogopite was only qualitative, no further assignment for each band was attempted at the present stage. However, the infrared absorption spectra mentioned above revealed that the Al-free phlogopite has at least two different hydroxyl orienta-

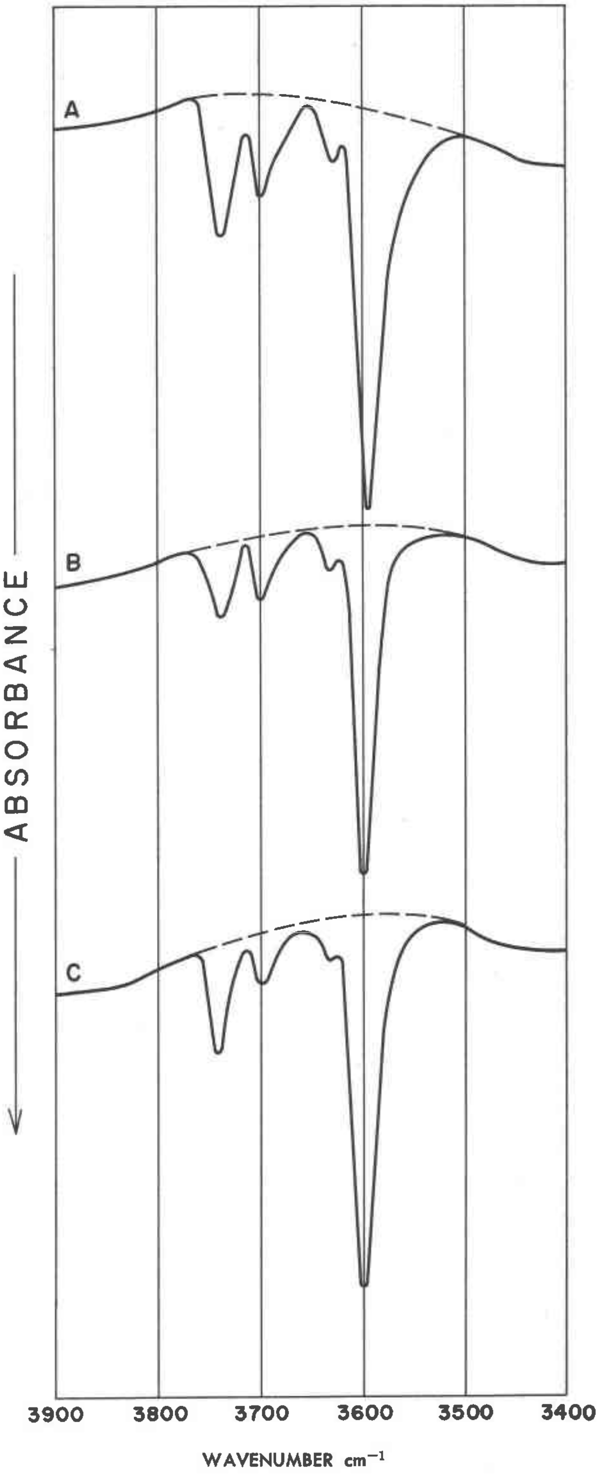

FIG. 1. Infrared absorption spectra in the OH region of the Al-free phlogopite. **A**, random orientation (by ordinary Nujol method); **B**, preferred orientation on a KBr disc (prepared by smearing Nujol paste of sample) with 90° of incidence to the surface of the KBr disc; **C**, 45° tilt from the position **B**.

tions, one nearly parallel to the c^*-axis as in phlogopites and another more inclined to the basal plane with an angle possibly similar to that of muscovite ($\simeq$ 16°). Since electron microscopic observations indicated that the mean particle size of phlogopite was much smaller than that of Al-free phlogopite, the < 0.4 μm fraction was collected by means of sedimentation and centrifugation and prepared for the comparative K exchange study. Potassium and magnesium analyses confirmed that the real compositions of the samples were practically identical to the corresponding ideal formulas.

Potassium was exchanged with Ca by treating 20 mg of sample with 100 ml 0.2 N $CaCl_2$ in a polypropylene bottle at 75°C in a water bath. Preliminary experiments showed that the equilibrium concentration of K, *i.e.*, the concentration at which no more K was released, was attained after two days reaction. Thus, after a three-day reaction period the solution was separated by centrifugation and siphoning, and then a fresh 100 ml portion of $CaCl_2$ solution was added to the sample. This procedure was repeated several times and gave a measure of K over Ca selectivity. Concentrations of K in the solutions were determined on a Techtron atomic absorption spectrophotometer. In order to examine hydration-dehydration behavior of hydrated mica layers, residues (Ca-saturated) of both samples after a total reaction time of 21 days were suspended in one ml water, pipetted onto a 37.5- by 25-mm glass slide and allowed to dry. The oriented aggregates were equilibrated for one hour under humidity conditions ranging from 0 to 100 percent and then subjected to X-ray analysis. After one additional hour from the first equilibration, X-ray analysis was repeated to confirm the previous results.

Results and Discussion

Figure 2 shows that the K from the Al-free phlogopite, whose charge originated in the octahedral sheet, was exchanged at a lower rate than the K from the phlogopite, whose charge arose in the tetrahedral sheet. This is contrary to the expectation that because of closer proximity of charge to the interlayer cation, the tetrahedrally charged mica would be more effective in holding the interlayer K than the octahedrally charged mica. Obviously a factor of greater importance than charge location was controlling K exchange in these micas. It is suggested that this factor is the hydroxyl orientation. As shown by infrared absorption spectra, the O-H bond direction of Al-free phlogopite is, unlike phlogopite, inclined from the normal to the octahedral sheet. This inclination is undoubtedly generated by the vacancy in octahedral sites. The resulting semi-dioctahedral nature, therefore, may increase the stability of K.

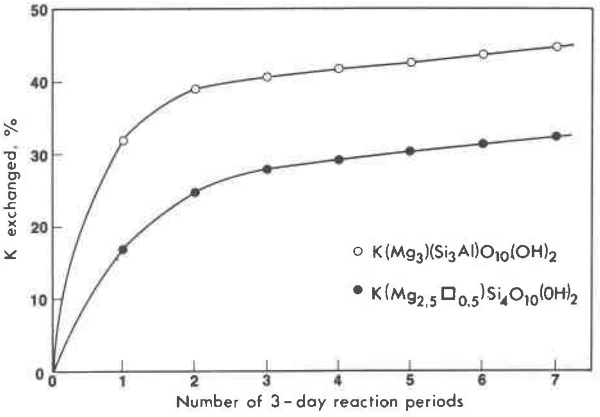

FIG. 2. Rates of exchange of K with Ca for the phlogopite and the Al-free phlogopite.

After 21 days, approximately 45 percent and 32 percent of total K, respectively, were extracted from phlogopite and Al-free phlogopite. The presence of hydrated mica layers was indicated in both samples by a distinct peak at about 15 Å with a 10 Å peak for the original micas under intermediate relative humidity conditions. Figure 3 shows that the basal spacing of hydrated layers in the Al-free phlogopite was increased to 18.6 Å with a minor peak at 15 Å under an extremely humid condition and decreased gradually to 12 Å with

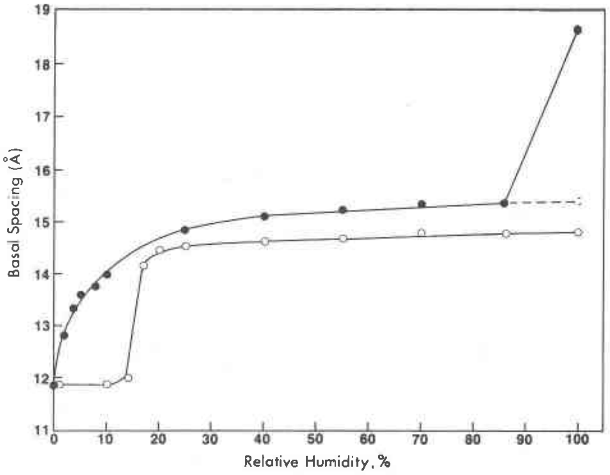

FIG. 3. Hydration-dehydration behavior of hydrated layers derived by the exchange reaction from the two synthetic phlogopites. ○, phlogopite; ●, Al-free phlogopite.

decrease in humidity. In the phlogopite a sharp reduction of the spacing to 12 Å occurred in a narrow range of relative humidity from 20 to 10 percent, and no expansion to a spacing higher than 14.8 Å was observed under high humidity conditions. Although the amount of K replaced from the Al-free phlogopite was less than that from the phlogopite, the former produced a highly hydrated layer of 18.6 Å. Nevertheless, the hydrated layers of the Al-free phlogopite exhibited a much stronger resistance to dehydration than those of the phlogopite. These observations are consistent with results of previous comparative experiments on a Mg form of K-depleted muscovite and Mg-vermiculite (Kodama and Ross, 1972). Thus, it is likely that expansibility of hydrated layers is more closely related to its layer charge location and that contractibility of hydrated layers is rather related to degree of trioctahedral nature, *i.e.*, hydroxyl orientation normal to the octahedral sheets.

Conclusions

For phlogopites with the same total layer charge and particle size, the following conclusions may be deduced:

1) A determinant factor for the rate of K exchange is hydroxyl orientation rather than layer charge location.
2) Hydrated mica layers are more expansible when their layer charge is located octahedrally.
3) Tetrahedrally located layer charge inhibits further expansion of hydrated mica layers.
4) Contractibility of hydrated mica layers is more influenced by the hydroxyl orientation than by charge location, perhaps because of a weaker affinity between an interlayer cation and basal oxygens in trioctahedral micas which could result in a less organized water molecule association around the cation in comparison with the hydrated dioctahedral micas.

It is evident from this work that the effect of layer charge location on K exchange and subsequent hydration is complicated by the effect of hydroxyl orientation and that, strictly speaking, the effect of each factor may not be evaluated in straightforward terms. The present attempt, however, suggests that location of the layer charge controls the expansibility of hydrated mica layers, an octahedrally located charge permitting more expansion of the interspace of hydrated layers than a tetrahedrally located charge.

Acknowledgments

The authors thank Messrs. M. Jaakkimainen and N. M. Miles for their technical assistance, and Dr. J. E. Brydon for reviewing the manuscript.

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Manuscript received, October 29, 1973; accepted for publication, January 3, 1974.