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FAR-INFRARED STUDY OF POTASSIUM IN MICAS

R. PROST AND V. LAPERCHE

Station de Science du Sol, Institut National de la Recherche Agronomique, Route de Saint-Cyr, 78026 Versailles Cédex, France

Abstract—The characterization of cations associated with clay materials has generally been approached by the sequential use of specific chemical reagents. To avoid the disturbing effect of the chemical reagents on the state and location of compensating cations of clays and to get information *in situ*, far-infrared spectroscopy was used. The far-infrared vibrational spectra of the potassium cation in muscovite, phlogopite, and biotite were recorded before and after heating at the dehydroxylation temperature. The vibrational frequency of K in micas before dehydroxylation was found to be a function of the di- or trioctahedral character and of the Fe content. After dehydroxylation or deprotonation, shifts of the K absorption band to lower frequencies were observed for the heated muscovite, in which K exchangeability increased, and to higher frequencies for the heated biotite, in which K exchangeability decreased. These results suggest that the vibrational frequency of potassium is characteristic of the state of K in these minerals and of its ability to be exchanged.

Key Words—Biotite, Dehydroxylation, Far-infrared spectroscopy, Muscovite, Phlogopite, Potassium.

INTRODUCTION

Both pedologists and agronomists are interested in understanding the mechanisms by which K is exchanged in micaceous minerals. The vermiculitization process of micas was the subject of a symposium at the International Clay Conference in 1972. Norrish (1972) reported that potassium was almost completely released with Na-tetraphenylboron if particles were >50 μm, and that the rate at which micas can be weathered followed the order, lepidomelane > biotite > phlogopite > muscovite > lepidolite.

The dominant factors controlling the rate of exchange and the equilibrium K concentration in the various micas appear to be the orientation of structural-OH groups and the content of divalent iron. These conclusions have been drawn from K-exchange isotherms or K-release kinetics obtained for different micas having well-defined structure and chemical composition (Rousseaux *et al.*, 1972) or by changing the K-release behavior of individual micas, for example, by heating (Scott *et al.*, 1972). Unfortunately, these data obtained at a macroscopic level give little information at a molecular level on the specific interactions of K with the structure of the different natural or modified minerals.

If the K of K-feldspar, mica, and illite constitutes stocks for plant nutrition (Quémener, 1976), its availability depends on the rate of release. Time scales of pedological processes can be of the order of centuries or more. In agronomy, they are of the order of a few months. Therefore, a better knowledge of the K-release mechanisms from these minerals is needed to evaluate the bioavailability of K of these soil materials.

The purpose of the present paper is to show (1) how the far-infrared (FIR) adsorption band of K in micas may give indications of the K-lattice interactions at the molecular level; and (2) the possibility of using the frequency of the K-absorption band to predict the nature of potassium release from micaceous minerals.

MATERIALS AND METHODS

Representative samples of muscovite (Madagascar), phlogopite (Madagascar), and biotite (Bancroft, Ontario) were used, having the following chemical formulae:

muscovite: $(Si_{3.09}Al_{0.91})\ (Al_{1.66}Mg_{0.08}Fe^{3+}_{0.23}Fe^{2+}_{0.05})O_{10}(OH)_2(K_{0.9}Na_{0.08})$; phlogopite: $(Si_{2.9}Al_{1.1})(Mg_{2.58}Fe^{2+}_{0.1}Fe^{3+}_{0.07}Al_{0.15}Ti_{0.03})O_{10}(OH_{1.45}F_{0.55})(K_{0.9}Na_{0.06})$; biotite: $(Si_{2.77}Al_{1.23})(Mg_{0.87}Fe^{2+}_{0.94}Fe^{3+}_{0.65}Al_{0.03}Mn_{0.02}Ti_{0.13})O_{10}(OH_{1.6}F_{0.4})(K_{0.93}Na_{0.04})$.

Data concerning the rate of release of K from micas were taken from the paper by Scott *et al.* (1972). These authors extracted K from the <5- or the <50-μm fraction of micas by putting the minerals in contact for different periods with Na-tetraphenylboron (NaTB) solutions, after they had been heated at different temperatures. Heating induced an increase of the rate of K release for muscovite, but a decrease for biotite.

Because dehydroxylation or deprotonation may occur with heating, the stretching bands of structural-OH groups of unheated and heated micas were recorded at room temperature on a Perkin-Elmer 580 spectrometer. The absorption bands of the interlayer K of micas were recorded under vacuum with a BRUKER IFS 113 instrument equipped with a DTGS detector. Spectra were obtained from polyethylene pellets or single crystals at room temperature.

RESULTS

Figure 1 shows the absorption spectra of muscovite, phlogopite, and biotite between 220 and 20 cm^{-1}. The

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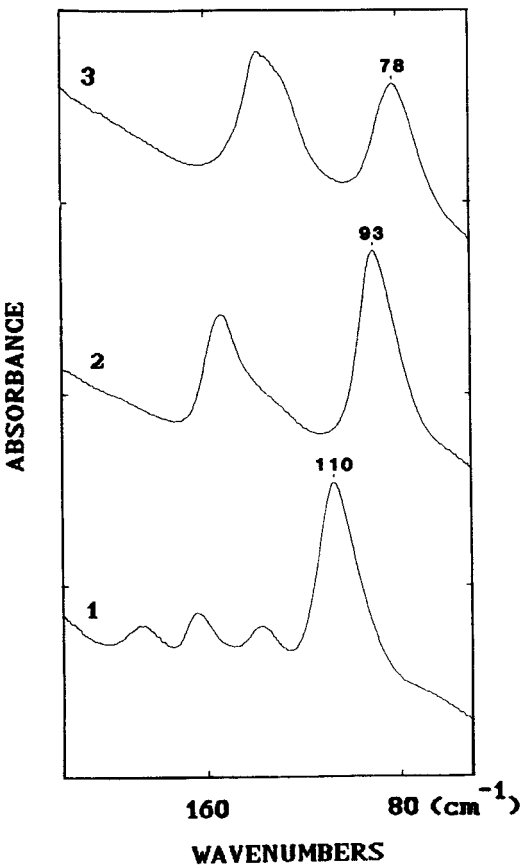


Figure 1. Infrared absorption spectra of (1) muscovite, (2) phlogopite, and (3) biotite in polyethylene pellets between 220 and 20 cm^{-1}.

absorption spectra are characteristic of the mineral. According to Ishii (1967), the bands at 110, 93, and 78 cm^{-1} are due to K in the interlamellar spaces of muscovite, phlogopite, and biotite, respectively. The absorption bands at higher frequencies are not discussed here.

To check if modifications in the state of K induced changes in the K-absorption band frequency, spectra of samples heated for 24 hr at different temperatures between 30° and 1150°C were recorded. The stretching modes of the structural-OH groups of the same samples were also recorded. The spectra obtained from muscovite (Figure 2, top) show that the K-absorption band frequency shifted from 110 to 97 cm^{-1} as dehydroxylation occurred (Figure 2, bottom). At that temperature the structure of muscovite is stable (Eberhart, 1963). No frequency shift was noted for phlogopite until the dehydroxylation process was completed (Figure 3). At that temperature drastic changes appeared in the structure (Vedder and Wilkins, 1969) and the FIR spectra (Figure 3, top). For biotite heated at 550° and 650°C the band at 78 cm^{-1} progressively shifted to 91 cm^{-1} (Figure 4, top). Changes were also observed in the stretching modes of the structural-OH groups (Figure 4, bottom). The 3676-, 3658-, and 3552-cm^{-1} bands disappeared after heating the sample at 550°C, as did the 3584-cm^{-1} band after heating the sample at 650°C. Thus, K-band shifts for heated muscovite and biotite were in opposite directions.

DISCUSSION

The vibrational frequency of K characterizes its state in interlamellar spaces. This frequency is a function of the electric potential in the cage where K is located. The potential function is related to structural and chemical factors. The di- or trioctahedral character and the iron content of the structure must therefore be considered in order to analyze the observed frequencies. The relation between the K-band frequency and the rate of release of K from these minerals must also be considered.

Relation of K absorption-band frequency to mineral characteristics

Of the micas studied, only muscovite is dioctahedral. Its structural-OH groups make an angle of 16° with the (*a, b*) plane (Vedder and McDonald, 1963). Oxygen atoms of structural-OH groups, further abbreviated as O_1, expose an atomic orbital with two electrons to K, and thereby induce an attractive effect on K giving rise to the highest frequency observed (Figure 1). On the other hand, the structural-OH groups of the trioctahedral phlogopite are nearly perpendicular to the (*a, b*) plane. The repulsive effect of the protons on K in trioctahedral minerals may give rise to a lower frequency (93 cm^{-1}) in phlogopite than in muscovite (110 cm^{-1}). According to its chemical formula, biotite has 2.63 octahedral sites of 3 occupied; only ⅓ of structural-OH groups belong to dioctahedral configurations. Thus, a question remains concerning the difference in K frequency of phlogopite (93 cm^{-1}) and biotite (78 cm^{-1}), both of which have a trioctahedral character. That difference is apparently due to the high Fe content of biotite.

Heating these minerals induced the dehydroxylation of muscovite or deprotonation of biotite as a consequence of the oxidation of Fe^{2+} to Fe^{3+} (Scott *et al.*, 1972). These processes drastically changed the K–OH group interaction. Figure 2, top shows that the K band of muscovite shifted from 110 to 97 cm^{-1} as dehydroxylation took place (Figure 2, bottom). At the dehydroxylation temperatures, the structure of muscovite was not destroyed; only very small changes in the unit-cell parameters were noted, and, according to Eberhart (1963), the oxygen atom which results from the dehydroxylation process ($R–(OH)_2 \rightarrow R–O + H_2O$) migrates into the vacant octahedral site of the structure increasing the K–O_1 distance. The result is the decrease of the specific interaction between K and structural-

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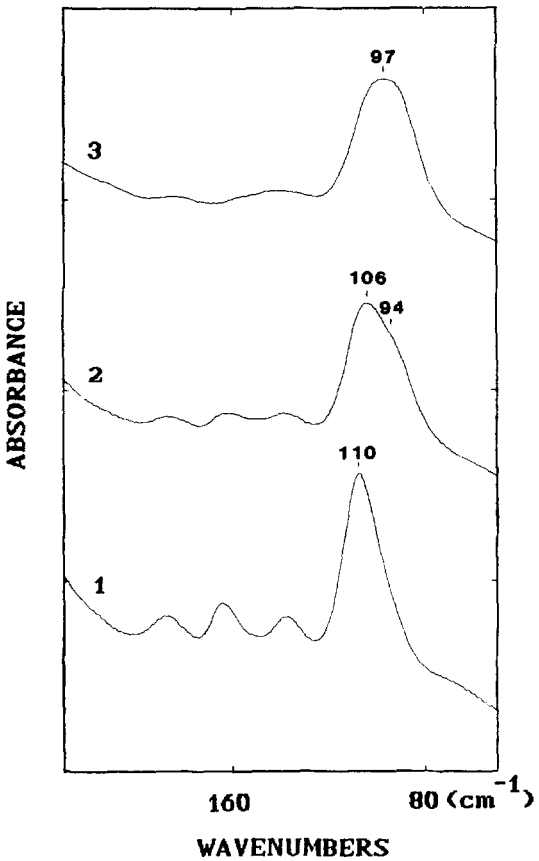
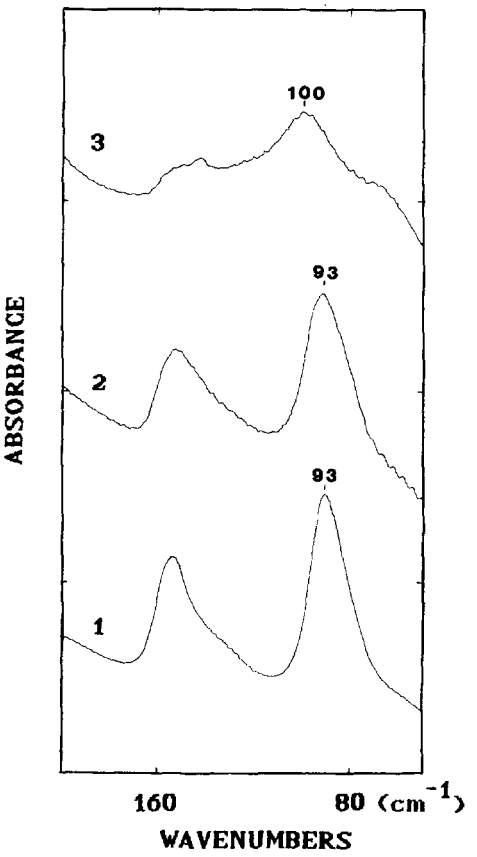


Figure 2. Infrared spectra of (top) K and (bottom) structural-OH groups of muscovite as a function of temperature: 1, 30°C; 2, 650°C; and 3, 750°C. Upper spectra were obtained in polyethylene pellets; lower spectra, with single crystals.



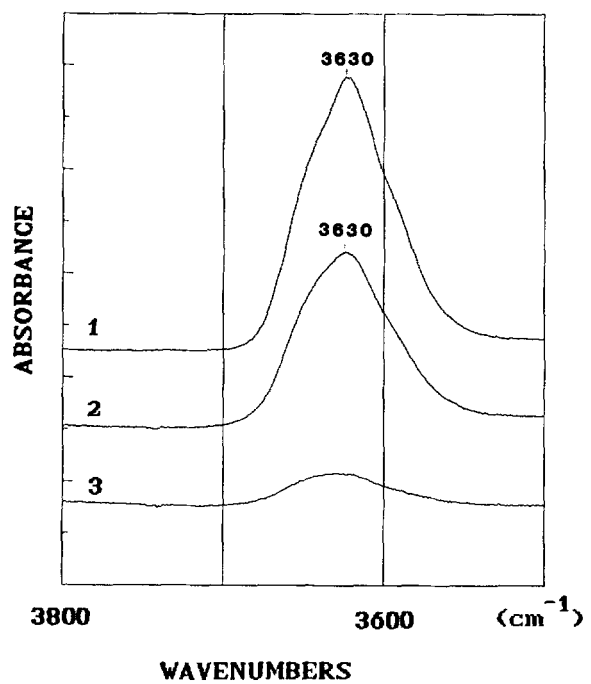
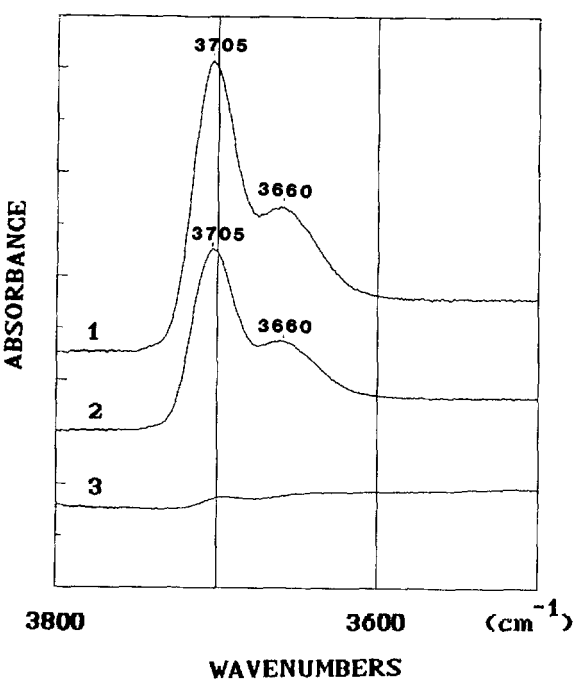


Figure 3. Infrared spectra of (top) K and (bottom) structural-OH groups of phlogopite as a function of temperature: 1, 30°C; 2, 1100°C; 3, 1150°C. Upper spectra were obtained in polyethylene pellets; lower spectra, with single crystals.



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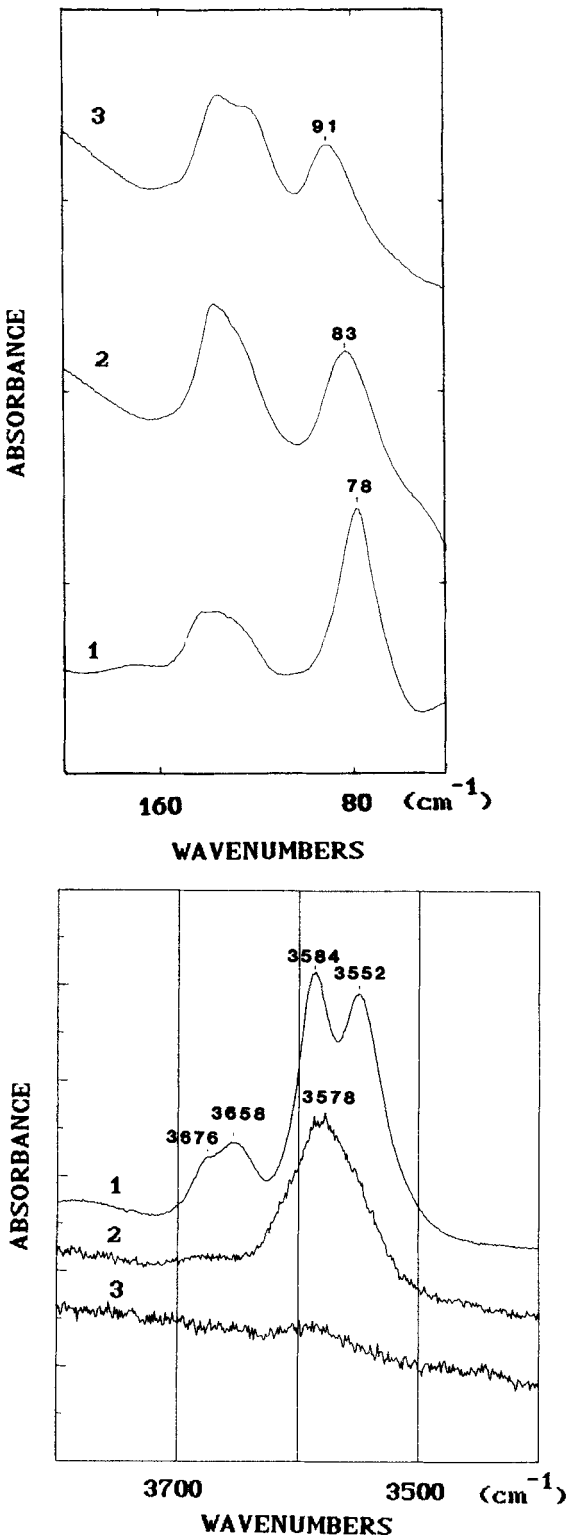


Figure 4. Infrared spectra of (top) K and (bottom) structural-OH groups of biotite as a function of temperature: 1, 30°C; 2, 550°C; 3, 650°C. Upper spectra were obtained in polyethylene pellets; lower spectra, with single crystals.

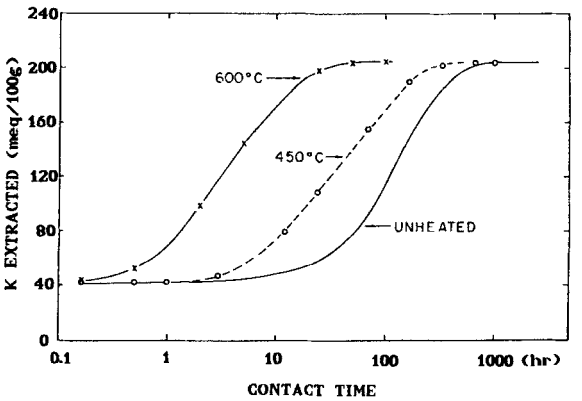


Figure 5. K extracted from <5-μm-size muscovite after different contact periods with Na-tetraphenylboron solutions after 24 hr of heating at different temperatures (Scott *et al.*, 1972).

OH groups. The increase of the distance between K and O induces a decrease of the interaction and consequently of the frequency. No frequency shift of the structural-OH groups occurred for heated phlogopite until the sample dehydroxylated (Figure 3). At the dehydroxylation temperature, the structure of phlogopite is destroyed (Vedder and Wilkins, 1969), and no conclusion can be made concerning the K-structure interaction. Spectra of the heated biotite are shown in Figure 4. The K band shifted progressively from 78 to 91 cm^{-1} as the temperature increased. A thermogravimetric analysis (TGA) showed that only 20% of the OH groups were lost at 600°C. Figure 4, bottom shows that the 3584-cm^{-1} band, the intensity of which decreased as the temperature increased to 400°C, corresponds to the structural-OH groups belonging to dioctahedral configurations. Between 400° and 600°C, the intensity of the 3676-, 3658-, and 3552-cm^{-1} components de-

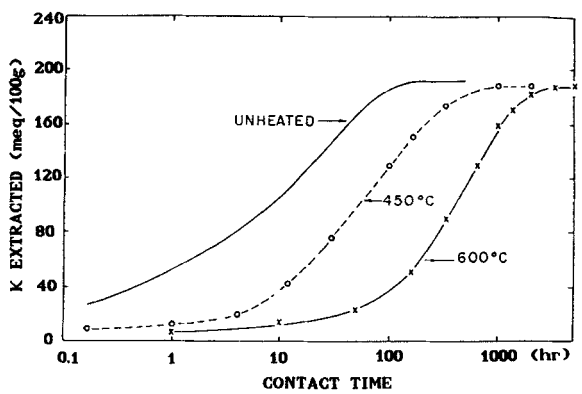


Figure 6. K extracted from <50-μm-size biotite after different contact periods with Na-tetraphenylboron solutions after 24 hr of heating at different temperatures (Scott *et al.*, 1972).

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creased without any visible change in the TGA analysis, due to the deprotonation process which resulted from the oxidation of Fe^{2+}. The K-band shift must therefore be related to the oxidation of Fe^{2+} to Fe^{3+}, which induces a deprotonation of structural-OH groups. As shown by Vedder and Wilkins (1969), this process occurs at lower temperatures than dehydroxylation of trioctahedral micas. The release of protons of OH groups increases the K–O_1 interaction and induces a shift of the K-band to higher frequency.

To summarize, we underline the determining influence of structural-OH groups and of Fe on the position of the K absorption band. For biotite, Fe^{2+} oxidation to Fe^{3+} on heating has an indirect effect, because it is accompanied by deprotonation of the OH. Thus, the K frequency gave an indication of the state of K in its site with respect to the crystal structure and the local physicochemical environment. The K frequency may therefore be reasonably related to the rate of release of K from micas.

Relation between IR frequency of K and its rate of release from micas

The present discussion mostly considers the data reported by Scott *et al.* (1972). Figures 5 and 6 from Scott *et al.* (1972) give the amounts of K extracted from <5-μm size muscovite or <50-μm size biotite after different contact periods with NaTPB solutions after 24 hr of heating at different temperatures.

The smaller rate of release of K observed on unheated samples by Scott *et al.* (1972) (Figures 5 and 6) for muscovite than for biotite was probably related to the stronger K–OH interaction in muscovite than in biotite, which is suggested by the higher IR frequency for muscovite (110 cm^{-1}) than for biotite (78 cm^{-1}).

The amount of K extracted as a function of time and of temperature of heating is reported in Figures 5 and 6. In heated samples these curves clearly show a greater rate of release of K from muscovite than from biotite. The rate of release was a function of the K–O_1 of OH group interactions. If these interactions increased, as has been found for heated biotite, the rate of release of K decreased and the K frequency increased, and vice versa for muscovite.

SUMMARY AND CONCLUSIONS

The frequency of the FIR band of K located in the interlamellar spaces of micas appears to be a function of the crystal structure and of the local physicochemical environment. The K-band was specific for each mica. The frequency was influenced by the orientation of structural-OH groups and by the Fe^{2+} content of the micas. FIR could be a useful tool for pedologists to study the vermiculitization process of micas. The K frequency has been shown to be related to the rate of release of K from these micas, an interesting point for agronomists if a relationship could be established between the state of K characterized by its IR frequency and the rate of release of that K. Such a function could be useful in estimating the stock of K in the soil available for plants.

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