

## FAR-INFRARED STUDY OF THE INFLUENCE OF THE OCTAHEDRAL SHEET COMPOSITION ON THE K<sup>+</sup>-LAYER INTERACTIONS IN SYNTHETIC PHLOGOPITES

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**Abstract**—Far-infrared (FIR) analysis of synthetic Mg-, Ni-, Co-, and Fe-phlogopites coupled with structural data from X-ray diffraction revealed that the K interlayer environments are directly related to octahedral sheet composition and geometry. The general phlogopite formula,  $KM_3^{2+}(Si_3Al)O_{10}(OH)_2$ , was varied according to octahedral compositions, where  $M^{2+} = Mg^{2+}, Fe^{2+}, Co^{2+},$  and  $Ni^{2+}$ . Octahedral substitutions have a direct effect on the *b* lattice parameter, which is related to the tetrahedral-octahedral sheet misfit and manifested by change in the tetrahedral rotation angle ( $\alpha$ ). The ditrigonal interlayer cavity geometry and the potential for retention of the compensating cations therefore varies according to the ionic size and the types and oxidation state of octahedral cations. These structural features appear as frequency shifts on FIR spectra. When  $Mg^{2+}$  is replaced by a smaller cation,  $Ni^{2+}$ , the *b* parameter decreases and the tetrahedral rotation angle,  $\alpha$ , increases, inducing the collapse of the ditrigonal ring. When this happens, the local anisotropy of the interlayer site increases, resulting in every other six out of 12 K–O bonds becoming shorter and the in-plane K–O vibration band shifts slightly to greater wavenumbers. Synthetic phlogopites with octahedral substitutions by cations of larger ionic radii (*i.e.*  $Co^{2+}$  and  $Fe^{2+}$ ) exhibit *b* parameter increases, where in the case of the annite end-member,  $\alpha$  decreases to almost 0°. As  $\alpha$  decreases, compensating cation sites become more hexagonal like and the nearest K–O bond increases in length. The K–O vibration bands move toward much smaller wavenumbers. Far infrared offers the potential for a new approach to study the retention of interlayer cations in other phyllosilicates and the mechanisms by which they are altered, such as heating or by weathering reactions in the environment.

**Key Words**—Annite, Biotite, Compensating Cation, Far-infrared Spectrometry, K<sup>+</sup>-layer Interactions, Octahedral Substitutions, Phlogopite, Synthetic, Tetrahedral Rotation.

### INTRODUCTION

General laws describing the exchange phenomenon of compensating cations in clays were established a few decades ago from thermodynamic data. To get a better understanding of the mechanisms of cation exchange, a study of cation–layer interactions at the molecular level is necessary. The study of far-infrared (FIR) absorption bands for fixed and exchangeable cations in micas and hydrous clay minerals is one such approach to monitoring these interactions (Ishii *et al.*, 1967; Schroeder, 1990, 1992; Prost and Laperche, 1990; Diaz *et al.*, 2002; Badreddine *et al.*, 2002a, 2002b).

The retention of cations compensating for layer-charge imbalances in 2:1 phyllosilicates is controlled by: (1) the physicochemical properties of cations and complexes within the interlayer site, (2) the crystal chemistry of the intralayer octahedral and tetrahedral sheets, and (3) the pressure, temperature, and composition of surrounding aqueous environments (Diaz, 1999).

Cation retention is generally described in terms of interactions between compensating cations and the clay structure. The most significant factors are the charge, mass, and radius of the compensating cation and the geometry of basal oxygen atoms in the tetrahedral sheet. Potassium–oxygen bonds give rise to absorption bands in the far infrared (FIR) range in micas (Schroeder, 1990; Laperche and Prost, 1991), corresponding to both the in-plane normal vibration modes along the *a* and *b* crystallographic axes with wavenumbers (*i.e.* frequencies) between 110 and 80  $cm^{-1}$  and the out-of-plane normal vibration mode between 140 and 130  $cm^{-1}$  (Diaz *et al.*, 2000). Study of the dichroic character of FIR absorption bands of K<sup>+</sup> in muscovite (Diaz *et al.*, 2000) showed the existence of two in-plane modes at 107 and 110  $cm^{-1}$ . Several authors have studied the mass and charge effects of cations and anions in the octahedral (*O*–) and tetrahedral (*T*–) sheets on the vibrations of compensating cations in the FIR range (Farmer, 1974; Tateyama *et al.*, 1977; Fripiat, 1981; Velde and Couty, 1985). Prost and Laperche (1990) and Schroeder (1990) established relations between an increasing in-plane stretching K–O wavenumber and the respective oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  in biotite and phlogopite, which can be attributed to OH-group orientations or removal in these micas upon heating. Laperche (1991) described the

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positive influence of the tetrahedral rotation angle ( $\alpha$ , which is a measure of *T*- and *O*- misfit) on the K–O wavenumber. Schroeder (1990) further proposed the following empirical equation correlating the in-plane stretching K–O wavenumber ( $\sigma$ ) with the stoichiometry of various di- and trioctahedral true micas:

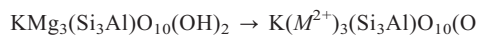
$$\sigma \text{ (cm}^{-1}\text{)} = 79.6 + 0.96 \text{ Mg}^{2+} - 4.23 \text{ Fe}^{2+} + 7.61 \text{ Al}^{3+} + 9.09 \text{ Fe}^{3+} - 4.65 \text{ Li}^{+} + 2.20 \text{ F}^{-}$$

Additional support for the correlation between interlayer *T*- and *O*- dimensions and intralayer chemical compositions has also been seen from X-ray diffraction (XRD) evidence. Among these modifications are changes in the size and geometry of polyhedra within the *T*–*O*–*T* layer, and modifications of the size and shape of the interlayer site (Bailey, 1984). The structural modifications induced by the size of octahedral cations in synthetic phlogopites were studied by Hazen and Wones (1972) and Redhammer *et al.* (1993, 1995), which showed that good correlation exists between the in-plane K–O wavenumber and the chemical composition of micas.

The objective of the present study was to provide additional molecular data, obtained by FIR spectroscopy, and to analyze the influence of the chemical composition of the octahedral sheet on the in-plane stretching K–O wavenumber in synthetic phlogopites. The aim was to obtain more information about the K<sup>+</sup>-layer interactions in micas and to confirm the structural changes resulting from different octahedral site occupancies. Attention was focused on the FIR absorption band corresponding to the in-plane normal vibration modes of K<sup>+</sup>.

## MATERIALS AND METHODS

The samples used were synthetic phlogopite solid-solution series, where Ni<sup>2+</sup>, Co<sup>2+</sup>, and Fe<sup>2+</sup> progressively replace octahedral Mg<sup>2+</sup>. The ionic radii (*ir*) of octahedrally coordinated Ni<sup>2+</sup>, Mg<sup>2+</sup>, Co<sup>2+</sup>, and Fe<sup>2+</sup> are 0.69 Å, 0.72 Å, 0.745 Å, and 0.78 Å, respectively (Shannon, 1976). Synthetic compositions were prepared along the following ideal series:



where  $\text{M}^{2+} = \text{Ni}^{2+}, \text{Co}^{2+}, \text{Fe}^{2+}$  according to the gelling method of Hamilton and Henderson (1968). The octahedral composition is described on a molar basis as  $X_M^{2+} = \text{M}^{2+}/(\text{M}^{2+} + \text{Mg}^{2+})$ . The starting compounds were introduced in sealed gold tubes, with distilled water, using a constant water/solid ratio of 15 wt.%. The syntheses were performed at 600°C, 1 kbar, for a run duration of 2 weeks, in Tuttle-type pressure vessels (Tuttle, 1949). The presence of variable-valence cations (Ni<sup>2+</sup>, Co<sup>2+</sup>, and Fe<sup>2+</sup>) in the systems investigated required control of the oxygen fugacity. This control was realized by a variation of the double-capsule

technique (Eugster, 1957), using the nickel-nickel oxide assemblage (NNO) as a buffer ( $\log f_{\text{O}_2} = -20$  at 600°C, 1 kbar, after Eugster and Wones, 1962).

Phase identification and structural parameters were determined by XRD in reflection mode, using a Siemens diffractometer (40 kV, 20 mA, CoK $\alpha$  Fe-filtered radiation,  $\lambda = 1.78897$  Å).

The FIR spectra were recorded under vacuum with a Bruker IFS 113V instrument, using polyethylene (PE) pressed powder pellets consisting of 10 mg of sample mixed with 30 mg of PE. Each sample was scanned 300 times with a nominal 2 cm<sup>-1</sup> resolution.

## RESULTS

### XRD data

The *b* lattice parameter is related to the deformation of the ditrigonal cavity by modification of the tetrahedral rotation angle,  $\alpha$ , and tetrahedral distortion is recognized as being largely a response to the varying dimensions of the octahedral sheet. Given the constancy of the tetrahedral sheet composition and consistent tri-octahedral nature of the octahedral sheet in the samples, the assumption is made here that  $\alpha$  is geometrically related to *b*. The value of  $\alpha$  was therefore calculated from the relation established by Donnay *et al.* (1964)

$$\cos(\alpha) = \frac{b}{4\sqrt{2}d_t} \quad (1)$$

where  $d_t$  is the average tetrahedral cation–oxygen distance, given by the equation of Hazen and Burnham (1973)

$$d_t(\text{Å}) = 0.163 \left( \frac{\text{Al}}{\text{Al} + \text{Si}} \right) + 1.608 \quad (2)$$

In the present case, all samples had the same tetrahedral composition (Si<sub>3</sub>Al), so the average cation–oxygen distance in tetrahedra,  $d_t$ , was constant and equal to 1.649 Å. The rotation angle was, therefore, calculated directly from the *b* cell dimension (Figure 1a inset). The experimental *b* parameter was determined from the  $d_{060}$  reflection on XRD patterns. The experimental *b* parameter and the calculated tetrahedral rotation angle,  $\alpha$ , of each sample along the Mg–Ni and Mg–Co synthetic phlogopites series and the phlogopite–annite solid solution series are reported in Table 1. The changes in the *b* parameter and in  $\alpha$  for the different phlogopites series (Figure 1) show an increase in *b* with increasing size of octahedral cations (*i.e.* in the following order: Ni<sup>2+</sup> < Mg<sup>2+</sup> < Co<sup>2+</sup> < Fe<sup>2+</sup>, Figure 1a), which agrees with the results of Hazen and Wones (1972) and of Redhammer *et al.* (1993, 1995). The inset in Figure 1a shows a decrease in the calculated  $\alpha$ , using  $d_t = 1.649$  Å, with increasing average size of octahedral cations, observations which agree well with the results of Hazen and Wones (1972).

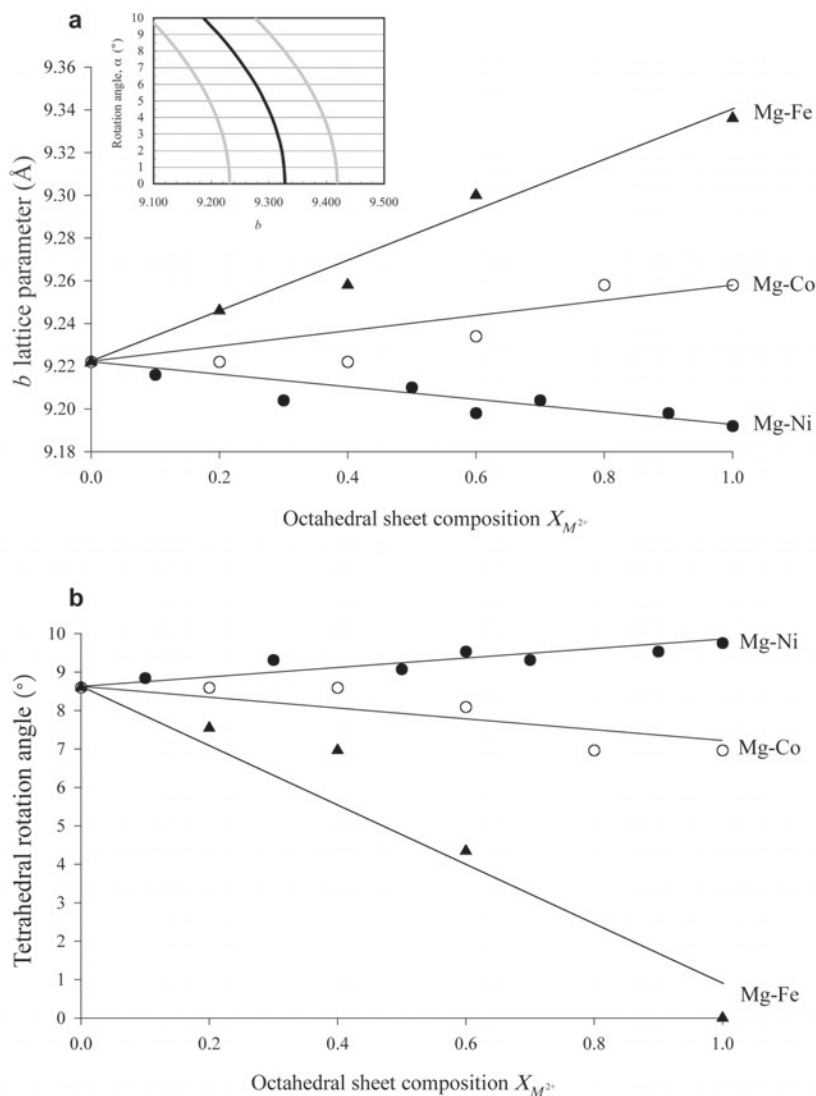


Figure 1. (a) Relationships between the  $b$  lattice parameter and (b) the tetrahedral rotation angle,  $\alpha$ , of synthetic phlogopite as a function of the octahedral sheet composition.  $\bullet$   $X_{Ni}^{2+} = Ni^{2+}/(Ni^{2+} + Mg^{2+})$ ,  $\circ$   $X_{Co}^{2+} = Co^{2+}/(Co^{2+} + Mg^{2+})$ ,  $\blacktriangle$   $X_{Fe}^{2+} = Fe^{2+}/(Fe^{2+} + Mg^{2+})$ . Inset to (a) shows variation in  $\alpha$  using equation 1 and assuming a  $d_{060} = 1.649$  Å (dark line). Gray lines show  $\pm 1\%$  error of  $d_{060}$  as determined from XRD.

### FIR spectra

The FIR spectra of the Mg-Ni, Mg-Co, and Mg-Fe phlogopites series (Figures 2, 3, and 4, respectively) revealed K–O vibration bands at  $80\text{ cm}^{-1}$  and  $141\text{ cm}^{-1}$ , which are consistent with in-plane and out-of-plane vibration modes, respectively, of  $K^+$  in synthetic phlogopite (Laperche, 1991; Diaz, 1999). In natural phlogopite, Laperche and Prost (1991) found these bands to be at  $91\text{ cm}^{-1}$  and  $152\text{ cm}^{-1}$ , respectively. The  $10\text{ cm}^{-1}$  up-shift between FIR of K–O vibrations in synthetic and natural phlogopite may be associated with the greater  $F^-$  content of natural samples, in which  $F^-$  substitution for  $OH^-$  reduces the repulsive  $H^+K^+$

interactions and increases K–O attractive forces (Schroeder, 1990). The  $82\text{ cm}^{-1}$  absorption band of Mg-phlogopite has an asymmetric character, which may be due to the existence of two in-plane modes of vibration, as it is for muscovite (Diaz *et al.*, 2000).

The doublet at  $162\text{--}157\text{ cm}^{-1}$  corresponds to the broad  $156\text{ cm}^{-1}$  band of natural phlogopite observed by Laperche and Prost (1991). Ishii *et al.* (1967) suggested that these bands are related to vibration modes involving octahedral cations. McKeown *et al.* (1999) used model calculations to attribute these bands, and associated the  $161$  and  $156\text{ cm}^{-1}$  bands with  $A_u$  and  $B_u$  modes, respectively, (Harris and Bertolucci, 1989) (*i.e.* where  $A$

Table 1. Value of the experimental  $b$  parameter ( $6 \times d_{060}$ ) and the calculated tetrahedral rotation angle,  $\alpha$ , for Mg–Ni, Mg–Co, and Mg–Fe synthetic phlogopite series.

Samples series	Octahedral composition $X_M^{2+} = M^{2+}/(M^{2+}+Mg)$	$b$ parameter (Å)	Tetrahedral rotation angle, $\alpha$ (°)
Mg-phlogopite	0	9.222	8.6(2)
	0.1	9.216	8.8(2)
	0.3	9.204	9.3(2)
	0.5	9.210	9.1(2)
Mg-Ni	0.6	9.198	9.5(2)
	0.7	9.204	9.3(2)
	0.9	9.198	9.5(2)
	1	9.192	9.8(2)
	0.2	9.222	8.6(2)
	0.4	9.222	8.6(2)
Mg-Co	0.6	9.234	8.1(2)
	0.8	9.238	7.0(2)
	1	9.258	7.0(2)
	0.2	9.246	7.5(2)
Mg-Fe	0.4	9.258	7.0(2)
	0.6	9.300	4.0(2)
	1	9.336	$\approx 0$

and  $B$  are the Mulliken symbol notations of one-dimensional modes + and –, respectively, and  $u$  is the anti-symmetric representation with respect to inversion) assigned to both  $M-O$  and in-plane  $K-O$  translations. No sufficient experimental FIR data are available to assign these two bands precisely. The bands may also be related to a doublet at  $177-169\text{ cm}^{-1}$  observed in talc and

corresponding to in-plane vibrations of octahedral  $Mg^{2+}$ , as described by Farmer (1974) and Ishii *et al.* (1967). Collectively, the observations suggest that the doublet at  $162-157\text{ cm}^{-1}$ , observed for the synthetic phlogopite, is, in part, due to  $M-O$  and/or  $M-OH$  vibrations.

As octahedral  $Mg^{2+}$  cations are progressively substituted by smaller  $Ni^{2+}$  cations, the  $K-O$  vibration band

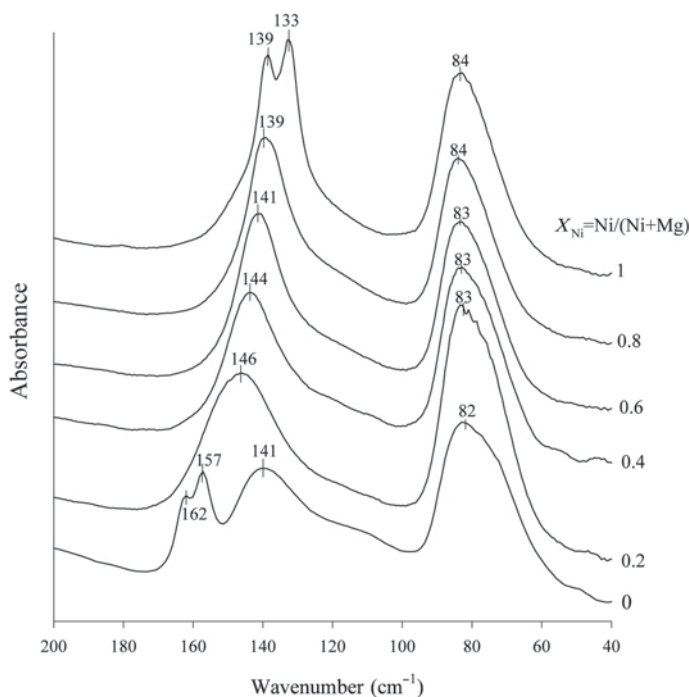


Figure 2. FIR spectra of Mg-Ni synthetic phlogopites.

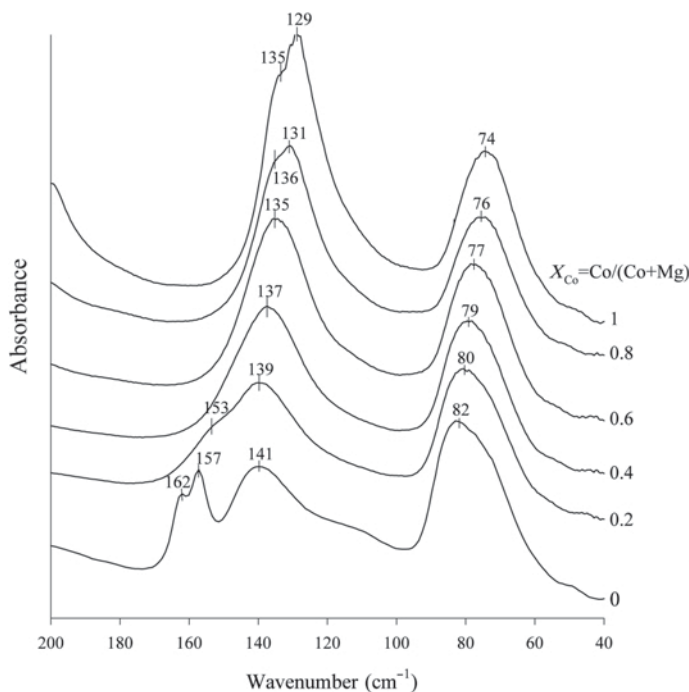


Figure 3. FIR spectra of Mg-Co synthetic phlogopites.

shifts upward slightly to  $84\text{ cm}^{-1}$ , while the doublet at  $162\text{--}157\text{ cm}^{-1}$  shifts downward considerably to  $139\text{--}133\text{ cm}^{-1}$  (Figure 2). The out-of-plane K–O  $141\text{ cm}^{-1}$  band overlaps with the shifted

$162\text{--}157\text{ cm}^{-1}$  bands, which displace as the  $\text{Ni}^{2+}$  content increases. As  $\text{Mg}^{2+}$  is replaced by larger  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$ , the K–O mode decreases from  $82$  to  $74\text{ cm}^{-1}$  for the Mg–Co phlogopite series (Figure 3) and from  $82$

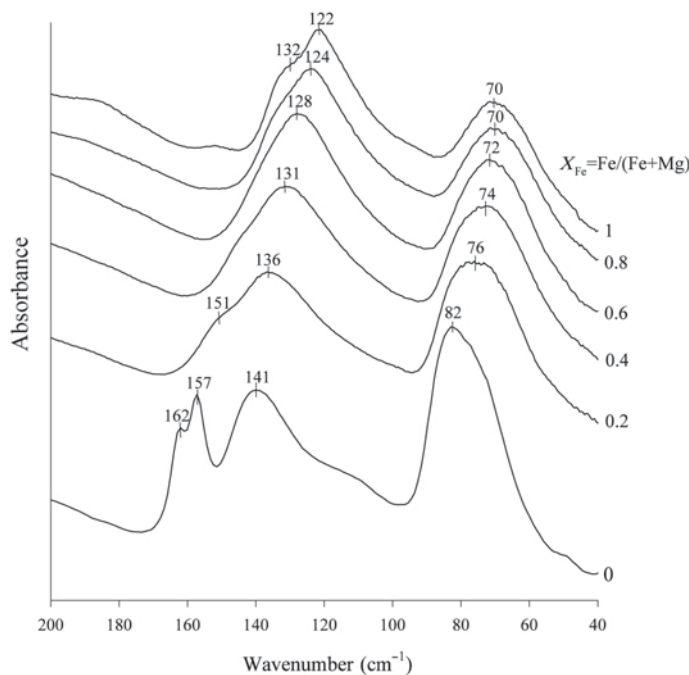


Figure 4. FIR spectra of Mg-Fe synthetic phlogopites.

to  $70\text{ cm}^{-1}$  for the phlogopite–annite series (Figure 4). The  $162\text{--}157\text{ cm}^{-1}$  doublet shifts downward to  $135\text{--}129\text{ cm}^{-1}$  and  $132\text{--}122\text{ cm}^{-1}$  when  $\text{Mg}^{2+}$  is replaced by  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$ , respectively. This shift overlaps the out-of-plane K–O  $141\text{ cm}^{-1}$  band for both series, explaining the visible broad band in spectra of samples with octahedral composition from  $X_M^{2+} = 0.2$  to  $X_M^{2+} = 0.8$ . The modifications in the  $180\text{--}120\text{ cm}^{-1}$  region are difficult to explain because of a lack of band-assignment knowledge for the bands in this range. The shift of the  $162\text{--}157\text{ cm}^{-1}$  doublet of Mg-phlogopite to a smaller wavenumber in Ni-Co-phlogopite, and annite can be attributed to an octahedral cation mass effect (*i.e.* atomic mass units of Mg = 24.32, while Ni = 58.69, Co = 58.93, and Fe = 55.85). Similar changes were observed by Ishii *et al.* (1967) on a biotite (lepidomelane), in which the Mg atoms were partially substituted by the Fe atoms in the octahedral sheet. Farmer (1974) also observed a shift of the Mg-talc doublet  $169\text{--}177\text{ cm}^{-1}$  to  $143\text{--}151\text{ cm}^{-1}$  for the Ni-talc. In addition to a mass effect, the FIR absorption-band positions of the octahedral cation vibrations should also be influenced by the size effect and resultant distortion of the octahedral site (as supported by observed modifications of the  $b$  parameter).

The variation of in-plane K–O stretching wavenumber vs.  $X_M^{2+}$  shown in Figure 5 along the three series investigated appears linear for the Mg–Ni and the Mg–Co series, but not in the case of the phlogopite–annite solid solution. These data indicate that the  $\text{K}^+$  environment also changes with the chemical composition of the octahedral sheet.

## DISCUSSION

### Structural modification

Hazen and Wones (1972) noted “octahedral substitutions have a profound influence on  $b$ , while  $d_{001}$  remains

virtually constant.” Variations of the octahedral-sheet composition effectively modify the cell  $a$  and  $b$  dimensions within the mica layer, which are theoretically related by  $b/a = \sqrt{3}$  (Donnay *et al.*, 1964). The dimensional misfit between octahedral and tetrahedral sheets is accommodated by polyhedral distortions that include tilt of apical oxygens, rotation of the ditrigonal oxygen cavity ( $\alpha$ ), and the thickness of the octahedral sheet (Bailey, 1984; Radoslovich and Norrish, 1962). The tetrahedral rotation angle,  $\alpha$ , is the most robust parameter for the evaluation of the tetrahedral-sheet deformation. Several authors studied the variations of  $\alpha$  as a function of unit-cell parameters and the composition of mica layers (Radoslovich and Norrish, 1962; Donnay *et al.*, 1964; McCauley and Newnham, 1971; Hazen and Wones, 1972; Hazen and Burnham, 1973; Redhammer *et al.*, 1993, 1995). As octahedral  $\text{Mg}^{2+}$  ( $ir = 0.72\text{ \AA}$ ) is replaced by a smaller cation,  $\text{Ni}^{2+}$  ( $ir = 0.69\text{ \AA}$ ), the  $b$  parameter decreases (Figure 1). Indeed, the presence of smaller cations decreases octahedral-sheet dimensions. As a consequence, the tetrahedral sheet becomes smaller by a diminution of the ditrigonal cavity, which is manifested by increasing  $\alpha$  from  $8.6^\circ$  to  $9.8^\circ$ . In contrast, as  $\text{Mg}^{2+}$  is replaced by larger cations such as  $\text{Co}^{2+}$  or  $\text{Fe}^{2+}$ , the  $b$  parameter increases (Figure 1). The  $\alpha$  response to  $\text{Fe}^{2+}$  is more profound than with  $\text{Co}^{2+}$  because of their differing ionic radii ( $0.78\text{ \AA}$  and  $0.745\text{ \AA}$ , respectively), where the ranges are  $8.6^\circ$  to  $7.0^\circ$  for the Mg–Co phlogopites series and from  $8.6^\circ$  to  $\sim 0^\circ$  for the phlogopite–annite series.

### Influence of $\text{K}^+$

The tetrahedral rotation modifies the geometry of the interlayer site. When  $\alpha = 0^\circ$ , the phlogopite  $\text{K}^+$ -site is a hexagonal polygonal ring and the twelve nearest-neighbor K–O distances are equal. As  $\alpha$  increases, the ring forms a ditrigonal cavity where every other six out of the 12 oxygen atoms are positioned closer to the

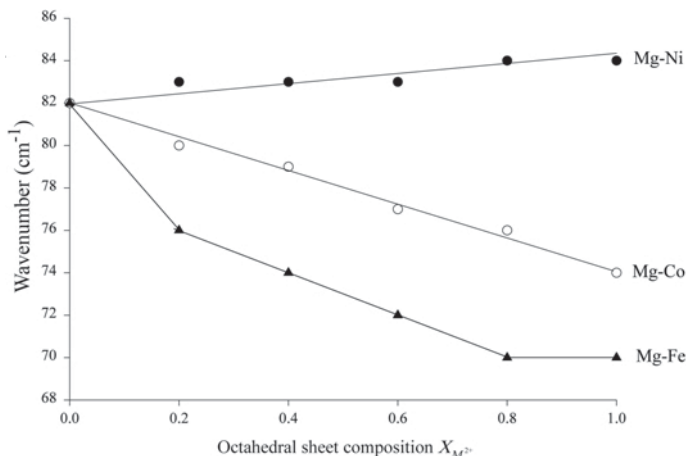


Figure 5. Shifts of the in-plane stretching K–O wavenumber as a function of different octahedral sheet compositions  $\bullet X_{\text{Ni}}^{2+} = \text{Ni}^{2+}/(\text{Ni}^{2+} + \text{Mg}^{2+})$ ,  $\circ X_{\text{Co}}^{2+} = \text{Co}^{2+}/(\text{Co}^{2+} + \text{Mg}^{2+})$ ,  $\blacktriangle X_{\text{Fe}}^{2+} = \text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg}^{2+})$ .

interlayer cation and the six others are more distant. This ditrigonal distortion defines short K–O ( $d_{\text{K-O inner}}$ ) and long K–O distances ( $d_{\text{K-O outer}}$ ). A clear difference between inner and outer K–O bond lengths (2.97 Å and 3.31 Å, respectively) for phlogopite was shown by Hazen and Burnham (1973). Redhammer *et al.* (1995) used single-crystal XRD data from a natural annite to demonstrate a near ideal hexagonal ring with  $d_{\text{K-O inner}} = 3.14$  Å and  $d_{\text{K-O outer}} = 3.22$  Å (*i.e.*  $\alpha \approx 0^\circ$ ). The FIR spectrometry is complementary to XRD in that it can evaluate the interactions between  $\text{K}^+$  and the six nearest oxygen atoms of the ditrigonal cavity directly (Diaz 1999). Tateyama *et al.* (1973) showed a linear inverse relationship between FIR, in-plane K–O wavenumbers in micas and  $d_{\text{K-O inner}}$ , suggesting that the  $\text{K}^+$ –basal oxygen interactions are stronger as the in-plane K–O wavenumber increases.

Data presented here indicate that as octahedral  $\text{Mg}^{2+}$  is replaced by  $\text{Ni}^{2+}$ , the increase in  $\alpha$  causes a slight shortening of  $d_{\text{K-O inner}}$ , which is seen by a slight increase in the in-plane K–O wavenumber, from 82 to 84  $\text{cm}^{-1}$ . The shift is small because the ionic radius of  $\text{K}^+$  (1.33 Å) is optimally close to the dimensions of the ditrigonal cavity. If the octahedral sheet is occupied by cations which are larger than  $\text{Mg}^{2+}$ , such as  $\text{Co}^{2+}$  or  $\text{Fe}^{2+}$ , then  $\alpha$  is smaller and the  $d_{\text{K-O inner}}$  is greater, explaining the shift in in-plane K–O band toward smaller wavenumbers as  $\text{Mg}^{2+}$  was progressively replaced by  $\text{Co}^{2+}$  (*i.e.* from 82 to 74  $\text{cm}^{-1}$ ). The downward shift is more pronounced in the case of the phlogopite–annite series (82  $\rightarrow$  70  $\text{cm}^{-1}$ ). Such relations are illustrated where the in-plane stretching K–O wavenumbers are plotted vs.  $b$  parameters (Figure 6a) and vs. the tetrahedral rotation angles  $\alpha$  (Figure 6b). The in-plane stretching K–O wavenumber increases linearly with decreasing  $b$ . Interestingly, the in-plane stretching K–O wavenumber does not vary with  $\alpha$  in a single linear fashion, but perhaps as two linear trends with an intersection at an  $\alpha$  of  $\sim 7^\circ$ .

The phlogopite–annite series is of particular interest because the in-plane K–O wavenumber does not shift in a linear fashion with changing  $X_{\text{Fe}}$ . The ditrigonal cavity distorts with the increasing tetrahedral-sheet  $b$  dimension in response to the increasing octahedral dimension, thus eliminating the misfit between the sheets. Takeda and Morosin (1975) noted that the rotation angle,  $\alpha$ , in the annite series changed suddenly from  $\sim 7^\circ$  to  $\sim 2^\circ$  within a very narrow composition range of  $0 \leq X_{\text{Fe}} \leq 0.4$ . Beyond this, they noted that for greater Fe contents the decrease in  $\alpha$  is very slight, up to  $\sim 1^\circ$  in the  $0.4 \leq X_{\text{Fe}} \leq 1$  range. A closer look at the in-plane K–O wavenumber shift in the annite series revealed that the data can be viewed as two trends which converge at  $\sim X_{\text{Fe}} = 0.4$  content, suggesting that the misfit between octahedral and tetrahedral portions of the 2:1 lattice geometry experience stresses that make  $\alpha$  unstable in the range of  $4^\circ$  to  $5^\circ$ .

#### Application to natural systems

The FIR analysis of  $\text{K}^+$ –layer interactions in synthetic micas can be applied to various natural examples. Prost and Laperche (1990) observed a shift of the in-plane stretching K–O vibration band of biotite from 78 to 91  $\text{cm}^{-1}$  when biotite was heated from 30°C to 650°C and related this shift to a deprotonation process induced by the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  during heating, as described by Scott *et al.* (1972), though no further explanation was given by the latter authors. Schroeder (1990) suggested that asymmetry of the charge distribution in the trioctahedral sites may explain changes. The shift cannot be explained in terms of thermal expansion of the K site which becomes more and more regular upon heating (Takeda and Morosin, 1975) and the shift should be toward smaller wavenumbers. Another factor may explain such a shift: the effect of the relative size of  $\text{Fe}^{2+}$  ( $ir = 0.78$  Å) and  $\text{Fe}^{3+}$  ( $ir = 0.645$  Å) in six-fold coordination on the  $b$  parameter and resulting  $\alpha$  angle.

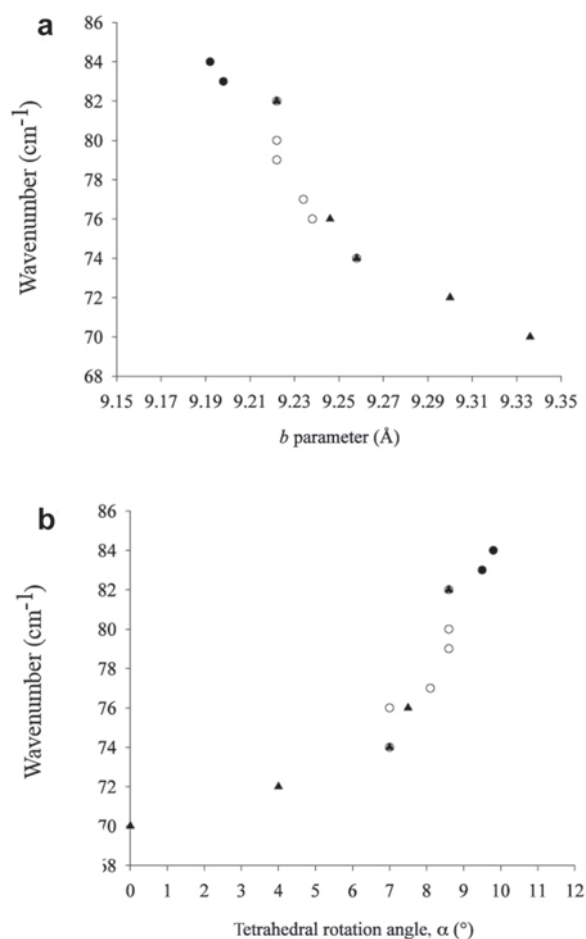


Figure 6. Shifts of the in-plane stretching K–O wavenumber as a function of the  $b$  parameter (a) and of the tetrahedral rotation angle,  $\alpha$  (b). ● Mg–Ni phlogopite series, ○ Mg–Co phlogopite series, ▲ phlogopite–annite series.

The increase in the octahedral  $\text{Fe}^{3+}$  content in heated biotite induced a decrease in  $b$ , as noted by Laperche (1991). Redhammer *et al.* (1993) also showed a decrease in the  $b$  parameter of synthetic annite with increasing  $\text{Fe}^{3+}$  content. The shift of the in-plane stretching K–O band toward a greater wavenumber value can thus be related to an increase in  $\alpha$  suggesting that the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in biotite during heating leads to stronger  $\text{K}^+$ -layer interactions, particularly in those regions of the octahedral sheet influenced by  $\text{Mg}^{2+}$  and other non-redox sensitive octahedral cations. Scott *et al.* (1972) observed a smaller rate of release of  $\text{K}^+$  in biotite heated to 600°C than in unheated samples, consistent with observations above, showing that a clear relation exists between the state of  $\text{K}^+$  in micas and the in-plane K–O stretching vibration band. Far infrared offers a new approach for the study of biotite and annite weathering, as Fe oxidation and compensating-cation expulsion are important mechanisms controlling rates of soil-mineral dissolution (Schroeder *et al.*, 1997).

The FIR study of Mg–Ni, Mg–Co, and Mg–Fe synthetic phlogopites shows the influence of the chemical composition of the octahedral sheet on the  $\text{K}^+$ -layer interactions, in particular the effect of Fe content. The interactions reflect the degree of retention of  $\text{K}^+$  in the mica structure. Prost and Laperche (1991) showed that the in-plane K–O wavenumber in micas increases with decreasing extractability of  $\text{K}^+$ , in the order biotite < phlogopite < muscovite. The extractability of  $\text{K}^+$  in phlogopite is known to increase with Fe content (Rousseaux *et al.*, 1972), and the present experimental study allows FIR spectrometry to be used to estimate  $\text{K}^+$ -retention potentiality in phyllosilicates as a function of the crystal-chemistry of the layer. Indeed, recent works indicate that the retention of exchanged cations in vermiculite can be studied by FIR spectrometry (Diaz *et al.*, 2002; Badreddine *et al.*, 2002a, 2002b).

### CONCLUSIONS

Far-infrared spectral data and associated structural data derived from XRD for three series of synthetic phlogopites show strong correlations. Synthetic phlogopites ( $\text{KM}_3^{2+}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ , where  $M$  = metal cation) varied according to octahedral compositions with increasing apparent size of octahedral cations in the following order  $\text{Ni}^{2+} < \text{Mg}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+}$ . Tetrahedral-octahedral sheet misfits were manifested by changes in the tetrahedral rotation angle,  $\alpha$ , in the order  $\text{Ni}^{2+} > \text{Mg}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+}$  for distortion of the ditrigonal interlayer cavity geometry. When  $\text{Mg}^{2+}$  in phlogopite is replaced by  $\text{Ni}^{2+}$ , the  $b$  parameter decreases and the tetrahedral rotation angle  $\alpha$  increases. This results in the nearest neighbor K–O bonds becoming shorter and the in-plane K–O vibration band shifting slightly to greater wavenumbers. Octahedral substitutions by  $\text{Co}^{2+}$  and  $\text{Fe}^{2+}$  exhibit  $b$  parameter increases, whereas in the annite end-

member case  $\alpha$  decreases to almost 0°. As  $\alpha$  decreases,  $\text{K}^+$  sites become more hexagonal-like and the nearest-neighbor K–O bond increases in length causing the K–O vibration bands to shift to smaller wavenumbers. Such a robust response of FIR to changes in the structural state of phlogopites offers the potential for a new approach to study the retention of interlayer cations in other phyllosilicates and, furthermore, will help to identify the mechanisms by which phyllosilicates alter through heating or weathering in the environment.

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