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TOPOTACTIC CATION EXCHANGE IN TRANSFORMED MICAS UNDER HYDROTHERMAL CONDITIONS

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Abstract—The formation of hydroxylated phases was investigated using K-depleted biotite (Na-biotite) and K-depleted muscovite (Na-muscovite) under hydrothermal treatment with alkali (Li^+, K^+, NH_4^+, Rb^+ and Cs^+), alkaline earth (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}), and aluminum (Al^{3+}) cations at 200ºC for 1 and/or 3 days. The K-depleted biotite treated with alkali cations produced anhydrous hydroxylated phases, while the K-depleted muscovite did not significantly exchange alkali cations but dehydrated to form Na-muscovite in all cases. The alkaline earth cations, however, produced hydrous hydroxylated phases with both K-depleted micas. The degree of hydration energy of cations and the charge density of micas were found to influence the formation of anhydrous and hydrous phases from the K-depleted micas. This type of topotactic cation exchange potentially could be used for fixation and immobilization of radioactive species such as Cs, Sr, Ra, *etc*. in the transformed micas. The K-depleted biotite and muscovite treated with Al^{3+} were transformed to hydroxy-Al interlayered vermiculites (HIV) because of hydrolysis and polymerization of Al^{3+}. These HIV phases could also serve as useful adsorbents for soil and groundwater contaminants.

Key Words—Hydrothermal Treatment, Hydroxy-Al Interlayered Vermiculite (HIV), K-depleted Biotite, K-depleted Muscovite, Topotactic Cation Exchange, Transformation.

INTRODUCTION

Ion exchange properties of artificially or naturally altered micas including their synthesis have been studied by many workers. The artificially K-depleted phlogopite, which is obtained by replacing interlayer K^+ ions with Na^+ ions, is an excellent candidate for selective Cs exchange (Komarneni and Roy, 1988). Another attempt to improve the ion exchange capacity of natural mica was made by Caseri *et al.* (1992), and they found that the specific surface area of Li-muscovite saturated with $LiNO_3$ solution was increased. Based on the above cleavage procedure, Osman *et al.* (1999) observed that Li^+ ions of Li-muscovite are readily exchanged by alkali metal ions (Na^+, K^+, Rb^+ and Cs^+). Natural micas also successfully separate some of the heavy metal cations such as Cu and Pb in soil solution and some radioactive species such as Cs and Sr from nuclear wastes because they have high negative charge density (Farquhar *et al*., 1997; Zachara *et al*., 2002; McKinley *et al*., 2004).

Topotactic reactions have been used for syntheses and transformations of clay minerals (Komarneni and Roy, 1986; Zhan and Guggenheim, 1995; Mendelovici, 1997; Vogels *et al*., 2005). Komarneni and Roy (1986) synthesized several hydroxylated phases including a Cs-mica for the first time under hydrothermal conditions using a K-depleted phlogopite mica which was created by the topotactic Na^+ ion exchange for K^+ of a natural phlogopite. They proposed that the K-depleted mica is a potential candidate for the immobilization of radioactive Cs (Komarneni and Roy, 1988).

In this study, we investigated the formation of anhydrous and hydrous hydroxylated phases using K-depleted biotite (Na-biotite) and K-depleted muscovite (Na-muscovite) by the topotactic cation-exchange method with different cations under hydrothermal conditions as this approach could be useful to immobilize some radioactive species, especially Cs and Sr (Stout *et al*., 2006).

MATERIALS AND METHODS

Clays and reagents

Natural biotite from Bancroft, Ontario and muscovite from Effingham Township were procured from Wards Natural Science Establishment. These micas were wet ground and <50 μm size fractions were obtained in wet conditions using a sieve. The K-depleted micas were produced according to the method developed by Scott and Smith (1966). Komarneni and Roy (1988) and Bortun *et al*. (1998) also showed that this conventional K-removal treatment effectively removes interlayer K^+ ions from natural micas. The micas were reacted repeatedly with 1.0 M NaCl–0.2 N sodium tetraphenylborate (NaTPB)–0.01 M disodium ethylenediaminetetraacetic acid (EDTA) solution at room temperature for several days to years. After equilibration, the solid and solution phases were separated by filtration and the solid portion collected was washed with 40% 0.5 N

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Table 1. d_{001} spacings (Å) of K-depleted biotite after hydrothermal and dry-heat treatment with alkali cations.

	After hydrothermal treatment at 200ºC for 1 day	After heating at 300ºC for 4 h	500ºC for 4 h
Li^+	10.18	10.18	10.18
K^+	10.09	10.04	9.97
NH_4^+	10.22	10.18	10.11
Rb^+	10.20	10.18	10.11
Cs^+	10.59	10.62	10.44

NaCl−60% acetone (volume basis) solution several times. The product was then washed repeatedly with deionized water. This series of procedures was repeated several times to remove K completely from biotite or muscovite. The two K-depleted micas used in the study were provided by the late Dr A.D. Scott. All the reagents used in this study were of analytical grade, and were used without further purification.

Hydrothermal formation of hydroxylated phases or transformation of micas

Several solutions containing different individual cations were prepared with a 3 N concentration of LiCl, KCl, NH_4Cl, RbCl, CsCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ or $AlCl_3$. 100 mg of K-depleted biotite or K-depleted muscovite and 10 mL of each different solution were sealed in teflon vessels of a stainless steel Parr reactor. After the Parr reactor was hydrothermally treated at 200ºC for 1 day, it was cooled to room temperature and pressure. As for $BaCl_2$ solution treatment, the reaction was also carried out for 3 days. The separation of solid and solution phases was achieved by centrifugation (HT centrifuge, IEC) at 5000 rpm. Powder X-ray diffraction (XRD) analysis was carried out to characterize solid phases using a Scintag diffractometer with CuKα radiation. In order to investigate the nature of the hydrous phases after the hydrothermal treatment, the solid samples were also heated in air at 300 and 500ºC for 4 h and XRD analysis was used to determine the nature of phases.

RESULTS AND DISCUSSION

Topotactic formation of hydroxylated phases from K-depleted biotite

Changes in the d_{001} spacing of the K-depleted biotite under both the hydrothermal and dry-heat treatments with different alkali and alkaline earth cations are summarized in Tables 1 and 2, respectively. The hydrothermal treatment using different alkali cations (Li^+, K^+, NH_4^+, Rb^+ and Cs^+) produced dehydrated hydroxylated phases from the K-depleted biotite (Table 1). The d_{001} spacing of the original K-depleted biotite obtained by the K-removal procedure is ~12.2 Å with a shoulder at 11.3 Å under dry conditions as revealed by the XRD pattern (Figure 1a). The K-depleted biotite, however, showed a 14.77 Å peak with a shoulder at 12.23 Å under wet conditions as revealed by the XRD (Figure 1b). This expansion of K-depleted biotite to 14.77 Å under wet conditions probably suggests a reduced charge density after K depletion. The hydrothermal treatments at 200ºC caused the collapse of the 12.20 Å interlayer spacing in the original K-depleted biotite to form mica-type hydroxylated phases (Figure 2). After heating at 300 and 500ºC, there were only small changes in the *d* spacings of these hydroxylated phases formed with alkali cations (K^+, NH_4^+, Rb^+ and Cs^+) which have relatively small hydration energies (Table 1). These results suggest that the alkali cations above led to the formation of anhydrous mica-type hydroxylated phases, while the

Table 2. d_{001} spacings (Å) of K-depleted biotite after hydrothermal and dry-heat treatments with alkaline earth and Al^{3+} cations.

	After hydrothermal treatment at 200ºC for 1 day	After heating at 300ºC for 4 h	500ºC for 4 h
Mg^{2+}	13.45, 10.20 (broad peaks)	10.11	9.86
Ca^{2+}	14.39, 10.77, 9.66 (broad peaks)	10.35 (broad peak)	10.02 (slightly broad)
Sr^{2+}	14.69, 12.34, 11.10 (broad peaks)	10.02	9.82
Ba^{2+}	12.20, 10.75, 10.20 (broad peaks)	10.09	10.04
Ba^{2+} (for 3 days)	10.59 (slightly broad)	NA*	NA*
Al^{3+}	15.23, 14.24 (broad peaks)	14.03, 13.34, 12.99 (quite broad peaks)	11.01, 10.74 (quite broad peaks)

* Not analyzed

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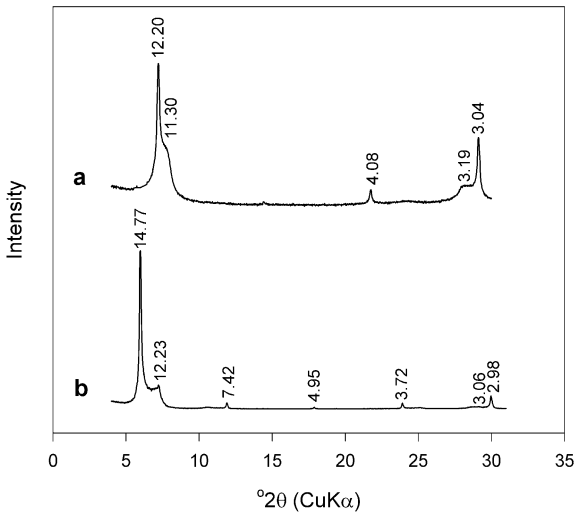


Figure 1. XRD patterns: (a) K-depleted biotite under dry conditions; and (b) K-depleted biotite under wet conditions, with *d* spacing values in Å.

hydrothermal treatment with Li^+ resulted in a slightly hydrated phase because Li^+ has a larger hydration energy than the other alkali cations. This hydrated Li phase did not show any collapse of the interlayer spacing even after heat treatment at 300 or 500ºC. Thus, it appears that some water molecules are trapped in the ditrigonal

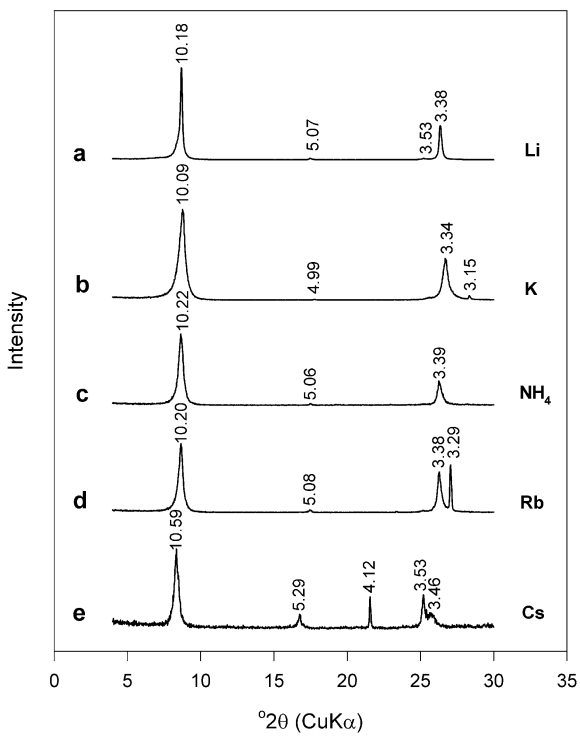


Figure 2. XRD patterns of the K-depleted biotite after hydrothermal treatment with LiCl, KCl, NH_4Cl, RbCl and CsCl (a: Li-biotite; b: K-biotite; c: NH_4-biotite; d: Rb-biotite; and e: Cs-biotite), with *d* spacing values in Å.

cavities of the interlayers along with the smaller Li ions. The XRD analyses after a series of heating treatments confirmed the formation of mica (anhydrous but hydroxylated) phases by using the K-depleted biotite under hydrothermal treatment with K^+, NH_4^+, Rb^+ and Cs^+. The *d* spacings, as determined by XRD of the micas formed by treatment with K^+, NH_4^+, Rb^+ and Cs^+, are dependent on their ionic radii as has been previously demonstrated by Komarneni and Roy (1986) with K-depleted phlogopite. These mica (anhydrous but hydroxylated) phases cannot be obtained by simple transformation of micas under natural conditions because the concentration of ions such as Rb^+ and Cs^+ would be very small. The use of K-depleted biotite with Cs-containing waste solutions could lead to the formation of Cs-mica and thus could be useful in the immobilization of Cs^+ (Komarneni and Roy, 1986, 1988; Stout *et al*., 2006).

The hydrothermal treatments using four alkaline earth cations (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) led to the formation of hydrated phases from the K-depleted biotite. There were differences in the degree of dehydration of these hydrated phases after heating at 300 and 500ºC as can be seen in Table 2. The dry heat treatments of the Ba-saturated biotite caused the interlayers to collapse to form a Ba-mica like phase. Although the treatment with $BaCl_2$ for 1 day led to a hydrated phase (Table 2), prolonged $BaCl_2$ treatment for 3 days resulted in almost complete dehydration which caused the further collapse of the interlayers to form a 10.59 Å mica-like phase (Figure 3d,e).

The d_{001} spacing of K-depleted biotite after hydrothermal treatment with Al^{3+} for 1 day increased from 12.20 Å to broad peaks at 15.23 and 14.24 Å (Figure 3f). This hydrothermal treatment caused K-depleted biotite to transform to HIV which may be an intermediate phase in the kaolinization of biotite (Rebertus *et al*., 1986; Karathanasis, 1988). These hydroxy-Al interlayers were apparently formed by hydrolysis and polymerization of Al^{3+} as well as through dissolution of the K-depleted biotite (Sawhney, 1968; Komarneni and Roy, 1986; Hsu, 1992). The *d* spacing of this hydroxylated phase changed after the heat treatment at 300 and 500ºC (Table 2). This collapse of the interlayer suggests that the product is HIV rather than chlorite since the *d* spacing of chlorite does not change after heat treatment (Barnhisel and Bertsch, 1989; McBride, 1994).

Topotactic formation of hydroxylated phases from K-depleted muscovite

The d_{001} spacing of the original K-depleted muscovite is 11.99 Å as revealed by the XRD pattern (Figure 4a). When the K-depleted muscovite was dried at 60ºC, it collapsed to 9.6 Å forming a Na-muscovite phase (not shown). Changes in the d_{001} spacing of the K-depleted muscovite after the hydrothermal and dry heat treatments with different alkali and alkaline earth

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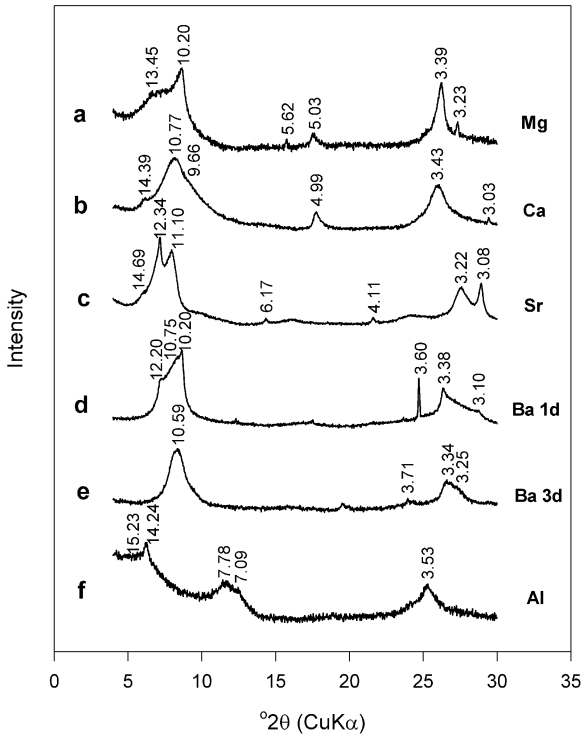


Figure 3. XRD patterns of the K-depleted biotite after hydrothermal treatment with $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ and $AlCl_3$ (a: Mg-biotite; b: Ca-biotite; c: Sr-biotite; d: Ba- biotite; e: Ba-biotite treated for 3 days; and f: Al-biotite), with *d* spacing values in Å.

cations are summarized in Tables 3 and 4, respectively. The treatment using different alkali cations (Li^+, K^+, NH_4^+, Rb^+ and Cs^+) produced an hydroxylated phase of

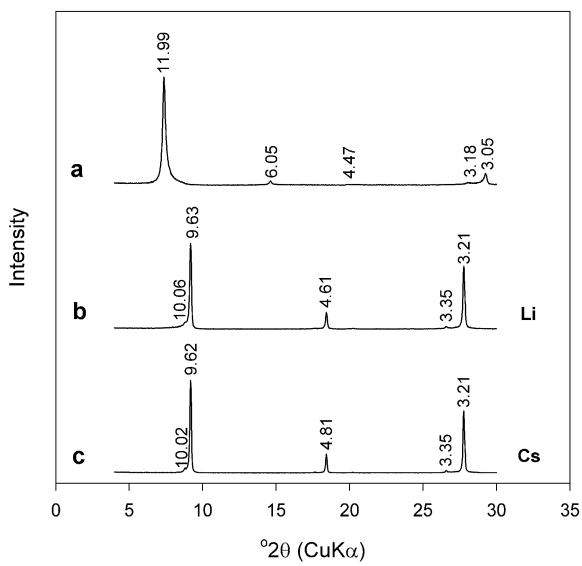


Figure 4. XRD patterns of original K-depleted muscovite and the K-depleted muscovite after hydrothermal treatment with LiCl and CsCl (a: K-depleted muscovite under dry conditions; b: Li-treated muscovite; c: Cs-treated muscovite), with *d* spacing values in Å.

Table 3. d_{001} spacings listed in decreasing order of intensity of K-depleted muscovite after hydrothermal treatment with alkali cations at 200ºC for 1 day.

Alkali cations	d_{001} (Å)
Li^+	9.63, 10.06
K^+	9.60, 9.99
NH_4^+	9.63, 10.06
Rb^+	9.62, 10.02
Cs^+	9.62, 10.02

~9.6 Å in all cases from the K-depleted muscovite. Thus the hydrothermal treatment at 200ºC caused the collapse of the 11.99 Å spacing in the K-depleted muscovite to 9.6 Å in all cases, apparently as a result of dehydration of the K-depleted muscovite to form Na-muscovite with little or no exchange of the different alkali cations in solution (Table 3; Figure 4b,c). This is in contrast with K-depleted biotite, which showed a significant difference between *d* spacings of the various mica-like hydroxylated phases formed by the almost complete exchange of different alkali cations under hydrothermal treatments. K-depleted muscovite has a higher charge density than K-depleted biotite and this is apparently responsible for the dehydration of Na ions and collapse of the interlayers forming a dehydrated Na-muscovite under hydrothermal conditions. There was no significant difference in the *d* spacings of the hydroxylated phases formed from K-depleted muscovite by hydrothermal treatments using Mg^{2+} and Ca^{2+} ions (Table 4; Figure 5). The d_{001} spacing of the Ba-saturated muscovite (Ba-muscovite) is larger than those of the other cations. The d_{001} spacing of the Ba-muscovite formed by the treatment for 1 day collapsed to 11.33 and 10.70 Å. However, prolonged Ba treatment for 3 days resulted in a uniform interlayer with an 11.35 Å phase (Figure 5d,e). The d_{001} spacings of Ba-muscovite with 1 and 3 days reflected different extents of Ba exchange. These results are consistent with those reported by Reichenbach and Rich (1969) who found that the d_{001} spacings of Ba-muscovite differed with the extent of Ba-K exchange. In case of the dry-heat treatments, significant changes in the degree of dehydration could be observed only for the Ba-muscovite after heating at 300 and 500ºC (Table 4).

Hydrothermal treatment with Al^{3+} for 1 day also caused the transformation of the K-depleted muscovite to HIV-type phase. However, the XRD peaks of the K-depleted muscovite treated with Al^{3+} are much sharper than those of K-depleted biotite (Figure 5f). This result suggests that K-depleted muscovite can fix Al hydroxides in the interlayer under this hydrothermal condition without destruction of structure. Some of the K-depleted muscovite collapsed to form dehydrated Na-muscovite as revealed by the 9.6 Å spacing (Figure 5f). However, K-depleted biotite appeared to transform completely to HIV compared to the K-depleted muscovite.

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Table 4. d_{001} spacings (Å) listed in decreasing order of intensity of K-depleted muscovite after hydrothermal treatment and dry-heat treatments with alkaline earth and Al^{3+} cations.

	After hydrothermal treatment at 200ºC for 1 day	After heating at 300ºC for 4 h	After heating at 500ºC for 4 h
Mg^{2+}	9.61, 10.02	9.61, 10.04	9.59
Ca^{2+}	9.60, 10.02	9.61, 9.99	9.61, 9.95
Sr^{2+}	9.67, 10.18	9.65, 10.15	9.61
Ba^{2+}	11.33, 10.70	10.04	10.02
Ba^{2+} (for 3 days)	11.35	NA*	NA*
Al^{3+}**	14.15, 9.61	13.80	12.51

* Not analyzed
** Results of treatment after 3 and 5 days are approximately the same. Ethylene glycol treatment does not lead to expansion of the 14.15 Å phase.

CONCLUSIONS

Topotactic exchange of alkali cations in K-depleted biotite under hydrothermal treatment at 200ºC successfully produced mica-type hydroxylated phases. K-depleted biotite resulted in Cs-biotite. K-depleted muscovite did not lead to the formation of mica-type phases with various alkali cations because the layers collapsed, preventing their exchange under these hydrothermal conditions and led to the formation of Na-muscovite mica instead. Treatment with alkaline earth cations of K-depleted biotite and muscovite led to different hydrated phases under hydrothermal conditions due to the greater hydration energy of the divalent cations. The hydrothermal treatments with Al^{3+} produced HIV from the K-depleted micas.

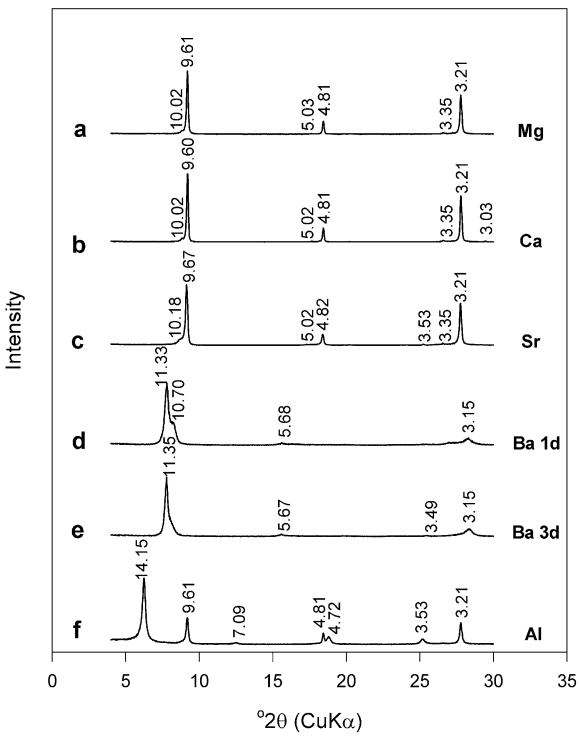


Figure 5. XRD patterns of the K-depleted muscovite after hydrothermal treatment with $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ and $AlCl_3$ (a: Mg-muscovite; b: Ca-muscovite; c: Sr-muscovite; d: Ba-muscovite; e: Ba-muscovite treated for 3 days; and f: Al-muscovite), with *d* spacing values in Å.

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