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THE CRYPTAND [222] FOR EXCHANGING CATIONS OF MICAS

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Abstract—Cation exchange experiments were carried out on phlogopite, biotite, and muscovite using cryptand [222] as a complexing agent, dioxane as solvent, and Li as the exchanging cation. The results indicate greater than 90% exchange of the analyzed cations K^+, Rb^+, and Sr^{++} in phlogopite and biotite after two days. Similar results for the exchange in muscovite are observed but it is apparently slower. The amount of exchange observed for mica depends mainly on pH, time and the exchanging cation at a constant temperature. Residues of the mineral phase were also investigated by X-ray diffraction and a significant change of the interlayer spacing was detected. Some samples of the residue were analyzed for Li content. The compositions of the treated samples were in good agreement with the determined exchange of K^+.

Key Words—Biotite, Cryptand, Exchange, Lithium, Mica, Muscovite, Phlogopite, Potassium, Rubidium, Strontium.

INTRODUCTION

Sr has four naturally occurring isotopes (^{88}Sr, ^{87}Sr, ^{86}Sr and ^{84}Sr), all of which are stable (Faure 1986). The isotopic abundances of Sr isotopes are variable because of the formation of radiogenic ^{87}Sr by the decay of naturally occurring ^{87}Rb. For this reason, the precise isotopic composition of Sr in a rock or mineral that contains Rb depends on the age and the Rb/Sr ratio of that rock or mineral. However, the content of ^{87}Rb and radiogenic ^{87}Sr is often influenced by exchange processes. Sometimes this leads to dates by the Rb-Sr-method, which are meaningless for geological events (Satir 1974; Satir and Friedrichsen 1986). Therefore, we have decided to study the exchange behavior of the trace elements Rb and Sr from the interlayer lattice sites of mica-type minerals and to study the influence of the exchange process on age determinations. This required development of a method which allows us to obtain a fast, selective and quantitative exchange of the interlayer lattice cations Rb and Sr, and isotopes ^{87}Rb and radiogenic ^{87}Sr.

Scott and Smith (1966) developed a method for exchanging K using sodiumtetraphenylborate to determine the exchange characteristics of micas. They found that the K exchange rate depends on the type of mica and the concentration of K in solution. Reichenbach and Rich (1978) used concentrated $BaCl_2$-solutions in an autoclave to exchange K quantitatively. We have found no work concerning the exchange of the trace elements Rb and Sr from micas in the literature, although these two elements have been used as exchange cations for K in micas (Reichenbach and Rich 1978; Reichenbach 1968; Bashour and Carlson 1984).

We present a method for the selective exchange of K, Rb, and Sr cations from natural phlogopite, biotite, and muscovite micas using the cryptand [222] and LiCl. To our best knowledge, this is the first study testing the use of the cryptand [222] to exchange cations from micas. Although the cryptand [222] has been used with muscovite to study the influence of counterion complexation on the Zeta potential (Scales *et al* 1988).

Cryptands are macrobicyclic ligands which are derived from crown ethers. They were first synthesized in 1973 when their surprising complexing abilities were also observed (Dietrich *et al* 1973). In contrast to Ethylenediamine Tetraacetic Acid (EDTA), they are able to complex monovalent cations in water and organic solvents. Each cryptand has a definite cavity size, which is illustrated in Figure 1. Only ions of an appropriate diameter fit into this cavity as shown by the complex stability constants in Table 1 (Weber *et al* 1989; Lehn and Sauvage 1975).

The cryptand [222] solution in water is alkaline because the nitrogen atoms of the molecule are easily protonated. Therefore, the complex stability depends strongly on the pH. The complex stability also increases with lower polarity and lower dielectric value of the solvent. The stability constants in methanol/water mixtures are higher for K^+, Rb^+, and Sr^{++} and low for Li^+ in comparison to water (Table 1). Li was used as an exchange cation because of its relatively low stability constant. Dioxane which has an even lower dielectric constant than methanol, is less volatile than methanol. It is miscible with water which is another advantage for handling, inclining to choose the organic solvent mixture dioxane/water for the final exchange procedure. The pH, solvent mixture, and concentra-

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Table 1. Acidic and stability constants (log K_s) of the alkaline and earth-alkaline cryptates.

Ligand	Solvent	pK_1	pK_2	Li	Na	K	Rb	Ca	Sr	Ba
[222]	w	7.28	9.60	<2.0	3.90	5.40	4.35	4.40	8.00	9.90
[222]	m/w	0.64	9.85	1.80	7.21	9.75	8.40	3.54	11.50	(12.00)
[222]	m	—	—	2.60	≫8	≫7	≫6	—	—	—
EDTA	w	—	—	2.85	1.79	0.96	0.59	11.00	8.80	7.78

w = water, m = methanol, m/w = methanol/water 9:1.

tion of reagents were varied for the different experiments and were tested on different micas to optimize the combination of the reagents (Bracke *et al* 1992).

MATERIALS

The international mica standards "phlogopite mica-Mg", "biotite mica-Fe" (Geostandards 1989), and mica standards for isotope dating "biotite Bern 4 B," "muscovite Bern 4 M" (Jäger *et al* 1963) have been used. The cryptand [222] was delivered by Merck in units of 1 g and was used without further preparation (mp.: 69° C, MG: 376.5 g/mol). Sr was not detectable in the 1 M water solution by AAS determinations with a graphite furnace (LLD<1 ppb). In a 1 M solution of $LiCl*H_2O$ in water 35 ppb Sr were found (blank value). The buffer solutions were prepared with 1 M LiOH with 2 M phosphoric acid in water (pH 2.5), 1 M LiOH with 2 M acetic acid in water (pH 4.5), and 0.3 M LiOH with 0.1 M phosphoric acid in water (pH 6.5). The cryptand [222] has a pH of 9 in a 1 M solution with LiCl.

METHODS

All glass and teflon containers were cleaned with 5 N hydrochloric acid and rinsed with double distilled water. Duplicate experiments on phlogopite, biotite, and muscovite were done in purified teflon centrifuge tubes. The micas were weighed after milling, sieving, and drying (ca. 40 mg, equivalent 0.1 mmol interlayer cations). The mesh size was less than 36 μm. One ml aliquots of the reagent solutions (1 mol/l in water, equivalent to a 10-fold molar excess to interlayer cations) were placed in the tubes, filled with solvent (water, methanol or dioxane to 10 ml) and sealed tightly with a cap and parafilm. The tubes were placed in an ultrasonic bath. The sealed tubes were cycled with 15 minutes of ultrasonic agitation followed by a 15-minute pause which was repeated during the course of the experiment. The temperature in the ultrasonic bath was 45 to 55° C. The tubes were centrifuged for 10 minutes at 6000 rpm to separate the solid residue and then carefully decanted. The solution was analyzed for K, Rb, and Sr. A fresh solution was introduced into the tubes containing the solid residue and exchange continued. The results are shown in Figures 2, 3 and 4. The K determination was examined after dilution with water on a Perkin-Elmer AAS 1100 B by flame atomic absorption. Rb and Sr were determined directly by a graphite furnace HGA 400 by standard addition. The solid residue was investigated on a Siemens x-ray diffractometer D 501 with $Cu_{K\alpha}$-radiation. Li was determined by flame atomic emission after dissolution

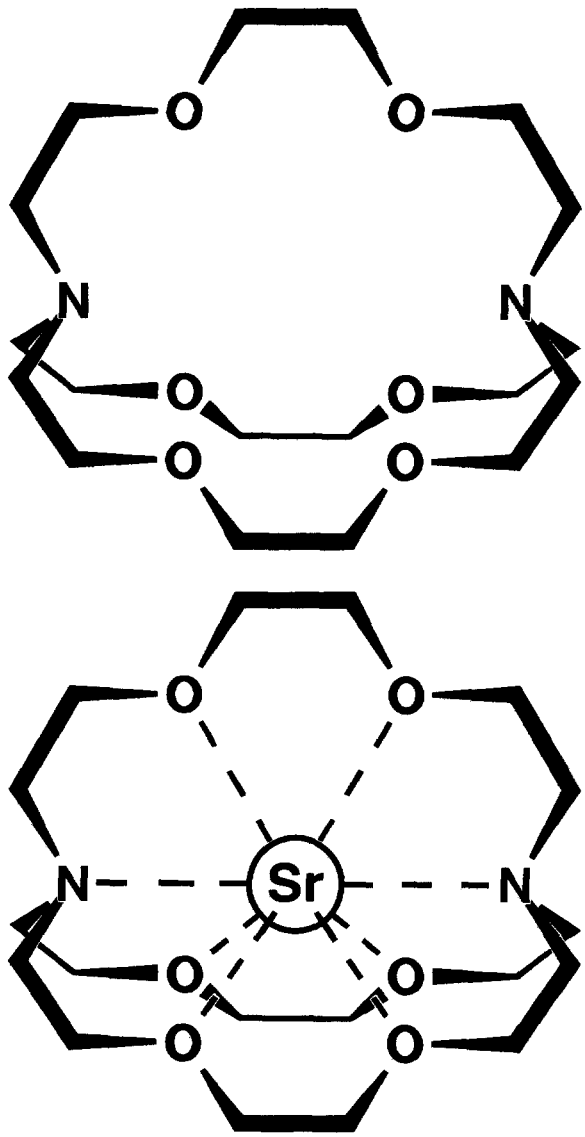


Figure 1. Structure of the cryptand [222] and of the Sr cryptate complex.

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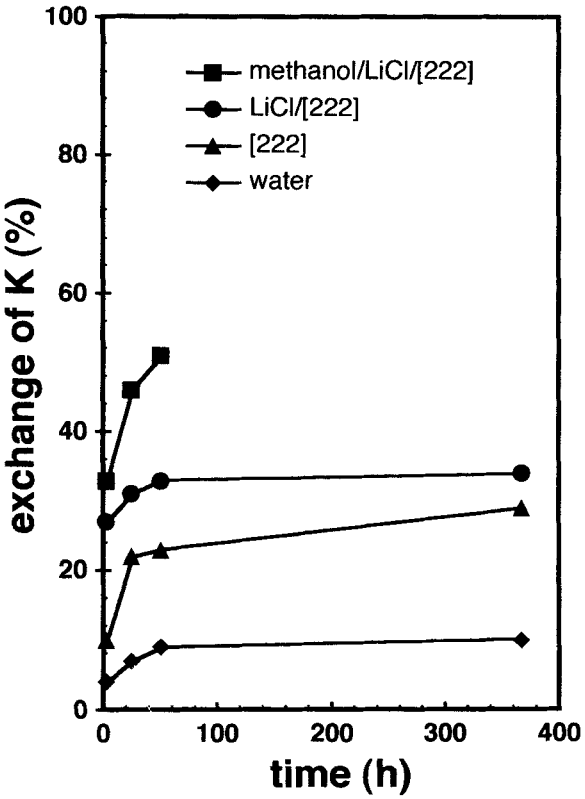


Figure 2. Exchange (%) of K of phlogopite mica-Mg against time (h). The labels give the combination of solvent and reagent solutions.

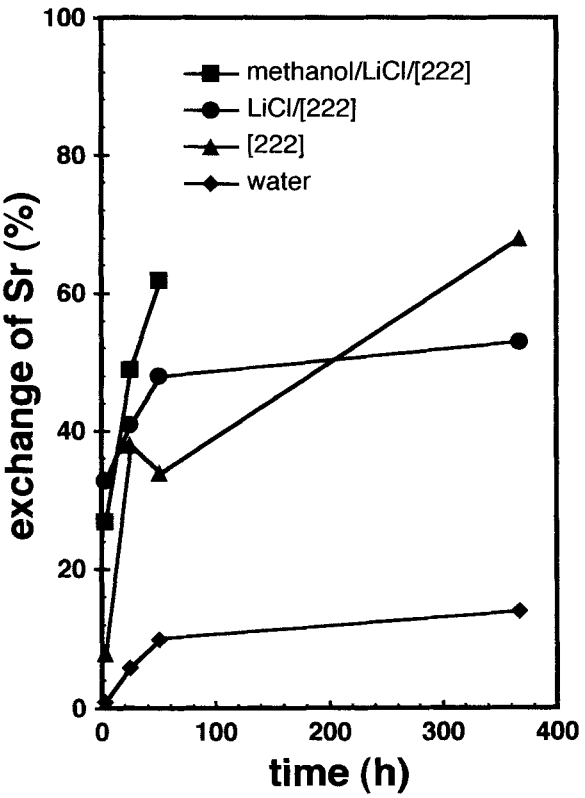


Figure 3. Exchange (%) of Sr of phlogopite mica-Mg against time (h). The labels give the combination of solvent and reagent solutions.

with HF/HNO_3. All results are given in percentage of total content. The relative error of the data is less than $\pm 5\%$.

RESULTS

Rapid exchange of K in phlogopite was demonstrated by Reed and Scott (1966). A quantitative exchange of interlayer K was produced in less than 5 days. Therefore, phlogopite was chosen as a starting material assuming that Rb and Sr show a similar behavior. Another advantage was that the concentrations of Rb and Sr in the standard phlogopite mica-Mg were high enough to produce easily measurable concentrations in the exchange solution.

Figure 2 shows the exchange (percentage of total content) of K on phlogopite vs. time in hours. A low exchange rate was found for water alone. The combination of the cryptand [222] and water gives a higher exchange. An even higher exchange was achieved with the combination of LiCl/[222] in water. The highest exchange in this experiment was obtained with methanol/LiCl/[222]. The last data point for the methanol/LiCl/[222] is not shown due to the evaporation loss of methanol, which changes the exchange behavior drastically. Sr exhibits the same exchange behavior as K. (Figure 3). The best exchange is achieved with methanol/LiCl/[222]. The exchange behavior of K and Sr correlates and equilibrium concentration is reached since the exchange does not increase linearly with time, as indicated in both Figures 2 and 3. A deviation of one data point of the [222]-solution from this common tendency occurred in this experiment.

Table 2. Alkaline-, earth-alkaline contents of the micas.

Mica	K	Rb	Sr	K-interlayer charge
Mica-Mg (phlogopite)	83,015 ppm	1300 ppm	27 ppm	212 mmol/100 g
Mica-Fe (biotite)	72,600 ppm	2200 ppm	5 ppm	186 mmol/100 g
Biotite Bern 4 B	73,833 ppm	594 ppm	2 ppm	189 mmol/100 g
Muscovite Bern 4 M	96,280 ppm	327 ppm	33 ppm	246 mmol/100 g

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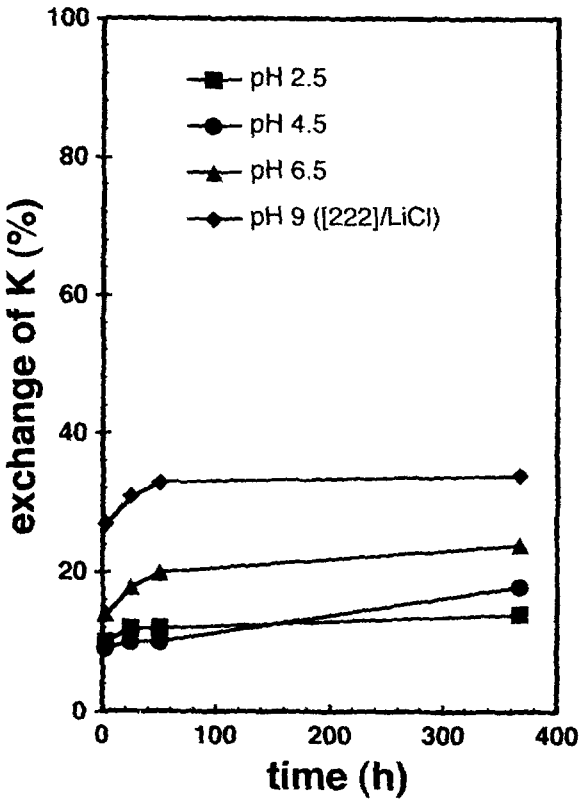


Figure 4. Exchange (%) of K of phlogopite mica-Mg against time (h) for different pH solutions.

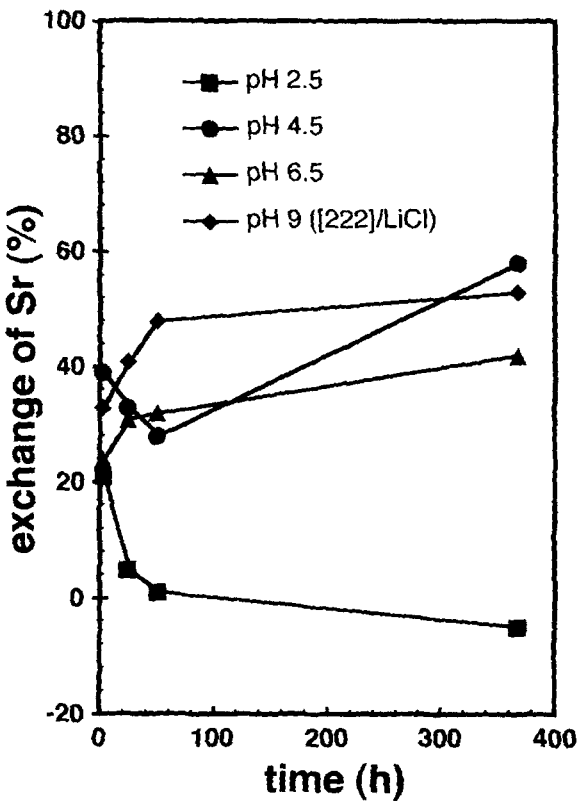


Figure 5. Exchange (%) of Sr of phlogopite mica-Mg against time (h) for different pH solutions.

We wanted to check the influence of pH on the exchange process since the exchange process between cryptand [222] and mica can be expected to be influenced by pH. The cryptand is protonated at low pH and H_3O^+ can replace cations in micas. Figures 4 and 5 show the exchange rate of K and Sr in phlogopite against time for different pH-values. All solutions are buffered and contain the cryptand [222]. Only the solution at pH 9 was not buffered. The exchange of K is increasing at all pH-values with time. The increase slows down with time which indicates an approach to equilibrium concentration. The lowest exchange is found at pH 2.5, whereas the highest exchange is found at pH 9.

An interesting effect of Sr is shown in Figure 5 where 20% by weight of Sr is in solution at pH 2.5 after one hour. This high value probably results from cations at the surface and the edges of the mica, which can be exchanged rapidly by a proton. The values decrease with time at pH 2.5 and even the Sr which is introduced by blank becomes resorbed after 368 h reaction time which accounts for the negative values. The cryptand [222] is positively charged at pH 2.5. Sr as a double charged cation is no longer as easily complexed by the cryptand as the single charged K. K replaces the small amount of Sr during the equilibration process because of its large excess and greater stability constant. Thus, this effect may only be obtained through low concen-

Table 3. Percent exchange of K, Rb and Sr of the micas.

Mica	Exchange solution with dioxane/water (8:2)/LiCl/[222]								
	Phlogopite Mica-Mg			Biotite Bern 4 B			Muscovite Bern 4 M		
Element	K	Rb	Sr	K	Rb	Sr	K	Rb	Sr
0–18 h	85	99	78	96	88	(64)	28	10	47
18–38 h	9	2	14	7	2	(10)	10	1	18
38–198 h	—	—	—	—	—	—	(30)	(30)	(23)
Added sum:	94	101	92	103	90	(74)	68	41	88

Italic: values for magnitude assessment (single determination or close detection limit).

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Table 4. Exchange without renewal of the solution containing cryptand [222].

Mica	Biotite Bern 4 B after 46 h	Muscovite Bern 4 M after 356 h
Exchange K:	104%	74%
Exchange Rb:	96%	69%
Exchange Sr:	LLD	86%

LLD = lower limit of detection error of date: ±5%.

trations of Sr and low pH. A similar but smaller effect is indicated at pH 4.5 though an unexpected high exchange was found after 368 h which we cannot explain.

These results led us to investigate an exchange solution consisting of dioxane/water (8:2), cryptand [222], and LiCl. This exchange solution was decanted at intervals and a fresh solution with the same composition was added. The final exchange results of this stepwise method are shown in Table 3. 85% of K, 99% of Rb and 78% of Sr of phlogopite was exchanged in the first step (0–18 h). Also 96% of K, 88% of Rb and 64% of Sr of biotite was exchanged in the first step. Only small additional amounts of cations are extracted from phlogopite and biotite during the second step (18–38 h). Muscovite exhibits a slower exchange. Only 28% of K, 10% of Rb and 47% of Sr of muscovite was exchanged in the first step. A second and a third step were done on muscovite which was allowed to stand longer (38–198 h). In total about 70% of K, 41% of Rb and 88% of Sr of the muscovite were exchanged this way. The exchange was also complete (better than 90%) for biotite Bern 4 B without renewal of the solution (Table 4). A slightly better exchange than in Table 3 was achieved on muscovite Bern 4 M with a longer reaction time.

The solid residue of the phlogopite mica-Mg and biotite mica-Fe was analyzed for Li content to confirm the extent of exchange. Two samples which have been investigated with the diffractometer were used. They were taken from the glass support on which they were fixed for X-ray analysis. This residue was not washed because a complete separation from water was not possible by centrifugation (Table 5). A slightly higher molar content of Li than the original molar content of K is observed.

The exchange is also evident on the diffractogram. The interlayer distance changes with replacement of K by Li (Figure 6). The original reflection at 0.993 nm loses intensity and a new reflection at 1.178 nm appears, other reflections of higher order are also lost. The relation of peak intensities (heights of reflections at 0.993 nm and 1.178 nm) on diffractograms agree with the determined exchange of K. Table 6 shows that the interlayer distance broadens for all types of mica from original 0.993 nm to 1.148–1.194 nm after exchange.

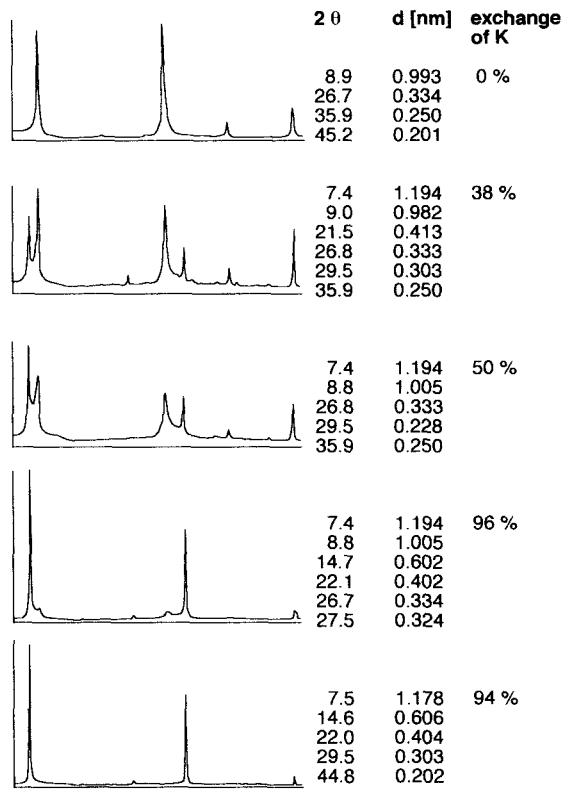


Figure 6. K-exchange and diffractometer spectra of phlogopite.

DISCUSSION

A cation (here Li) is necessary to replace the interlayer cations because of charge balance. Enough Li was found to account for the replacement of the interlayer cations. The agreement of peak intensities and exchange rate confirms that K is replaced by Li. The slightly higher molar content of Li in the treated residue can be explained partly by the replacement of other cations in the interlayer (mainly barium) and partly because the samples were not washed before dissolu-

Table 5. Content of K before exchange and content of Li after exchange.

Sample cation	Initial K	Final Li	Initial K/100 g	Final Li/100 g
Phlogopite mica-Mg	8.30%	1.66%	212 mmol	238 mmol
Biotite mica-Fe	7.38%	1.50%	186 mmol	216 mmol

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Table 6. Diffractometer spectra of the micas (d-values [nm] for the 001 reflections).

Mica	Initial	Final
Phlogopite mica-Mg (001)	0.993	1.178
Biotite mica-Fe (001)	0.993	1.148
Biotite Bern 4 B (001)	0.993	1.194
Muscovite Bern 4 M (002)	0.993	1.148

tion and analysis. The X-ray reflections of the treated micas show an increased interlayer distance of 1.148, 1.178 and 1.194 nm. This is surprising since Li is a smaller cation than K and therefore a smaller interlayer distance is expected. It is not possible to define here whether this interlayer distance is for micas where interlayer Li is accompanied (vermiculite) by water molecules or not. Keppler (1990) observed a similar interlayer distance of 1.21 nm for a synthetic dehydroxylated Li mica which was exposed to humid air. He was able to show that the uptake of water was reversible at high temperatures and loss of water results in a smaller interlayer distance of 0.934 nm.

CONCLUSIONS

We achieved a higher exchange of the cations K^+, Rb^+ and Sr^{++} with the use of the cryptand [222] in comparison to water without additions. This effect is enhanced by the additional use of LiCl salt. The influence of an organic solvent (methanol and dioxane) also enhances the exchange. Complete exchange (>95%) was achieved for K^+, Rb^+, and Sr^{++} on biotite and phlogopite with the final exchange solution after 38 h and 46 h. The percent exchange was still increasing for muscovite in spite of the long reaction time. This means that the exchange rate depends on the type of mica and furthermore that the solution is not degraded. The high Li content in the residue of the mineral phase leads to the conclusion that a Li bearing mica was produced. The molar Li content is slightly higher than the previous K content, which can be caused by not washing the samples and the exchange of other cations. The layer structure of the mica was retained according to X-ray diffractograms. The high interlayer distance indicates a water containing Li mica. These results lead to the conclusion that the final exchange solution was suitable to exchange the interlayer cations K^+, Rb^+, and Sr^{++} without destroying the layer structure of the mica.

The amount of Rb^+ and Sr^{++} remaining is low as the bulk of the total content was exchanged. If the exchange is incomplete the residue should show the same isotope composition as the Sr in the exchange solution. If there are any structural effects on the exchange process of Rb^+ and Sr^{++} the isotope composition of solution and residue will be different. Future isotopic investigation may show this more conclusively.

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