Sorption of cesium on weathered biotite: The effects of cations in solution

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ABSTRACT

Phyllosilicate minerals can control the mobility and distribution of nuclear elements in both natural environments and nuclear waste sites owing to their high reactivity. Radioactive ^{137}Cs is an important component of nuclear waste and can be used as a tracer for soil erosion assessment; therefore, information regarding the reaction of ^{137}Cs with phyllosilicate minerals is necessary to predict its fate in near-surface environments. Here, biotite samples were artificially weathered with low ph solutions containing k, ca, na, mg, rb, and cs. Cations in the solutions had varying effects on both Si release caused by the dissolution of biotite plates and K release influenced by ion exchange, and in addition to resultant Cs sorption on weathered biotite. Na and Mg had the most significant effects on weathering among the cations. Si release, pH increase, and the results of X-ray diffraction (XRD), and scanning electron microscopy (SEM) verified these effects. These two cations influenced the weathering of biotite through the formation of expandable layers. Monovalent cations such as Na, Rb, and Cs were similar to K in radius and charge and had significant effects on interlayer K replacement in the biotite. The results of this study suggest that plate weathering and cation exchange each differently affect Cs sorption on weathered biotite. Weathered biotite that reacted with Na and Mg solutions had the highest amount of Cs sorption owing to the presence of expandable layers. However, the biotite samples that reacted with Cs, Rb, and K had much lower amounts of Cs sorption possibly because these cations fit relatively well on the frayed edge sites in the weathered biotite and therefore blocked additional sorption of Cs.

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1. Introduction

Radiogenic Cs is released into the natural environment via nuclear weapons testing and nuclear accidents. Once released, Cs can be easily fixed to various minerals that control its mobility, fate, and ultimate environmental effect on an ecological system. Among the Cs-fixing minerals, despite being devoid of expandable layers such as those in smectite, mica is unique because it strongly fixes Cs at low concentrations. Illite has higher selectivity for Cs at low concentration levels than other expandable clays mainly due to the frayed edge sites formed by the weathering of mica edges (Bradbury and Baeyens, 2000; Poinssot et al., 1999; Sawhney, 1970, 1972). Francis and Brinkley (1976) reported preferential adsorption of ^{137}Cs on the micaceous component of a ^{137}Cs-contaminated freshwater sediment. Preferential ^{137}Cs sorption on illite has also been reported in marine sediments (Kim et al., 2006). Kim et al. (2007) found that compared with other minerals in coarse marine sediments, biotite selectively contains ^{137}Cs. They concluded that frayed edge sites on biotite play a significant role in fixing ^{137}Cs.

Biotite is one of the most important rock-forming minerals. It is a trioctahedral phyllosilicate mineral that is more vulnerable to weathering than dioctahedral micas such as muscovite (McBride, 1994). As a result, biotite plays a more important role than muscovite in the distribution

of elements (Arnold, 1960; Malmström and Banwart, 1997; Murakami et al., 2003; Sokolova et al., 2010). The formation of frayed edges on weathered biotite is very important for Cs sorption; thus, it controls the migration of Cs on the surface of the earth (McBride, 1994; McKinley et al., 2004; Tsai et al., 2009; Zachara et al., 2002). During biotite weathering, cations and hydrogen ions in solution replace K and form frayed edge sites. Therefore, information about the effects of cations in solution on biotite weathering is essential for understanding Cs sorption on biotite specifically and Cs behavior in soil and geological materials generally. For example, ^{137}Cs sorbed on soil containing phyllosilicates provides an effective method of tracing rates and patterns of erosion and deposition within landscapes (Alewell et al., 2014; An et al., 2014). However, the role of cations in biotite weathering has not been systematically studied thus far. It has been reported that a mechanism for K removal in solution is needed for the interlayer of biotite to constantly release and replace K with other cations (Gilkes and Young, 1974; Rausell-Colom et al., 1965). This cation replacement and resultant weathering will not proceed with only a small amount of K. In addition, the effects of Ca and Na were also studied on the weathering of biotite and phlogopite (Gilkes, 1973; Ross and Rich, 1974; Sánchez-Pastor et al., 2010). However, the effects of different cations on the weathering of biotite and resultant Cs sorption on weathered biotite have not been reported thus far. The formation of additional weathering products including clay and iron mineral phases such as vermiculite, smectite, gibbsite, kaolinite, goethite, and jarosite can also affect the sorption capacity of weathered

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biotite (Bhatti et al., 2011; Hu et al., 2014; Jeong, 2000; Murakami et al., 2003; Pachana et al., 2012). In the present study, we investigate the effects of alkali cations in low-pH solutions on biotite weathering and discuss the sorption capacity of the resultant weathered biotite for Cs.

2. Materials and methods

2.1. Samples

Biotite samples from Minas Gerais, Brazil, used for this study were provided by Minservice. The biotite chemical composition was determined by electronic probe microanalysis (EPMA; Shimadzu, EPMA1610) at the Korea Basic Science Institute. The mineral characterization of the biotite was determined by X-ray diffraction (XRD; Philips, X'pert APD) analysis by using a Phillips X-ray diffractometer with Ni-filtered Cu-Kα radiation at 40 kV and 30 mA at the Daegu Center of the Korea Basic Science Institute. An unoriented sample without pretreatment was used for XRD data collection from 5° to 60° 2θ with steps of 0.02° 2θ and a counting time of 1 s per step.

2.2. Weathering experiment

The biotite was cut into small pieces using scissors and was ground in a blender with deionized water for 5 min. The ground biotite was freeze-dried, and a sample with particle sizes between 55 μm and 100 μm was selected by using sieves. An ultrasonic cleaner was used to separate very fine particles from the sample, and a sieve was used to remove biotite particles <55 μm. The final sample was dried at room temperature. The surface area of the sample measured by nitrogen adsorption (BET) with BESORP-max (BEL Japan, Inc.) was $1.37 \ m^2 \ g^{-1}$.

To enhance the weathering reaction, highly concentrated cation solutions with low pH were used at high temperature. The weathering experiment required 0.2 g of biotite sample to be mixed in plastic HDPE bottles with separate 50 ml 1 M solutions of KCl, $CaCl_2$, NaCl, $MgCl_2$, RbCl, and CsCl. The dissolution of biotite is highly pH-dependent and shows a minimum around-neutral pH (Malmström and Banwart, 1997). Therefore, the pH values of the solutions were adjusted to pH 2 and 4 by using 0.1 M HCl solution to increase the reaction rate. The bottles were stored in an oven at 40 °C. Reaction times of 20, 40, 60, 80, 100, and 120 days were selected, during which times the bottles were frequently shaken.

At the end of each reaction time, the solid sample was separated from the solution by filtering through a 0.45 μm membrane filter. The pH was measured with a pH meter (Orion 420A). The solid samples were washed three times with deionized water and were dried at room temperature. XRD analysis was used to investigate phase changes and the formation of secondary minerals. Random powder mounts without pretreatment were used for XRD data collection. A scanning electron microscope (SEM; Hitachi S-4200) equipped with energy dispersive spectroscopy (EDS) was used to observe morphological changes and to determine the chemical compositions of the mineral phases. The K and Si concentrations in each solution were analyzed by atomic absorption spectrometry (AAS; Varian, 240FS) and by using the molybdemum-blue colorimetric method.

2.3. Sorption experiment of Cs

Prior to the sorption experiment, the weathered biotite was mixed with 50 ml of deionized water for 24 h and was then filtered through a 0.45 μm membrane filter to remove any salts remaining on the biotite. The samples were additionally washed with deionized water three times during filtering. The sorption experiment required a 10^{-5} M CsCl solution and adjustment to pH 7 by 0.1 M HCl and NaOH solutions. A solution of 0.1 M NaCl was used as the background. The sorption experiment involved mixing 0.1 g of each weathered biotite sample with 50 ml of prepared CsCl solution in plastic HDPE bottles. The bottles were shaken at 120 rpm in a water bath for 36 h at 25 °C. After the reaction time was completed, the solutions were separated from the solid by centrifuge. Solutions were acidified below pH 2 by using 1 N HNO_3 to avoid precipitation and adsorption onto the walls of the bottle. The samples were kept in a refrigerator pending further analysis. The amount of sorbed Cs was calculated from the difference in Cs concentration in solution prior to and following the reaction. The concentration of Cs was analyzed by inductively coupled plasma–mass spectrometry (ICP–MS; Perkin Elmer, ELAN 6100) at the Seoul Center of the Korea Basic Science Institute.

3. Results and discussion

3.1. Characterization of biotite

The XRD pattern in Fig. 1 proves our sample to be pure mica with no other mineral phases. The chemical composition analyzed by EPMA is $(K_{0.88}Na_{0.07}Ba_{0.01})(Si_{2.91}Al_{1.09})(Mg_{2.32}Fe_{0.46}Al_{0.12}Ti_{0.05})O_{10}OH_{1.75}F_{0.25}$, which corresponds to trioctahedral mica biotite with a composition close to phlogopite due to its high Mg content.

3.2. Changes in pH after weathering

Regardless of the initial pH values and cations in solution, the pH values after weathering increased with an increasing reaction time. During the weathering process of silicate minerals, the pH level increases through consumption of H ions, which leads to increases in alkalinity. Thus, pH increase can be used as an indicator of the weathering process (Kim, 2003). However, the trend in pH increase varied between the two different pH values at which the experiments were performed. An increase in pH was observed for all solutions at pH 2; however, the pH increases in the K, Cs, and Rb solutions were less than those of the other cations. This result indicates that the weathering rate of the biotite in solutions containing K, Cs, and Rb was lower than that in the solutions of the other cations. However, for the solutions at pH 4, no noticeable difference was observed among the different cations. For all samples, the rate of pH increase declined with an increase in reaction time, indicating that for all samples, the weathering rate was higher at the initial stage.

3.3. Effects of cations on the release of Si and K

Cations in a low-pH solution can affect weathering through biotite plate dissolution and ion exchange. Because Si is released from the plate edges, Si concentration is a good indicator of biotite weathering (Kalinowski and Schweda, 1996; Murakami et al., 2003, 2004). However, the release of K from the interlayer of biotite is related to ion exchange rather than plate dissolution (Sánchez-Pastor et al., 2010). Therefore, the concentrations of both elements are expected to differ under different weathering conditions. Fig. 2 shows that the concentrations of Si and K in solution are clearly affected by the cations in the solution, reaction time, and pH. Based on the concentration of K after 20 days, the weathering rates (log rate, mol m^{-2} s^{-1}) were calculated as −9.43 to −10.23. These values are significantly higher than those measured in a laboratory at 25 °C and pH 3–6 (−11.9 to −10.6) and those measured in field experiments (−15 to −12.9; Murphy et al., 1998; Taylor et al., 2000). Therefore, the geochemical and mineralogical changes observed in our study correspond to approximately 100–1000 years of weathering in the field. The concentration of Si in solutions at pH 2 was, in general, seven times higher than those at pH 4. This result indicates that pH is a very important factor in controlling biotite plate dissolution at lower pH levels (Acker and Bricker, 1992; Malmström and Banwart, 1997; Pachana et al., 2012). At pH 2, the difference in Si concentration for each cation was similar to the change in pH increase for that cation. The solution containing Na showed the highest increase in pH as well as the greatest effect on Si release; the