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OXYGEN ISOTOPE CHANGES DURING MICA ALTERATION

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Abstract—Oxygen isotope analyses (δO^{18}) of micas that were artificially depleted in K^+ indicate little or no isotope exchange during the transformation. The oxidation of iron in K-depleted, iron-rich micas by H_2O_2 treatment resulted in 1.6 to 4.6‰ decrease in δO^{18} due to the fact that the equilibrium fractionation factor is less than the initial difference between the starting δO^{18} of the fluid and micas. The oxygen isotope ratio of a saponite formed by the weathering of phlogopite showed a 9.7‰ increase in δO^{18} due to authigenic recrystallization. These results suggest that oxygen isotope ratios can be used to determine the nature of chemical transformation during the weathering of mica to vermiculite and/or smectite.

Key Words—Mica, Oxygen isotopes, Potassium, Recrystallization, Saponite, Weathering.

INTRODUCTION

Oxygen and hydrogen isotope compositions of ocean sediments (Savin and Epstein, 1970) and Quaternary soils (Lawrence and Taylor, 1971) that consist largely of authigenic minerals are in isotopic equilibrium with the coexisting waters. According to Savin and Epstein (1970) detrital clays, however, show no major oxygen isotope exchange with the coexisting waters, but these authors were unable to make a definitive statement about hydrogen isotope exchange of detrital clays in sea water. Unweathered minerals in soil profiles developed on igneous and sedimentary rocks also undergo no appreciable oxygen or hydrogen isotope exchange with meteoric water in the weathering environment (Lawrence and Taylor, 1972). Thus, O^{18}/O^{16} ratios may be used to distinguish authigenic minerals from detrital components because detrital minerals originating from igneous and metamorphic rocks have lower O^{18}/O^{16} ratios than most minerals formed at low temperatures (Hoefs, 1980). The above statement, however, may not be applicable to assemblages found at high latitudes and high altitudes where meteoric waters are depleted in O^{18} (S. M. Savin, Case-Western Reserve University, Cleveland, Ohio, personal communication, 1984).

Quaternary soils commonly contain appreciable quantities of detrital micas and their transformation products, as well as varying amounts of authigenic minerals. Detrital micas transform to vermiculite and then to minerals of the smectite group (Jackson *et al.*, 1952). These mineralogical changes result in the replacement of K^+ from micas by hydrated cations, with concurrent decrease in layer charge. The decrease in layer charge results from compositional changes such as the oxidation of iron, the ejection of structural cations such as Mg^{2+}, Fe^{3+}, and Al^{3+} (Veith and Jackson, 1974), and the incorporation of Si in the layers (Sridhar and Jackson, 1974). The clays formed from the alteration of micas swell in water (Sridhar *et al.*, 1972) and commonly have aluminous and/or ferruginous coatings (Roth *et al.*, 1969). Although the changes in chemical composition during the above transformations have been studied by many workers, the extent of isotope exchange between the aluminosilicate framework and the associated waters has received little or no study. The objective of the present study is to determine the extent of oxygen isotope exchange in various structural layers during the weathering of micas to expanding layer silicates, both in nature and in the laboratory.

EXPERIMENTAL

Materials

Phlogopite and saponite were separated from the Hills Pond peridotite, Woodson County, Kansas. Here, phlogopite in the parent peridotite has weathered in part to saponite through a vermiculite intermediate (Jackson and Sridhar, 1974). Phlogopite of igneous or metamorphic origin from near Perth, Lanark County, Ontario, was obtained as large sheets from Ward's Nat-

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ural Science Establishment, Rochester, New York. Biotite from Bancroft, Ontario, Canada (<50 μm size, courtesy, A. D. Scott), biotite from an unknown locality (20–250 μm), and an iron-rich mica, lepidomelane (20–250 μm) were also obtained as large sheets from Ward's Natural Science Establishment. Muscovite mica (5–10 μm) from Norway was also used.

Sample preparation

Phlogopite flakes (>500 μm) were isolated from the Kansas peridotite by wet sieving and hand picking and then washed with water to remove the adhering fine particles. The saponite (<0.2 μm) was separated from the peridotite by dispersing the sample in water and centrifuging the dispersion. The clay-size fraction was treated with pH 5 N NaOAc, H_2O_2, and citrate-bicarbonate-dithionate to remove calcite, organic matter, and free iron oxides, respectively (Jackson, 1956), as described below. The purity of this material was tested by X-ray powder diffraction (XRD) and quantitative mineralogical analysis (Jackson and Sridhar, 1974). Samples of phlogopite (Ontario), biotite (Ward's), lepidomelane, and muscovite (Norway) were wet ground in a blender and the respective size fractions obtained by sedimentation and centrifugation (Jackson, 1956). Biotite (Bancroft) was ground dry and screened into different size fractions.

Deferration. Saponite and the iron-rich biotite micas were treated to remove iron oxide and oxyhydroxide coatings (i.e., deferration) using sodium dithionate ($Na_2S_2O_4$) as a reducing agent, sodium bicarbonate as a buffer, and sodium citrate as a chelating or complexing agent for ferrous and ferric iron (Jackson, 1956). After the treatment, the samples were washed free of all salts.

NaOAc and H_2O_2 treatments. To eliminate carbonates and organic matter in the <0.2-μm fraction of saponite, the sample was washed with 1 N NaOAc at pH 5 and digested in 30% H_2O_2. The Kansas phlogopite (>500 μm) and the various mica samples were not treated this way because carbonates and organic matter were not apparent in these samples under the light microscope.

K-depletion of micas. To simulate natural vermiculitization, the various micas were treated with sodium tetraphenylboron (NaTPB) in 1 N NaCl solution (Scott and Smith, 1966). This process lowers the K^+ activity in the suspending liquid by the precipitation of potassium tetraphenyl boron. Muscovite mica was heated to 550°C prior to the NaTPB treatment to enhance the K-depletion process (Scott *et al.*, 1972). Heating muscovite at 550°C should not affect its isotope exchange properties because this temperature is well below its dehydroxylation temperature (Jackson, 1956). The NaTPB treatment results in a Na^+-saturated vermiculite with H_2O in the interlayers. The NaTPB treatment was carried out to determine the extent of isotope exchange with water which entered the interlayers. The artificial K^+-depletion process also resulted in the partial oxidation of iron in iron-rich micas (Sridhar and Jackson, 1974).

Fe^{2+}-oxidation treatment. The iron-rich micas, biotites and lepidomelane, after K^+-depletion, were digested with 30% H_2O_2 at ~90°C for 6 hr to oxidize most of the structural Fe^{2+} present (Jackson, 1956). The exact amount of iron oxidized by the H_2O_2 treatment, however, was not determined.

Oxygen isotope determination. Oxygen from the micas and their weathering products was extracted by reacting 10 to 20 mg of solid with BrF_5 at 550°C in nickel reaction vessels for 12–14 hr (Clayton and Mayeda, 1963). The evolved O_2 was then converted to CO_2 for mass spectrometric analysis by combustion with graphite (Taylor and Epstein, 1962). Analyses of CO_2 for oxygen isotopes were made using an isotope-ratio mass spectrometer. The isotopic data are reported as δO^{18} values in per mil (‰), where δO^{18} is defined as:

$$\delta O^{18} = \left[\frac{O^{18}/O^{16}\ \text{sample}}{O^{18}/O^{16}\ \text{standard}} - 1\right] \times 1000,$$

with Standard Mean Ocean Water (SMOW) (Craig, 1961) as a reference.

RESULTS AND DISCUSSION

The oxygen isotope ratios of various micas and their transformation products are presented in Table 1. Simple exchange of interlayer K^+ by Na^+ in the artificially weathered phlogopite and muscovite caused no significant change in the oxygen isotope composition. In two iron-rich micas (Bancroft biotite and Ward's lepidomelane), the δO^{18} value decreased significantly after K^+-depletion. This decrease in iron-rich micas may have been related to the partial iron oxidation that took place (Table 1) during K^+-depletion as found by Sridhar and Jackson (1974). The effect of iron oxidation on the oxygen isotope (δO^{18}) ratio was investigated further by treating the samples with H_2O_2 (Table 1). Oxidation of structural iron should have increased with the H_2O_2 treatment, but the exact amount was not determined. The H_2O_2 treatment resulted in a large δO^{18} decrease in iron-rich micas. This decrease in δO^{18} accompanying Fe^{2+} oxidation by H_2O_2 treatment may reflect oxygen isotopic exchange between the clay and the interlayer water which was introduced during K^+-depletion; however, there is no clear cut correlation between the Fe^{2+} contents of these micas (as reported by Sridhar and Jackson, 1974) and the decrease in δO^{18} by Fe^{2+} oxidation. The distilled water used in the K-depletion experiments had a δO^{18} value of −8 to −12‰. The oxidation of iron results in the ejection of Fe^{3+} and/or Mg^{2+} cations from octahedral sites in order to

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balance the charge (Veith and Jackson, 1974). Deuteration experiments have suggested that the hydroxyls become exchangeable even at room temperature (unpublished results). The extent of exchange of hydroxyls with interlayer water is not known. A substantial hydroxyl exchange with the low O^{18} water might have led to a lower δO^{18} value after oxidation.

A second explanation for the lower δO^{18} value after K-depletion is related to the hydrolysis of iron ejected from the octahedral sites. The ejected iron could have hydrolyzed with the interlayer water, resulting in low δO^{18} phases in the interlayer positions and hence an overall lower δO^{18} value for the depleted mica. In an equilibrium system, this decrease in δO^{18} for the mica transformation product results only if the equilibrium fractionation factor is less than the initial difference between the starting δO^{18} of the fluid and solid. The fact that the iron-rich micas were originally rich in O^{18} suggests some low-temperature interaction prior to treatment. Because the starting micas were already enriched in O^{18}, some depletion took place during the K^+-replacement. If these micas were originally depleted in O^{18} (as expected for an igneous or metamorphic source), significant enrichment could have resulted. The effect of H_2O_2 treatment on the δO^{18} of K-depleted, iron-poor phlogopite and muscovite needs to be investigated before the effect of iron oxidation on δO^{18} can be confirmed.

The lack of oxygen isotope exchange during the simple mineral transformation involving Na^+ and water exchange with K^+ for the iron-poor micas, phlogopite, and muscovite suggests that the oxygen isotope ratio can be an indicator of partial authigenic recrystallization, i.e., breakdown of framework metal–oxygen bonds leading to the removal and incorporation of cations in transformation products. Authigenic recrystallization by the removal of tetrahedral Fe and Al and the incorporation of Si has been proposed (Sridhar and Jackson, 1974) as the mechanism for the decrease in layer charge in the natural transformation of phlogopite to saponite. If the layer-charge decrease during this natural transformation was indeed caused by the removal and incorporation of structural ions with the breakdown of framework metal–oxygen bonds, this transformation might have led to oxygen isotope exchange. To test this possibility, the oxygen isotope ratios of phlogopite and its natural weathering product, saponite, were determined (Table 1). Phlogopite from Kansas has a δO^{18} value of 6.7‰ which indicates its high-temperature (igneous) origin. On the other hand, the saponite transformation product of this phlogopite has a significantly higher δO^{18} value of 16.4‰. This drastic increase (9.7‰) of δO^{18} in saponite compared to the parent phlogopite indicates extensive oxygen isotope exchange during weathering. Because this phlogopite contains little iron and because no deuteric alteration appears to have taken place, the change in δO^{18} from phlogopite to saponite could be due to oxygen isotope exchange resulting from the breakdown of framework metal–oxygen bonds. Thus, these oxygen isotope data support the Sridhar and Jackson's (1974) hypothesis of authigenic recrystallization by the removal of tetrahedral Fe^{3+} (and Al^{3+}) and incorporation of Si^{4+} during the transformation of phlogopite to saponite. The chemical process of phlogopite transformation to saponite with the accompanying oxygen isotopic change can be summarized as follows:

$$\text{Phlogopite} + Si^{4+} \xleftrightarrow{\text{Oxygen isotope exchange}} \text{Saponite} + Fe^{3+}(Al^{3+}) + K^+$$

The removal of Fe^{3+} or Al^{3+} and the incorporation of Si in the tetrahedral sheets of this mica led to a breakdown in framework metal–oxygen bonds, and this breakdown facilitated oxygen isotopic exchange.

Table 1. Oxygen isotope abundance of micas and their transformation products.

Sample	Isotopic composition δO^{18} (‰) SMOW	Fe^{2+} oxidized, mmole/100 g
Micas and artificially weathered micas		
Phlogopite, Ontario	16.7	NA[1]
Phlogopite, Ontario, K^+-depleted	17.2	NA[1]
Muscovite, Norway	11.3	NA[1]
Muscovite, Norway, K^+-depleted after heating to 550°C	11.4[2]	NA[1]
Biotite, Bancroft, Ontario[3]	11.1[2]	NA[1]
Biotite, Bancroft, Ontario, K^+-depleted	10.2	31
Biotite, Bancroft, Ontario, K^+-depleted and Fe oxidized with H_2O_2	9.5	ND[1]
Biotite, Ward's Natural Science Establishment[3]	12.0	NA[1]
Biotite, Ward's Natural Science Establishment, K^+-depleted	11.8	17
Biotite, Ward's Natural Science Establishment, K^+-depleted and Fe oxidized with H_2O_2	7.7	ND[1]
Lepidomelane, Ward's Natural Science Establishment[3]	11.5	NA[1]
Lepidomelane, Ward's Natural Science Establishment	10.1	56
Lepidomelane, Ward's Natural Science Establishment,[3] K^+-depleted and Fe oxidized with H_2O_2	6.9	ND[1]
Phlogopite and its natural weathering product		
Phlogopite, Woodson County, Kansas	6.7[2]	NA[1]
Saponite formed from phlogopite, Woodson County, Kansas[4]	16.4[2]	NA[1]

[1] NA = not applicable; ND = not determined; the values for Fe^{2+} oxidation were taken from Sridhar and Jackson (1974).
[2] Average of duplicates.
[3] Treated with citrate-bicarbonate-dithionate.
[4] Treated with H_2O_2, pH 5 N NaOAc and citrate-bicarbonate-dithionate.

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CONCLUSIONS

Little or no oxygen isotope exchange occurred in vermiculite by artificial K^+-depletion. The oxidation of iron in Fe-rich micas by H_2O_2 treatment led to a decrease in the δO^{18} value probably due to oxygen isotope exchange with the water introduced into the interlayers and/or by forming low-O^{18} oxide phases by the hydrolysis of ejected iron in the interlayers. This depletion of δO^{18} in mica transformation products was likely due to the fact that the equilibrium fractionation factor was less than the initial difference between the starting δO^{18} of the fluid and mica. Authigenic recrystallization during the mineral transformation of phlogopite to saponite was supported by an increase in the δO^{18} ratio.

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Резюме—Изотопный анализ кислорода (δO^{18}) в образцах слюды, содержание K^+ в которых было искуственно уменьшено, указывают на незначительный или нулевой изотопный обмен во время превращения. Результатом окисления железа в K-обедненных, обогащенных железом слюдах, при помощи обработки перекисью было уменьшение δO^{18} на 1,6 до 4,6‰. Это было вызвано тем, что величина равновесного коэффициента разделения была меньше, чем разница начальных значений δO^{18} для течи и слюд. Отношение изотопов кислорода для сапонита, образованного путем выветривания флогопита показало 9,7‰ увеличение значения δO^{18}, вызванное аутогенной рекристаллизацией. Эти результаты указывают на то, что отношения изотопов кислорода могут быть использованы для опредедения природы химического превращения во время выветривания слюды и формирования вермикулита и/или смектита. [E.G.]

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Resümee—Sauerstoffisotopen-Analysen (δO^{18}) von Glimmern, denen K^+ künstlich entzogen wurde, zeigen geringen oder gar keinen Isotopenaustausch während der Umwandlung. Die Oxidation von Eisen in K^+-verarmten, Eisen-reichen Glimmern durch H_2O_2-Behandlung führte zu einer Abnahme von 1,6 bis 4,6‰ bei δO^{18}, aufgrund der Tatsache, daß der Gleichgewichtsfraktionierungsfaktor kleiner ist als der ursprüngliche Unterschied zwischen dem Ausgangswert δO^{18} der Flüssigkeit und dem der Glimmer. Das Sauerstoffisotopenverhältnis eines Saponits, der durch Verwitterung von Phlogopit gebildet wurde, zeigte eine Zunahme von 9,7‰ des δO^{18}-Wertes aufgrund autigener Rekristallisation. Diese Ergebnisse deuten darauf hin, daß die Sauerstoffisotopenverhältnisse dazu verwendet werden können, die Art der chemischen Umwandlung während der Verwitterung von Glimmer zu Vermiculit und/oder Smektit zu bestimmen. [U.W.]

Résumé—Des analyses d'isotope oxygène (δO^{18}) de micas dont on a artificiellement retiré K^+ ont indiqué peu ou pas d'échange d'isotopes pendant la transformation. L'oxidation du fer dans des micas riches en fer, privés de K par traitement H_2O a resulté en une diminution d'1,6 à 4,6‰ de δO^{18} à cause du fait que le facteur de fractionation d'équilibre est plus petit que la différence initiale entre le δO^{18} de départ du fluide et des micas. La proportion d'isotope oxygène d'une saponite formée par l'altération d'une phlogopite a montré une augmentation de 9,7‰ de δO^{18} à cause de la recristallisation authigénique. Ces résultats suggèrent que les proportions d'isotope oxygène peuvent être utilisées pour déterminer la nature de la transformation chimique pendant l'altération du mica en vermiculite et/ou en smectite. [D.J.]

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