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Experimental alteration of a subvolcanic rock with 1 M NaOH solution

Alteración experimental de una roca subvolcánica con una solución 1 M NaOH

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INTRODUCTION

Smectites are widely distributed over the earth's crust as the weathering products of volcanic glasses or rock-forming minerals. They have been synthesised at low temperature using various starting materials. On the other hand, berthierine is commonly considered to be typical of marine sediments, undoubtedly as a result of its frequent occurrence in marine oolitic ironstone formations. But, there are still few experimental works dealing with its formation. Because most syntheses of clays were carried out using synthetic starting materials under hydrothermal conditions, the aim of the present study is the formation of clay minerals from a subvolcanic rock during its interaction with 1 M NaOH solution at room temperature.

Material and experimental methods

The subvolcanic rock used in the present study is characterised by the presence of olivine, calcic plagioclase and pinkish Ti-rich augite associated in ophitic texture. Ti-rich amphibole, biotite, are accessory minerals together with apatite and Fe-Ti ores. The absence of clays in the starting rock was confirmed by a previous TEM/AEM study using copper grids. The subvolcanic rock was gently ground in an agate mortar. The specific surface area obtained was 3.16 m2/g. Three g were then placed in a glass flask with 500 ml of 1 M NaOH solution. The experiments were performed at room temperature for 1, 3, 14 and 40 days. After each reaction period, solids and solutions were separated. The residual material was then cleaned by distilled-deionized water to remove adhering salts. The solid fraction of each reaction was then studied by X-ray diffraction (XRD) and analytical transmission electron microscopy (TEM/AEM). Smectite from the subvolcanic derived soil was used for further comparison.

Results and discussion

The structural formulas of the smectite precipitated in the third day of the experiment, calculated from AEM analyses show that both Si and Al contents range widely. Silica varies between 3.23 and 3.98 pfu while Al ranges from 2.16 to 1.44 pfu. The ranges in which Mg and Fe vary are wide as well, suggesting that different kinds of smectites are present. The Fe content is, in general, higher than that of Mg. These analyses showed a very heterogeneous interlayer composition with regard to the interlayer cations. At 14 days of reaction, TEM lattice fringe images show the presence of smectite layers and berthierine-smectite mixed-layer (B-S). The structural formulas of B-S, calculated from AEM analyses performed on B-S packets of TEM images revealed a composition which is compatible with that previously reported in the literature for berthierine. In addition, TEM images also revealed the presence of amorphous materials tightly intergrown with smectite particles: one of them corresponds to an Fe-Si-Ca amorphous substance and forms ovoidal to ellipsoidal structures and two others tightly associated with smectites the composition of which is quite similar to that of the adjacent smectite. At 40 days into the experiment we found similar characteristics to the 14-day reaction were found. Randomly interlayered 0.7 and 10 nm packets were observed. However, their chemical composition showed that the 0.7-nm phase is a Mg-rich-greenalite-smectite mixed-layers (Mg-G-S) instead of the 14-day berthierine.

The use of HRTEM/AEM was indispensable to characterise the different phases generated during the alteration process, their chemical compositions, and their textural relationships. In the first steps of the alteration process, experimental interaction with 1 M NaOH solution led to the formation of dioctahedral beidellite to Fe-rich montmorillonite after 1 and 3 days of reaction. This range of smectite composition is similar to that from natural subvolcanic-derived soil formed from the same parent material. After 14 days of reaction, a berthierine-smectite (B-S) mixed-layer clay had partially replaced the smectite. Although, the presence of smectite interlayers prevented analysis of pure berthierine, berthierine-rich B-S mixed-layers have a composition similar to pure berthierine. After 40 days, the alteration process led to a 7Å-S mixed-layer the composition of which falls between greenalite and lizardite. In fact, the increase in Si in the tetrahedral sheet produced a decrease in Al (in both the tetrahedral and octahedral sheets) and a concomitant increase in Mg in the octahedral sheet, that is, the Tchermack substitution favored by the progressive increase with time of the Si/Al ratio into the solution. Because of the precipitation of Si-Ca-Fe amorphous material as a sink of Fe, such substitution involved Mg rather than Fe.

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