

Fixation of radium by weathered granite from the view point of dependence of ionic size on adsorption reaction

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Introduction

Clay minerals can adsorb many ions and are abundant at earth surfaces, which controls dissolved concentrations of various trace ions in natural soil/sediment-water systems. Thus, clay minerals affect various phenomena observed at earth surfaces. In my previous study, it was revealed that ions adsorbed on clay minerals mainly form two types of surface complex, either outer-sphere (OS) or inner-sphere (IS) complex. Furthermore, it was shown that ions smaller than Ba form OS complexes, while ions larger form IS complexes, which suggested that Ba has specific interaction with clay mineral surface. In general, ions forming IS and OS complexes have low and high ion exchangeability, respectively. Therefore, behavior of ion can be predicted by the ionic size. In this study, radium (Ra), which has been rarely studied, because Ra is one of the radioactive elements, causing the difficulty to study in particular in natural system. In this study, we focused on the migration of Ra in an abandoned mine (Ningyo Toge, Japan), where the interaction of Ra with clay minerals can be examined.

Methods

In this study, soil core samples in Ningyo-Toge in Japan was collected by boring. Ningyo-Toge was a uranium (U) deposit and also has high concentration of Ra because ^{234}U disintegrates into ^{226}Ra through ^{230}Th . Furthermore, weathered granite with clay minerals was present below the sediments with uranium enrichment part at underground of Ningyo-Toge. To reveal mineral and major element compositions, X-ray diffraction (XRD) and X-ray fluorescence (XRF) were conducted, respectively. The results of XRF were used to calculate chemical alteration index (CIA). To determine the concentration of U, Ra, and other elements, Ge semiconductor detector and ICP-MS were used. To identify local structures, X-ray absorption fine structure (XAFS) was conducted for iron (Fe), manganese (Mn), and U.

Results & Discussion

The samples were separated to three types; weathered sand stone exposed to chemical processing (upper layer), original weathered sand stone with U enrichment (medium layer), and granite (lower layer). U in the upper layer was already extracted by chemical processing. The medium layer is same with the layer used as the uranium deposit. The lower layer has weathered or fresh granite depending on the depth.

According to the XAFS results, U in most of the samples is UO_2^{2+} , which is mobile. On the other hand, chemical species of Fe and Mn showed different characteristics at each sample. The chemical species of Fe and Mn in some samples were identified as carbonate, while that in others were biotite. These results are helpful to understand the mechanism of migration of U and Ra.

As for the samples at the medium layer, the $^{226}\text{Ra}/^{238}\text{U}$ activity ratio was less than 1. This result suggested that a larger amount of Ra migrated to deeper layer more readily compared with U. As for the samples at the lower layer, some samples at upper area (weathered granite) with higher CIA, which suggests that the samples were more weathered had the peaks identified as clay minerals. Furthermore, the $^{226}\text{Ra}/^{238}\text{U}$ activity ratio was much higher than 1 (about 2.4), which suggests that Ra is selectively fixed in clay minerals in weathered granite. These results were consistent with the prediction based on the relationship of ionic size and adsorption structure, the latter of which is closely related to the affinity of each ion to clay minerals.

Keywords: radium, ionic size, adsorption, surface complex