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Synthesis of ferrian and ferro-saponites: Implications for the structure of (Fe,Mg)-smectites formed under reduced conditions

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Abstract

Clay minerals are widely distributed on the surface of Earth, Mars, and Ceres in the solar systems. Among numerous clay minerals, smectites can record the history of the environment through the exchange of interlayer cations with those in water or through redox reactions with the atmosphere. Therefore, characterization of chemical compositions and crystal structures of smectites is crucial for revealing the paleoenvironment. For instance, the crystal structure within octahedral sheets of iron-bearing smectites changes to trioctahedral sheets under reduced or dioctahedral sheets under oxidizing conditions. Orbital infrared and X-ray diffraction (XRD) analyses by Mars orbiters/rovers revealed the presence of (Fe,Mg)-smectites on the surface of Mars; however, it has been difficult to characterize the properties of these (Fe,Mg)-smectites, which are rare on the surface of Earth. In this study, we synthesized ferrian (ferric ion-rich) and ferrous (ferrous ion-rich) (Fe,Mg)-saponite and revealed the effect of valence states and iron contents on the crystal structures. These saponites were synthesized using a hydrothermal method under reduced conditions. The crystal structures and valence states of iron were analyzed by XRD, Fourier-transform infrared spectroscopy, transmission electron microscopy, Mössbauer spectroscopy, and X-ray absorption near edge measurements. The synthesized clays were trioctahedral swelling clays and were identified as saponites. The valence state of iron in these synthesized saponites is altered by oxygen and a reducing agent in water; however, the trioctahedral structures are maintained under both oxidizing and reduced conditions, following a reversible reaction. This mechanism can be interpreted by the desorption and adsorption of hydrogen in the hydroxyls of the octahedral sheets of the smectite layers. The maximum basal spacing of the (02*l*) lattice plane in the octahedral sheets was defined by compiling various smectite data. When the basal spacing of (02*l*) is larger than the maximum in dioctahedral smectites, smectite can be identified as trioctahedral smectite. The redox state of iron in the octahedral sheet cannot be determined from the basal spacing of (02*l*). We revealed that the iron content in the trioctahedral sheet has a linear relationship with lattice parameter *b*. This provides a method to estimate the iron content in saponite from XRD data. The XRD profiles of smectites found at the Yellowknife Bay on Mars can be explained only by trioctahedral smectites, and the iron content in the octahedral sheet is roughly estimated to be 0.5–1.7 in a half-unit cell. These results indicate that the presence of (Fe,Mg)-saponite implies a reduced environment during the formation and that this iron-bearing saponite has both oxidation and reduction capabilities depending on the environment.

Keywords: Reduction, oxidization, smectites, XRD, XANES, clay mineralogy, Mars