

論文の内容の要旨

論文題目 Study of Fe-rich chlorite and 7Å-14Å interstratified minerals
using high-resolution electron microscopy

(高分解能電子顕微鏡法による鉄に富む緑泥石と
7 Å-14 Å 混合層鉱物の研究)

氏名 井上 紗綾子

Chlorite is one of the most common phyllosilicates in sedimentary, low-to medium-grade metamorphic and hydrothermally altered rocks. Changes in the polytypic structure, interstratification, and variations in the chemical composition are believed to be functions of temperature, and possibly many other intensive variables such as total pressure, partial pressure of oxygen and sulfur, and activities of metal cations in solution. Elucidation of the relationships between chlorite and the formation condition may lead to the better understanding of geologic environments where chlorites occur. Correlations between crystal structure of chlorite and its formation conditions, however, have not been fully understood. Particularly, the structure of Fe-rich chlorite remains ambiguous because of some difficulties with X-ray diffraction (XRD).

The present study focuses on characterizing the stacking structures of so-called Fe-rich chlorites filled in quartz veins of epithermal to xenothermal vein-type ore deposits using high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) along with XRD and chemical analysis. Samples studied here

have a wide range of Fe/(Fe+Mg) ratios from 0.38-0.98 and tetrahedral Al substitutions for Si from 0.94-1.44 atoms per formula unit (apfu). The formation temperatures estimated by chlorite geothermometry ranged between 190°C-320°C. Low magnification HRTEM images showed that most of the samples made an interstratification between 7-Å, 14-Å, and sporadically smectite layers. The proportion of 7-Å layers increased progressively with Fe content. The proportion of 7-Å layer reached >80% in Fe-rich samples with Fe/(Fe+Mg) > 0.9. Layer stacking structures in the high Fe-rich samples were complex with disorder of 7- and 14-Å layers, differences in the polarity of the tetrahedral sheets, variations of the slant of the octahedral sheets, and positional disorder between octahedral and tetrahedral sheets involving the hydrogen bonding as indicated from HRTEM observations along one of the Y_i directions of the phyllosilicates. From chemical point of view, the 7-Å layer is close to Fe-rich berthierine. Berthierine commonly occurs in sedimentary rocks and is believed to be a low temperature precursor of Fe-rich chlorite. Despite our previous knowledge about berthierine, the present Fe-rich 7-Å component layer was directly precipitated from solution at temperatures >200°C.

To better understand the relationships between chemical composition and structural irregularities, the octahedral cation distributions in 7Å-14Å interstratified minerals with Fe/(Fe+Mg)>0.9 were investigated in combination with HAADF-STEM observations and image simulations. In 14-Å layers, octahedral Al concentrated in M4 site of the interlayer sheet based on HAADF-STEM observations from one of the X_i directions. Two types of 7-Å layers with different octahedral cation distributions, named disordered- and ordered- types in this study, were observed. Octahedral cations were randomly distributed in the disordered-type 7-Å layer, while in ordered-type 7-Å layer octahedral Al is preferentially concentrated in the A position octahedral sites defined in Bailey (1969). Vertical arrangements of 14-Å layers and disordered- and ordered- type 7-Å layers were random in the interstratified structure. Types of octahedral cation distributions varied laterally at the

contact of opposite polar tetrahedral sheets.

To clarify the differences between commonly observed sedimentary 7-Å-14-Å interstratified minerals as transformation product and studied hydrothermal samples, the stacking structures of Fe-rich pore-lining chlorites in siliciclastic reservoir sandstones were investigated by HRTEM. Samples have a Fe/(Fe+Mg) ratios between 0.75-0.80, and the formation temperatures ranged between 105°C-220°C. Previous studies suggested that, berthierine was formed as a precursor at shallower depth, and then transforms to chlorite by way of berthierine-chlorite interstratified mineral with increasing burial depth. The interstratification of 7-Å and 14-Å layers was identified in powder XRD patterns and HRTEM. The proportion of 7-Å layer increased with decreasing temperature. The polytypic structure of samples is, in general, expressed as a mixture of *Ib* and *Ia* polytypic groups. The structural irregularities observed in the hydrothermal chlorites such as differences in the polarity of the tetrahedral sheets, and variations of the slant of the octahedral sheets were not observed in these samples. It is, therefore, concluded that the degree of structural irregularity in pore-lining chlorites is lower than hydrothermal chlorites although the pore-lining samples were formed at lower temperatures. The differences in pore-lining and hydrothermal samples are brought about the differences in the genesis of minerals. That is hydrothermal 7-Å-14-Å interstratified minerals were directly precipitated from solution under disequilibrium condition; on the other hand, pore-linings were an intermediate stage of transformation from berthierine to chlorite. Although HAADF-STEM observation of the interstratified mineral as transformation product has not been performed, the regular alternation of disordered- and ordered-type 7-Å and the lateral contact of ordered-type 7-Å layer and interlayer sheet may be expected in this type of 7-Å -14-Å interstratified minerals from other occurrences.

The results suggested that Fe-rich chlorite contains more or less structural irregularities including the interlayering of 7-Å layers and a mixture of different polytypic groups. Although such features

can only be identified using high resolution electron microscopy, they may be a key to understand the formation mechanism of chlorite structure.