SEM, FTIR, and NMR studies of dumortierite from an Al-rich clay deposit, Korea

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Occurrence of dumortierite

Dumortierite occurs as veinlets or thin layers in the Milyang clay deposit, southeastern part of Korea, which was formed by hydrothermal alteration of the late Cretaceous andesitic tuff. Chemical analysis shows that dumortierite in this area has higher contents of Al, which is closely related to associated Al-rich minerals such as dickite, pyrophyllite, diaspore, and tourmaline. Most dumortierites consist of radiating fibers or aggregates. Cell-dimensions of dumortierite are determined as a = 11.71 ° , b = 20.39 ° , c = 4.70 ° , and volume = 1129.48 ° 3.

Results and discussion

Dumortierite was commonly altered to pyrophyllite along the radiating needles. Microcrystalline pyrophyllite with pseudohexagonal outline grew on the dumortierite crystallites, showing successive replacements. FTIR spectra of dumortierite demonstrated a strong stretching band at 1386 cm^{-1}, showing that boron exists as nearly symmetric trigonal boron(BO_3). The ^{11}B NMR spectrum contains one broad peak and it has typical quadrupole pattern (^{11}B spin number I=3/2) with very small asymmetry parameter (_ ˜ 0), indicating that trigonal boron in dumortierite is axially symmetric or nearly so. ^{29}Si MAS NMR spectrum shows well resolved two peaks at -90.9 and -95.5 ppm, representing two crystallographically different sites. ^{27}Al NMR spectrum shows only one octahedral Al peak.

Conclusions

FTIR and NMR spectroscopic studies on dumortierite reveal that boron in dumortierite exists entirely as trigonal boron(BO_3). The common occurrence of dumortierite indicates an important role of boron in Al-rich clay mineralization in acidic volcanic rocks.

References

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Morphological and structural changes during transformation of Green Rust – Fe(II)(III)-hydroxide

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Uptake of a contaminant by a sediment or soil mineral can immobilise it or allow it to remain available for release again if solution conditions change. Transformation of the mineral to a new, often more stable phase can alter this behaviour. A better understanding of transformation processes will lead to improved ability to model the fate of environmental contamination.

Green Rust (GR) is the general name given to a family of Fe(II)-Fe(III) compounds. They are most commonly found in environments where conditions are near the Fe(II)/Fe(III) redox boundary, such as in marine sediments and in soil. Recent developed waste management technologies that use zero-valent iron in reactive barriers are also certain to contain Green Rust (GR). The mineral is built of Brucite-like Fe(II)-Fe(III) hydroxide layers with anions such as SO_4^{2-}, Cl^- or CO_3^{2-} and water filling the interlayers. Green Rust is believed to be an important intermediate in the oxidative transformation of Fe(II) phases.

By using X-ray diffraction (XRD) and atomic force microscopy (AFM), we have followed the transition of a sulfate form of Green Rust (GR(SO_4^{2-})) into a Fe(III)-oxyhydroxide, such as Goethite, α-FeOOH, Feroxyhyte, δ'-FeOOH or Lepidocrocite, _-FeOOH, as well as Magnetite, $Fe(II)Fe(III)_2O_4$. Oxygen partial pressure, pH, solution composition, and time all play a role in defining the morphology and structure that result during transformation.

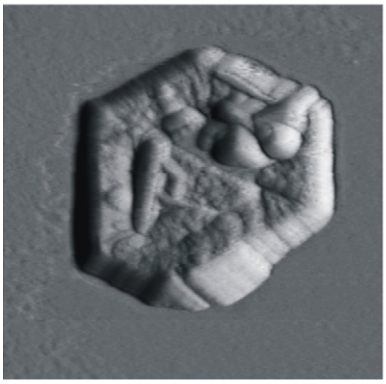

Figure 1: AFM deflection image of GR(SO_4^{2-}) with transformation products on top. Size of image is about 500 nm.