

Transformation of halloysite and kaolinite into beidellite under hydrothermal condition

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ABSTRACT

Understanding clay mineral transformation is of fundamental importance to unraveling geological and environmental processes and to better understanding the unique structure and property of phyllosilicates. To date, two pathways have been identified, i.e., the transformation among 2:1 type clay minerals (e.g., illitization of smectite) and from 2:1 type to 1:1 type (e.g., kaolinization of smectite). However, the transformation of 1:1 to 2:1 type is less commonly observed. In this study, hydrothermal experiments were conducted to investigate the possibility of the transformation of 1:1 type clay minerals (i.e., halloysite and kaolinite) into 2:1 ones (i.e., beidellite). The obtained products were characterized by XRD, TG, FTIR, ²⁷Al and ²⁹Si MAS NMR, and HRTEM. XRD patterns of the hydrothermal products display characteristic basal spacing of smectite group minerals at 1.2–1.3 nm with dramatic decrease/disappearance of the (001) reflection of halloysite and kaolinite. This is consistent with HRTEM observations, in which clay layers with a thickness of 1.2–1.4 nm are observed in all hydrothermal products and the Si/Al ratio determined by EDS analysis is close to that of beidellite. The basal spacing increases to ~1.70 nm upon ethylene glycolation, displaying swelling ability of the resultant minerals. The consumption of surface OH in precursor minerals during the transformation leads to a dramatic decrease of mass loss of dehydroxylation and merging of the well resolved OH stretching vibrations in precursor minerals into one at ca. 3667 cm⁻¹, which is indicative of beidellite. These results demonstrate that both halloysite and kaolinite can be converted to 2:1 beidellite under hydrothermal condition, and the transformation of halloysite is easier than that of kaolinite. Such transformation of 1:1 clay minerals to 2:1 ones could be a new pathway for the transformation of clay minerals in nature. Meanwhile, the substitution of Al³⁺ for Si⁴⁺ is found in all newly formed beidellite, suggesting the chemical composition of the newly formed Si-O tetrahedral sheet is different from the one inherited from the precursor clay minerals. This can well explain the formation of “polar layer” in mixed-layer phyllosilicates. These findings are of high importance for better understanding the transformation among clay minerals and unique structure of mixed-layer phyllosilicates.

Keywords: Clay transformation, hydrothermal condition, halloysite, kaolinite, beidellite