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Research paper

Reprint of Genesis of halloysite from the weathering of muscovite: Insights from microscopic observations of a weathered granite in the Gaoling Area, Jingdezhen, China

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ABSTRACT

Halloysite is a 1:1 clay mineral typically derived from the hydrothermal alteration of alumino-silicate minerals such as biotite and feldspar. In this paper, microscopic observations are used to describe the formation of halloysite on weathered muscovite plates from a granite outcrop near Gaoling village, Jingdezhen, eastern China, where kaolinite was first discovered approximately 1000 years ago. X-ray diffraction (XRD) and Fourier transform infrared spectra (FTIR) analyses are used to identify halloysite, while field emission scanning electron microscopic (FESEM) observations reveal two types of halloysite that have different shapes and spatial distributions around muscovite. Most of the halloysite is present as long filaments with a uniform occurrence and is found on both the exposed (001) surfaces and edges of muscovite. In contrast, a small amount of the halloysite-like mineral occurs as stumpy, sheet stacking, which has an irregular appearance and occurs mainly at the margins of the muscovite plates. It is proposed that the halloysite was derived from the surface leaching of muscovite by two possible mechanisms: dissolution–precipitation or local dissolution–rearrangement of residue structure. Interestingly, similar phenomena were also found in historic tailings at Gaoling village, which most likely suggests a short-term process of formation for the nano-sized halloysite.

1. Introduction

Kaolin is an unusual rock type dominated by kaolin group minerals (Schroeder and Erickson, 2014), making it an important deposit type for these non-metallic mineral resources. Over the past 1000 years, kaolin has played a prominent role in the paper making industry in addition to having significant cultural, industrial, and engineering applications (Zhou and Keeling, 2013; Schroeder and Erickson, 2014), which have ranged from its use in the ceramics industry (Detellier and Schoonheydt, 2014) and pottery that gives clues to civilizations, to nano-composites, drug delivery (Tan et al., 2014), and diverse technological uses (Williams and Hillier, 2014).

Kaolin group minerals include kaolinite, halloysite, dickite, and nacrite; all of these minerals have similar crystallochemical characteristics (Bergaya and Lagaly, 2013). The unit layers in halloysite are separated by a monolayer of water molecules, which distinguishes it from kaolinite, dickite, and nacrite (Churchman and Carr, 1972; Joussein et al., 2005). Nonetheless, the interlayer water is so weakly held that halloysite-(10 Å) can readily and irreversibly dehydrate to halloysite-(7 Å) (Joussein et al., 2005). Halloysite can adopt a variety of morphologies, the most common of which is an elongate tubule that typically has a length of 0.1–30 μm and width of 0.05–0.20 μm (Giese, 1988). In addition, short tubular, spheroidal and platy particle shapes have also been widely reported (Dixon and McKee, 1974; Tazaki, 1982; Noro, 1986; Singer et al., 2004; Joussein et al., 2005).

Kaolin group minerals commonly form from the weathering and/or hydrothermal alteration of aluminosilicates (Weaver, 1989). The different types of the kaolin group minerals are strongly influenced by the primary mineralogy of the parent rocks, particularly in relatively young weathering profiles (Jeong, 2000). It has been shown that the kaolin group minerals form from the weathering (Singh and Gilkes, 1991; Dong et al., 1998) and hydrothermal alteration of micas (Craw et al., 1982; Nicolini et al., 2009). While the alteration of biotite has been well studied (Ahn and Peacor, 1987; Banfield and Eggleton, 1988; Fordham, 1990; Kretzschmar et al., 1997; Dong et al., 1998; Papoulis et al., 2009), the alteration of muscovite has received little attention. Muscovite is mainly altered by topotaxial or epitaxial alteration (Banfield and Eggleton, 1990; Robertson and Eggleton, 1991; Singh and Gilkes, 1991) due to the relatively small structural and chemical modifications required for its transformation, which is quite different from the weathering mechanisms of biotite (i.e., partial dissolution and recrystallization) (Kretzschmar et al., 1997). Stoch and Sikora (1976) suggested the existence of a temporal transition from two muscovite layers to three kaolinite layers in weathered crust,

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based on the results of X-ray diffraction (XRD), electron microprobe (EMP) analysis, and optical microscopy. During this transition, montmorillonite and regular mixed-layer mica–montmorillonite may occur as unstable intermediate phases. Banfield and Eggleton (1990) described a process involving the epitactic growth of kaolinite onto an intermediate illite and smectite phase. Robertson and Eggleton (1991) concluded that the weathering of granitic muscovite to kaolinite was topotatic, with each 10-Å muscovite layer being transformed to a 7-Å kaolinite layer. They also noted that kaolinite was partly altered to halloysite and that a series of sharp kinks was present in the kaolinite plate in which alteration had occurred. Singh and Gilkes (1991) found that kaolinite crystals developed from muscovite invariably preserved the crystallographic orientation of their parent mica. Jiang and Peacor (1991) suggested that the muscovite–kaolinite transitions during hydrothermal alteration proceeded via smectite as an intermediate phase. These previous studies were mainly based on lattice-fringe images obtained from transmission electron microscopic (TEM) analysis and contain limited micromorphological observations; however, morphologies are the direct result of the crystallization method (Banfield and Eggleton, 1990; Jiang and Peacor, 1991). More persuasive and direct morphological evidence, derived from TEM and scanning electron microscope (SEM) analyses, is required to verify the proposed genetic models. The present study, therefore, focuses on micro-textural and micro-analytical investigations of the weathering of muscovite in order to determine the alteration mechanism of muscovite to halloysite.

The samples analyzed in this study were collected from a weathered granite near Gaoling village (historically known as "Kauling village"), Jingdezhen city, located in the northeastern part of Jiangxi Province, eastern China, and where kaolin was first described and named after the mountain 'Kauling' (Dana and Ford, 1949; Grim, 1953; Chen et al., 1997). Gaoling village has been an important source of kaolin for China and has been producing kaolin since the Tang Dynasty (approximately 800 AD) (Chen et al., 1997). The main type of kaolin in the Gaoling deposit is locally called 'bright sands' due to its high contents of quartz and glittering muscovite, which are the final weathering products of a muscovite granitoid (Xia et al., 1979; Li et al., 1982). The kaolin is composed mainly of moderately to poorly ordered kaolinite and halloysite-(7 Å) (Chen et al., 1997). The deposit has been abandoned for the past 100 years. It has been completely mined out and all that remains to be seen is dumps of sand tailings from historic kaolin mining.

Muscovite from both the weathered granite and sand tailings is investigated by SEM, TEM, EMP, XRD, and Fourier transform infrared spectroscopy (FTIR), in order to clarify the conversion mechanism of muscovite to halloysite. Moreover, it is anticipated that the findings of this study may encourage the processing of the sand tailings due to the considerable amount of muscovite that remains.

2. Sample preparation and analytical methods

2.1. Sample location and preparation

The Gaoling kaolin deposit, located ~50 km northeast of Jingdezhen (Fig. 1), is situated in the middle of the Fuliang granite (Xia et al., 1979; Li et al., 1982). There are many small kaolin ore-bodies located around the Gaoling village, which are closely related to outcrops of Jurassic granite plutons, such as the Nankang, Dazhou, and Fuliang granitic masses (Xia et al., 1979; Chen et al., 1997). In this study, the weathered muscovite granite was sampled ~1.0 km northeast of Gaoling village. The local ceramics workshops generally isolate kaolinite clays from this granite, which is a weathered, coarse-grained, gray-colored granite that is easily dispersible (Fig. 2). The historic tailings were also sampled for mineralogical analyses. Numerous muscovite plates were hand-picked from both the weathered granite and tailing samples for SEM and EMP analyses. The centrifuge method (Sudo, 1981) was used to isolate the fine-grained fractions for XRD and FTIR analysis.

Fig. 1. Location map of the Gaoling Area, Jingdezhen, China, showing the sampling site (triangle).

2.2. Instrumental analysis

XRD patterns of the weathered granite and kaolin tailings were acquired to identify their respective mineral components. The samples were ground into powders (~200 mesh) using an agate mortar to prepare un-oriented powdered specimens. Furthermore, gravity sedimentation according to Swith Stokes' law was used to obtain the clay fractions for analysis. The XRD patterns of both the bulk rock and clay fraction powders were recorded using an ARL XTRA-X-ray diffractometer with CuKα radiation at 40 kV ($K\alpha 1 = 1.5406$ Å; scan step of 0.02°/0.3 s; $2\theta = 3°–65°$). The FTIR analysis was performed using the KBr tableting method with a NICOLET-NEXUS870 Fourier transform infrared spectrometer. A total of 1–2 mg of sample powder (<2.0 μm) was mixed with 100–200 mg of KBr powder and then pressed into disk-shaped wafers. The XRD and FTIR analyses were carried out at the Modern Analytical Center, Nanjing University, Nanjing, China.

A field emission scanning electron microscope (FESEM, Zeiss Supra55) equipped with an energy dispersive spectroscope (EDS, Oxford Instruments, Inca X-Max 150 mm^2) was used to observe the micromorphology of weathered muscovite particles and their chemical compositions. The samples were attached to the sample stage using a 1:1 type carbon glue, then air dried and coated with C/Pt/Cr. Photo freezing was performed with an accelerating voltage of 5 or 10 kV, while the component testing was performed using an accelerating voltage of 15 kV in order to obtain sufficient count points. The suspension of mica plates was observed by dropping them on amorphous

Fig. 2. Photograph of a hand sample of the weathered granite examined in this study.