Structure of prismatic halloysite

TOSHIHIRO KOGURE,1,* KIYOFUMI MORI,2 VICTOR A. DRTS,3 AND YOSHIKO TAKAI2

1Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan
2Department of Material and Life Science, Graduate School of Engineering, Osaka University, 2-1 Yamada-Oka, Suita, Osaka, 565-0871, Japan
3Geological Institute of the Russian Academy of Sciences, Pyzhevsky per 7, Moscow 119017, Russia

ABSTRACT

The crystal structure of halloysite, despite being one of the most commonly occurring clay minerals on the Earth’s surface, remains elusive. This paper reports on a multi-methodological study to shed more light on the atomic arrangement of halloysite from Olkhon Island, Lake Baikal, Russia, which has a prismatic morphology. It has been investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), selected-area electron diffraction (SAED) and, in particular, high-resolution transmission electron microscopy (HRTEM), to reveal its atomic structure and formation process. XRD analysis indicated a basal spacing of ca. 7.2 Å and two characteristic peaks with d = 4.28 and 4.03 Å on the tail of the 02,11 band. The halloysite grain cross sections displayed various prismatic forms, ranging from a rectangle to a regular 18-sectored polygon in SEM and TEM. The SAED pattern from a sector of the polygonal prisms with the incident beam parallel to the prism axes showed a regular one-layer oblique reciprocal lattice, similar to that of kaolinite along Yi-directions. HRTEM imaging performed with the new computer-assisted minimal-dose system and an incident beam perpendicular to the prism axis showed stacking of most dioctahedral 1:1 layers with their pseudo-mirror plane perpendicular to the prism axis and an almost random, or rather, alternating lateral stagger to the right or left from the preceding layer, which corresponds to interlayer displacements of t+ and t− in Zvyagin symbols, or layer displacements of t1 and t2 used to describe the stacking in kaolinite. This stacking feature explains the SAED pattern from the side of the prismatic grains and the two characteristic peaks on the tail of the 02,11 band in the XRD pattern. Based on these results, it is proposed that tubular halloysite initially forms as a hydrated one with the pseudo-mirror plane of the kaolinite layers perpendicular to the tube axis, then dehydrates with, possibly, partially hydrogen-bonded interlayers, and finally transforms to a prismatic one consisting of sectored flat layers with the complete hydrogen-bonded interlayers. During this transformation, stacking with comparable ratio and frequent alternation of t+ and t− is formed, to minimize morphological change of the tubes.

Keywords: Halloysite, stacking sequence, prismatic form, hydrogen bonding, HRETM, SAED

INTRODUCTION

Halloysite, Al2Si2O5(OH)4·nH2O, is one of the most common and ubiquitous clay minerals on the terrestrial surface. However, it is also true that the real structure of halloysite has yet to be fully understood despite the amount of research devoted to this mineral. Actually, no three-dimensional periodicity has been reported for halloysite because of very limited information from conventional diffractometry, which leads to the possibility that halloysite contains intense structural disorder. Moreover, from the standpoint of electron microscopy, halloysite is too beamsensitive to apply recent high-resolution structure imaging techniques to analyze its atomic structure.

Halloysite is one of the kaolinite group minerals consisting of dioctahedral 1:1 layers, which are termed “kaolinite layers” in this study, and hydrated/dehydrated interlayers. In cases involving halloysite with a tubular morphology, the kaolinite layers are rolled to compensate for the misfit between the tetrahedral and octahedral sheets (Bates et al. 1950). Bailey (1990) suggested ditrigonal rotation in the tetrahedral sheet, which reduces the misfit in the other kaolin group minerals may not be realized in halloysite due to water molecules and exchangeable cations possibly existing at the interlayer region. On the contrary, Singh (1996) proposed that the rolling mechanism of the kaolinite layers is preferable to ditrigonal rotation, if Si-Si repulsion in the tetrahedral sheet is considered. With respect to the stacking structure of halloysite, much research has suggested a two-layer periodicity for the dehydrated form, halloysite (7 Å), based on selected-area electron diffraction (SAED) taken with the incident beam perpendicular to the tube-axis (Honjo and Mihara 1954; Honjo et al. 1954; Chukhrov and Zvyagin 1966; Kohyama et al. 1978; Singh and Gilkes 1992). Among them, probably only...