Imaging of dioctahedral 2:1 layers by high-resolution transmission electron microscopy (HRTEM): Possibility of recording the dehydroxylate

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ABSTRACT
High-resolution transmission electron microscopy (HRTEM) images of dioctahedral 2:1 phyllosilicates (muscovite, paragonite, pyrophyllite, etc.) acquired by intense electron radiation may not record the natural state but rather the dehydroxylate phase, e.g., NaAl$_2$Si$_4$AlO$_{10}$(OH)$_8$. Intense electron radiation on paragonite changes its electron diffraction pattern by a small increase in cell edges and a considerable decrease of the $\beta$ angle, which are consistent with dehydroxylation. Comparison between experimental and simulated HRTEM images also indicates that the experimental image contrast is in better agreement with that for the dehydroxylate structure than the natural state. Thus, special care is necessary when analyzing the structures of dioctahedral 2:1 phyllosilicates from their HRTEM images, e.g., positions of octahedral cations that were proposed to change by migration during the dehydroxylation process.

Keywords: Electron microscopy, dioctahedral 2:1 phyllosilicates, paragonite, electron diffraction, phase transition

INTRODUCTION
Some dioctahedral 2:1 phyllosilicates, e.g., illite and dioctahedral smectite, are fine-grained phases and the distribution of cations among the octahedral sites in these minerals is a controversial issue (e.g., Ylagan et al. 2002; Drits 2003; Zviagina et al. 2004; Sainz-Díaz et al. 2005; Drits et al. 2006). There are two kinds of octahedral sites (cis- and trans- sites) in a 2:1 layer, depending on the location of coordinating hydroxyls. In the ideal dioctahedral sheet, one third of the total octahedral sites are vacant. If these vacancies are at the trans-site (or one cis-site), the structure is called “trans-vacant” (or “cis-vacant”) (Drits 2003). Single-crystal X-ray structure analyses of dioctahedral 2:1 phyllosilicates with sufficient crystal size for analyses (e.g., muscovite, paragonite, margarite, pyrophyllite) showed that they are trans-vacant (e.g., Jackson and West 1931; Lin and Bailey 1984; Takéuchi 1966; Lee and Guggenheim 1981). However, some montmorillonite and illite samples were interpreted as cis-vacant structures (e.g., Tsipursky and Drits 1984; Drits et al. 1993, 1995), although their grains are too minute such that occupancies at the octahedral sites cannot be determined directly.

High-resolution transmission electron microscopy (HRTEM) of mica, if the specimen is observed with the incident electron beam parallel to the layers, can analyze the layer stacking and the occupancy at the interlayer sites semi-quantitatively (Kogure and Murakami 1996; Kogure et al. 1997; Banfield and Murakami 1998). Dioctahedral and trioctahedral 2:1 layers can be distinguished by the image contrast at the octahedral sheet (Kogure 2002). This technique may give insights to the trans- and cis-site occupancies in dioctahedral micas. Several illite specimens that were expected to contain cis-vacant 2:1 layers were investigated but image contrast indicated that the cis-vacant 2:1 layer is not present (details will be reported elsewhere). An interesting phenomenon occurred in the HRTEM investigation of paragonite, a Na-bearing dioctahedral mica. The recorded HRTEM contrast showed features that are inconsistent with the reported crystal structure of paragonite. The results and conclusions obtained here are essential for the proper interpretation of octahedral cation occupancies in the dioctahedral 2:1 phyllosilicates using HRTEM techniques.

SAMPLES AND METHODS
The paragonite specimen used is a colorless, large flake from Kabo, Oyama-chi, Hyogo-Prefecture, Japan (Geological Survey of Japan, GSI-M 16481). The recorded composition and cell dimensions (Sekino et al. 1975) are (Na$_{1.006}$K$_{0.035}$Ca$_{0.031}$)(Al$_{1.841}$Fe$^{3+}_{0.159}$)Si$_{2.870}$Al$_{1.130}$O$_{10}$(OH)$_2$ and $a = 5.140$ (4), $b = 8.909$ (7), $c = 19.357$ (8) Å, $\beta = 94.58$ (1)°. The muscovite specimen used is a colorless, large plate from pegmatite in Yamanoo, Ibarki-Prefecture, Japan. The composition and cell dimensions were not determined and typical values (e.g., Brigatti et al. 1998) were assumed.

Specimens for TEM examination were prepared by using the method in Kogure (2002). A cleaved plate was embedded with epoxy resin between two glass slides. After hardening, the glass slides were cut using a diamond wheel to laths of ~1 mm thickness. The laths were thinned to ~50 μm by mechanical grinding and then argon ion milled. HRTEM examination was performed at 200 kV using a JEOL JEM-2010. HRTEM images were recorded on films with magnification of ×400,000 or ×500,000. Selected images were digitized using a CCD camera for image processing. Noise from amorphous materials in HRTEM images was removed using Wiener-filter (Marks 1996; Kilaas 1998) developed by K. Ishizuka (HREM Research Inc.) and implemented with Gatan DigitalMicrograph version 3.10.0. A Gatan ES-500W CCD camera equipped at a port of the column just above the phosphor screen of the TEM was used to acquire diffraction patterns. For the accurate measurement of angles in HRTEM images or diffraction patterns, the images or patterns must be free from distortion. The distortion for the TEM images or patterns was estimated using HRTEM images and diffractions from silicon oriented...