LETTER

Novel 2:1 structure of phyllosilicates formed by annealing Fe$^{3+}$, Mg-rich dioctahedral mica

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ABSTRACT

A new modification of the 2:1 phyllosilicate layer has been discovered in annealed celadonite, a Fe$^{3+}$, Mg-rich dioctahedral mica. Plan-view diffraction patterns in TEM indicate a base-centered supercell with $A = 3a$ and $B = b$, where $a$ and $b$ are the cell dimensions of the original mica. Basic $h0l$ reflections with $h = 3n$ form an orthogonal lattice with one-layer periodicity, which is not expected for normal micas. The high-resolution TEM image along the <100> or related directions is similar to that expected from normal micas but the image along the <010> directions is completely different. From these images, it is concluded that the two tetrahedral sheets in a 2:1 layer are facing each other with no lateral $a/3$ staggering. In the proposed model that explains the high-resolution TEM images, two thirds of the spaces surrounded by two facing tetrahedral six-member rings accommodate three (Fe$^{3+}$,Mg) cations and one third of the spaces are completely vacant. The (Fe$^{3+}$,Mg) cations are coordinated by six or five oxygen atoms forming trigonal prisms or square pyramids, respectively.

Keywords: Crystal structure, electron microscopy, electron diffraction, mica, phase transition, phyllosilicates

INTRODUCTION

The 2:1 or TOT (Tetrahedral-Octahedral-Tetrahedral) layer is one of the basic structural units for phyllosilicates or clay minerals, which occur universally and are abundant on the global surface. Pauling (1930) was the first to determine the structure of the 2:1 layer by X-ray structure analysis and to report its di- and trioctahedral variation by pointing out the counterpart minerals, such as pyrophylite and talc, muscovite and muscovite, etc. About half a century later another variation in the dioctahedral 2:1 layer was reported (Tsipursky and Drits 1984). There are two kinds of octahedral sites ($cis$ and $trans$ sites) in the octahedral sheet, depending on the location of coordinating hydroxyls. The structure is called “$trans$-vacant” or “$cis$-vacant” depending on whether the octahedral vacancy is in the $trans$ site or in one of two symmetrically independent $cis$ sites (e.g., Drits 2003). Most dioctahedral 2:1 phyllosilicates are $trans$-vacant, but some illite and montmorillonite specimens were reported to have $cis$-vacant 2:1 layers. However, except for these variations in the octahedral site occupancy, the structure of the 2:1 layer is basically identical for all 2:1 phyllosilicates.

Dioctahedral 2:1 layers are topotactically dehydroxylated at elevated temperatures. Such dehydroxylation, as well as the dehydroxylated structure, was reported for pyrophyllite (Wardle and Brindley 1972), muscovite (Udagawa et al. 1974) and paragonite (Comodi and Zanazzi 2000). For instance, the dehydroxylation of muscovite is formulated as KAl2Si3AlO10(OH)2 → KAl2Si4AlO10(OH)2 + H2O. As a result, aluminum becomes fivefold-coordinated with four apical oxygen atoms of the tetrahedral sheets and one residual oxygen atom that has the same $z$ coordinate as aluminum (Wardle and Brindley 1972). These minerals are $trans$-vacant both in the natural state and in the dehydroxylated form. Drits et al. (1995) suggested that in the case of $cis$-vacant illite, dehydroxylation destabilizes aluminum in the $trans$ site, which results in the migration of the aluminum to the vacant $cis$ site. As a result the dehydroxylated 2:1 layer in $cis$-vacant illite is identical to that in dehydroxylated muscovite or $trans$-vacant illite.

On the other hand, celadonite and glauconite, dioctahedral micas with Fe$^{3+}$ as the dominant octahedral cation, behave in a different way. They have $trans$-vacant structures in the natural state, and in the course of dehydroxylation by annealing, the octahedral cations migrate from the $cis$ sites to the vacant $trans$ sites (Tsipursky et al. 1985). Muller et al. (2000a) studied the structure of dehydroxylated celadonite and glauconite by fitting the experimental and calculated powder X-ray diffraction patterns. Furthermore, they reported the formation of supercells in dehydroxylated celadonite in the electron diffraction patterns along the layer normal (plan-view) in TEM (Muller et al. 2000b). They suggested that these supercells result from the long-range ordering in the octahedral cation distribution.

During a further investigation of these dehydroxylated celadonite samples using TEM, we have found that the supercell with triple length along the $a$-axis consists of 2:1 layers completely different from the normal ones. This paper describes the experimental results and proposes a structure model for this novel 2:1 layer.

SAMPLES AND METHODS

The sample investigated was a celadonite specimen named Z1 that has been investigated in several previous works (Drits et al. 1997; Muller et al. 2000a, 2000b). X-ray diffraction indicated that the specimen is completely monomin-