Semi-ordered crystalline structure of the Santa Olalla vermiculite inferred from X-ray powder diffraction

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ABSTRACT

A sample of Mg-vermiculite from Santa Olalla (Spain) was studied by X-ray powder diffraction, electron microprobe, and thermo-gravimetry. The 3D structure is described as a disordered stack of two types of 2D building blocks, which are made up of one talc-type layer and one interlayer space containing hydrated Mg$^{2+}$ cations. We have succeeded in the refinement of both the atomic positions and occupancies of exchangeable cations and water molecules in the interlayer space of this vermiculite using the program package DIFFaX+. The position of the Mg$^{2+}$ cations is the only difference between the two layers. Besides the water molecules associated to the octahedrally coordinated Mg$^{2+}$, we also located water molecules in the interlayer space. The structural analysis confirms that vermiculite is a semi-ordered crystalline material characterized by the existence of a large density of defects due to random ~±b/3 translations along the crystalline [010] direction. In this way, this structure can no longer be described by means of a unit cell repeated in 3D space. Instead, long-range order is only recognized in the a-b plane. The 3D structure is described by means of a recursive method.

Keywords: Mg-vermiculite, stacking faults, X-ray diffraction, DIFFaX+

INTRODUCTION

Vermiculite is an interesting mineral both from the basic and applied point of view (Strand and Stewart 1983; Hindman 1992; Bergaya et al. 2006). The possibility of atomic intercalation makes it suitable for the sorption of heavy metals (Lee et al. 2002) and organic contaminants (Redding et al. 2002; Huang et al. 2005), whereas the low gas permeability (Takahashi et al. 2006) and the interesting mechanical properties (Tjong et al. 2002) renders vermiculite useful for the production of clay-based nanocomposites (Matějka et al. 2006).

Vermiculite is a 2:1 phyllosilicate, similar in appearance to mica. The thickness of the structural unit (assemblage of 2:1 layer and interlayer space) is about 14 Å, depending on the water interlamellar layers and the interlayer cations. Isomorphic substitutions in tetrahedral and/or octahedral positions are common. The structure of natural vermiculite was first studied via X-ray powder diffraction (XRD) by Gruner (1934) who proposed a monoclinic Cc or C2/c cell. Hendricks and Jefferson (1938) confirmed Gruner’s conclusions from single-crystal diffraction, but also suggested the presence of a partial random displacement of layers parallel to the y-axis. Subsequently, other authors (Mathieson and Walker 1954; Mathieson 1958) demonstrated that in Kenyan vermiculite water molecules and exchangeable cations occupy well-defined sites within the interlayer space. Shirozu and Bailey (1966) were able to add more details to the picture by working on a specimen from Llano as ordered structure (2-layer ordered structure, c = 28.89 Å): the shift between successive 2:1 layers is always of −a/3 along the x-axis and alternates between +b/3 and −b/3 along the y-axis. De la Calle et al. (1975a) concluded that the observed intensities and diffuseness of k ≠ 3n reflections in the Llano vermiculite indicate that many stacking faults are present, disrupting the regular alternation of +b/3 and −b/3 interlayer shifts. Thus de la Calle et al. (1988) proposed a random model alternating ±b/3 shifts for a sample from Santa Olalla (Spain).

It is now well known that vermiculites have various possible layer-stacking sequences (de la Calle et al. 1975a, 1975b, 1978, 1985) depending on the nature of the interlayer cation and of relative humidity. Some systematization of the disorder sequences in vermiculites was presented by Weiss and Durovic (1980) using the order-disorder (OD) theory developed by Dornberger-Schiff (1956), based on the algebra of groupoids.

The reference state of Mg-vermiculites under natural conditions in the soil shows an average d_{001} ~ 14.3 Å (see e.g., Walker 1956; Zhou et al. 1993) and has both Mg$^{2+}$ and two layers of water in the interlayer (2-water layer hydration state or 2-WLHS, notation after Suzuki et al. 1987).

By ordered phase, we mean one in which the position of any atom in the crystal follows both point group and space group symmetry. In layered materials (e.g., clays), disorder can however be present. This disorder can range from faulting in the sequence of one type of layer (random rotations and/or translations from one layer to the next, e.g., turbostratic disorder) to the presence of different kinds of layers randomly alternating in the stack (interstratified phases, see e.g., Marcos et al. 2003).