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TEM investigation of the domain structure and superstructure in hillebrandite, $Ca_2SiO_3(OH)_2$

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ABSTRACT

Selected-area electron diffraction, dark-field images, and high-resolution transmission electron microscope images show that there are pervasive domains in hillebrandite from Mexico. The domains are in thin layers that are almost parallel to (010). They range from one to several unit cells thick across the *b* direction, with an average thickness of about 10 nm. The actual repetition period (7.28 Å) along the *a* crystallographic direction is that of the wollastonite-like chain in the hillebrandite structure. Neighboring superstructure domains are related by stacking faults, with stacking vector of $\pm\frac{1}{2}a_{sup}$. Nonperiodic arrangements of the superstructure domains give an average structure of hillebrandite with a 3.64 Å repetition period along the *a* axis and one-half occupancies of Si atoms in the tetrahedral sites in the two Si-O chains.

INTRODUCTION

Hillebrandite is a natural analog of the calcium silicate hydrate (CSH) phase that forms a major part of Portland cement (Bye 1983; Taylor 1990). Despite decades of investigation of hillebrandite and its synthetic CSH analog, the crystal structure remained poorly understood because of the rarity of ideal single crystals for X-ray diffraction. Recently, however Dai and Post (1995) found a suitable crystal and determined an average structure with $Cmc2_1$ symmetry and unit-cell parameters $a = 3.6389$, $b = 16.311$, and $c = 11.829$ Å. Its structure contains one-half occupancies of Si atoms in the two wollastonite-type tetrahedral chains. The wollastonite-type chain is an average structure of two symmetrically equivalent chains related by a mirror perpendicular to the *a* axis. Preliminary selected-area electron diffraction (SAED) patterns revealed streaking parallel to b^* at $\frac{1}{2}a^*_{sub}$ *in h0l* reflections, which suggests that hillebrandite contains thin domains (Dai and Post 1995). The results may indicate a superstructure with a doubled repetition period along the *a* axis, as suggested by Heller (1953) and Ishida et al. (1992). Information concerning the ideal and defect structures in hillebrandite may provide a better understanding of hydration reactions and strength development of Portland cement. In this paper, we discuss the domain structures and superstructure in hillebrandite as revealed by SAED and high-resolution transmission electron microscope (HRTEM) images, and discuss the relationships among superstructure, domain structure, and average structure (i.e., substructure).

SPECIMEN AND EXPERIMENTAL METHODS

The hillebrandite sample (NMNH 95767-7) used in this study is from Velardena, Durango, Mexico. The same sample was investigated by Dai and Post (1995). Petrographic examination shows that it forms fibrous aggregates having a radiolitic texture and an anomalous, dark blue interference color. The crystals for the transmission electron microscopy (TEM) study were selected from a petrographic thin section and mounted on copper grids. Thin specimens were thinned by Ar-ion bombardment and then coated on one side with a thin carbon layer. SAED and conventional TEM were performed with a JEOL 2000FX analytical transmission electron microscope operated at 200 keV. HRTEM images were obtained by using a JEOL 4000EX high-resolution transmission electron microscope operated at 400 keV. The main obstacle in the TEM investigation was extremely fast electron-irradiation damage.

RESULTS AND DISCUSSION

A [100]-zone-axis SAED pattern from the hillebrandite shows sharp diffractions (Fig. 1A). Systematic absences were observed for reflections of the types 0*kl* ($k \neq 2n$) and 00*l* ($l \neq 2n$) in accordance with the *b* glide and 2_1 screw symmetry in space group $Cmc2_1$. A $[40\bar{1}]$-zone-axis pattern shows continuous streaking along the b^* direction at $\frac{1}{2}(114)^*$ (Fig. 1B). A [001]-zone-axis pattern also shows sharp reflections and continuous streaking along the b^* direction at $\frac{1}{2}a^*_{sub}$ (Fig. 1C), where subscript "sub" means subcell. The sharp reflections characterize the average substructure determined by Dai and Post (1995). However, the streaking at $\frac{1}{2}a^*_{sub}$ indicates that the periodicity of the crystal along the *a* axis (a_{sup}, where subscript "sup" means supercell) is doubled with respect to that of the average structure (a_{sub}), i.e., $a_{sup} = 2a_{sub}$. Continuous streaking along the b^* direction in the SAED patterns in Figure 1 also indicates that there are thin domains perpendicular to the *b* axis. The neighboring domains are possibly related by a stacking fault with a

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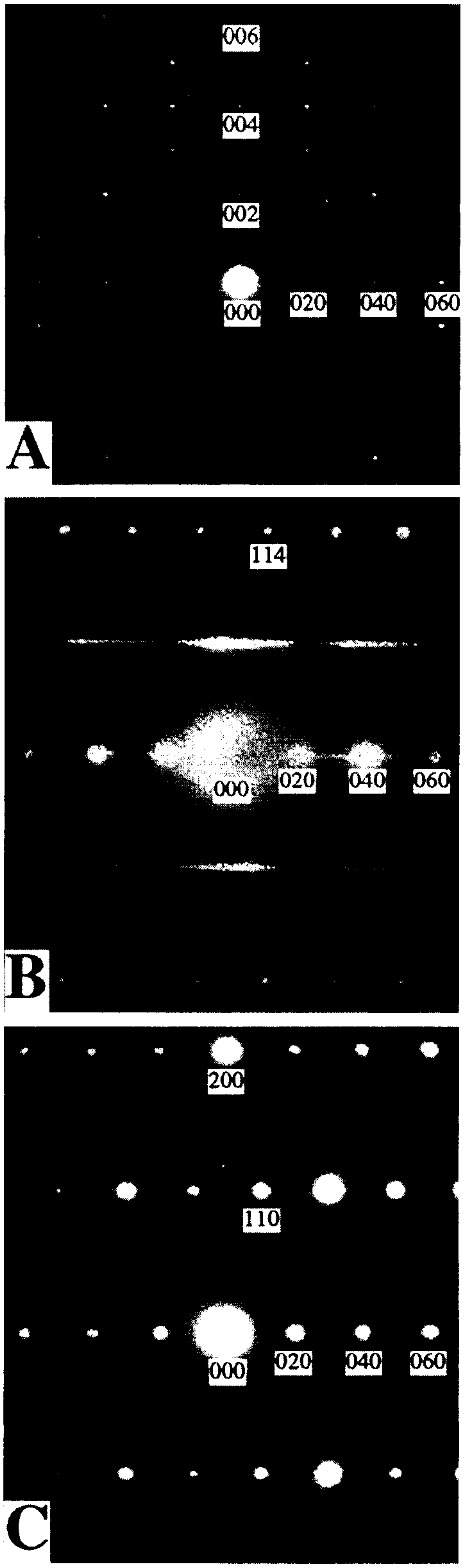

Figure 1. SAED patterns of hillebrandite. (**A**) The [100]-zone axis, (**B**) the [40$\bar{1}$]-zone axis, and (**C**) the [001]-zone axis. All indices are based on a subcell of the average structure determined by Dai and Post (1995).

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stacking vector of ½a_{sup}. Two dark-field (DF) images obtained by selecting part of the streaking at ½a^*_{sub} and ½(114)* show layer domains with average thicknesses of 10 nm (Fig. 2). An HRTEM image (Fig. 3) corresponding to the orientation of the SAED pattern in Figure 1C shows that the superstructure periodicity along the *a* direction is 7.28 Å. Neighboring domains are shifted by ±½a_{sup} or ±a_{sub} along the *a* direction.

The average structure of hillebrandite with dense stacking faults contains two wollastonite-like Si-O tetrahedral chains in the channels formed by Ca-O(OH) octahedra along the *a* axis. These chains are one-half occupied by Si1 and Si2 atoms (Dai and Post 1995). Actually, they can be considered as two distinct tetrahedral chains shifted by ½a_{sup} in different parts of the crystal (Fig. 4). Dai and Post (1995) proposed that there is only one set of tetrahedral chains in a given channel. Here we propose that there is only one type of tetrahedral chain (i.e., either A or B in Fig. 4) in each domain. The repetition period of the tetrahedral chain along the *a* axis is 7.28 Å, which is double the periodicity of the *a* axis in the average structure determined by Dai and Post (1995). Unit cells of the average (subcell) and superstructure are illustrated in Fig-

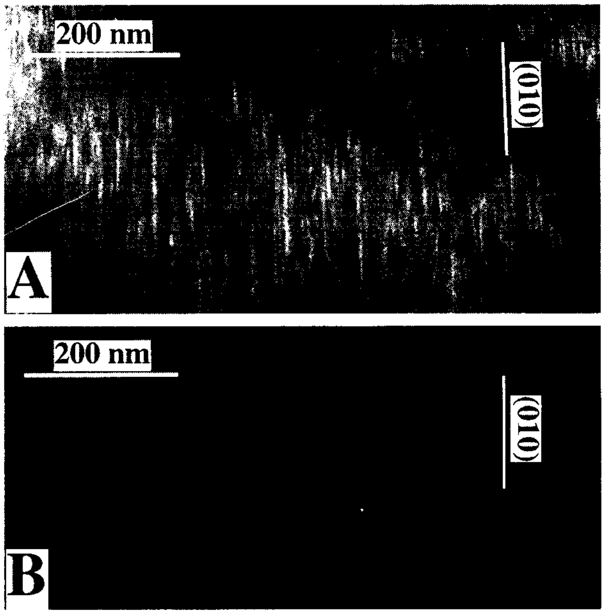

Figure 2. Dark-field images from selected parts of the streaked reflections in the SAED patterns in Figures 1B and 1C at ½a^*_{sub} (**A**) and ½(114)* (**B**), respectively. Both images show pervasive (010) layer domains.

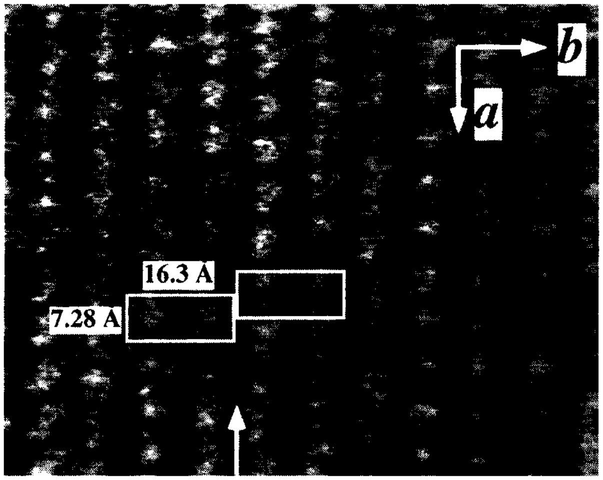

FIGURE 3. HRTEM image of the hillebrandite showing 7.28 Å periodicity along the a direction and stacking faults (for instance, the one indicated by an arrow), with a stacking vector of ½a_{sup}.

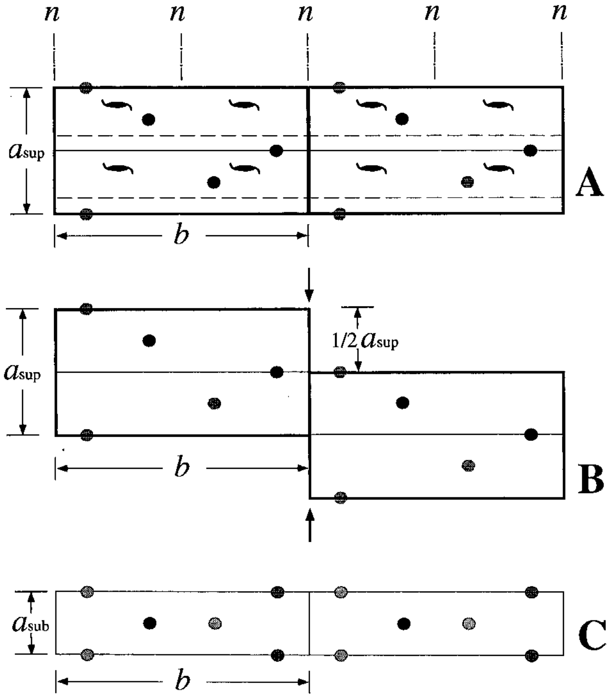

FIGURE 5. Diagram showing (**A**) a unit cell of the superstructure with $Pbn2_1$ symmetry, (**B**) a stacking fault between two supercells, and (**C**) the average structure with $Cmc2_1$ symmetry of the crystal with pervasive domains. The gray and black dots in **A** and **B** show only Si2 atoms with full occupancies in the supercell at heights of 0 and ½, respectively. The light gray and dark gray dots in **C** show Si2 atoms with one-half occupancies in the subcell of the average structure at heights of 0 and ½, respectively.

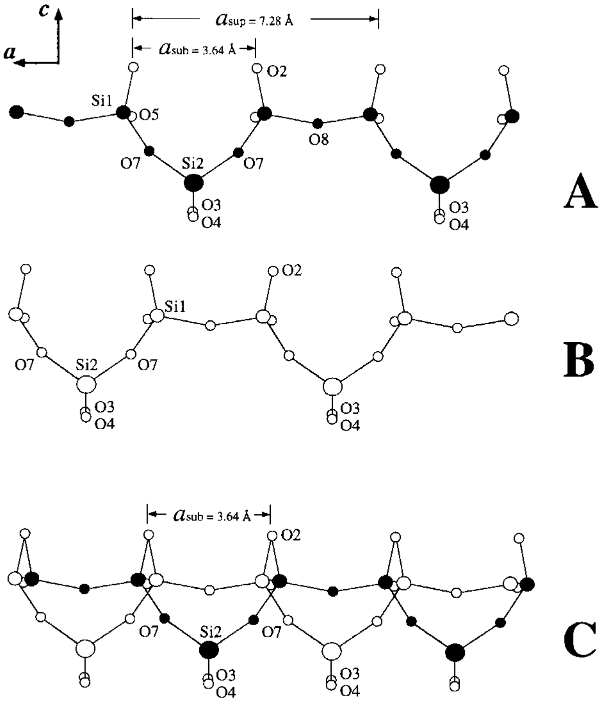

FIGURE 4. The wollastonite-like chains in the neighboring superstructure domains related by a stacking vector of ½a_{sup} (**A** and **B**), and the chains with partial occupancies of Si1 and Si2 atoms in the average structure (**C**). The chain in the average structure (**C**) can be considered as an overlapping of the chains in **A** and **B** with one-half occupancies. However, in real crystals there are no chains of the type shown in **C**. (Modified from Dai and Post 1995.)

ure 5. Figure 5A shows Si2 atoms with full occupancies in the supercell, and Figure 5B shows the relationship between neighboring superstructure domains. On the basis of the extinctions of the SAED pattern in Figure 1A, we propose that the probable symmetry for the supercell is $Pbn2_1$ (Fig. 5A). Actually, the tetrahedral chains with partial occupancies observed by Dai and Post (1995) in the average structure locally violate the mirror symmetry normal to the a axis. The removal of this mirror from space group $Cmc2_1$ yields the subgroup $Pbn2_1$.

Nonperiodic arrangements of domains related by ±½a_{sup} stacking vectors result in streaking along the b direction at ½a^*_{sub}. The doubled periodicity (7.28 Å) in the supercell is the repetition period of the wollastonite-like chains (Fig. 4). The shift between neighboring domains does not affect the arrangement of Ca-O(OH) octahedra. The periodicity of 3.64 Å in the average structure reflects the repetition period of the octahedra along the a axis. The crystal structure determined from sharp reflections has one-half periodicity of the true chain repetition along the a axis and one-half occupancies of Si atoms in the tetrahedral chains (Fig. 5C). The dense stacking faults and the intergrown layers with different structures may be responsible for the abnormal interference color of the crystal. The fibrous habit with radiolitic texture may indicate fast crystallization. It is proposed that the hillebrandite with dense stacking faults crystallized relatively fast from a supersaturated solution.

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