

## Jerrygibbsite-leucophoenicite mixed layering and general relations between the humite and leucophoenicite families<sup>1</sup>

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### ABSTRACT

TEM images of jerrygibbsite from Franklin, New Jersey, reveal random and ordered mixed layering with leucophoenicite on (001) and periodic twinning that gives rise to complex superperiodicities within the leucophoenicite. The differences between the structures of the Mn-humite and leucophoenicite families, as defined by the cation-stacking relations of White and Hyde (1983, *Acta Crystallographica*, B, 39, 10–17), are shown to be generally due to simple unit-cell twinning. Ordered twinning sequences in leucophoenicite can therefore be alternatively viewed as due to periodic mixed layering of leucophoenicite and manganhumite. Leucophoenicite and Mn-humite family members are characterized by an absence of F and significant F contents, respectively.

### INTRODUCTION

White and Hyde (1983a) have shown that the structures of the members of the humite family and those of the leucophoenicite family are simply related. They focused on a closest-packing sequence in which 1, 2, and 3 octahedrally coordinated cations were shown to be equivalent to sequences found in CrB, Ni<sub>2</sub>In, and Re<sub>3</sub>B; such sequences give rise to slabs parallel to (001) having thicknesses of 1.6, 3.1, and 4.7 Å, respectively. The magnitudes of *a* and *b* for both families are approximately 4.8 and 10.7 Å, respectively. Humite structures have sequences designated as (3,2\*) and those of the leucophoenicite family have sequences (1,2\*). For example, leucophoenicite has the sequence (1,2<sup>3</sup>) and therefore has  $d_{001} = 11 \text{ \AA}$ .

Dunn et al. (1984) described jerrygibbsite, Mn<sub>9</sub>(SiO<sub>4</sub>)<sub>4</sub>(OH)<sub>2</sub>, as a new mineral, noting that the lattice parameters were consistent with one of two structural relations: either (1) it is a member of the leucophoenicite family having the sequence (1,2<sup>4</sup>)<sup>2</sup>, because  $d_{001} = 2 \times 14 \text{ \AA}$ , or (2) it is a unit cell–twinned polymorph of sonolite, because  $d_{001}$  of jerrygibbsite is approximately twice that of sonolite ( $d_{001} = 14 \text{ \AA}$ ), the *a* and *b* lattice parameters have the same magnitudes within error, and the compositions are apparently the same. Presumably jerrygibbsite would be classed as a member of the humite group in the latter case. Dunn et al. (1984), however, found that leucophoenicite, Mn<sub>7</sub>(SiO<sub>4</sub>)<sub>3</sub>(OH)<sub>2</sub>, is intimately associated with jerrygibbsite, implying that jerrygibbsite is a member of leucophoenicite group. Indeed, the intergrowths were so pervasive that no Debye-Scherrer photographs of jerrygibbsite could be obtained that were entirely free of diffraction peaks of leucophoenicite.

In part in order to clarify these relations, we have carried

out a TEM study of jerrygibbsite. In the meantime, Kato (pers. comm.) has determined the crystal structure of jerrygibbsite. The structure is describable either as a (1,2<sup>4</sup>)<sup>2</sup> leucophoenicite-family type or as the unit cell–twinned polymorph of sonolite. We report here on our results of the mixed layering and unit-cell twinning in jerrygibbsite and leucophoenicite, and we show how the unit-cell twinning relation serves as a simple model for a one-to-one relation between all members of the leucophoenicite and Mn-humite families. An additional aim of this study was to attempt to determine the cause of formation of one group versus the other, in hope of providing insight into the lack of leucophoenicite-like structures among the Mg-humites.

A holotype specimen (USNM R18772) of jerrygibbsite from Franklin, New Jersey, was used for this study. The specimen was cut approximately perpendicular to (001) and ion-thinned in preparation for TEM studies, which were carried out utilizing the University of Michigan JEOL JEM 100 CX STEM. All references to indexing are based on unit cells in which *c* is parallel to octahedral chains, such that the structure can be viewed as constructed of slabs parallel to (001) (Francis and Ribbe, 1978).

### RESULTS

Figure 1 shows a lattice fringe image of homogeneous jerrygibbsite in which the 28-Å *c*-axis repeat and 14-Å subunit are clearly shown (also see Figs. 4 and 6). Such homogeneous areas never exceeded a few micrometers in thickness. Figure 2 shows a lattice fringe image of leucophoenicite from the same sample as for Figure 1, with characteristic 11-Å periodicity. The light and dark contrast bands are due to random twinning (White and Hyde, 1983b), as shown in part by the inserted electron-diffraction pattern in which reflections from both twin orientations are superimposed and separated in alternate rows.

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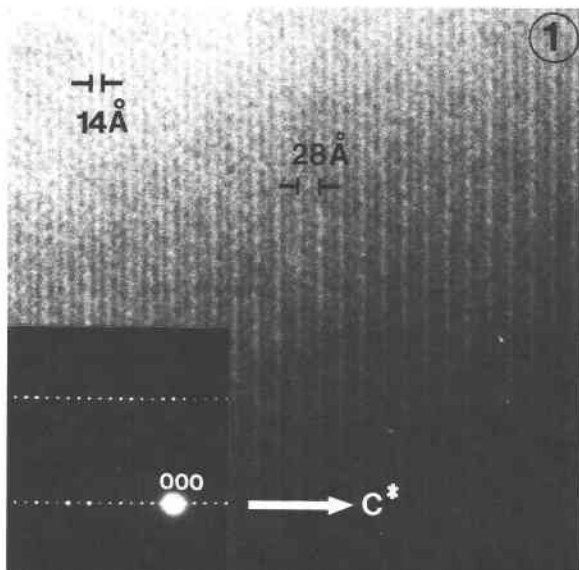


Fig. 1. (001) lattice fringe images and electron-diffraction pattern of jerrygibbsite, showing that 14-Å half-unit fringes display light and dark alternating contrast.

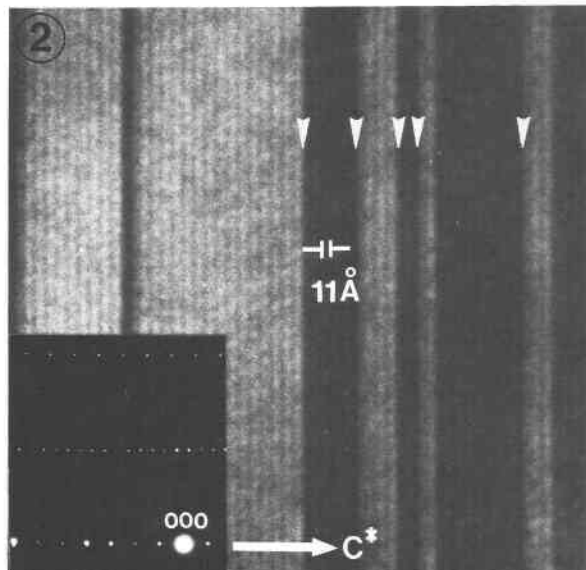


Fig. 2. (001) lattice fringe images and electron-diffraction pattern of twinned leucophoenicite showing bands of alternating contrast indicative of two twin orientations. Arrows point to the twin planes.

Figure 3 is also a lattice fringe image of leucophoenicite, but it shows an exceptional feature. The twin operation is periodically repeated over a distance of approximately  $1 \mu\text{m}$ . The periodicity of the twinning is approximately  $165 \text{ \AA}$ , although there are local deviations from a perfect repeat. The inserted electron-diffraction pattern displays twinning-induced superlattices and streaking parallel to  $c^*$  owing to "stacking" faults.

Jerrygibbsite and leucophoenicite were invariably found to be intercalated, as shown in Figure 4. As illustrated, the mixed layering is generally random, with units of jerrygibbsite being more numerous. However, ordered mixed layering was also found. For example, Figure 5 shows ordered mixed layering of one unit of jerrygibbsite with eight or nine units of leucophoenicite, resulting in superlattices with maximum spacing of  $127 \text{ \AA}$ . Similar features were observed by White and Hyde (1983b) in a TEM study of leucophoenicite. In general, the intergrowths are coherent and homogeneous, but occasionally faults are observed, as shown in Figure 6. Contrast due to strain is associated in Figure 6 with an offset of  $66 \text{ \AA}$ . However, the faulted area is limited by strain-free regions containing straight fringes, implying that the faulting occurred before crystallization was completed.

The complex stacking relations shown above provide a ready explanation for the intimate association of jerrygibbsite and leucophoenicite found by Dunn et al. (1984). More importantly, they imply that a crystal chosen as the basis of a crystal-structure analysis could not be homogeneous. Although Kato determined the structure of jerrygibbsite (pers. comm.), several features of the structure

are not satisfactory, including Si-O distances outside of the normally accepted range. The TEM data provide a ready explanation for such features, but are consistent with the validity of the average structure relations.

#### UNIT-CELL TWINNING

White and Hyde (1983a) pointed out that the manganimite structure [cation sequence  $(3,2^2)^2$ ] can be viewed as a unit cell-twinning polymorph of leucophoenicite  $(1,2^3)$ . Similarly, Kato (pers. comm.) has shown that jerrygibbsite  $[(1,2^4)^2]$  is the unit cell-twinning polymorph of sonolite  $(3,2^3)$ . Kato showed that the twinning operation is a glide plane which causes the CCP sequence of three octahedra to become the sequence (1,2). These relations can be generalized such that a similar glide in every member of the humite family  $(3,2^x)$  results in a structure of the leucophoenicite family  $(1,2^{x+1})$ . Where a member of one family is monoclinic, the polymorph in the other family is orthorhombic, with  $c$  double that of the monoclinic phase. The orthorhombic phase must have a sequence of the form  $(1,2^x)^2$  or  $(3,2^x)^2$  where  $x$  is an even number, such that doubling of the basic sequence produces translation periodicity. Peacor (unpub. data) has noted that a phase has been found at Kombat, Namibia, that is apparently an orthorhombic member of the leucophoenicite family  $(1,2^2)^2$ , and the unit cell-twinning polymorph of alleghenyite  $(3,2)$ .

Winter et al. (1984) and Dunn (1985) have postulated that leucophoenicite family structures may be stabilized relative to those of the humite family by the presence of Ca and/or Zn in solid solution for Mn. The unit cell-

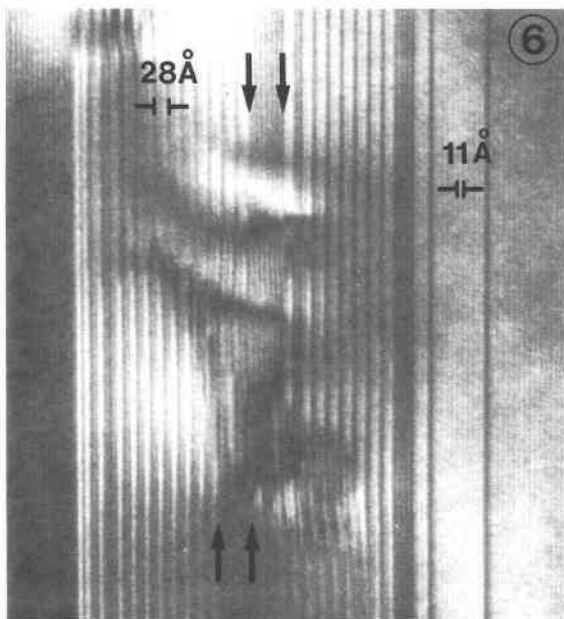
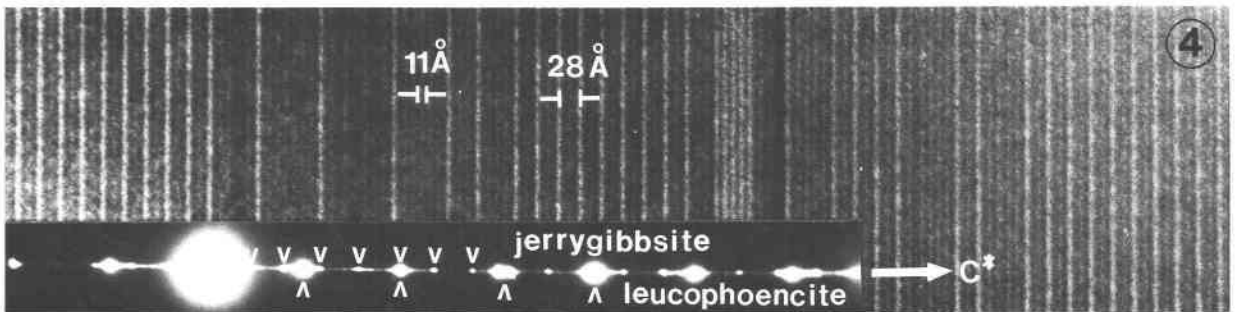
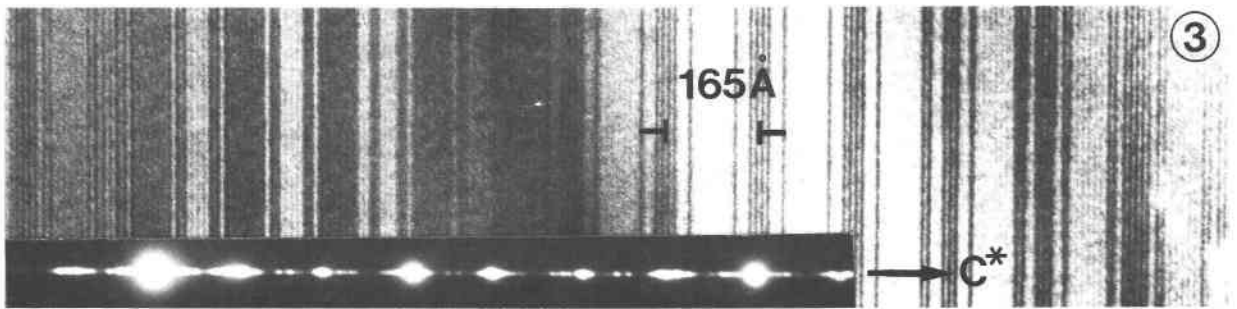


Fig. 3 (upper photograph). An ordered sequence of twinning in leucophoenicite resulting in a superperiodicity with  $d_{(001)} = 165 \text{ \AA}$ .

Fig. 4 (middle photograph). (001) lattice fringe image and electron-diffraction pattern showing extensive mixed layering of jerrygibbsite and leucophoenicite.

Fig. 5 (lower photograph). Superstructures resulting from ordered mixed layering of one jerrygibbsite unit and eight to nine leucophoenicite units.

twinning mechanism suggests another cause, however. The structure of jerrygibbsite is derived from that of sonolite by unit-cell twinning, where the glide plane operation relates (OH,F)-coordinated octahedra, as opposed to those with oxygen ligands. Jerrygibbsite and leucophoenicite are both characterized as being F-free, but the Mn-humites

Fig. 6. Strain contrast associated with diagonal faults. Parallel fringes above and below are shifted by  $66 \text{ \AA}$  parallel to  $c^*$ .

ubiquitously have significant F contents (Dunn, 1985). We tentatively hypothesize that the unit cell-twinning operation and (OH,F) contents are coupled (perhaps through H-bond systems in the OH-rich leucophoenicite family members).

Lastly, it is puzzling that the Mg-humites have no leucophoenicite family equivalents. We note, however, that they invariably contain substantial F substituting for OH. Indeed, F is usually in excess of OH (Dunn, 1985). We therefore also tentatively suggest that the lack of Mg-leucophoenicites may result from such factors. Mg-humites should be carefully examined for the presence of leucophoenicite family-type domains, especially in samples with minimum F content.

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