

## Perception of structural complexity: Fillowite revisited and $\alpha$ -iron related

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### ABSTRACT

All 23 cations in the asymmetric unit of fillowite, including two ordered vacancies,  $a = 15.28$ ,  $c = 43.51$  Å,  $R\bar{3}$ ,  $18(\text{Na}_2\text{CaMn}_3)(\text{Mn}_4\text{□}_2\text{P}_6)\text{O}_{24}$  can be related to the hexagonal (rhombohedral) cell of  $\alpha$ -Fe,  $a(\text{h})_\alpha = 4.05$ ,  $c(\text{h})_\alpha = 4.96$  Å,  $R\bar{3}c$ , 6Fe. This relation corresponds to  $3a(\text{h})_\alpha$  and  $6c(\text{h})_\alpha$  and has  $3^2 \cdot 6 = 54$  unit cells of  $\alpha$ -Fe in hexagonal setting or  $54 \cdot 6 = 324$  metals in the expanded  $\alpha$ -Fe cell. There is a 1:1 correspondence with the 324 cations (including 36 ordered vacancies) in fillowite. In  $c/a$  ratio, fillowite is dilated 14% along  $c$  relative to its  $\alpha$ -Fe counterpart. This is believed due to insertion of many oxide anions in the (001) plane of fillowite. The largest difference between cation centroids of fillowite and corresponding invariant centroids of  $\alpha$ -Fe is  $\Delta = 1.34$  Å for Na(3) compared with perpendicular bisection of  $t/2 = 1.47$  Å in the (001) plane and  $t/2 = 1.81$  Å parallel to  $c$ , the calculations based on the fillowite cell.

All cations fall within their respective Dirichlet domains in the projection on (001). It is believed that the two ordered vacancies, □(1) and □(2) in general positions, arise from near-eclipsing of terminal tetrahedral bases, in this case five beads of T–M–T–M–T. Such sections of rods are called *stalks* and appear in other structural colossi such as palmierite, cerite, and arrojadite-dickinsonite. These stalks may force a large number of atoms in a unit cell. Fillowite's cell alone has 756 atoms as its contents. Yet only three distinct rods, each of 12 cation beads in the  $c$ -repeat, occur in the unit cell: rod I ( $\times 3$ ), rod Ia ( $\times 6$ ), and rod II ( $\times 18$ ). The I and Ia correspond to pole points on (001) as (00) for ( $xy$ ), and II corresponds to  $(\frac{2}{3}\frac{1}{3})$  for the parent structures  $\alpha$ -Fe(h),  $\text{Ni}_2\text{In}$ , and glaserite  $[(\text{K}_3\text{NaS}_2)\text{O}_8]$ , respectively.

### INTRODUCTION

Chemical crystallography has many ramifications. It does not stop with the solution of a crystal structure. In fact, it is a dendritic and unending activity. Sir J.B.S. Haldane once remarked that "things are interesting insofar as they relate themselves to other things." He also once declared something like "The universe is rather queer, and the more one looks at it the queerer it becomes." These observations stress the unending process of scientific inquiry, and the need for constant re-evaluation of values and of the things we study. My contribution is such "old wine in a new bottle."

Fillowite is one of the monsters in the mineralogical menagerie. Its Brobdingnagian structure taunts us by its presence. With a relatively simple composition,  $\text{□}_2\text{Na}_2\text{CaMn}_7(\text{PO}_4)_6$ , it has 324 cations and ordered vacancies alone in its unit cell. The  $\alpha$ -Fe, on the other hand, has 2 Fe atoms in its body-centered,  $Im\bar{3}m$  cell. The hexagonal (rhombohedral) cell of  $\alpha$ -Fe has 6 Fe atoms. Yet, I hope to show that this Lilliputian with its 1:54 metal: cation relationship to fillowite suggests that the monster is capable of being tamed somewhat.

Inspiration for my unusual approach began with a book by Arthur L. Loeb (1976) entitled *Space Structures*. Loeb's book includes a chapter on Dirichlet domains, where

points distributed in space were compared to communities. Neighborly, adjacent, contiguous points about one reference point were conceived as occurring in a parish, and many reference points created other parishes. These parishes are called *domains* and help sort out connected communities within crystal structures as well.

Words like *isostructural*, *isomorphic*, etc. although well-defined are rarely used with any rigor. More complicated structures invariably have some atoms with at least one degree of freedom. This is the essence of the fillowite problem. Fillowite's cations alone have 53 degrees of freedom in the asymmetric unit, whereas  $\alpha$ -Fe has none—all atoms are equivalent and occupy fixed, invariant points. Behind this study is one nagging question: just what do we mean by complexity?

### PERCEIVING THE FILLOWITE STRUCTURE (OR TAMING OF THE MONSTER)

#### Description of the structure: Preparatory notes

The essential details of the fillowite crystal structure and its 45 atoms in the asymmetric unit appeared in Araki and Moore (1981). However, at that time, this elephantine design suggested "a glaserite-derived structure," but the more detailed aspects of that relation were not pursued further. Actually, glaserite itself had a rather con-

founded history, and no clear nomenclatural distinction between that phase and apthitalite exists. In this study, I adopt ordered  $2\text{KNa}(\text{SO}_4)$ , trigonal,  $P3m1$ ,  $a = 5.61$ ,  $c = 7.18 \text{ \AA}$  as *apthitalite* and  $1\text{K}_3\text{Na}(\text{SO}_4)_2$ , trigonal,  $P\bar{3}m1$ ,  $a = 5.68$ ,  $c = 7.31 \text{ \AA}$  as *glaserite*. The cell criteria follow from the definitive structure study on these two compositions by Okada and Ossaka (1980), the chief distinction being that one is polar whereas the other (*glaserite*) is centrosymmetric. Early samples of these phases would have been practically impossible to differentiate: mixtures as overgrowths of or exsolutions involving the two types and optical and chemical similarities easily have confounded these two related substances in the past.

The key feature of the fillowite structure is its decomposition into three distinct rods along [001] as depicted in Araki and Moore (1981, especially Fig. 1a). In this figure, it was shown that in projection on (001), one rod consisting of M alternating with T (M = larger cation, T = tetrahedral cation) defined a  $(6^3)$  hexagonal net and that the remaining two unique rods consisting of only the larger M cations resided approximately in the hexagonal centers of this net. The inversion centers,  $3_1$  and  $3_2$  screw axes, and 3-fold rotors automatically generated the entire structure from all three unique rods. In that study, rods I and II were shown in their Figures 1b and 1c. For reasons that will become obvious, I will redefine these as rods I and Ia, respectively. The poles pierce (001) at  $(00)$ ,  $(\frac{2}{3}\frac{1}{3})$ ,  $(\frac{1}{3}\frac{2}{3})$  for rod I; and  $(\frac{1}{3}0)$ ,  $(0\frac{1}{3})$ ,  $(\frac{1}{3}\frac{1}{3})$ ,  $(\frac{2}{3}0)$ ,  $(0\frac{2}{3})$ , and  $(\frac{2}{3}\frac{2}{3})$  for rod Ia. The former are on 3-fold rotors and the latter weave around 3-fold screws. Thus, nine rods ( $3 \times \text{I}$  and  $6 \times \text{Ia}$ ) are contained within the cell. I will further redefine the general rod III of the Araki-Moore paper, with M alternating with T and situated in (001) at the nodal points of the  $(6^3)$  net. In this study, it is redefined as rod II. Its pole point emerges at general  $(\frac{2}{9}\frac{1}{9})$ , etc. The composition of the plane group with the R-centering and with inversion leads to

$$\{p3\} \cdot \{R\} \cdot \{\bar{1}\} = R\bar{3}$$

$$3 \cdot 3 \cdot 2 = 18$$

and forces the hexagonal-shaped cell. Thus, there are 18 such equivalent rod II's in the unit cell. Rod II includes  $6\text{T} + 4\text{M} + 2\Box$  (where  $\Box$  = ordered vacancy) as the beads that collectively define the  $c$ -axial repeat. The 12 beads are each unique, the vacancies included among the beads. Rods I and Ia also have twelve beads each, all populated with atoms, in the  $c$ -axial repeat, but of these, only seven are unique in rod I and four are unique in rod Ia. Thus, the total unique cations in the cell are  $7 + 4 + 12 = 23$ . The two missing cations in Araki and Moore (1981, Table 1) are the two ordered vacancies,  $\Box(1)$  and  $\Box(2)$ , in rod II. Their coordinates were obtained by taking the mean between adjacent T atoms above and below, that is,  $\Box(1) = (0.220, 0.094, 0.458)$  and  $\Box(2) = (0.221, 0.117, 0.960)$ . Later, I will advance an argument that these ordered vacancies are what lead to fillowite's structural "complexity." These vacancies break the necklace of beads

into discrete units of five beads, as is readily perceived in Araki and Moore (1981, Fig. 1a).

A synthetic cement phase, phase Q in the system  $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{P}_2\text{O}_5$ , bears a striking resemblance to fillowite. Its structure was recently deciphered by Domanskii et al. (1982). The cell formulae of both fillowite and phase Q can be conveniently partitioned according to the three kinds of rods: rods I and Ia contain  $18(\text{Na}_2\text{CaMn}_3)$  in fillowite and  $18(\frac{1}{6}\text{Na}_4\frac{1}{3}\text{Ca}_4\frac{1}{3}\text{Mg}_3)$  in phase Q; rod II contains  $(\text{Mn}_4\frac{1}{2}\text{P}_6)\text{O}_{24}$  in fillowite and  $(\text{Mg}_4\frac{1}{2}\text{P}_6)\text{O}_{24}$  in phase Q.

Rod II in both structures is nearly equivalent, but rod I in phase Q has missing Na(1), which results in a bead sequence of 3 and 7, respectively, separated by two intervening vacancies in the  $c$ -axial repeat at  $(00z)$ , etc.

### The cation aristotype (parent structure) is $\alpha$ -Fe

The  $\alpha$ -Fe structure type defines a body-centered cubic cell. It is  $Im\bar{3}m$ ,  $a = 2.866 \text{ \AA}$ ,  $Z = 2$ , Fe at  $(000)$ ,  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  (Thomas, 1948). Transforming to the hexagonal cell by projection along [111], we get  $a(\text{h})_\alpha = 4.053$ ,  $c(\text{h})_\alpha = 4.964 \text{ \AA}$ ,  $Z = 6$ . The hexagonal Fe equivalences are  $(000)$ ;  $00\frac{1}{2}$ ;  $\frac{1}{3}\frac{2}{3}\frac{4}{6}$ ;  $\frac{1}{3}\frac{2}{3}\frac{1}{6}$ ;  $\frac{2}{3}\frac{1}{3}\frac{2}{6}$ ;  $\frac{2}{3}\frac{1}{3}\frac{5}{6}$ . These correspond to Wyckoff position (6b) for space group  $R\bar{3}c$ . An infinitesimal compression or dilation of  $\alpha$ -Fe along [111] will force the "equivalent" rhombohedral group. The relation of  $\alpha$ -Fe ( $\alpha$ ) to its fillowite ( $\text{F}_\alpha$ ) cell becomes obvious by noting  $a(\text{F}_\alpha) = 3a(\text{h})_\alpha$  and  $c(\text{F}_\alpha) = 6c(\text{h})_\alpha$  or  $a(\text{F}_\alpha) = 12.159$ ,  $c(\text{F}_\alpha) = 29.784 \text{ \AA}$ . Fillowite has  $a = 15.282$ ,  $c = 43.507 \text{ \AA}$ , 324 cations in the unit cell. These relations are forced by the earlier remarks on rods I, Ia, and II and the cell formula given above. Note that  $a(\text{F}_\alpha), c(\text{F}_\alpha) \rightarrow a, c$  of fillowite states that  $3^2 \cdot 6 = 54$   $\alpha$ -Fe hexagonal cells in  $R\bar{3}c$  occur in that cell. Furthermore, the cell contains  $54 \cdot 6 = 324$  Fe atoms, precisely the number of cations and ordered vacancies in the fillowite cell. The axial ratios are  $c(\text{F}_\alpha)/a(\text{F}_\alpha) = 2.450$  and  $c/a = 2.847$  for fillowite. This suggests that fillowite can be thought of as layers of cations with interleaving layers of oxide anions; many such oxide layers parallel to (001) lead to an anisotropic expansion of some 14% along the  $c$  axis relative to  $a$ . This expansion is readily apparent in Figure 1b of Araki and Moore (1981). Relative to the  $a(\text{F}_\alpha), c(\text{F}_\alpha)$  cell of  $\alpha$ -Fe, the volume increase is 56% based on the fillowite cell. The expansion through oxide insertion does not generally apply to all intermetallic  $\rightarrow$  oxy-salt relations. For example, for  $\text{Ca} \rightarrow \text{CaO}$ , there is a decrease in cell volume. Moore et al. (1989) in an exhaustive study on kornrupine discussed in some detail that if an intermetallic has only  $s$  valence electrons, the  $\text{Me} \rightarrow \text{MeO}$  will involve a decrease; but for  $\text{Me}$  with  $s, p$ , etc. electrons, the  $\text{Me} \rightarrow \text{MeO}$  isopunctal relation will involve an increase in cell volume.

### The difference $\Delta$ ( $\text{\AA}$ ) and Dirichlet domains

The cation rods of fillowite emerge as pole points in simple relation to the  $\alpha$ -Fe subcell. Rod I emerges at the 3-fold rotors and rod Ia at the 3-fold screws in the fillowite cell. Noting that fillowite's  $a$  axis is trebled that of

TABLE 1. Rods in fillowite and differences,  $\Delta$  (Å), compared with equivalent  $\alpha$ -Fe and  $\text{Ni}_2\text{In}$ 

Rod I							
	00z	z	$z = \frac{1}{12}(n), n = 0, 1, \dots, 11$		$\Delta$ (Å)		
3 M(1)		.000		.000	0.000		
6 M(3)		.101		.083	0.783		
6 Na(1)		.175		.167	0.348		
6 Na(2)		.249		.250	0.044		
6 M(4)		.325		.333	0.348		
6 M(5)		.399		.417	0.783		
3 M(2)		.500		.500	0.000		
		+ { $\bar{1}$ }		+ { $\bar{1}$ }	+ { $\bar{1}$ }		
Mean		0.384			0.384		

Rod Ia							
	$0\frac{1}{2}z$		$z = \frac{1}{12}(n), n = 0, 1, \dots, 11$		$\Delta$ (Å)	$\Delta a_1 \times a_2$ (Å)	$\Delta c$ (Å)
18 Ca	-.025	.266	-.001	0.000	0.897	0.896	0.044
18 M(8)	.003	.324	.082	0.083	0.171	0.165	0.044
18 Na(3)	.079	.427	.165	0.167	1.340	1.337	0.087
18 M(9)	-.003	.399	.247	0.250	1.041	1.032	0.130
		+ { $3_2$ }			+ { $3_2$ }		
Mean					0.862	0.858	0.076

Rod II										
	$\frac{1}{3}(\frac{2}{3}\frac{1}{3})z = \frac{1}{6}\frac{1}{2}z$			z		$\Delta$ (Å)		$\Delta a_1 \times a_2$ (Å)	$\Delta c$ (Å)	
				A	B	A	B		A	B
18 P(6)	.200	.116	.054	.056	.042	0.387	0.644	0.377	0.087	0.522
18 M(11)	.222	.108	.134	.139	.125	0.222	0.395	0.046	0.217	0.392
18 P(4)	.218	.123	.210	.223	.208	0.581	0.161	0.135	0.566	0.087
18 M(6)	.239	.086	.281	.306	.292	1.223	0.736	0.559	1.088	0.479
18 P(1)	.233	.090	.361	.389	.375	1.292	0.746	0.430	1.218	0.609
18 □(1)	.220	.094	.458	.472	.459	0.657	0.250	0.246	0.609	0.044
18 P(5)	.206	.097	.555	.556	.542	0.235	0.611	0.231	0.044	0.566
18 M(7)	.222	.095	.629	.639	.626	0.499	0.277	0.244	0.435	0.131
18 P(2)	.218	.086	.706	.722	.709	0.782	0.378	0.355	0.696	0.131
18 M(10)	.252	.174	.791	.806	.792	1.059	0.835	0.834	0.653	0.044
18 P(3)	.242	.118	.866	.889	.876	1.036	0.511	0.269	1.001	0.435
18 □(2)	.221	.117	.960	.972	.959	0.532	0.109	0.100	0.522	0.044
Mean						0.709	0.471	0.319	0.595	0.290

Note: Individual beads in the asymmetric unit are denoted. Equipoints, differences (Å), their components in principal directions, and mean differences are also listed. Difference  $\Delta$  is computed based on the fillowite cell. A:  $z = \frac{1}{18} + \frac{1}{12}(n), n = 0-11$  ( $\alpha$ -Fe model). B:  $z = \frac{1}{24} + \frac{1}{12}(n), n = 0-11$  ( $\text{Ni}_2\text{In}$  model).

$\alpha$ -Fe in  $R\bar{3}c$  representation, rod I is made up of twelve beads at (00z), rod Ia is ideally at  $\frac{1}{2}(11)z = \frac{1}{2}\frac{1}{3}z$ , and rod II is ideally at  $\frac{1}{3}(\frac{2}{3}\frac{1}{3})z$  or  $\frac{1}{6}\frac{1}{2}z$ , a general position. Since twelve beads, including ordered vacancies, constitute a rod, the z coordinates can be ideally related to  $\alpha$ -Fe. For rods I and Ia, it is simply  $z = \frac{1}{12}(n), n = 0, 1, \dots, 11$ , where n is the bead in the sequence. Six  $\alpha$ -Fe,  $R\bar{3}c$  cells repeat along c in one fillowite cell translation. Therefore, with  $(\frac{2}{3}\frac{1}{3}\frac{1}{3})$  in  $\alpha$ -Fe, the z coordinates are ideally  $z = \frac{1}{6}(\frac{1}{3}) + \frac{1}{12}n$  or  $\frac{1}{18} + \frac{1}{12}n, n = 0, 1, \dots, 11$ . The related  $\text{Ni}_2\text{In}$ ,  $P6_3/mmc, Z = 2$  (see Table 2), has one site at  $(\frac{2}{3}\frac{1}{3}\frac{1}{4})$  with a fillowite cell sequence  $z = \frac{1}{6}(\frac{1}{4}) + \frac{1}{12}n$  or  $\frac{1}{24} + \frac{1}{12}n, n = 0, 1, \dots, 11$ . I include  $\text{Ni}_2\text{In}$  as well. Not only does it give a much better fit to fillowite's cations in rod II but suggests that prudent choice of intermetallic model to compare with cation mimic is necessary. These ideal coordinates head columns in Table 1, which list beads in fillowite. The difference,  $\Delta$  in angstroms, was taken between the ideal coordinates and the real coordinates, which were rounded off to three significant digits from Araki and Moore (1981, Table 1). The remainder was multiplied by the appropriate fillowite cell translation. Mean differences are listed at the end of each column for unique

rods I, Ia, and II. In addition, the differences for rods Ia and II are listed as components in the  $a_1 \times a_2$  plane and along c. The largest displacement from the ideal model is  $\Delta = 1.340$  Å (1.337 Å in the  $a_1 \times a_2$  plane) for Na(3) of rod Ia. The largest displacement along c is  $c\Delta z = 1.218$  (with  $\alpha$ -Fe) or 0.609 Å (with  $\text{Ni}_2\text{In}$ ) for P(1) of rod II. What does this mean?

Araki and Moore (1981, their Fig. 1a) showed the plan of fillowite's cell on (001) and drew circles that enveloped the cations in the distinct rods. How are the rods related to each other and which beads belong to them? For the  $\alpha$ -Fe model, the invariant points define 14-coordination of neighboring Fe atoms around a central Fe atom. Since all atoms are equivalent, only one coordination polyhedron is defined, the rhombic dodecahedron with  $N_0 = 8$  vertices that are each 3-connected and possess 3-fold rotational symmetry plus 6 vertices that are each 4-connected and possess 4-fold rotational symmetry. The edges,  $N_1 = 24$ , are each equivalent. The faces,  $N_2 = 12$ , are all of the same kind, and each consists of a rhombus composed of two coplanar isosceles ( $70.53^\circ$ ) triangles that share an edge. Thus, the Euler characteristic  $N_0 - N_1 + N_2 = 14 - 24 + 12 = 2$ , a map on the sphere (= a convex

polyhedron). Rhombic dodecahedra have an additional property: they are F edorov solids, that is, they pack to fill space.

The  $\text{Ni}_2\text{In}$  structure is related, but it is geometrically distorted. The three equivalent rhombic dodecahedra at (000),  $(\frac{2}{3}\frac{1}{3}\frac{2}{6})$  and  $(\frac{2}{3}\frac{1}{3}\frac{5}{6})$  in  $\alpha$ -Fe (hexagonal setting) are split into two distinct polyhedra: one *bicapped hexagonal prism* at (000) with  $12 + 2 = 14$ -coordination or  $\text{Ni}(1)$ - $[\text{In}_6\text{Ni}(2)_6\text{Ni}(1)_2]$  and two pentacapped *trigonal prisms*, at  $(\frac{2}{3}\frac{1}{3}\frac{1}{4})$  with  $6 + 3 + 2 = 11$ -coordination or  $\text{Ni}(2)$ - $[\text{Ni}(1)_6\text{In}_3\text{In}_2]$  and at  $(\frac{2}{3}\frac{1}{3}\frac{3}{4})$  with  $6 + 3 + 2 = 11$ -coordination or  $\text{In}[\text{Ni}(1)_6\text{Ni}(2)_3\text{Ni}(2)_2]$ . For the last two polyhedra, each has three extra coordinating spheres usually regarded as second nearest neighbors. [These spheres would complete the rhombic dodecahedron.] This follows from Dirichlet domain construction: the basal-cap perpendicular bisection truncates them. These polyhedra all arise from some symmetric distortion of  $\alpha$ -Fe. A vast number of such compounds exists as does a large literature on the subject, but to my knowledge no rigorous topogeometric analysis has ever been done. A systematic study of the distortion of the rhombic dodecahedron would be a most challenging and fruitful study indeed! It would help in deciphering body-centered cubic structures.

This small introduction on the rhombic dodecahedron can be applied to fillowite. The beads in rods I and Ia of the fillowite cell are each coordinated by 14 nearest-neighbor beads defining a distorted bicapped hexagonal prism where the bases are covered by caps. For rod I, the coordinating beads are 2 from rod I and 12 from rod II. Rod Ia has 2 from rod Ia and 12 from rod II. For rod II, the coordinating beads define a distorted pentacapped trigonal prism. Here, all trigonal prism faces are covered by caps. A bead in rod II is 11-coordinated: 4 from Ia and 2 from I defining a trigonal prism, and 5 from II defining the 3 equatorial and 2 apical caps. The same polyhedra occur for  $\text{Ni}_2\text{In}$  but with less distortion.

Fischer et al. (1971) in an analysis of  $\text{CaCl}_2$  and Pearson (1985) on  $\text{BaAl}_4$ , the most populous (400 phases) of intermetallic structure types, discussed and demonstrated the utility of the Dirichlet domain (Wirkungsbereich) in defining regions of nearest-neighbor coordination. In the plane, a point will exist within its boundary or domain. Its coordinating spheres in crystal space will define edges of the polygonal domain in the dual space. In three dimensions, a polyhedron (also called the Voronoi polyhedron) ensues, and the coordinating points correspond to faces of that polyhedron. The Voronoi polyhedron is of special interest to the crystallographer, and an excellent menu, replete with diagrams and equations for finding planar intersections, exists in David and David (1982). In both dimensions  $R^2$  and  $R^3$ , their relative contiguity is determined by the length of the edge or the area of the face: the closer a coordinating point occurs to the central point, the larger the edge or face. More distant points correspond to smaller edges or faces, beyond which the adjacent point will define neither an edge nor a face. That adjacent point belongs to a different domain.

Construction of the Dirichlet domain is straightfor-

ward. All potential coordinating points are each connected to the central point and perpendicular bisectors are constructed (either lines or planes). The resulting enclosure (polygon or polyhedron) about the central point is the Dirichlet domain. In constructing domains for spheres of identical radius, the problem is straightforward. Fischer et al. (1971) extended the problem to spheres of differing radii and performed constructions based on radius ratio, for example  $r_1/r_2$ , where the perpendicular bisector is located between two points by the "lever rule." In fillowite, a simpler approach was taken since the points for each rod consist of at most 12 beads and radius for the aggregate as such is not defined. When rod II centroids on the (001) plane are connected together for fillowite, the result is the  $(6^3)$  net, but when all rods—I, Ia, and II—are connected, the triangular net  $(3^6)$  obtains. This projection of fillowite on (001) would have edge length  $t = 2.94 \text{ \AA}$  and bead repeat along  $[001]$  of  $c/12 = 3.62 \text{ \AA}$  based on the perfect  $\alpha$ -Fe hexagonal net applied to the fillowite cell. The perpendicular bisectors would be located at  $t/2 = 1.47 \text{ \AA}$  and  $\frac{1}{2}(c/12) = 1.81 \text{ \AA}$ . Both these distances are each longer than the longest  $\Delta$  ( $\text{ }$ ) in Table 1.

The Dirichlet domains were constructed for the  $\alpha$ -Fe arrangement of the fillowite cell containing the beads of rods I, Ia, and II. In effect, the dual  $(6^3)$  of  $(3^6)$  is constructed. Figure 1 shows this construction, and all real beads fall within their respective domains. As expected, Na(3) in rod Ia is the farthest outlying point. For rod I on the 3-fold rotor, only the  $c\Delta z$  component need be considered. The largest deviants are M(3) and M(5) with  $\Delta = 0.78 \text{ \AA}$ . The largest displacement in this direction is  $c\Delta z = 1.22 \text{ \AA}$  for P(1), comfortably within the range of the average perpendicular bisector of  $1.81 \text{ \AA}$ . Using the  $\text{Ni}_2\text{In}$  model, it is  $c\Delta z = 0.61 \text{ \AA}$ .

What does this mean? Fillowite, one of the most "complex" of mineral structures can be considered an oxygen-stuffed derivative of  $\alpha$ -Fe in  $R\bar{3}c$  representation. The difference,  $\Delta$ , is a consequence of a variety of atom species and a range of anion coordinations about cations. Shared anion edges and faces in particular are known to disrupt cation centroids for ideal arrangements by cation-cation repulsion effects across the shared edge or face. It is surprising that all 23 cations (including 2 vacancies) in fillowite fit so well. The oxide anions, on the other hand, present no sensible arrangement according to well-known principles such as crystallographic dense-packing. This appears to be the sternest example yet of the role of cations and their relation to intermetallic phases, discussed by O'Keeffe and Hyde (1985).

Then, why is fillowite so complex? Its cell is enormous, with a volume of over  $8799 \text{ \AA}^3$ , and contains 47 distinct atom positions or 756 atoms in the cell. There is no evidence of a substructure in X-ray films. The severe restrictions placed by  $R\bar{3}$  on the structure allow all cations to be arrayed into two distinct sheets: tier A ( $z = \frac{1}{4}$ ) and B ( $z = \frac{3}{4}$ ) for centers and nodes of the  $(6^3)$  net (see Fig. 2); and tier A' ( $z = \frac{3}{4}$ ), A'' ( $z = \frac{1}{4}$ ), and B' ( $z = \frac{1}{4}$ ) (see Fig. 3). Most interesting is Figure 4, the ordered vacancies

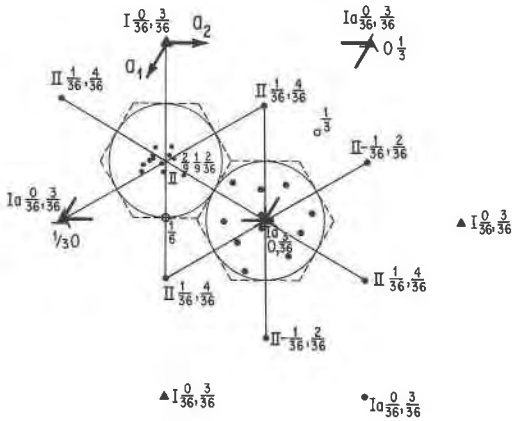


Fig. 1. Dirichlet domain construction on (001) based on  $\alpha$ -Fe equivalent of fillowite. The fillowite beads are superimposed.

$\square(1)$  and  $\square(2)$  in the unit cell. No hexagonal or trigonal subcell can be found for these vacancies. For a given rod II, these vacancies contain stalks P(6)–M(11)–P(4)–M(6)–P(1) and P(5)–M(7)–P(2)–M(10)–P(3) in between. It is further noted that the bases of the terminal  $[PO_4]$  tetrahedra are nearly perpendicular to the  $c$  axis. This is rem-

iniscent of cerite,  $RE_9Fe(SiO_4)_6(SiO_3OH)(OH)_3$ , another huge structure with at least 288 atoms in the unit cell, where Si(2)–RE(1)–RE(3)–RE(2)–Si(1) stalks occur (Moore and Shen, 1983a). Again, the bases of  $[Si(1)O_4]$  and  $[Si(2)O_4]$  are nearly perpendicular to the  $c$  axis (Moore and Shen, 1983a). These terminal tetrahedral orientations would render continued polymerization to form a string unlikely owing to high-charged cation-cation repulsion effects across the tetrahedral bases. Other examples of parallel to near-parallel eclipsed and staggered tetrahedral bases abound: steenstrupine (Moore and Shen, 1983b) with at least 339 atoms in the unit cell and palmierite  $K_2Pb(SO_4)_2$  (see Moore, 1973) are a few cases. The staggered and eclipsed tetrahedra with voids in between are illustrated for cerite, palmierite, and fillowite in Figure 5. Symmetry forces a  $\{3\}$  staggering of two  $[SO_4]$  tetrahedra in palmierite. In cerite, the facing  $[SiO_4]$  tetrahedra are tilted versions of palmierite. In fillowite, the tilting is even more pronounced, but near-eclipsing of tetrahedral pairs forces the vacancies  $\square(1)$  and  $\square(2)$ . The successive bead distances along  $c$  range from T– $\square(2) \approx 4.1 \text{ \AA}$  in fillowite, T(1)–T(2)  $\approx 4.1 \text{ \AA}$  in cerite and T–T  $\approx 4.8 \text{ \AA}$  in palmierite. In all the structures mentioned, the ordered vacancies are between tetrahedral bases.

The recurrence of such stalklike units among oxysalt

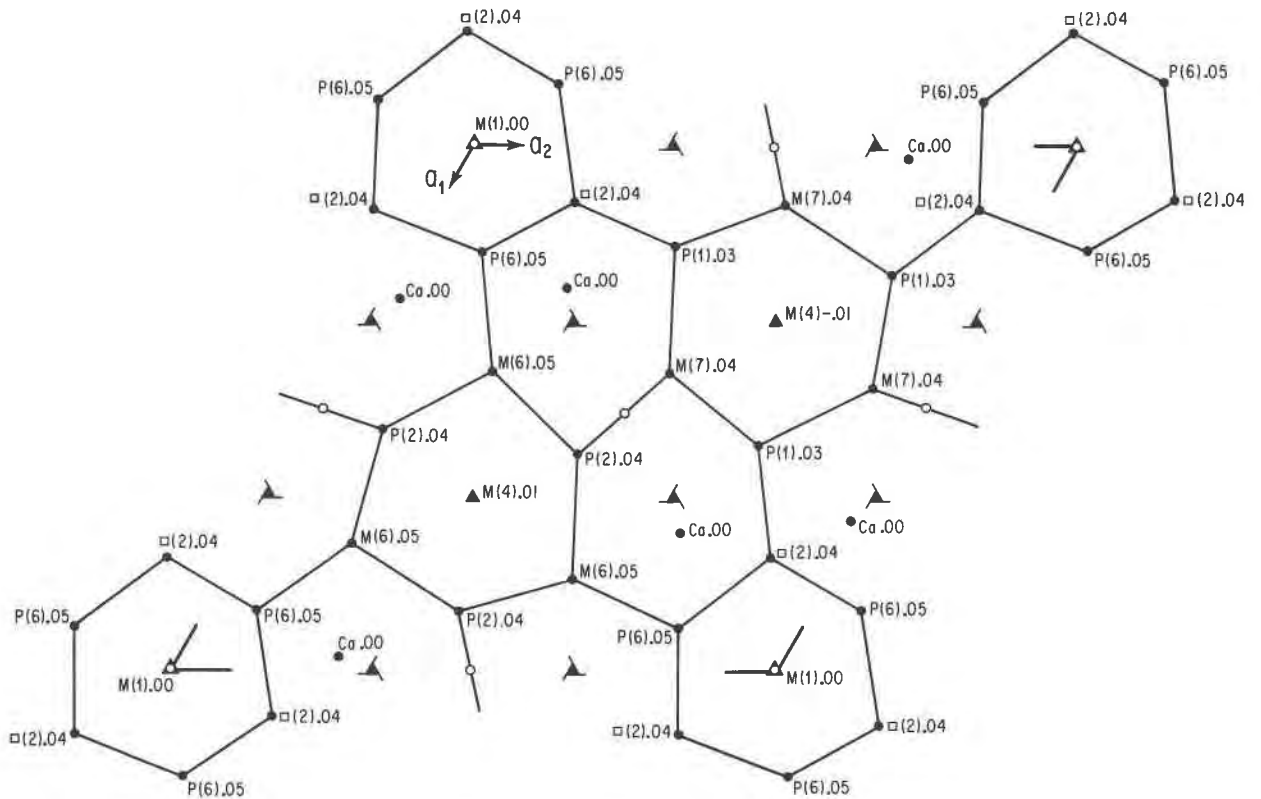


Fig. 2. Section of fillowite based on coordinates of Araki and Moore (1981). Tier A at  $z \approx \frac{3}{4}$  includes M(1), M(4), and Ca at hexagon centers. Tier B at  $z \approx \frac{1}{4}$  includes P(1), P(2), P(6), M(6), M(7), and  $\square(2)$  at hexagon nodes. The distorted (6) net is shown. Atom heights in this and succeeding figures are given as fractional coordinates.

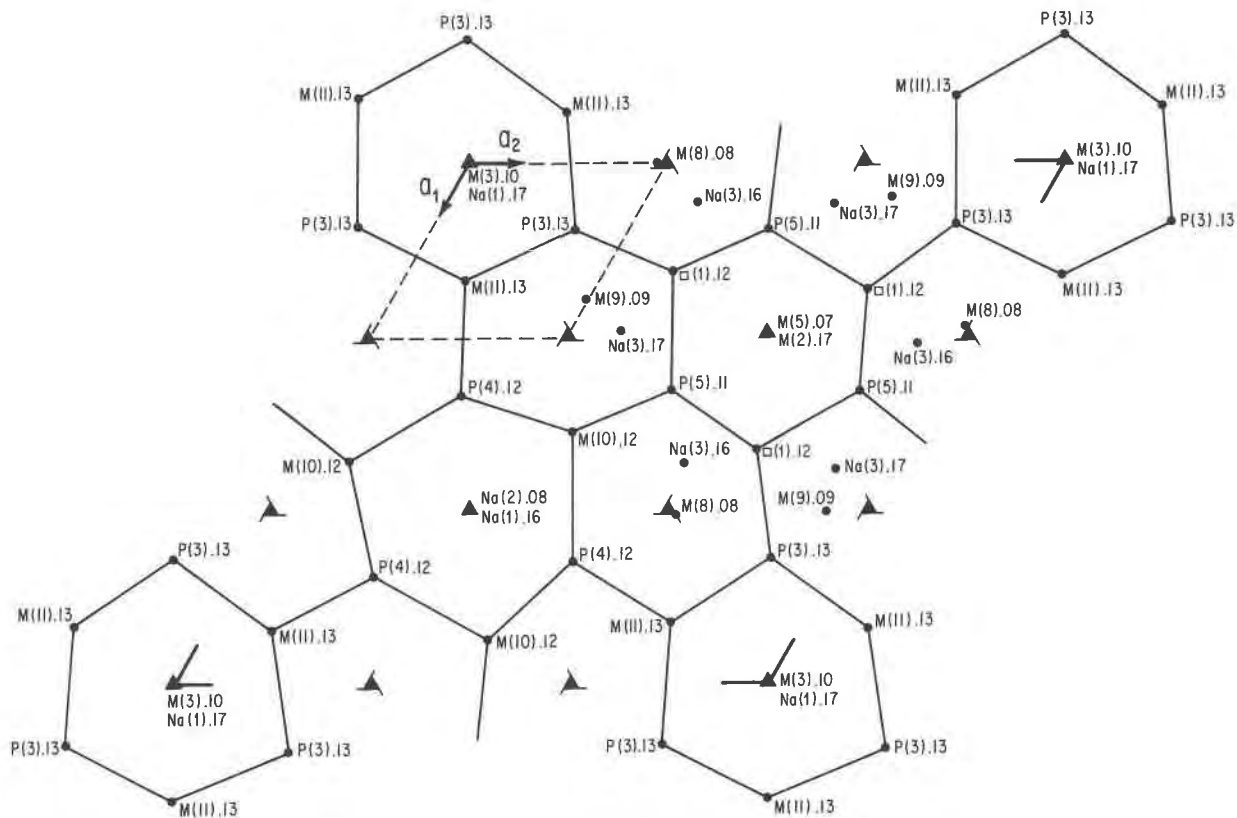


Fig. 3. Continuation of Fig. 2 with  $\alpha$ -Fe(h) cell dashed in. Tier A' at  $z \approx \frac{1}{24}$  includes Na(2), M(3), M(5), M(8), and M(9) and tier A'' at  $z \approx \frac{1}{24}$  includes Na(1), Na(3), and M(2), both tiers at hexagon centers. Tier B' at  $z \approx \frac{1}{24}$  includes P(3), P(4), P(5), M(10), M(11), and  $\square(1)$  at hexagon nodes. The distorted ( $6^3$ ) net is drawn in.

structures is intriguing. Furthermore, these regions in the various structures are well-ordered, whereas disorder occurs in the regions remaining (note especially steenstrupine and cerite); therefore such an intuitive model of clustering and crystal growth—at least for these phases—is appealing.

#### Some other candidates for relation to $\alpha$ -Fe

Table 2 lists cell criteria, differences ( $\Delta$ ), and shortest perpendicular bisections,  $t/2$ , between beads for  $\alpha$ -Fe,

$\text{Ni}_2\text{In}$ , and glaserite [ $\text{K}_3\text{Na}(\text{SO}_4)_2$ ]. These candidates have been frequently used in the literature when crystal-structure types have been compared. Only cations and/or metals are listed and compared. Space groups and bonding characters are quite different among these compounds.

Differences in  $z$  coordinates occur only along the 3-fold rotors at  $(x, y) = (\frac{2}{3}, \frac{1}{3})$  for  $\text{Ni}_2\text{In}$ - $\alpha$ -Fe and glaserite- $\alpha$ -Fe. However, all differences are within  $t/2$ , the perpendicular bisections. This suggests the Dirichlet domains about individual cations and/or metals in all three structure types

TABLE 2. Comparative crystallography of  $\alpha$ -Fe,  $\text{Ni}_2\text{In}$ , and glaserite,  $\text{K}_3\text{Na}(\text{SO}_4)_2$

Rank	$\alpha$ -Fe			$\text{Ni}_2\text{In}$				$\Delta$ ( $\text{\AA}$ )	Glaserite			$\Delta$ ( $\text{\AA}$ )	
1	0	0	0	Ni(1)	0	0	0	0.000	K(3)	0	0	0	0.000
1	0	0	$\frac{1}{2}$	Ni(1)	0	0	$\frac{1}{2}$	0.000	Na	0	0	$\frac{1}{2}$	0.000
2	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{5}{6}$	In	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{3}{4}$	0.426	K(2)	$\frac{2}{3}$	$\frac{1}{3}$	0.683	1.096
2	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{5}{6}$	Ni(2)	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	0.426	S	$\frac{2}{3}$	$\frac{1}{3}$	0.234	0.724
	<i>F</i> 3 <i>c</i>			<i>P</i> 6 <sub>3</sub> / <i>m</i> <i>m</i> <i>c</i>					<i>P</i> 3 <i>m</i> 1				
	$t/2 = 1.24 \text{ \AA}$			$t/2 = 1.28 \text{ \AA}$					$t/2 = 1.64 \text{ \AA}$				
	$a = 4.053 \text{ \AA}$			$a = 4.179 \text{ \AA}$					$a = 5.680 \text{ \AA}$				
	$c = 4.964 \text{ \AA}$			$c = 5.131 \text{ \AA}$					$c = 7.309 \text{ \AA}$				
	$c/a = 1.225$			$c/a = 1.228$					$c/a = 1.287$				
	Thomas (1948)			Laves and Wallbaum (1942)					Okada and Ossaka (1980)				

Note: The references refer to original reports on structures. The hexagonal cell is used in this study for  $\alpha$ -Fe. Differences refer only to the  $c$ -axis translations based on the  $\text{Ni}_2\text{In}$  and glaserite cells, respectively. The perpendicular bisection,  $t/2$ , refers to the closest sequence of beads. All differences  $\Delta$  compare the larger cell with  $\alpha$ -Fe; the remainder is multiplied by the appropriate larger cell translation.

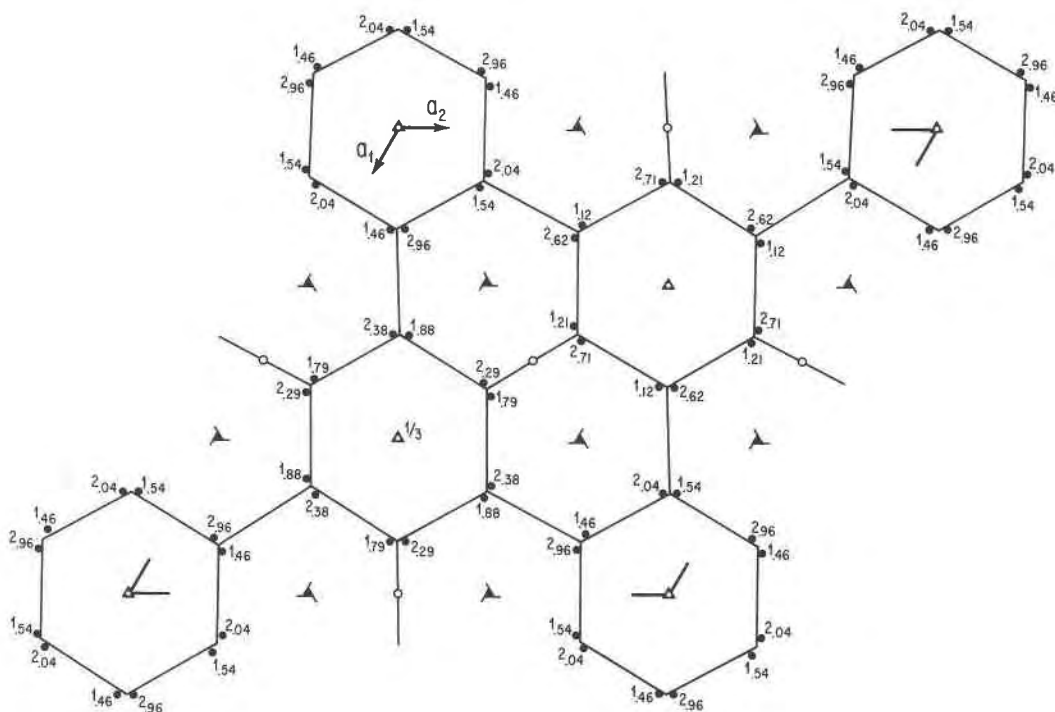


Fig. 4. The ordered vacancies,  $\square(1)$  and  $\square(2)$ , which define termini of P-M-P-M-P stalks are placed in the fillowite unit cell. The distorted ( $6^3$ ) net is drawn in.

have similar faces with somewhat dissimilar relative areas. In this sense, the cations and/or metals are not isomorphic but are certainly related. A more detailed comparative analysis of the Wirkungsbereichen (Dirichlet domains) following Fischer et al. (1971) and Pearson (1985) is now in progress. Here, comparison of the constructed polyhedral domains is important. The large number of unique polyhedral domains in fillowite is a big challenge. For this reason, only the simple polygonal model and perpendicular bisections were used in this study.

I have been re-examining the reported crystal structures of triplite, triploidite, graftonite, arrojadite-dickinsonite, griphite, and garnet. All are very dense (see Moore, 1981, for a short review on these dense structures). It is becoming increasingly apparent that they are elaborations of stalklike units that pack in glaserite-, palmierite-like cells but possess even lower symmetry groups. Such relationships are usually masqueraded, and cell transformations can be very complex indeed.

### SUMMARY

The enormous fillowite cell includes  $18(\text{Na}_2\text{CaMn}_3)(\text{Mn}_4\text{P}_6)\text{O}_{24}$  where the cation beads in the first parentheses are included in rods I and Ia and beads in the second parentheses are included in rod II. Twelve beads make up the  $c$ -axial repeat, which includes two unique cation vacancies in rod II. Poles of the rods project on (001), and they can be conveniently related to the  $\alpha$ -Fe cell in hexagonal setting with  $a(h)_\alpha = 4.05$  and  $c(h)_\alpha =$

$4.96 \text{ \AA}$ , space group  $R\bar{3}c$ . The cations in these structures are arranged according to body-centered cubic packing. The axial relation is  $a(F)_\alpha = 3a(h)_\alpha$  and  $c(F)_\alpha = 6c(h)_\alpha$ , where F denotes the  $\alpha$ -Fe multiple cell to be compared with fillowite. Note that  $3^2 \cdot 6 = 54$  corresponds to the number of  $\alpha$ -Fe cells or  $54 \cdot 6 = 324$  cations as found in fillowite, including the ordered vacancies. The ratio  $c(F)/a(F) = 2\sqrt{3}/\sqrt{2} = 2.450$  compares with  $c/a = 2.847$  for fillowite, a 14% dilation for the latter along  $c$  relative to  $a$ . This dilation is believed to result from laminations of many of the added oxide anions in the plane parallel to (001) to derive fillowite from  $\alpha$ -Fe. The three unique rods in fillowite are organized according to the  $\alpha$ -Fe structure in multiple hexagonal orientation. They are  $(00z) \times 3$  for rod I,  $\frac{1}{3}(11)z = (\frac{1}{3}\frac{1}{3}z) \times 6$  for rod Ia and  $\frac{1}{3}(\frac{2}{3}\frac{1}{3})z = (\frac{2}{3}\frac{1}{3}z) \times 18$  for rod II. The fillowite cell can be considered as the composition  $\{p3\} \cdot \{R\} \cdot \{\bar{1}\} = R\bar{3}$  composed of  $3 \cdot 3 \cdot 2 = 18$  elements.

Dirichlet domains based on perpendicular bisection,  $t/2$ , of the ideal  $\alpha$ -Fe centroids in hexagonal representation and expanded to the complex fillowite cell, lead to  $t/2 = 1.47 \text{ \AA}$  in the (001) plane and  $t/2 = 1.81 \text{ \AA}$  parallel to the  $c$  axis. The net is ( $6^3$ ), but its Dirichlet domain is ( $6^3$ ). All cation beads fall within their respective domains for a fillowite-shaped cell. The greatest cation deviant is Na(3) with  $\Delta = 1.34 \text{ \AA}$  from its ideal  $\alpha$ -Fe derived centroid.

It is believed that the ordered cation vacancies,  $\square(1)$  and  $\square(2)$ , are the cause for the enormous ( $V = 8799 \text{ \AA}^3$ )

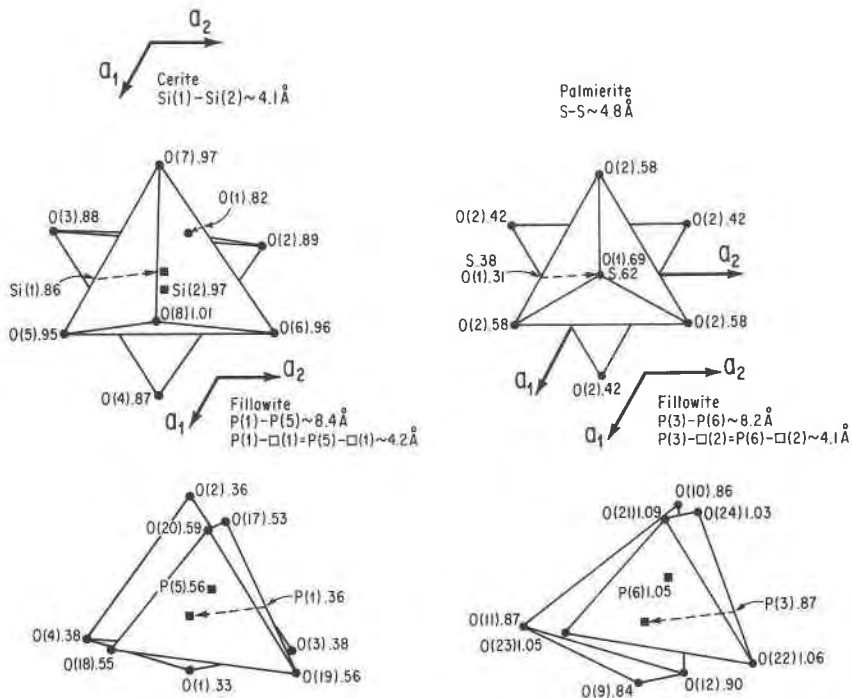


Fig. 5. Eclipsing of tetrahedral termini of stalks in cerite, palmierite, and fillowite.

cell in fillowite. These vacancies create *stalks* of five continuous polyhedral connections along [001] of the type P–M–P–M–P. Such stalks result in the seeming cell complexity. Related “simple” structures include  $\text{Ni}_2\text{In}$ , glaserite  $[\text{K}_3\text{Na}(\text{SO}_4)_2]$ , and palmierite  $[\text{K}_2\text{Pb}(\text{SO}_4)_2]$ , the last which has stalks S–K–Pb–K–S. Structures believed to contain stalklike units with cells often of lower symmetry but of complexity similar to or greater than that of fillowite include triplite, triplodite, graftonite, arrojadite-dickinsonite, and griphite. Cerite, a complex structure, contains similar stalks of the type Si–REE–REE–REE–Si. In all cases examined, the  $(\text{TO}_4)$  tetrahedral termini form

staggered to eclipsed or near-eclipsed arrangements with similar tetrahedra, thus terminating a structural rod into a stalk of finite length. Knowledge of the stalks composed with the appropriate symmetry group may lead to cells of awesome complexity but whose underlying principles are based on relative simplicity.

Several years ago, I found a tree that illustrates the transition from simple  $\rightarrow$  complex. Burdett (1988) illustrated a version of this tree in a review and noted that I would soon publish it. So here in Table 3 I give it in publication!

#### ACKNOWLEDGMENTS

This study stems from a mosaic of variegated information, which appears in the references. The present study acknowledges the National Science Foundation Grant EAR-87-07382.

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TABLE 3. Tree for cell contents from  $\alpha$ -Fe metals to fillowite cations

Contents	Substance	Space Group
2	$\alpha$ -Fe	$Im\bar{3}m$
6	$\alpha$ -Fe hexagonal setting	$R\bar{3}c$
1	(FeFe) (FeFe) <sub>2</sub>	
2	$\text{Ni}_2\text{In}$	$P6_3/mmc$
1	(NiNi) (NiIn) <sub>2</sub>	
1	glaserite $\text{K}_3\text{Na}(\text{SO}_4)_2$	$P\bar{3}m1$
1	(KNa) (KS) <sub>2</sub> O <sub>6</sub>	
18	fillowite $\square_2\text{Na}_2\text{CaMn}_2^+(\text{PO}_4)_6$	$R\bar{3}$
18	$(\text{Na}_2\text{CaMn}_3) (\text{Mn}_2\square_2\text{P}_6)\text{O}_{24}$	
54	(MM) (MT) <sub>2</sub> O <sub>6</sub>	



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MANUSCRIPT RECEIVED AUGUST 19, 1988

MANUSCRIPT ACCEPTED MARCH 21, 1989