An Alternative Description of the Paulingite Structure

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The paulingite structure can be described as an invariant transformation of the gismondine structure. Packets of a fourling construction of the gismondine structures, which is closely related to the merlinoite structure, are used to build the structure of paulingite as an interpenetrating sixling.

The paulingite structure is considered to be one of the most complex of all silicate structures. The cubic unit cell, with $a = 35.09$ Å, contains 672 silicon and aluminum atoms, 1344 oxygen atoms in the zeolitic framework, and about 800 more atoms in the cages. Samson *et al.* (*1*), who determined the composition and structure (space group $Im3m$), describes it as built up of the structural units A, B, C, $D_{1,2}$, and $H_{1,2}$. Of these, A has been observed in Linde A (*2*) and B in ZK-5 (*3*), but the configurations C, $D_{1,2}$, and $H_{1,2}$ seem to be unique for paulingite.

With due respect to Samson, who showed tremendous enterprise in solving a structure of such formidable size, we cannot help but find his original description difficult to understand. After deriving the relationship between gismondine, phillipsite, and merlinoite (*4, 8*), we think that the giant structure of paulingite can now be described in a very simple way.

In Fig. 1 we show how a gismondine (*5, 7*) unit repeats by cyclic translation to a fourling unit, with slabs of phillipsite (*6*) formed in the twin planes and a large column of the merlinoite structure in the center. In Fig. 2 we show in projection that part of the gismondine fourling which is used to build the structure of paulingite. In Fig. 3a two of these packets are shown in the form of a model with only (Si, Al) atoms.

By using the merlinoite unit cell orientation, it is easy to find the matrix which interrelates the atomic positions of these different structures:

$$\begin{matrix} \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & \overline{\frac{1}{2}} & 0 \\ 0 & 0 & \frac{1}{2} \end{matrix}$$

A "unit cell" similar to that for merlinoite[1] may be derived from this matrix for the regular tetrahedra in Fig. 2. This has $a = 2d(\sqrt{3} + 1)$ and $c = 4d(\sqrt{2}/\sqrt{3})$, where d is a tetrahedral edge, and the atomic coordinates are

$$x = \frac{\sqrt{3}}{6(\sqrt{3} + 1)}, \qquad y = \tfrac{1}{4}, \text{ and } z = \tfrac{1}{6}.$$

The 7×96 (Si,Al) atoms are divided into two sets of positions, 2×48 and 6×96. The

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[1] Note that the unit in Fig. 2 is not exactly merlinoite, because the eight tetrahedra in the corners still have to be inverted.
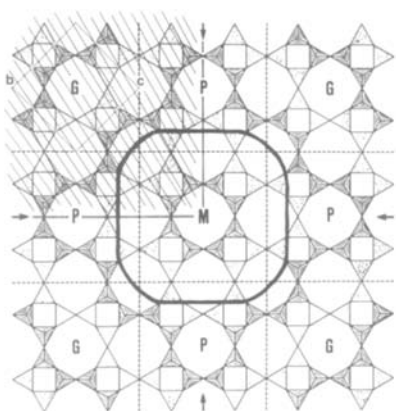
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FIG. 1. A fourling construction of the gismondine structure (shaded, upper left) which gives the phillipsite and merlinoite structures. The frame in the center contains a column of the merlinoite structure and the twin planes (arrowed) contain the phillipsite structure.
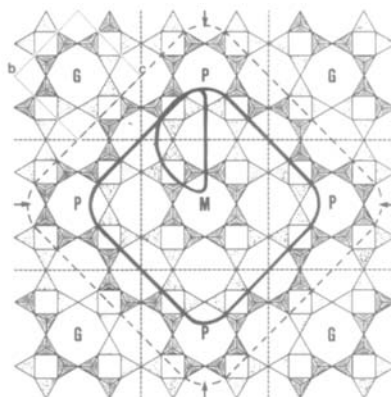

FIG. 2. The smallest frame represents the gismondine unit used to calculate the coordinates for paulingite structure. The middle-sized frame shows, in projection, the sixling unit that builds into the paulingite structure (see blue unit in Fig. 3). Such sixling units interpenetrate so that even larger units of the fourling construction (framed by dashed lines) can be found in paulingite (see Fig. 3).

eight atoms in the asymmetric unit can be seen in Fig. 2 and in the blue unit packet of Fig. 3. By using the matrix given above a general expression for the (Si,Al) atom coordinates of the paulingite structure is obtained:

$$x = \frac{n}{42}; n = 13, 17, 13, 19, 17, 13, 11, 7;$$

$$y = \frac{n + \sqrt{3}}{42};$$

$$n = -12, -12, -12, -6, 6, 6, -6, -6;$$

$$z = \frac{n + \sqrt{3}}{42};$$

$$n = 6, -6, -6, 0, 0, 0, 0, 0.$$

These coordinates are compared in Table I with those of Samson et al. (1).

The smallest unit of Fig. 2, which corresponds to the assymmetric unit of the paulingite structure, is a piece of the gis-

TABLE I

|	Coordinates calculated from regular tetrahedra			Samson's coordinates			Coordinates calculated from the gismondine structure		
	x	y	z	x	y	z	x	y	z
1	0.310	0.245	0.184	0.3137	0.2500	0.1863	0.3130	0.2497	0.1869
2	0.405	0.245	0.102	0.4021	0.2500	0.0979	0.4013	0.2497	0.0987
3	0.310	0.245	0.102	0.3132	0.2498	0.0979	0.3133	0.2433	0.0932
4	0.452	0.105	0.041	0.4558	0.1072	0.0443	0.4559	0.1069	0.0442
5	0.405	0.184	0.041	0.4019	0.1782	0.0448	0.4007	0.1748	0.0497
6	0.310	0.184	0.041	0.3126	0.1785	0.0441	0.3120	0.1793	0.0432
7	0.262	0.102	0.041	0.2592	0.1073	0.0445	0.2581	0.1104	0.0491
8	0.167	0.102	0.041	0.1708	0.1076	0.0441	0.1701	0.1069	0.0442
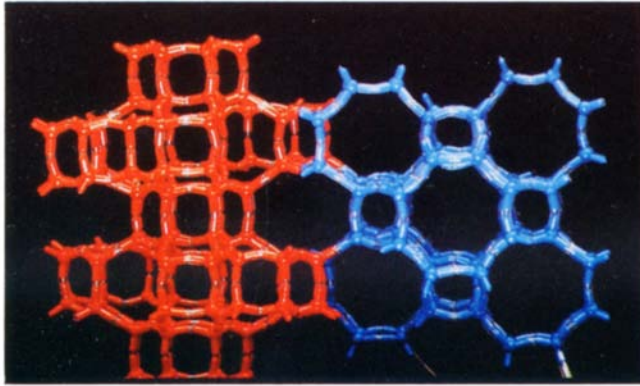
FIG. 3. Two fourling units of the gismondine structure which build packets of the paulingite structure.

mondine structure which, in a recent refinement (5, 7), was reported as pseudotetragonal, with the monoclinic cell $a = 10.226$, $b = 10.432$, $c = 9.884$ Å, and $\beta = 88°19'$, space group $I2$.

The matrix which interrelates the coordinates of the gismondine and the paulingite structures now becomes

$$\begin{array}{ccc} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} \end{array}$$
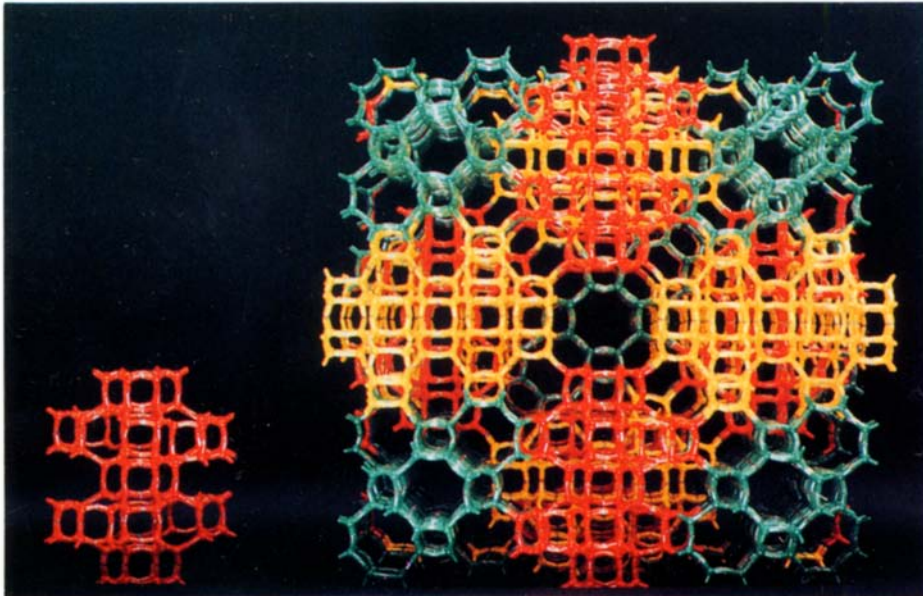

FIG. 4. The structure of paulingite, with only the (Si, Al) atoms shown. The red unit is the fourling of the gismondine structure (shown in Fig. 3) which builds into the paulingite structure by a reflection translation operation, shown by the red, green, and yellow units, which are identical with the blue. The green units are at the corners of the cubic unit cell.

The coordinates, shown in Table I, are calculated after allowing for the appropriate coordinate system shifts. The agreement with the observed coordinates for paulingite is excellent, and shows that the symmetry of gismondine is conserved during this transformation, or very nearly so.

The full structure of paulingite is shown in Fig. 4. The green, red, and yellow structure packets are all identical fourling units of the gismondine structure, put together with a reflection translation operation. This provides an excellent example of the general description of crystal structures formulated recently (8), in which it is said that a part of a structure is used in various operations to yield another (more complex) structure. Of the new structure obtained a new part may be repeated to form a new structure again etcetera.

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