AN ICOSAHEDRAL SILICATE QUASICRYSTAL MODEL

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ABSTRACT

Putting silicon atoms in the corners of a regular pentagonal dodecahedron as well as oxygens in the mid-points of edges, silico-dodecahedrane units are obtained. These, in turn, linking together by face sharing, provide a "decoration" of the icosahedral PENROSE-MACKAY quasilattice. Thus, a silicate quasicrystal model is obtained. Some of the properties and relations of this hypothetical structure are discussed in the paper.

INTRODUCTION

The notion of quasilattice has been introduced by ALAN MACKAY (1981), who described it as a non-periodic space filling composed of two kinds of rhombohedra. The two different rhombohedral unit cells, by repeated juxtaposition, fill the space without gaps and overlaps in such a way that the structure exhibits icosahedral orientational symmetry (i.e. the characteristic directions are parallel to the axes of a regular icosahedron; a mathematically rigorous association of the icosahedral point group to such type of quasilattices has first been given by KRAMER and NERI 1984).

This construction arose from purely mathematical considerations, and as MACKAY (1981) admitted in his paper, "we cannot find any evidence for the actual appearance of our pentagonal structure". However, the experimental discovery of Al-Mn alloys exhibiting icosahedral diffraction symmetry (SHECHTMAN *et al.* 1984) changed the situation radically. Mackay's idea became the starting point of a series of models attempting to explain the structure of such alloys (see e.g. LEVINE and STEINHARDT 1984, 1986; JARIĆ 1986; KATZ and DUNEAU 1986; SOCOLAR and STEINHARDT 1986; GRAMLICH 1987; PRINCE 1987; YANG and KUO 1987; YAMAMOTO and HIRAGA 1988; JANOT *et al.* 1989). LEVINE and STEIN-HARDT (1984, 1986) coined the name "quasicrystal" (quasiperiodic crystal) for such structures. Now this term is used in a very broad sense independently of the contradictions which arise theoretically and conceptually (PAULING 1987; SENE-CHAL and TAYLOR 1990).

In what follows, we raise the question of what the structure of a silicate quasicrystal may be like. The question is not totally meaningless, since the plenty of quasicrystalline samples obtained in various laboratories of the world from various alloys can give the impression that quasiperiodicity is reserved by Nature for alloys only. In an earlier issue of this journal we shortly discussed a related problem (GÉVAY and SZEDERKÉNYI 1987—1988). In the present note it is shown

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that, at least theoretically, such construction is possible. Our arguments are largely geometrical and the question of a possible crystal chemical or even mineralogical reality of the model is left open.

DESCRIPTION OF THE SILICATE QUASICRYSTAL MODEL

A hierarchical organization is assumed, thus we take the individual levels one after the other.

Our basic unit is the silica tetrahedron $(SiO_4)^{4-}$ which is common in almost all silicates. These tetrahedra are assumed to link together forming five-membered rings by corner sharing. Since we consider regular pentagonal rings, this point is a definite departure from classical crystal chemistry in that such rings are unknown in the world of minerals, although *irregular* pentagonal rings do occur (ZOLTAI and STOUT 1984). (This lack is clearly related to the crystallographic prohibition of pentagonal symmetry.) On the other hand, the status of our regular pentagonal ring is rather peculiar, as we shall see at once. ZOLTAI and BUERGER (1960) performed electrostatic energy calculations for rings with different numbers of tetrahedra taking into consideration several possible symmetries of the tetrahedral arrangements. They found that for the symmetry that is also relevant to our case (*Fig. 1*), five tetrahedra per rings is the energetically most favourable number. We consider this result as somewhat supporting our conception.
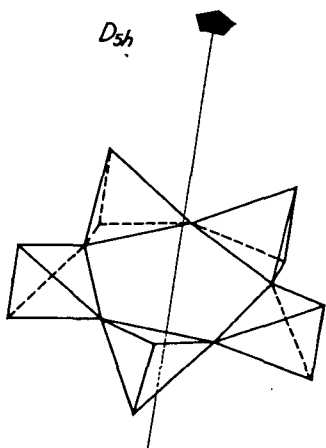

Fig. 1. The five-membered ring of silica tetrahedra. Symmetry of this arrangement is D_{5h} - $\overline{10}m2$

At the next stage these tetrahedral pentagons are considered as faces of a regular pentagonal dodecahedron (*Fig. 2*). This idea originates from our work on a related field (GÉVAY and KEDVES 1990) where we assumed a hydrocarbon $C_{20}H_{20}$ molecule in the same manner, i.e. at the vertices of the dodecahedron carbon atoms are located. In the meantime we got to know that our hypothetical dodecahedrane was an existing compound synthesized recently and some of its properties had already been established (PAQUETTE *et al.* 1981). It seems quite natural to transmit the schema to silicates taking into account the close chemical relationship between carbon and silicon.

Thus, in our "silico-dodecahedrane" the silicon atoms are located at the vertices and three of the oxygens coordinated around a silicon atom are at the mid-points of edges and every fourth oxygen is directed outwards. The formula of the frame can be given as $(Si_{20}O_{50})^{20-}$.
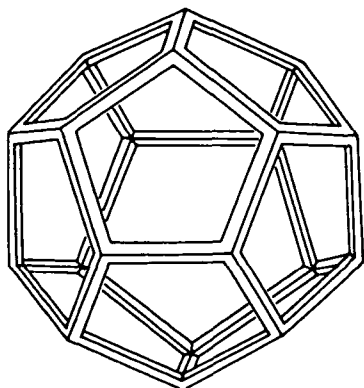
Fig. 2. Regular pentagonal dodecahedron, the geometric skeleton of the silico-dodecahedrane $(C_{20}O_{50})^{20-}$ units.

There are numerous ways to go on further. For the bio-organic case work is in progress (KEDVES 1988; GÉVAY and KEDVES in preparation.) Here we consider one way of linkage of the silico-dodecahedrane units, notably that by face sharing (this does not contradict Pauling's rules, as the dodecahedron here is not a coordination polyhedron). Even face sharing itself offers a variety of possibilities to form chains of dodecahedra having face in common. Taking into account that the interfacial angle of a regular pentagonal dodecahedron is π-arctan 2 = 116°34' (the interaxial angle of five-fold rotations is arctan 2 = 63°26'), the only values of the angle that is formed by the centers of three consecutive dodecahedra in a chain are 63°26', 116°34' and 180°. These angles are realized in a rhombic arrangement of 16 dodecahedra (*Fig. 3*) at the acute angle, obtuse angle and at the edge of the rhombus, respectively (see the dotted lines).
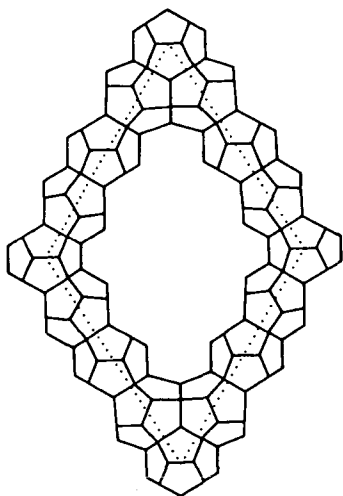

Fig. 3. The „golden rhombus" composed of 16 dodecahedral units. The dodecahedra are drawn as non-transparent solids for the sake of better visualization. The abstract rhombus skeleton is indicated by dotted lines.

We obtained a "golden rhombus" of silico-dodecahedrane units, as the ratio of its diagonals is $\tau = (1+\sqrt{5})/2 \approx 1.618$, the golden section (actually, tan 1/2 arctan2 = τ). At the acute angles of this rhombus three adjacent dodecahedra have pairwise one face in common, hence some distortion is to be presupposed: the interfacial angles at the common faces must be somewhere between 116°34' and 120°. (On the other hand, small distortions occur at the "edge-dode-

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cahedra" as well, since the tetrahedral and dodecahedral geometry are not perfectly compatible, being the relevant angles 109°28' and 108°, respectively. We assume that the Si-O-Si bond chains can relax to an appropriate state so that the structure will be relatively strain-free).

Now the rhombuses can be the faces of two different rhombohedra, with acute angle or with obtuse angle meeting at the poles (*Fig. 4*). These rhombohedra correspond just to the unit cells of the Mackay quasilattice, the copies of which
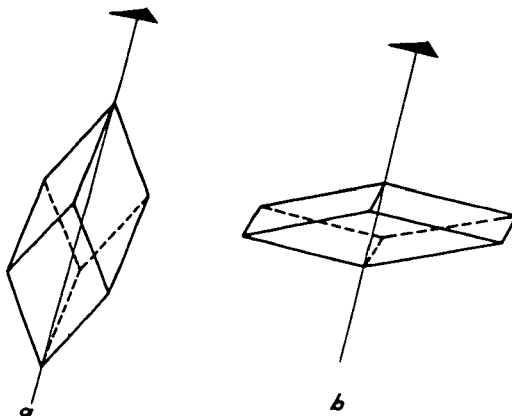

Fig. 4. The prolate (a) and oblate (b) rhombohedron composed of golden rhombuses. Their volume ratio as well as ratio of frequency in the icosahedral Mackay quasilattice is τ.

"tile" the three-dimensional space. The icosahedral orientational symmetry appears as follows. There are 10 distinct orientations (up to central inversion) for the three-fold axes of rhombohedra — these are just the directions of three-fold rotations of a regular icosahedron. On the other hand, the directions of edges of the rhombohedra are parallel to the five-fold axes of icosahedron (the axes of icosahedron are shown in *Fig. 5*). Thus the chemical bonds fit to definite directions,
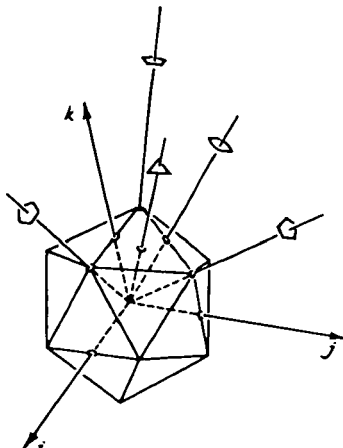

Fig. 5. Rotation axes of the icosahedron, the dual counterpart of the regular pentagonal dodecahedron.

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hence the bond orientation order (declared as one of the defining properties of a quasicrystal by LEVINE and STEINHARDT 1986) is ensured.

There are a number of papers discussing various properties of abstract (icosahedral) quasilattices (see e.g. the references in this note). Here only we note that in one of the simplest cases there are altogether (up to rotations and inversion) 24 distinct arrangements of cells ("vertex neighbourhoods"), which involve from four to twenty rhombohedra (KATZ and DUNEAU 1986, GINGL 1988). At the same time, it is an interesting fact that in this case the average number of cells meeting at a vertex is 8 (cf. the classical lattices !) (GINGL 1988.)

It is somewhat difficult to illustrate packing of the rhombohedra. Here we show (*Fig. 6*) an appropriate projection of one layer of the rhombohedral packing which provides just the famous PENROSE pattern (a two-dimensional quasilattice with decagonal orientational symmetry: the prototype for MACKAY's construction that has therefore been called 3-dimensional PENROSE lattice).
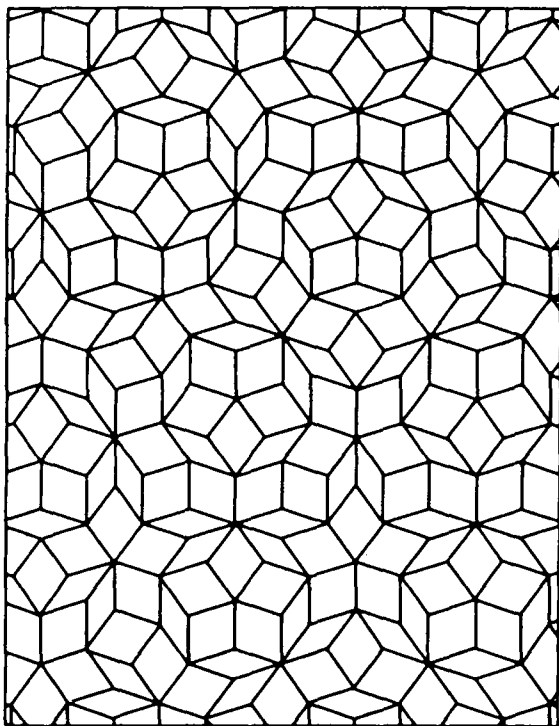

Fig. 6. The 2-dimensional Penrose quasilattice.

To sum up, the levels of the hierarchy are as follows:
(a) The silica tetrahedra $(SiO_4)^{4-}$;
(b) the regular pentagonal ring of tetrahedra;
(c) the regular pentagonal dodecahedron $(Si_{20}O_{50})^{20-}$;
(d) the "golden rhombus" composed of 16 dodecahedra;
(e) rhombohedra, prolate and oblate;
(f) the silicate quasicrystal itself.

The reverse conception (which is more usual in solid state physics) is as follows. Take an abstract quasilattice (i.e. the bare geometric skeleton) and decorate it by *atoms* (or *clusters of atoms*). In this sense our silicate quasicrystal is an icosahedral quasilattice decorated appropriately by silico-dodecahedrane units. "Appropriateness" may mean a lot of things, but let us see here some elementary geometric relations.

Observe that the symmetry elements of the lattice as well as of the decorating dodecahedra coincide (apart from small local distortions that may occur). Furthermore, the rather elementary requirement is met that the silico-dodecahedrane units have enough room within the rhombohedra (that is why the rhombohedron edges should be assumed to consist of three dodecahedra: the poles of the oblate rhombohedron are rather close to each other).

This is the point to mention the free oxygen bonds. Our quasilattice is not a pure $(SiO_2)_{\infty}$ structure, because not all corners of the dodecahedra are shared by other dodecahedra. Thus, one should suppose presence of cations compensating the net negative charge of the frame.

SOME FURTHER REMARKS AND CONCLUSIONS

It would be difficult to assign our silicate to any of the traditional classes of silicate structures. It is not a proper ring silicate, because a five-membered group is not an isolated unit here but part of a polyhedral cage (the difference is reflected in the distinction between the terms *ring* and *loop* (ZOLTAI and STOUT 1984); in our case *loop* would be more suitable). With the dodecahedra as repeating units, this structure is similar to, for example, the well known sodalite structure where the characteristic units are truncated octahedra. But it is not a proper network silicate either, because of the cavities within the rhombohedra (actually, as YANG and KUO (1987) observe, in an icosahedral quasilattice the prolate rhombohedra form the main skeleton and the oblate rhombohedra fill the empty space left by the former). Thus, it could perhaps be termed as a "quasi-network" silicate (or quasiperiodically polymerized silicate).

On the other hand, like in network silicates, we assume the possibility of substitution of silicon by other suitable cation (e.g. Al^{3+}) in the tetrahedral sites, with simultaneous appearance of the necessary charge compensating secondary cations.

What is more, just as we exploited the analogy between carbon and silicon, one may take into consideration the Si-Ge analogy as well. Indeed, as classification of the silicate minerals served as a pattern for classification of germanates (STRUNZ 1960), it is natural to suppose that our model can be considered a hypothetical germanate quasicrystal as well.

Some of the features of this structure, not discussed here, provides analogies to other non-classical structures. The well-known self-similarity property as well as the hierarchical organization relates it to the structure discussed e.g. by SCHNEER (1988). The unit $(Si_{20}O_{50})^{20-}$ might well be a building element of less polymerized structures, or of structure built by other construction principles (GÉVAY and KEDVES 1990), etc.

In sum, we demonstrated geometrically that a certain variant of quasicrystalline silicate structure is possible. Although we did not apply arguments that would go beyond the limits of a field which might be called a "solid state geometry", our hope is that the model will bring us closer to the reality of non-metallic quasicrystals.

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