

QUASICRYSTALS AND THEIR SPONTANEOUS FORMATION POSSIBILITIES IN THE NATURE

G. GÉVAY, T. SZEDERKÉNYI

Department of Mineralogy, Geochemistry and Petrography
Attila József University

ABSTRACT

Quasicrystals are a recently (1984) discovered family of structures producing X-ray diffraction diagrams with five-fold symmetry. This non-crystallographic symmetry can be explained by supposing that the strict periodic order is replaced here by a weaker order, called quasiperiodicity. Some of their properties as well as the possibility of formation in natural geological processes are discussed briefly in the paper.

A BRIEF INTRODUCTION TO QUASICRYSTALS

Quasicrystals were discovered by SHECHTMAN *et al.* (1984). A puzzling aspect of this discovery is that the BRAGG diffraction diagram of quasicrystals consists of sharp spots that indicates long-range order, however, it exhibits *five-fold* rotational symmetry. It is well known that this kind of symmetry is forbidden by the fundamental laws of classical crystallography (BARLOW's theorem, COXETER, 1961). Thus it is supposed that we are facing a new type of order, called quasiperiodicity (ROMERIO, 1971). Indeed, as it turned out, the mathematics of diffraction does not require strict periodicity in order to produce sharp peaks, but quasiperiodicity is sufficient (LEVINE and STEINHARDT, 1984). This latter means, in a descriptive sense, that a quasiperiodic structure is built of two (or more) different unit cells instead of one, such that the ratio of their corresponding geometric parameters (e.g. volume) is irrational number (and so is their relative frequency, i.e. occurrence in at least in principle, an infinite structure). Thus, the translational order is lacking here. On the other hand, the long-range rational order is replaced by a long-range "orientational" order. This means that the characteristic bonding directions fit to some straight lines of different orientation.

A two-dimensional model of such a quasiperiodic structure is visualized in *Fig. 1*. It is directly seen that picking out any lattice point and considering the densest packed straight lines passing through it, these lines succeed one after the other by an angle $360/5 = 72^\circ$. "Thus, the symmetry of this "quasilattice" reveals itself in such an indirect way (or, as mentioned above, through the symmetry of its diffraction pattern).

In three dimensions, taking another such pentagyre through the same point, further five-fold axes are induced, thus we have altogether six pentagyres. Actually, ten three-fold axes and fifteen two-fold axes will be generated at the same time. This configuration of symmetry elements corresponds just to the point group consist-

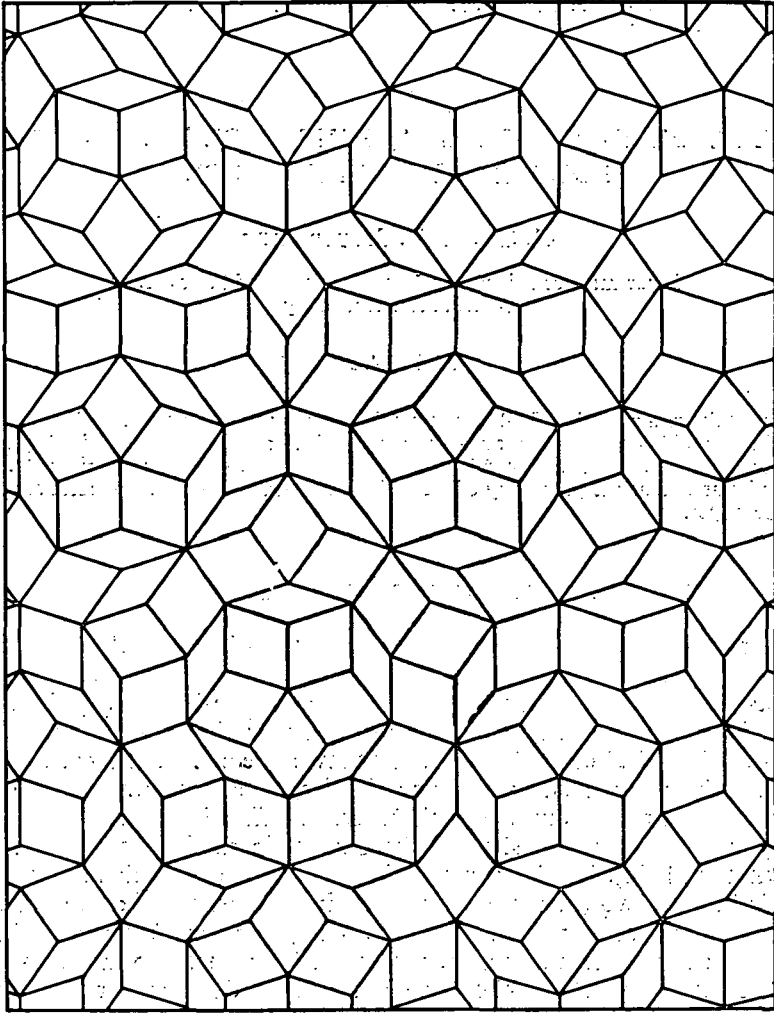


Fig. 1. A two-dimensional quasicrystalline structure: the Penrose pattern

ing of all rotations of an icosahedron (Fig. 2), or of a regular pentagonal dodecahedron (Fig. 3). So, these two regular polyhedra (Platonic solids), exorcised from the classical crystallography, appear in the geometry of quasicrystals. The symmetric axes listed before can be more easily perceived on a combination of these two Platonic solids (Fig. 4), which is an intermediate form recalling the cubooctahedron of the classical crystals. The stereographic projection of the point group $I-235$ considered is shown in Fig. 5. This may be regarded as a hemihedral "quasicrystal class" and, as it contains only rotational axes, an enantiomorphic one. Adding inversion centre to it, fifteen additional mirror planes are induced and the holohedral class $I_h - m\bar{3}5$ is obtained (Fig. 6), which is the full symmetry group of the icosahedron. The corresponding general (i.e. having faces of maximal number) "quasicrystal form" consists of 120 faces ("hecatonicosahedron", Fig. 7). This form is obtained from a single face

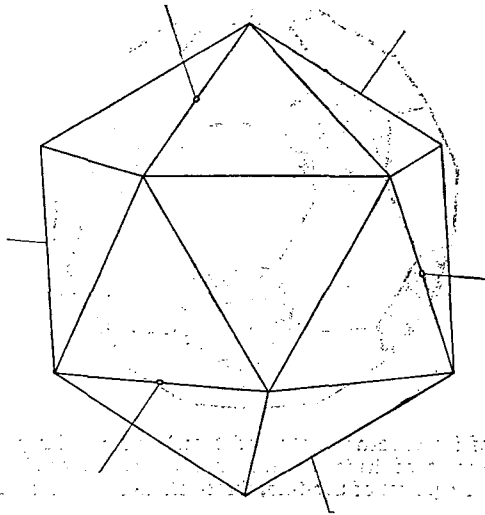


Fig. 2. Icosahedron, representing quasicrystalline symmetry

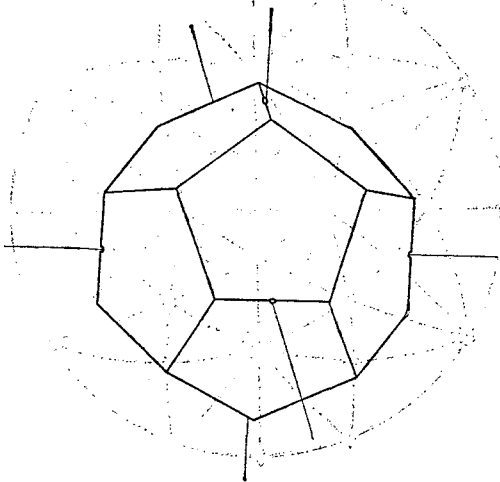


Fig. 3. The regular pentagonal dodecahedron

situated so that it is orthogonal to none of the symmetry elements of I_h : in this case each element of the point group will multiply it.). For completeness, we note that the 3-dimensional quasilattice of icosahedral symmetry is built also of two unit cells, acute and obtuse rhombohedra with edges of equal length (just as the two-dimensional pentagonal quasilattice is built of acute and obtuse rhombuses, cf. Fig. 1). Moreover, any section through a lattice point and orthogonal to a five-fold axis provides just the PENROSE pattern (for further details of this quasilattice see e.g. GINGL, 1988).

As a matter of fact, the "shechtmanite" $Al_{0.86}Mn_{0.14}$ described by SHECHTMAN *et al.* (1984) exhibits this icosahedral symmetry and phases like that have been called

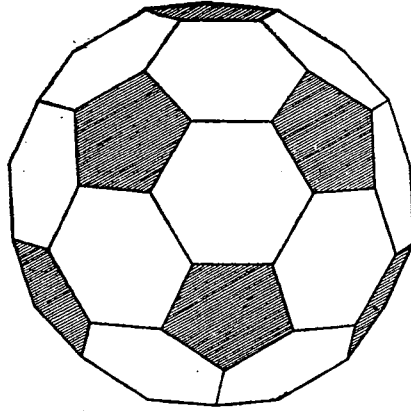


Fig. 4. A combination of icosahedron (unshaded faces) and regular pentagonal dodecahedron (shaded faces). The central points of shaded faces, unshaded faces and of edges between two unshaded faces are the emergence points of five-fold, three-fold and two-fold axes, respectively

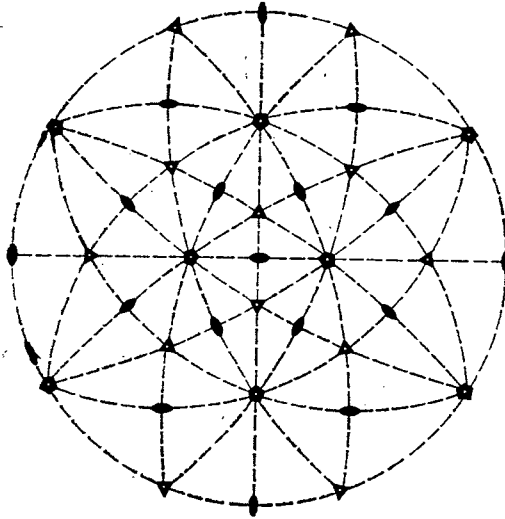


Fig. 5. Stereographic projection of the point group I—235.

since then icosahedral phase (IP). One should note, however, that this is not a unique type of quasicrystals: there are other phases which are characterized by ten-fold (BENDERSKY, 1985), moreover, by twelfefold (ISHIMASHA *et al.* 1985) rotational axis.

CONSIDERATIONS ON THE FORMATION OF QUASICRYSTALS

The first publications on quasicrystals described preparations produced in laboratory conditions. Naturally arises the question, in what circumstances can quasicrystals be expected to form spontaneously in Nature. Such a possibility cannot

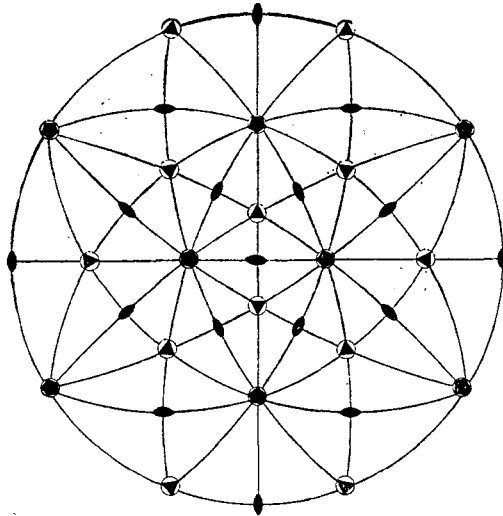


Fig. 6. Stereographic projection of the point group $I_h-m\bar{3}5$.

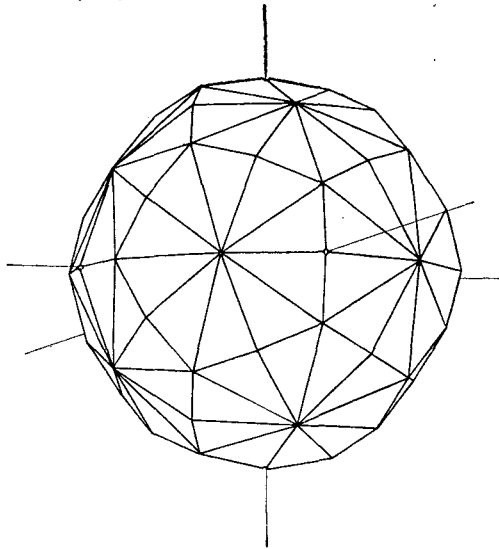


Fig. 7. Hecatonicosahedron, the form of maximal face number corresponding to the point group $I_h-m\bar{3}5$. It has 120 faces, 180 edges and 62 vertices. It is an icosahedral analogue of the hexakis octahedron of cubic symmetry

be excluded *ab ovo*, as it is indicated by some analogies in connection with other "exotic" structures, as follows.

In a sense, silicon atoms in octahedral position can be considered strange enough. However, stishovite, a high pressure modification of SiO_2 known from the Arizona meteor crater (STRUNZ, 1966) contains $[SiO_6]$ octahedra (type rutil). In extreme conditions, silicon atoms are forced into such a coordination (formation at 1200—

1400 °C, > 160,000 atm), though, here is no indication of violating the strict periodicity.

A real deviation from strict periodicity can be observed in a continuously broadening group of structures which are called modulated structures. Modulation means that a periodic perturbation occurs in the lattice (GÜGGENHEIM and EGGLETON, 1987). These phases were discovered in the sixties on the basis of the observation that in their diffraction diagram extra (satellite) reflections could be found. The satellite reflections cannot be indexed in the usual way, actually, they often have irrational indices, violating the classical law of rationality (DE WOLFF, 1974). The irrationality is considered as a consequence of incommensurability between the translational and modulation period (i.e. their ratio cannot be represented as a ratio of two integer numbers). Since the discovery, a number of modulated crystals have been found and described (see e.g. the review by GÜGGENHEIM and EGGLETON, 1987), indicating that the world of minerals is more abundant than one might imagine merely on the basis of classical crystallography.

The relation of modulated (incommensurate) crystals and quasicrystals is still a debated problem. However, it is worth pondering on the possibility of proper quasicrystals among minerals. For example, BOISEN JR. and GIBBS (1985) speculate on a possible quasicrystalline form of skutterudite. In the skutterudite ($\text{Co}_4\text{As}_{12}$), there are icosahedral units As_{12} which, combining with interstitial Co atoms, form a lattice of cubic (m3) symmetry. The authors cited refer to the fact that the dominant crystal form of skutterudite, the pyritohedron, closely resembles the regular pentagonal dodecahedron. Their supposition that this mineral may have passed through a quasicrystalline state prior to its final crystallization, is in accordance with OSTWALD'S rule. By this rule, a stable modification often does not form directly, but the action progresses through successive steps in which intermediate phases appear. Its application here is justified by the observation that formation of quasicrystals is a non-equilibrium process and they are generally in metastable state. It is also worth mentioning that skutterudite has a metalloid structure and the quasicrystalline substances (according to our present knowledge) are generally alloys. Thus the crystal chemical resemblance also supports the idea due to the above authors.

Let us see now the laboratory formation circumstances of quasicrystals. By now a series of methods is known, see RONCHETTI (1987). From our point of view, the most important methods are those in which rapid melt cooling (quenching) is applied (with often a simultaneous spinning of melt). A common and important feature of these and other methods is the high nucleation rate in comparison with growth rate. This seems to be a rather characteristic condition for the formation of quasicrystals.

In what follows we try to give some geological examples where physico-chemical conditions mentioned just above might be expected to favour formation of natural quasicrystals.

A. *Rapid cooling* resulting in highly supercooled melt in which crystallization is characterized by high nucleation rate is a typical feature of magma intrusion. An additional parameter intensifying nucleation is the strong convective motion of the melt: the intruding magma is forced in the magma chamber into an intense motion controlled by several interconnected thermodynamical parameters. Actually, at least three types of convection are distinguished (MORSE, 1988) thermal convection (due to thermal gradient, especially that between floor and roof of the chamber), two-phase convection (involving crystal+liquid suspensions that can move much faster than small individual crystals can settle), and compositional convection (due

to rejection of solute by growing cumulates). Study of layered intrusions show that competition between nucleation, growth, and cooling rates (THY *et al.* 1988) can often lead to an oscillatory behaviour of the multisaturated liquid, which is reflected in the rhythmic layering (MAALØE, 1978) of the product phases. Though nucleation theories aiming at explaining rhythmic layering are, at least partly, in controversy with each other, they admit that abrupt changes in parameters controlling nucleation can occur, giving rise to burst of nucleation. This is the very point which is important to our discussion: the magmatic dynamic patterns may create appropriate physico-chemical conditions for the formation of quasicrystals.

B. *Shock-hardened meteorites*: in these substances a number of specific transformations can be traced. Hardening, multiple twinning and polymorphic transition are typical alterations induced by terrestrial or preterrestrial shock.

From the point of view of solid state physics, hardening is due to blocking the motion of dislocations (KITTEL, 1978). This can be achieved, for example, by homogenizing the dislocation density, a transformation which results e.g. from explosive deformation. A related process that also blocks the motion of dislocations is the formation of short-range order. As quasiperiodicity is an intermediate case between long-range (periodic) order and total disorder, a factor of hardening may be such partial disordering, i.e. formation of quasicrystalline domains. In this respect, a phenomenon called "preferred disorder" respectively "preferred orientation" (JAIN and LIPSCHUTZ, 1970) may be worthy of attention. This roughly means that disordering is confined to certain directions and it is revealed by radial streaks in X-ray diffraction photographs, which is called asterism. In a more recent work by HORZ *et al.* (1986), Debye—Scherrer patterns of experimentally shocked augite and naturally shocked pyroxenes from the Shergotty meteorite are shown. As it is noted there, substantial disturbance of long-range order and preferred orientation are indicated, the latter by discontinuous and streaky reflections. Moreover, what is mainly essential from our point of view, the asterism exhibits nearly 14-fold symmetry (Fig. 1 in the paper referred to; the relevant photographs cannot be adequately reproduced here because of their small dimension). These figures originate from discrete grains of 220—250 μm diameter and are said to be hybrids between single crystals and fine-grained powders, and the lattice is considered as mechanically disaggregated by shock. It is stressed by the authors that "crystallographic control becomes impractical for such highly fragmented samples". However, despite of the difficulties, such and similar phenomena perhaps would be worthy to be subjected to further investigation, in our opinion.

As for the other two phenomena, viz. multiple twinning and polymorphism in meteorites, here we only refer to the fact that there exists an alternative notion of quasicrystals emphasized by LINUS PAULING (1987), according to which the properties of quasicrystals can be satisfactorily explained by supposing certain multiple twinning structures. The debate has not been concluded yet (WOLNY *et al.*, 1988).

CONCLUDING REMARKS

Of course, the train of thought in A and B is a tentative one and even does not pretend to be anything more. This is because the knowledge on quasicrystals is in an accumulation period and theoretical (e.g. geometric) description of their structure is not completed yet, in contrast to classical crystals for which at least the geometric point lattice theory essentially was completed at the beginning of the century. On the other hand, actually in *any* geological sample having more or less

peculiarity in its formation circumstances one may find (at least small domains of) quasicrystals. Perhaps a number of researchers have already met without recognizing them: surely all of us are more or less confined to scientific "dogmas", like for example the strict crystallographic prohibition of five-fold symmetry.

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