Quasicrystals and Other Aperiodic Structures in Mineralogy

Carlos M. Pina [1,2,*] and Victoria López-Acevedo [1,3]

[1]   Department of Crystallography and Mineralogy, Faculty of Geological Sciences,
      Complutense University of Madrid, 28040 Madrid, Spain; vcornejo@geo.ucm.es
[2]   Geosciences Institute IGEO (Universidad Complutense de Madrid-Consejo Superior de Investigaciones
      Científicas), 28040 Madrid, Spain
[3]   Museum of Geology at the Complutense University of Madrid, 28040 Madrid, Spain
[*]   Correspondence: cmpina@geo.ucm.es; Tel.: +34-91-394-4879; Fax: +34-91-394-4872

Abstract: In this article, we first present and discuss eighteenth-century descriptions of minerals that contributed decisively to the development of crystallography. Remarkably, these old crystallographic descriptions included morphologies with symmetries incompatible with an internal periodic order of atoms, which, however, have been recognised to be characteristics of quasicrystals. Moreover, we also review a number of studies of minerals with aperiodic crystal structures, including recently reported natural quasicrystals of extra-terrestrial origin. Finally, we discuss the current investigations addressing the search for new quasicrystalline minerals in nature.

Keywords: quasicrystals; aperiodic mineral structures; crystal and quasicrystal morphologies; quasicrystalline minerals; skutterudite; cobaltine

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1. Introduction

The development of crystallography has been closely interwoven with mineralogical investigation. Minerals were the first accessible crystalline solids that scientists were able to study and measure systematically in order to derive the first crystallographic laws. In the eighteenth century, mineralogists already realised that the external polyhedral forms of minerals were constant and determined by an internal order of their constituting atoms or molecules [1,2]. Despite this remarkable finding, it took about a century to fully establish the crystallographic principles that govern such an order [3–6]. These principles were derived theoretically on the basis of the concept of periodicity; that is, it was assumed that the order of crystal structures is periodic in all three space dimensions. At the beginning of the twentieth century, internal periodicity of crystals was nicely demonstrated by X-ray diffraction experiments using minerals [7,8]. Notwithstanding this, diffraction studies soon showed that the structures of a number of minerals are occasionally not strictly periodic (e.g., calaverite, quartz, and feldspars). These anomalous structures usually resulted from phase transformations and were interpreted as being more or less complex modulations of average periodic lattices. By doing this, the crystallographic paradigm was preserved for some time. However, the discovery of quasicrystals, whose pentagonal symmetries are noticeably incompatible with a periodic order of atoms [9], definitively challenged the fundamentals of crystallography. The scientific community was then forced to review the traditional concepts of crystal and crystal lattices to include internally ordered solids without translational symmetry. Consequently, in 1991, the International Union of Crystallography stated that "a crystal is any solid having an essentially discrete diffraction diagram", a definition which intentionally avoids the term "periodic" [10]. In this case, the new developments in crystallography and the subsequent redefinition of crystal resulted from the study not of minerals but of synthetic alloys.

Nevertheless, in 2009, the first mineral with a quasicrystalline structure, named icosahedrite, was found within a meteorite from Khatyrka (eastern Russia), and in 2015 a new natural quasicrystal with decagonal symmetry was also identified in the same meteorite [11–13]. Although mineral quasicrystals formed on Earth have not been recorded to date, it is quite conceivable that some minerals may exist in a quasicrystalline state on our planet. Synthesis experiments and crystallochemical analyses suggest that a number of minerals could be transformed into quasicrystals under extreme pressure and temperature conditions on Earth [14–16]. Hence, finding such mineral quasicrystals of terrestrial origin is relevant to the investigation of the formation conditions of aperiodic crystals in nature and would constitute a new contribution of mineralogical studies to the advancement of crystallography.

The aim of this article is to review some of the main contributions of mineralogy to the study of aperiodic and quasicrystalline structures and to discuss mineral structures that could be related to the formation of quasicrystals on Earth.

2. Before Crystallography

The foundation of crystallography as a modern science was the result of several centuries of careful observations and mathematical thinking about the origin of the polyhedral shapes of minerals. Initially, the researchers did not make any distinction between minerals, rocks, sediments, and fossils, and the term *fossilis* referred to all materials that can be found under the ground [17,18]. It was not until the end of the sixteenth century that the difference between fossils (of organic origin) and minerals with polyhedral shapes (formed by the addition of material) began to be recognised [19]. Once the inorganic origin of minerals became apparent, the interest of scientists focussed on their regular external morphologies. As early as 1669, Nicolaus Steno realised that the angles between analogous faces of quartz crystals were always identical [20]. This important observation was subsequently generalised by Romé de L'Isle [21], who measured a large number of interfacial angles of many different crystals and formulated the first law of crystallography: *The Law of the Constancy of Interfacial Angles*. But we also owe to him one of the earliest and broadest inventories of crystal forms. In his book *Cristallographie* [1], he described up to 746 crystals of different minerals and presented ten tables with drawings of observed and idealised crystal morphologies. Some of them were also carefully reproduced in baked clay and complemented his book.

Crystal morphologies reported by Romé de L'Isle can be divided into two categories. The first of these categories includes both crystal shapes that he apparently observed in minerals from his own collection (At present, part of the mineral collection of Romé de L'Isle can be found at the Muséum National d'Histoire Naturelle in Paris (France)) and descriptions of minerals reported by other scientists [22,23]. The second category of morphologies described in *Cristallographie* [1] is constituted by several idealised crystal shapes obtained after virtual cutting of vertices and/or bevelling of edges of forms considered by Romé de L'Isle as "primitives" (i.e., parallelepipeds, prisms, and pyramids). Interestingly, in both categories of crystal shapes, some forms with pentagonal symmetries (i.e., morphologies incompatible with a periodic internal order of crystal structures) can be found (Figure 1).

Although Romé de L'Isle could only see crystal forms with approximately fivefold symmetries, it is worth considering his descriptions in detail. According to him, all the morphologies with pentagonal faces shown in Figure 1 are variants of the cube and they can be considered as characteristic of the minerals pyrite and *marcassite* (the name commonly given in the seventeenth and eighteenth centuries to any pyrite with a high content of sulphur and variable amounts of zinc, copper, and other metals). In the case of the dodecahedron and the icosahedron, it seems obvious that Romé de L'Isle tried to reconcile his observations to the forms of the Platonic solids, which fascinated scientists and philosophers in ancient times. Similarly, the description of the triacontahedron and the pyramidal dodecahedron were attempts by Romé de L'Isle to approximate observed mineral forms to regular polyhedra. While Romé de L'Isle admitted in his *Cristallographie* that he never observed an isolated triacontahedron, he claimed to have a *marcassite* crystal with the shape of a pyramidal dodecahedron in

his personal mineral collection. *Marcassite* crystals of similar shape to that described by Romé de L'Isle were also reported by Démeste [22], indicating that the morphologies with apparent pentagonal symmetries are not infrequent in this mineral (Figure 2).
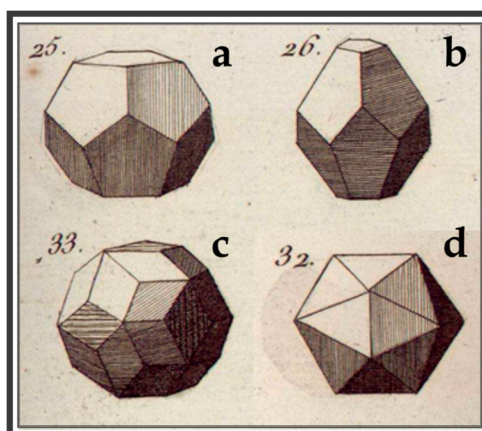

Figure 1. Forms with non-crystallographic pentagonal external symmetries by Romé de L'Isle. (**a**) Regular dodecahedron; (**b**) Elongated or pyramidal dodecahedron; (**c**) Regular triacontahedron; (**d**) Icosahedron. Illustration adapted from Table II (*Le Cube ou L'Hexaèdre et ses Modifications*) in Volume IV of *Cristallographie* [1].
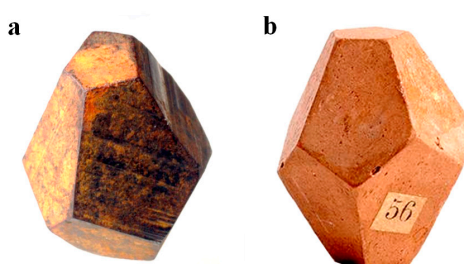

Figure 2. (**a**) Photograph of a limonitised pyrite from Jarapalos, Málaga (Spain), showing a pyramidal dodecahedron-like morphology (size of the crystal: ≈2 cm). Collection and picture from J.M. Bruguera. This crystal is similar to the *marcassite* reported by Romé de L'Isle in his book *Cristallographie* [1]. (**b**) Photograph of an eighteenth-century baked clay model of a pyramidal dodecahedron from the collection of the Geology Museum at the Complutense University of Madrid (size of the model: 2.5 cm × 2.3 cm). This model reproduces a single crystal of *marcassite* from Romé de L'Isle's personal mineral collection. Photograph by Toya Legido.

A symmetry analysis of the morphologies described by Romé de L'Isle shows that the dodecahedron, the icosahedron, and the triacontahedron have identical symmetry, that is, six fivefold roto-inversion axes, ten threefold roto-inversion axes, fifteen twofold axes, fifteen mirror planes, and a centre of symmetry. Differently, the symmetry content of the pyramidal dodecahedron only contains one fivefold roto-inversion axis, five twofold axes, five mirror planes, and a centre of symmetry. Using an extended Hermann-Mauguin notation, the dodecahedron, icosahedron, and triacontahedron belong to the m$\overline{3}\overline{5}$ quasicrystal class, while the pyramidal dodecahedron belongs to the $\overline{5}$m2 quasicrystal class [24–26] (Figure 3).
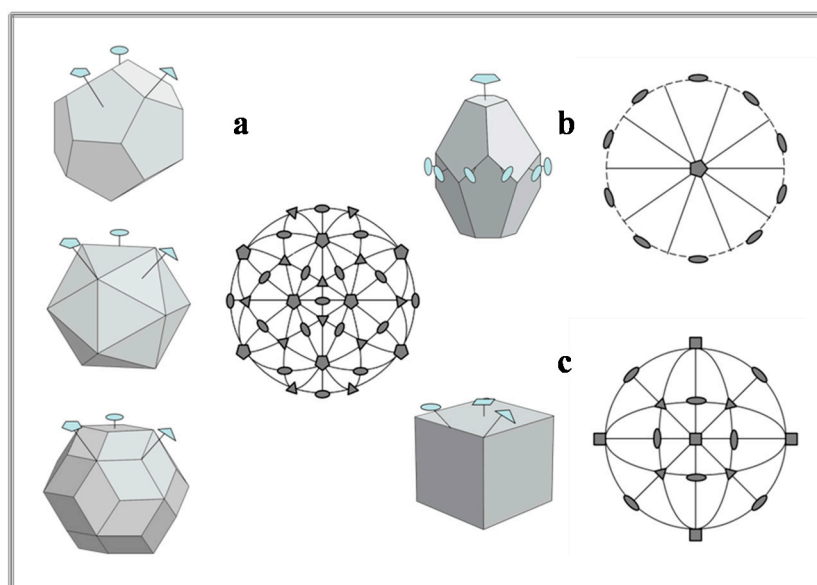
Figure 3. Crystal morphologies reported by Romé de L'Isle [1] and the corresponding stereographic projections of their symmetry elements. (**a**) Forms belonging to the m$\overline{3}\overline{5}$ icosahedral quasicrystal class (from top to bottom: dodecahedron, icosahedron, and triacontahedron); (**b**) elongated dodecahedron showing the symmetry of the $\overline{5}$m2 quasicrystal class; and (**c**) cube belonging to m$\overline{3}$m crystal class. Symbols: ellipses, triangles, squares, and pentagons indicate the orientations of the twofold, threefold, fourfold, and fivefold axes respectively. The full lines in the stereographic projections represent mirror planes.

Interestingly, recent investigations have shown that the morphologies with symmetries described above are commonly exhibited by quasicrystals [27–29] (Figure 4a). Obviously, Romé de L'Isle did not predict the existence of quasicrystals but only described some forms that he considered plausible for natural crystals (Figure 4b). In fact, icosahedral quasicrystal classes (e.g., m$\overline{3}\overline{5}$ and $\overline{5}$m2) and cubic crystal classes (e.g., m$\overline{3}$m and m$\overline{3}$) are symmetrically and topologically not so different from each other, since they are related to the most efficient ways of filling the three-dimensional space with atoms. Furthermore, it is now known that a cubic lattice and an icosahedral quasi-lattice can both be obtained by projecting a six-dimensional hypercube on the three-dimensional space [30]. The fundamental difference between the two types of projections is that periodicity is preserved in the former and lost in the latter.
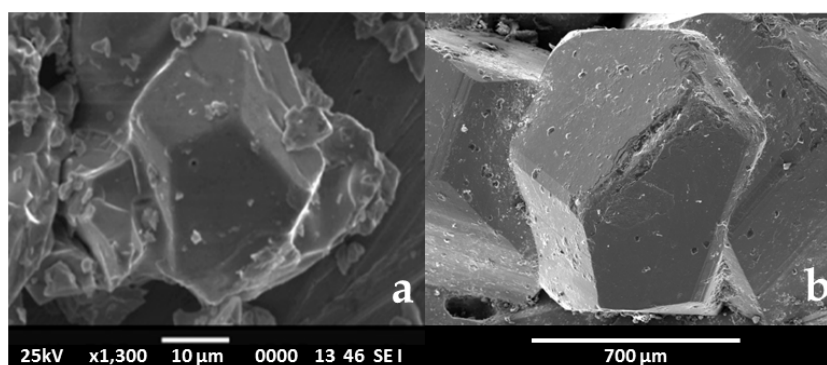

Figure 4. (**a**) Scanning electron microscopy image of an $Al_{62.2}Cu_{25.3}Fe_{12.5}$ quasicrystal with the shape of an elongated dodecahedron (reproduction from [28]); (**b**) Scanning electron microscopy image of a limonitised pyrite with the approximate shape of an elongated dodecahedron, similar to the *marcassite* described by Romé de L'Isle [1].

Romé de L'Isle was not the only scientist interested in the shapes of crystals at that time. His contemporary, René Just Haüy, also devoted much effort to describing and studying the morphology of minerals. Haüy presented most of his observations and ideas about crystals in his *Traité de Mineralogie* [2], which also contains numerous drawings of natural crystals and geometrical constructions. From many observations and measurements, Haüy deduced that crystals are built up from fundamental units with a parallelepipedic shape, repeated in three dimensions. Such repetitions imply that the internal order of crystals is periodic. Haüy's measurements of angles between crystal faces are consistent with a periodic stacking of crystal unit cells (or *molécules intégrantes*, according to Haüy's definition) and allowed him to formulate the second law of crystallography, *the law of rational indexes,* which states that the intercepts of the natural faces of a crystal form with the unit-cell axes are inversely proportional to prime integers. As a consequence of this law, external crystal morphologies with real pentagonal symmetries must be considered impossible. Haüy was aware of the incompatibility of pentagonal symmetries with the law of rational indexes. Accordingly, in his review of the forms described by Romé de L'Isle, Haüy explicitly discarded the dodecahedron, the icosahedron, and the triacontahedron as morphologies exhibited by real crystals. After that, we had to wait almost two centuries until scientists reconsidered such forms as the result of a highly ordered (but not periodic) arrangement of atoms within solids.

The law of rational indexes paved the way for the development of crystallography in the following two centuries by excluding the possibility of any internal crystal order other than periodic. However, as we will see in the next section, the impressive achievements of the research in crystallography in the nineteenth and twentieth centuries were also accompanied by the discovery of mineralogical cases in which violation of the periodic internal order of crystals was evident. Some of these cases were found to be difficult or impossible to explain within the classical crystallographic paradigm and were often ignored or forgotten.

3. The Crystallographic Paradigm and "Dissident" Minerals

The hypothesis that crystals are formed by a periodic arrangement of unit cells was the starting point for the development of modern crystallography. In the decades following the publication of Haüy's works, scientists reported descriptions and goniometric measurements of a large number of minerals with polyhedral shapes [31–33]. These investigations led to the establishment of the geometrical principles of crystallography. One of the first contributions to so-called geometrical crystallography was a demonstration by Hessel [34,35] that all crystal shapes can be grouped into 32 symmetry classes; that is, there are only 32 possible combinations of symmetry elements consistent with solids with internal periodic order. A few years later, Bravais [3] derived the possible three-dimensional lattices that describe the periodic repetition of unit cells within the crystals, that is, the so-called 14 Bravais lattices. Finally, Fedorov, Schoenflies, and Barlow [4–6] independently derived the 230 space groups, that is, the combinations of symmetry elements compatible with a periodic order which describe all possible crystal structures. The 32 crystal classes, the 14 Bravais lattices, and the 230 space groups constitute the fundamentals of crystallography that allow us to explain both the external symmetries and the structures of all crystalline materials.

The discovery of the diffraction of X-rays by crystals in 1912 and the subsequent use of diffraction techniques provided an experimental support for the abovementioned fundamentals of crystallography [7,8]. Moreover, diffraction data allowed scientists to determine in a few years the structure of a multitude of minerals and synthetic compounds. This led to unprecedented knowledge of the solid matter and the principles that govern its internal order. The structure of the mineral halite (NaCl) was the first crystal structure determined by X-ray diffraction, that is, the positions of the sodium and chlorine atoms within a cubic lattice [36]. After that, the number of structures solved increased rapidly [37,38]. Currently, there are more than 50,000 known crystal structures. Among them are about 4500 minerals.

As the knowledge of mineral structures and external morphologies of crystals increased, mineralogists and crystallographers discovered that some crystals showed features that were clearly inconsistent with the idea of a perfect and periodic internal atomic order. Investigations conducted at the beginning of the twentieth century already demonstrated that crystals usually exhibit more or less severe alterations of their internal periodicity. These could affect single atomic positions, rows of atoms, or even reticular planes. While some of these violations of the crystallographic order were interpreted as simple "crystal defects", others posed really serious problems for the crystallographic paradigm, thereby warranting further analysis.

In the early twentieth century, morphological studies of the mineral calaverite ($Au_{1−x}Ag_xTe_2$) revealed an astonishingly complex crystal morphology defined by more than 90 different crystallographic forms [39,40] (Figure 5). The first attempts to index all calaverite faces required the use of different lattices, which led questioning the universality of the law of rational indexes for the first time. Far from clarifying the "calaverite problem", X-ray diffraction data showed satellite spots, which indicated that calaverite had a complex superstructure whose explanation was still elusive. Subsequent electron diffraction patterns confirmed the existence of satellite diffraction spots. A detailed analysis of such spots revealed that calaverite has a modulated structure [41]. Such a modulation results from both the displacement of Te and the occupation of Ag atoms (which partially substitute the Au atoms), resulting in a deviation from the average C2/m monoclinic structure of calaverite [42]. Since the period of modulation is not an integral number of lattice translations, the structure of calaverite is defined as incommensurate. Remarkably, the incommensurability of the calaverite structure has a morphological expression consisting in the coexistence of many crystal forms, whose indexation was conducted by the simultaneous use of different lattices. Recently, the problems associated with using this cumbersome and artificial indexation have been overcome by the use of face Miller indexes consisting of four numbers, where the fourth number describes the modulation [43–46], and references therein].
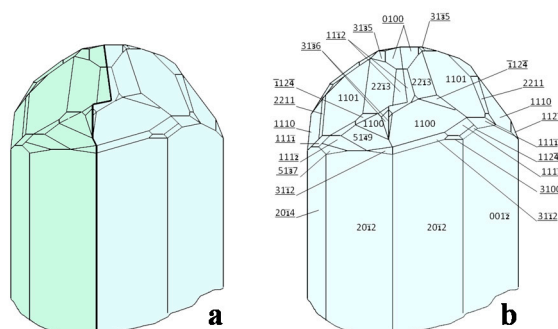

Figure 5. Morphology of calaverite. (**a**) Calaverite twinned crystals; (**b**) Indexed morphology of calaverite according to Janner and Dam [45]. Modified and redrawn from Chapuis [46].

Far from being exceptional, modulated structures are relatively common in minerals. In all cases, transmission electron microscopy (TEM) observations have shown that structural modulations result in the presence of satellite reflections and irregular arrangements of Bragg maxima in the diffraction patterns. As for the mineral calaverite, modulated structures are commonly described by a basic (average) periodic structure to which periodic lattice distortions are introduced by means of one or more modulation vectors. When modulation vectors can be expressed by a linear combination of the lattice vectors of the basic structure, superstructures are formed and an ordinary space group can be assigned to them. Otherwise, modulations are incommensurate and crystal structures are aperiodic along one or more crystallographic directions.

The origin of periodic lattice distortions in crystals is diverse, and modulated structures can arise from cationic ordering, exsolution phenomena involving two or more chemical components, transformation twinning, formation of stacking faults, development of antiphase boundary domains, and so on [47,48]. These modulated structures usually appear during transitions from high-temperature

to low-temperature phases. Within the mineral world, the complex modulated structures of feldspars due to Al/Si and Ca/Na ordering and the incommensurable structure formed during the polymorphic transition of quartz can be considered some of the most remarkable mineralogical cases of aperiodicity in crystal structures (Figure 6).
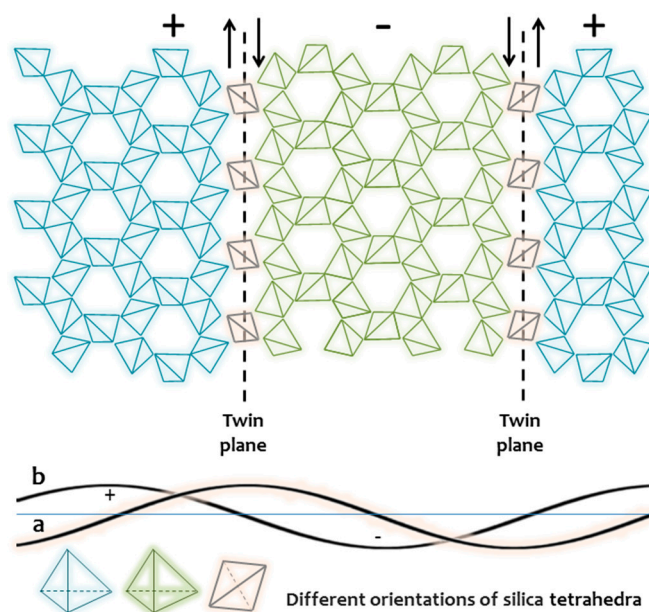

Figure 6. Incommensurate structure of quartz (modified from Putnis [48]). This structure is formed during the transformation from high to low quartz. Both regions of lattice distortion (+ and −) and shear on the Dauphiné twin boundaries (↑↓ and ↓↑) oscillate. Since the oscillations (represented by the waves a and b) are not an integral multiple of the translational periodicity of the quartz lattice, the structure is termed incommensurate and shows a "periodicity" of ≈150 Å.

The introduction of the concepts of modulation and incommensurability to describe those crystal structures that partially depart from periodic order allowed crystallographers to avoid a profound revision of the crystallographic paradigm for some time. By assuming aperiodicity in crystal structures is somewhat "pathological" and, as a result of more or less extensive deviations from perfect and ideal periodic arrangements of atoms, the main axioms of crystallography could be preserved. However, this conservative approach could no longer be maintained when quasicrystals were discovered and scientists realised that their structures could not be described at all in terms of the classical concepts of the unit cell and periodicity.

4. Quasicrystals and Minerals

The discovery of quasicrystals by Shechtman in 1984 had a great impact on crystallography [9,49,50]. Once the existence of solids whose diffraction patterns are inconsistent with a periodic internal order of their atoms had been confirmed, crystallographers were forced to admit that ordered matter can exhibit rotational symmetry that violates the *crystallographic restriction theorem*. This important theorem states the symmetry axis of crystals must fulfil the condition *$2cos\theta = Z$* (where *Z* is an integer and *θ* is the rotation angle corresponding to the symmetry axis); that is, symmetry axes must be compatible with periodicity.

To date, most reported quasicrystals are synthetic alloys that show morphologies and electron diffraction patterns with fivefold and tenfold symmetries, which are incompatible with the *crystallographic restriction theorem.* Although quasicrystals can be easily recognised by their electron diffraction patterns, currently the number of these patterns is limited. In contrast, there is a published collection of over 80,000 powder diffraction patterns, called "ICDD PDF" [51], which includes synthetic

inorganic and organic compounds as well as about 9000 files of mineral phases. Unfortunately, powder diffraction patterns do not allow us to directly detect quasicrystal symmetry. Therefore, some scientists considered the possibility that some of the listed powder diffraction patterns in the ICDD-PDF could correspond in reality to quasicrystals [52].

In order to identify possible "hidden" icosahedral quasicrystals within the ICDD-PDF, Lu et al. [52] proposed a searching method based on two figures of merit: $\overline{Q}$ and $|\Delta|$. While $\overline{Q}$ quantifies the match between the wave vectors of a given diffractogram and the wave vectors of an ideal icosahedral diffraction pattern, $|\Delta|$ measures the match between the corresponding relative intensities [52–54]. Figure 7 shows a plot of the distribution of the quantities $\overline{Q}$ and $|\Delta|$ for about 60,000 diffraction patterns in the ICDD-PDF (grey dots), including the currently known icosahedral quasicrystals (circles). As can be seen in this figure, all quasicrystals are plotted far away from the dense cluster of ordinary crystalline compounds. This allows one to identify quasicrystals from their powder diffraction patterns alone.
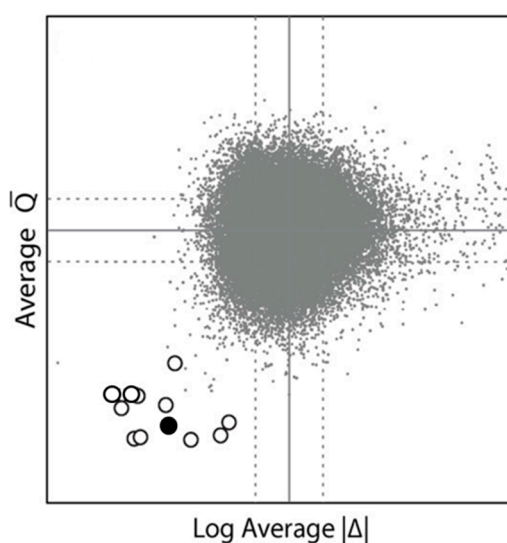

Figure 7. Plot of $\overline{Q}$ versus $|\Delta|$ of X-ray diffraction patterns listed in the ICDD-PDF. The main cluster of grey dots corresponds to crystalline materials and the open circles correspond to the known synthetic quasicrystals with icosahedral symmetry. The black circle represents the new mineral icosahedrite, whose $\overline{Q}$ and $|\Delta|$ values are within the cluster of quasicrystals. Reproduced with permission from Bindi [54].

From inspection of the figures of merit, $\overline{Q}$ and $|\Delta|$, Lu et al. [52] proposed a list of 19 quasicrystal candidates within the ICDD-PDF, that is, materials whose $\overline{Q}$ and $|\Delta|$ values plot closer to the cluster of quasicrystals shown in Figure 7. This list included the following minerals: aktashite ($Cu_6Hg_3As_4S_{12}$), tantalite ($(Fe,Mn)Ta_2O_6$), and gratonite ($Pb_9As_4S_{15}$). In 2007, Luca Bindi began to study samples of these minerals from the Mineralogical Collection of the Museo di Storia Naturale, Università di Firenze. Unfortunately, he concluded one year later that none of these minerals are quasicrystals. Then, he and his collaborators focussed their search for natural quasicrystals on materials of extra-terrestrial origin. After a few years of investigations, they discovered the first natural quasicrystal within a meteorite found in 1979 in the Khatyrka region of the Koryak Mountains in the Kamchatka Peninsula (Russia) and which has been stored in the Florence Museum since 1990 [11,55]. This quasicrystalline mineral of ideal composition $Al_{63}Cu_{24}Fe_{13}$ was named icosahedrite for its icosahedral symmetry (with probable space group $Fm\overline{3}\overline{5}$) and its name was approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (2010-042). More recently, a second natural quasicrystal with the composition $Al_{71}Ni_{24}Fe_5$ and decagonal symmetry has been found in the same meteorite from the Koryak Mountains [12,13]. Figure 8 shows two electron diffraction patterns,

which nicely revealed the fivefold and tenfold symmetries of the quasicrystals found in the Khatyrka meteorite. The fact that the only natural quasicrystals found to date have a meteoritic origin, together with recent shock-induced synthesis experiments, suggests that the formation of quasicrystals in nature may be the result of asteroid collisions [16,56].
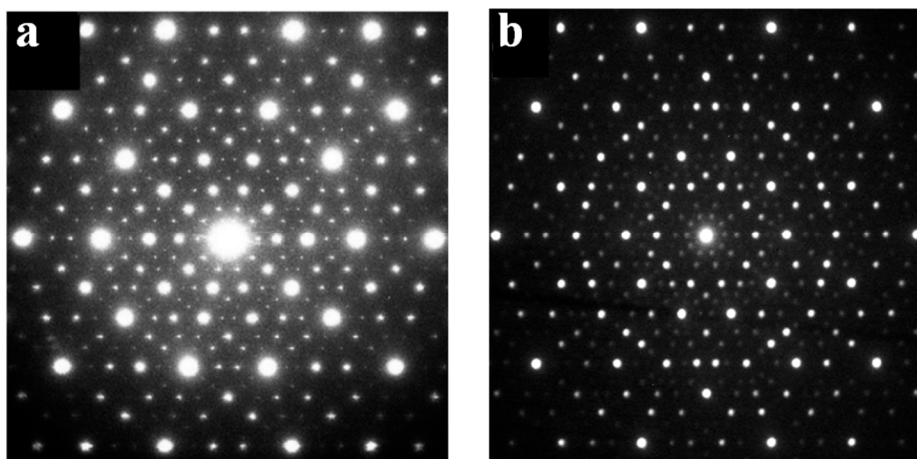

Figure 8. Electron diffraction patterns of quasicrystals found in the Khatyrka meteorite. (**a**) icosahedrite [11] and (**b**) quasicrystal with decagonal symmetry [12].

Even though both the findings of meteoritic quasicrystals and the conclusions drawn from recent shock experiments may shed light on the origin of natural quasicrystals, a fundamental question remains: Is there any place on Earth with suitable conditions for the formation of quasicrystals? Considering the diversity of the chemical compositions of minerals and the vast temperature–pressure ranges in the geological systems, it seems reasonable to think that the formation of quasicrystal minerals could also occur in our planet. Obviously, occurrences of quasicrystals must be rare on Earth and should be related to very specific geochemical and formation environments. Therefore, the search for them cannot be random but must focus on those known minerals with compositional and structural characteristics that could develop quasicrystalline order under certain conditions. In this regard, minerals containing transition metals in their formulas and showing external and internal (structural and/or textural) features with apparent dodecahedral or icosahedral symmetries can be considered as good candidates for continuing the search for natural quasicrystals. Among these mineral candidates, some sulphides and arsenides of cobalt, iron, and nickel, and their solid solutions, show a number of morphological, textural, and diffraction peculiarities that deserve special attention. In this article, we will focus our analysis on two minerals: skutterudite and cobaltine.

Skutterudite ($CoAs_3$) is the endmember of extensive solid solution series in which cobalt can be substituted by nickel and minor amounts of iron (skutterudites with Fe: (Co + Ni) ratios higher than 1 have not been found in nature). Depending on both the extent of the cationic substitution and the arsenic content, different mineral names are used: skutterudite *sensu stricto*, with the formula $(Co,Ni,Fe)As_3$ (with Fe < 12%), and the arsenic-deficient varieties smaltite and chloanthite with a general formula $(Co,Ni)As_{3-x}$ and variable Co:Ni ratios [57].

Regardless of compositional variations, skutterudite is considered cubic and the space group $Im\bar{3}$ has been assigned to its structure [58–61]. However, skutterudites frequently exhibit "flame textures" and an anomalous optical anisotropy inconsistent with a cubic symmetry, which can be attributed to exsolution and phase transition phenomena. Alternatively, such conspicuous textures and optical anisotropy could be the result of partial substitution of skutterudites by the related minerals safflorite and clinosafflorite, $(Co,Ni,Fe)As_2$, which crystallise in the orthorhombic and monoclinic systems respectively. In any case, it is clear that skutterudites experience major structural and/or compositional rearrangements when P-T conditions change.

Undoubtedly, the most striking feature of the structure of skutterudite is the existence of two icosahedral empty cavities per unit cell, which are defined by the positions of arsenic atoms (Figure 9a). Recently, these icosahedral voids have attracted much attention in the scientific community due to the possibility of filling them with a large variety of atoms (e.g., rare earths, alkaline earths), which provide interesting electronic, optic, and thermoelectric properties to the so-called filled skutterudites [62,63] and references therein.
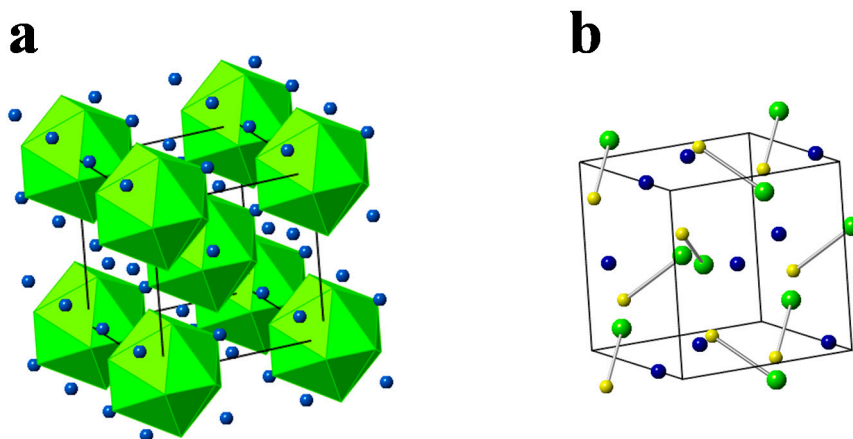
Figure 9. (**a**) Projection of the skutterudite structure showing icosahedral voids (green) defined by the positions of the arsenic atoms (not represented) and the cobalt atoms (blue); (**b**) Projection of the cobaltite structure showing the As–S pairs and the cobalt atoms (blue). Cobaltite and pyrite are isostructural only when the As–S pairs are fully disordered.

Despite the possibility that skutterudite icosahedral voids allow the synthesis of materials with new properties, such voids can also be relevant for the research on the formation of quasicrystals and other non-periodic structures. Skutterudite icosahedral cages formed by 12 arsenic atoms are presumably quite stable structural entities that seem to be related to the skutterudite 503 and 530 diffraction peaks, that is, corresponding to close-packed planes of icosahedral cages.

Icosahedral structural entities such as those found in skutterudite are characteristic of the local order in amorphous materials [64,65]. In the liquid state, icosahedral geometry ensures a dense packing of atoms, and icosahedral clusters have even been detected in metallic glasses formed by extremely fast cooling [66]. Although these clusters are energetically favourable in liquids, their fivefold symmetry prevents the formation of large structures with periodic long-range order (i.e., crystals) when the liquid–solid transitions occur. This is referred to as the "geometrical frustration" of icosahedral ordering, which seems to be related to vitrification processes [67–69]. Apparently, such a geometrical frustration can be overcome and structures with icosahedral order (i.e., quasicrystals) can form only under very specific solidification conditions.

Skutterudite and its solid solutions can be typically found in hydrothermal veins associated with magmatic systems, including the exceptional igneous complex of Sudbury (Canada), where magma was produced by the impact of a huge meteorite 1800 million years ago [70,71]. Considering the chemical variability of skutterudite, the singularity of its structure, and the variable pressures and cooling rates expected in the magmatic and hydrothermal systems where skutterudite appears, the formation of a natural quasicrystalline form of this mineral is plausible. Remarkably, as early as 1985 the possible existence of quasicrystalline polymorphs of skutterudite was already the object of speculation. Boisen and Gibbs [14] noticed the icosahedral As_{12} units in the skutterudite structure and suggested that the relatively frequent pyritohedral morphology of skutterudite crystals could reflect a previous quasicrystalline state. A few years later, Gévay and Szederkény [15] pointed out that the hypothesis proposed by Boisen and Gibbs [14] is in accordance with Ostwald's rule and, therefore, a possible quasicrystalline form of skutterudite could be considered as a metastable

precursor of crystalline skutterudite. Furthermore, Gévay and Szederkény [15] indicated that rapid cooling in magmatic systems and shock hardening due to meteoritic impacts may generate appropriate conditions for quasicrystal formation. In view of the recent discoveries of natural quasicrystals in meteorites [11–13,16], it seems clear that the search for quasicrystalline forms of skutterudite in natural environments such as Sudbury's igneous complex is worthwhile.

Cobaltite (CoAsS) is another cobalt mineral that frequently appears associated with skutterudite in high-temperature hydrothermal deposits. As in the case of skutterudite, cobalt atoms can be partially substituted by iron and nickel in the cobaltite structure, resulting in extensive solid solution series (e.g., cobaltite–gersdorffite). Nonetheless, the structure of cobaltite differs from that of skutterudite and it can be derived from the pyrite (FeS_2) structure by ideally replacing Fe by Co and S_2 by As–S pairs (Figure 9b). But only in the case of a complete As–S disorder would cobaltite be isostructural with pyrite. The ordering of the As–S pairs reduces symmetry, and therefore the orthorhombic space group *Pca2₁* has been assigned to cobaltite [72–74]. Despite this, cobaltite crystals with pyritohedral, elongated pyritohedral, and icosahedral shapes are relatively frequent (Figure 10). In addition, "flame textures" similar to those found in skutterudite are also common in cobaltite samples. Both the singular morphologies and the "flame textures" of cobaltite again suggest the existence of mineral precursors, some of which might correspond to a quasicrystalline state.
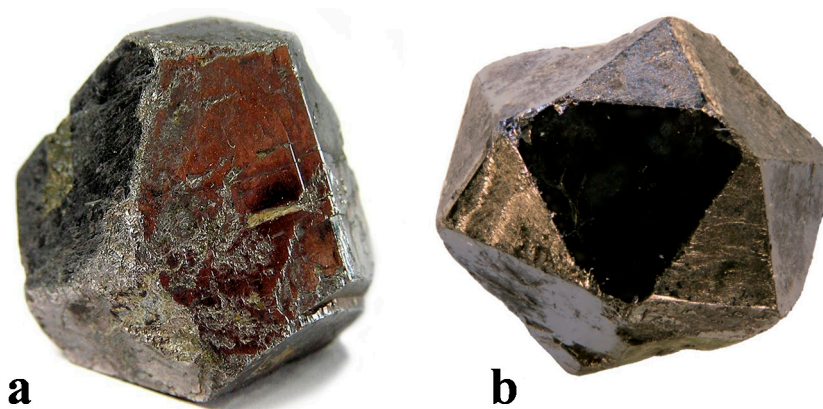

Figure 10. Cobaltite crystals with (**a**) elongated pyritohedral shape. Size: 2.5 × 2.3 × 2.2 cm (picture from Rob Lavinsky) and (**b**) icosahedral shape. Size ≈ 2.5 mm (crystal and picture courtesy of the Museo Geominero (IGME), Madrid, Spain).

At present, the idea that some cobaltites could have been formed from quasicrystalline precursors is highly speculative. However, in this regard, diffractograms of cobaltite have revealed anomalous features that can be relevant for the search for aperiodic atomic order in the cobaltite structure. The most striking of these features is that the most intense diffraction peaks often correspond to the planes that define the {120} cobaltite pyritohedron. Giese and Kerr [72] proposed that at high temperatures (above 850 °C), As and S are completely disordered in the cobaltite. As a result, cobaltite crystallises in the cubic space group *Pa3*; i.e., it is isomorphic with pyrite. At temperatures lower than 850 °C, As and S tend to become ordered and a complete As–S ordering results in the orthorhombic (pseudo-isometric) space group *Pca2₁*. This would partially explain the importance of the 120 reflections in the cobaltite diffractograms. Nevertheless, cubic cobaltite has not yet been found in nature, and X-ray diffraction patterns of natural cobaltites also show a number of reflections forbidden by the space group *Pca2₁* [73]. In order to explain the presence of such forbidden reflections in the diffractograms of cobaltite, Bayliss [73] proposed a complex twinning model consisting of six interpenetrated domains related by a $\bar{3}$ twin axis parallel to the [1$\bar{1}$1] direction of the orthorhombic *Pca2₁* cobaltite unit cell (Figure 11).
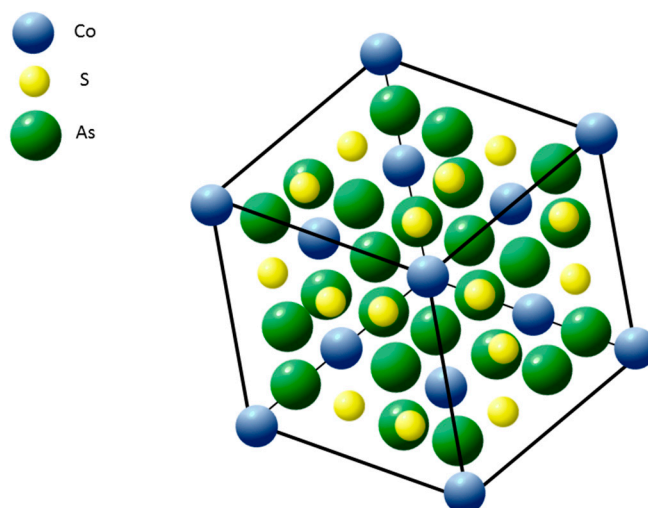
Figure 11. Model of the cobaltite multiple twin according to [73]. Projection along the [111] direction. In this cell, there are 52 atoms (4 Co, 24 S, and 24 As).

The cobaltite twin model by Bayliss [73] has been, however, questioned by Fleets and Burns [74]. On the basis of new X-ray diffraction data and optical observations of "flame textures" using reflected light, Fleets and Burns [74] proposed a simpler twin model in which two twin domains with incoherent boundaries are related by a single threefold axis along the [111] direction. Even though this second model seems to describe diffraction data better (i.e., forbidden reflections), the origin and exact nature of cobaltite complex twinning have not yet been completely elucidated.

The proposed cobaltite twin models resemble the attempts by Linus Pauling to provide an explanation for the first recorded diffraction patterns of quasicrystals within the framework of classical crystallography. Pauling claimed that diffraction patterns of materials with external icosahedral symmetry could be explained by a model of multiple twinning of cubic domains with huge unit cell dimensions and sharing a threefold axis and three mirror planes [75–79]. Further investigations showed that Pauling's twinning model was not the simplest way of explaining diffraction patterns with fivefold symmetries and the quasicrystal model imposed [80,81]. The fact that X-ray powder diffraction patterns of non-twinned cobaltite crystals have not been recorded to date indicates that the proposed cobaltite twinning must occur at the nanometre or subnanometre scales, similarly to the complex twinning model described by Pauling. Considering this, it is plausible that the anomalous diffraction patterns of cobaltite could be more easily explained through an alternative description of the cobaltite structure and, particularly, of the arrangement and ordering of S–As within it. In this regard, both a detailed TEM study of cobaltite and a structural analysis of its structure based on the concepts of Zintl-Klemm, Pearson's generalised octet rule, and cation substructures [82–84], and references therein] may be revealing.

Skutterudite, cobaltite, and related minerals are certainly very interesting cases of minerals with puzzling structures that might be related to the formation of quasicrystalline atomic ordering under certain conditions. Nevertheless, taking into account the enormous variety of mineral structures and compositions, these minerals are surely not the only candidates to be precursors or approximates of quasicrystals. The search for quasicrystal minerals has just started with the pioneering works by Bindi and collaborators on the Khatyrka meteorite. But there are still numerous minerals and geological environments to be investigated, including those of other planets and planetary bodies that are becoming accessible. However, new insights into the formation of quasicrystals in nature will be only gained by combining mineralogical exploration, detailed structural analysis, and experiments conducted using selected minerals (precursors) as starting materials.

5. Conclusions

The crystallographic paradigm based on a strict periodic atomic order was definitively established thanks to X-ray diffraction by crystals. However, investigations conducted in the twentieth century also showed an increasing number of mineral structures with more or less severe deviations from periodicity. These anomalous structures were found to be difficult to explain within the framework of classical crystallography. Finally, the discovery of quasicrystals led to a profound revision of some axioms and concepts of crystallography to include a new type of ordered matter that it was not possible to describe at all by periodic lattices.

Essentially, quasicrystals are solids with highly ordered structures that are rigorously aperiodic along one or more crystallographic directions and often show fivefold and tenfold symmetries. Notably, typical morphologies of reported quasicrystals are identical to those described by some early crystallographers and considered as impossible mineral forms for more than two centuries. After the first quasicrystals were synthesised in the laboratory, some mineralogists asked themselves whether minerals with quasicrystalline structures could be found in nature. Although only two natural quasicrystalline minerals of extra-terrestrial origin have been reported to date, the possibility of discovery of quasicrystals on Earth cannot be discounted. Taking into account some analogies with quasicrystal structures currently reported, some natural alloys, sulphides, and sulpharsenides (e.g., skutterudite, cobaltite) can be considered as suitable candidates for transformation into the quasicrystalline state under conditions still to be determined. Furthermore, some of these minerals display both structural features and external morphologies with striking icosahedral and dodecahedral symmetries. Although coordination polyhedra and crystal morphologies with fivefold symmetries do not provide direct evidence of internal quasiperiodic order, their recognition and analysis may be helpful in the future search for quasicrystals within the mineral world.

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