

Eighteenth-century forms of quasicrystals

Carlos M. Pina^{a,b,*} and Victoria López-Acevedo^{a,c}

^aDepartment of Crystallography and Mineralogy, Faculty of Geological Sciences, Complutense University of Madrid, 28040 Madrid, Spain, ^bGeosciences Institute IGEO (UCM-CSIC), 28040 Madrid, Spain, and ^cMuseum of Geology at the Complutense University of Madrid, 28040 Madrid, Spain. *Correspondence e-mail: cmpina@geo.ucm.es

Received 28 October 2015

Accepted 16 November 2015

Edited by J.-G. Eon, Universidade Federal do Rio de Janeiro, Brazil

Keywords: quasicrystals; crystallographic models; Romé de L'Isle; symmetry analysis.

A careful inspection of the drawings and baked clay models created by the mineralogist Romé de L'Isle in the 18th century has revealed the existence of a number of intriguing forms with pentagonal symmetries. These forms cannot be classified in any of the 32 crystal classes. They can thus be considered the first crystallographic descriptions of polyhedral forms found in quasicrystals two centuries later. This paper presents a symmetry analysis of the fascinating drawings and clay models with pentagonal symmetries described in the book *Cristallographie* published in 1783 by Romé de L'Isle, as well as a comparison with quasicrystals recently synthesized. The paper also briefly discusses what could induce Romé de L'Isle to consider forms with pentagonal symmetries as plausible crystal forms.

The origin of modern crystallography goes back to the first descriptions of polyhedral shapes found in minerals (Steno, 1669; Werner, 1774; Sequeiros, 2002). One of the aims of early crystal studies was to establish the laws governing the external polyhedra of minerals (Amorós, 1978, and references therein). First derivations of possible polyhedral shapes were essentially conducted by cutting vertices and bevelling edges of a number of crystal shapes which were considered as 'primitives' (e.g. a cube). Remarkably, polyhedra derived following this method were related to crystal symmetry much later (Weiss, 1815), and only about two centuries after the first systematic descriptions of mineral shapes, scientists confirmed that the external morphologies of crystals are determined by an internal structural order based on periodical patterns (Friedrich *et al.*, 1912). The rigorous analysis of the possible three-dimensional crystal shapes and internal patterns (*i.e.* lattices) led to the development of the current mathematical principles of crystallography, whose milestones were: (i) the identification of the 32 crystal classes by Hessel (1830, 1897), (ii) the construction of the 14 lattices by Bravais (1850) and (iii) the deduction of the 230 space groups (Fedorov, 1891; Schoenflies, 1891; Barlow, 1883).

The discovery of quasicrystals has recently challenged the established principles of crystallography (Shechtman *et al.*, 1984; Maciá Barber, 2010). Unlike crystals, atoms in quasicrystal structures are not repeated periodically but according to aperiodic patterns mathematically related to tessellations previously described by Penrose (1974). This means that quasicrystals violate the crystallographic restriction theorem, which states that only twofold, threefold, fourfold and sixfold rotational symmetries are compatible with a periodic arrangement of atoms in crystal structures (*i.e.* $2 \cos \theta = Z$, where Z is an integer and θ is the rotation angle corresponding to the symmetry axis). In other words, quasicrystals exhibit



crystallographically ‘forbidden’ external symmetries by sacrificing internal periodic order. The most common quasicrystals exhibit fivefold symmetries and they can be classified into nine quasicrystal classes (Rao *et al.*, 2007). These pentagonal quasicrystal classes describe all possible external symmetries of quasicrystals when fivefold axes are combined with mirror planes, twofold and threefold axes and a centre of symmetry. Unlike the 32 crystal classes, the quasicrystal classes are derived by neglecting the crystallographic restriction theorem.

In the 18th century, scientists began to describe and classify the possible forms that crystals can exhibit in nature (Amorós, 1978; Kubbinga, 2001). This required an idealization of the observed natural crystals, whose morphologies often deviated from regular polyhedra due to the unequal development of symmetrically equivalent faces. First descriptions of crystal forms and their classification in families paved the way for the development of modern crystallography. However, early crystallographers considered that crystals with pentagonal symmetries were possible since the lattice theory of crystal structures had not yet been developed and, therefore, the crystallographic restriction theorem was unknown. In addition, the fascination with Platonic solids since ancient times encouraged Romé de L’Isle and his contemporaries to look for regular dodecahedra and icosahedra within the mineral forms (Van Smaalen, 1995, and references therein).

In his book, *Cristallographie* (1783), Romé de L’Isle presented drawings of 448 crystal forms classified according to their geometrical and symmetrical analogies (Romé de L’Isle, 1783). To make his book more commercially attractive, Romé de L’Isle sold it together with a collection of 448 crystal models nicely sculpted in baked clay (see Fig. 1).

The National Museum of Natural Sciences in Madrid owns two second-edition copies of Romé de L’Isle’s *Cristallographie* and the Museum of Geology at the Complutense University of Madrid holds a large but incomplete collection of the accompanying crystal models (López-Acevedo & de Dios Celada, 2012). Recently, a careful inspection of both the



Figure 1

Two photographs of a baked clay model of an elongated or pyramidal dodecahedron belonging to the collection of the Geology Museum at the Complutense University of Madrid (size of the model 2.5 × 2.3 cm). Left: lateral view; right: top view. According to Romé de L’Isle, this model reproduces a single crystal of *marcassite* from his personal mineral collection. Photographs by Toya Legido.

drawings and models of Romé de L’Isle revealed a fact: some of the models do not represent real crystals but forms typically shown by quasicrystals. In particular, Romé de L’Isle described two Platonic solids (*i.e.* the dodecahedron and the icosahedron), a pyramidal dodecahedron and a regular triacontahedron (see Fig. 2).

Both the icosahedron and the regular triacontahedron are polyhedra formed by faceting the regular dodecahedron (see Figs. 2*a*, 2*c* and 2*d*). These three forms belong to the $2/m\bar{3}5$ quasicrystal class and show an identical combination of symmetry elements: six fivefold roto-inversion axes, ten threefold roto-inversion axes, 15 twofold axes, 15 mirror planes and a centre of symmetry. Although related to the regular dodecahedron, the pyramidal dodecahedron (see Fig. 2*b*) belongs to a different quasicrystal class, the $\bar{5}m2$, which only contains one fivefold roto-inversion axis, five twofold axes, five mirror planes and a centre of symmetry. Undoubtedly, the pyramidal dodecahedron is the most peculiar and enigmatic form described by Romé de L’Isle because its derivation cannot be seen as an attempt to approximate a mineral form to any highly regular and symmetric polyhedron (*e.g.* a Platonic solid). Romé de L’Isle claimed that a number of forms with fivefold symmetry can be observed in some pyrite crystals with variable contents of zinc, copper and other metals, which are frequently called *marcassites* by Romé de L’Isle, according to previous descriptions by Démeste (1779). Obviously, Romé de L’Isle could only see approximate forms of these regular solids with pentagonal symmetries. Pyrite has a well known crystal structure and its external pentagonal forms can only be the result of a singular combination of crystal faces. It was not until the end of the 20th century that

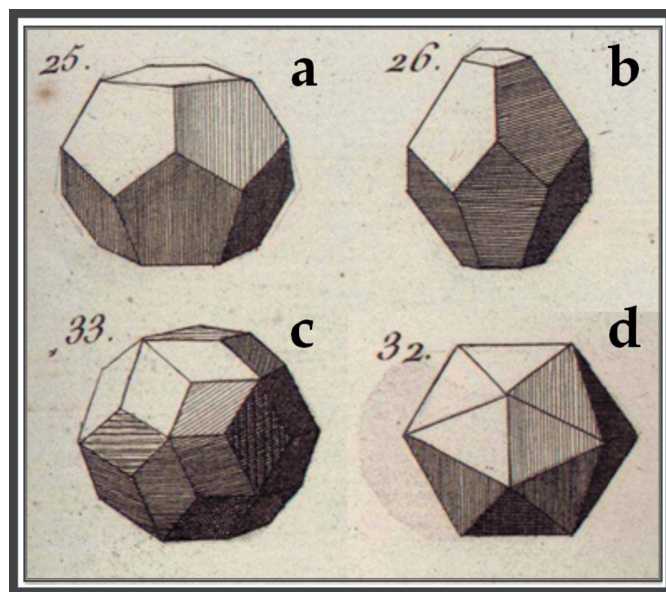


Figure 2

The ‘quasicrystal’ models of 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* by Romé de L’Isle (1783).

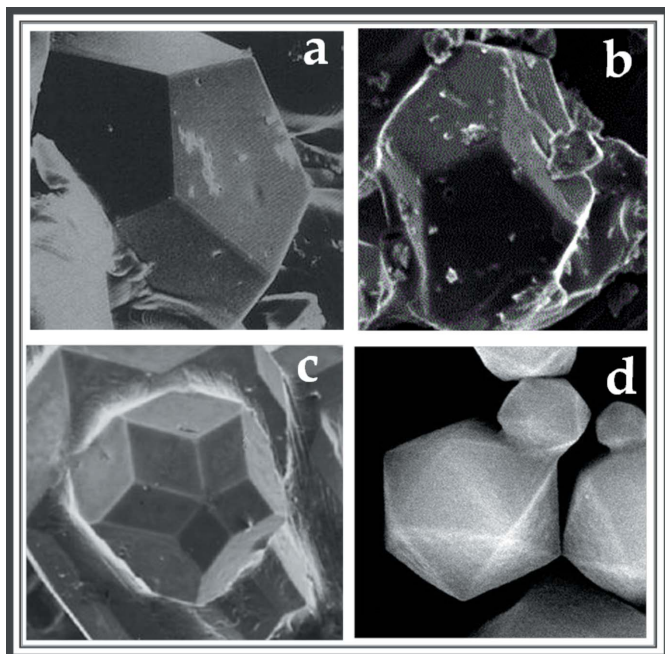


Figure 3

Scanning electron microscopy images of quasicrystals. (a) $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ dodecahedral quasicrystal (reproduced from Tsai *et al.*, 1987). (b) $\text{Al}_{62.2}\text{Cu}_{25.3}\text{Fe}_{12.5}$ quasicrystal with the shape of an elongated dodecahedron (reproduced from Jamshidi *et al.*, 2014). (c) Al–Cu–Fe quasicrystal with the shape of a regular triacontahedron [reprinted with permission from McGraw-Hill Education. *Concise Encyclopedia of Physics* (2005)]. (d) Icosahedral silica quasicrystal [reprinted by permission from Macmillan Publishers Ltd: *Nature* (Van Blaaderen, 2009) copyright (2009)].

the existence of solids with both external and internal pentagonal symmetries (*i.e.* quasicrystals) was reported (see Fig. 3).

Usually, quasicrystals are more or less complex synthetic metal alloys whose external morphologies are astonishingly similar to those reported by Romé de L'Isle. Interestingly, Romé de L'Isle, after studying and idealizing the external forms of numerous natural crystals, implicitly assumed that forms with pentagonal symmetries could be found in nature (*e.g.* the pyramidal dodecahedron shown in Fig. 1 is a baked clay model created after a single crystal of *marcassite* belonging to Romé de L'Isle's personal mineral collection). Furthermore, he recognized that some forms with pentagonal faces could be obtained by truncating, bevelling and distorting the corners and faces of a cube in various ways. This is not a trivial crystallographic observation since the $2/m\bar{3}5$ and the $\bar{5}m2$ quasicrystal symmetry classes share a number of symmetry elements with the cubic crystal class, which contains four threefold roto-inversion axes, three fourfold axes, six twofold axes, nine mirror planes and a centre of symmetry. Topological studies have demonstrated that cubic lattices and icosahedral quasilattices are closely related (Torres *et al.*, 1989). In fact, a cubic lattice and an icosahedral quasilattice can be considered two different three-dimensional projections or 'shadows' of a six-dimensional hypercubic lattice (Mackay, 1990). This means that periodic and quasiperiodic ordering of atoms in solid matter are symmetry-related alternatives to fill

the space in the most efficient way. Although Romé de L'Isle did not know anything about the topological relationships between icosahedral quasilattices and cubic and hypercubic lattices, such veiled relationships somehow induced him to consider forms with pentagonal symmetries as plausible forms shown by natural solids. The result was that Romé de L'Isle included in his book *Cristallographie* (1783), and in the accompanying collection of clay pieces, three-dimensional forms corresponding to quasicrystals whose existence was only recognized two centuries later: an interesting case of scientific premonition.

Acknowledgements

We thank Toya Legido for photographs shown in Fig. 1. Copies of the original plates by Romé de L'Isle were kindly provided by the Historical Library 'Marqués de Valdecilla' at the Complutense University of Madrid.

References

- Amorós, J. L. (1978). *La gran aventura del cristal. Naturaleza y evolución de la Ciencia de los cristales*. E-Prints Complutense. <http://eprints.ucm.es/33677/>.
- Barlow, W. (1883). *Nature (London)*, **29**, 186–188.
- Bravais, A. (1850). *J. Ec. Polytech.* **19–33**, 1–128.
- Concise Encyclopedia of Physics* (2005). New York: McGraw-Hill Education. ISBN 0071439552.
- Démeste, J. (1779). *Lettres du Docteur Démeste au Docteur Bernard. Sur la Chymie, la Docimasie, la Cristallographie, la Lithologie, la Minéralogie et la Physique en général*. Tome Second. Chez: Didot, Imprimeur de Monsieur, et Clousier, Imprimeur & Libraire. Paris.
- Fedorov, E. S. (1891). *Verhandlungen der Russisch-Kaiserlichen Mineralogischen Gesellschaft zu St Petersburg*, **2**(28), 1–145.
- Friedrich, W., Knipping, P. & Laue, M. (1912). *Sitzungsber. K. Bayer. Akad. Wiss. Math. Phys. Kl.* pp. 303–322.
- Hessel, J. F. Ch. (1830). *Gehler's Physikalisches Wörterbuch*, **7** (I–K), 1023–1340.
- Hessel, J. F. Ch. (1897). *Krystallometrie, oder Krystallonomie und Krystallographie*. Ostwald's Klassiker der exakten Wissenschaften, Vols. 88–89.
- Jamshidi, A. L. C. L., Nascimento, L., Rodbari, R. J., Barbosa, G. F., Machado, F. L. A., Pacheco, J. G. A. & Barbosa, C. M. B. M. (2014). *J. Chem. Eng. Process. Technol.* **5**, 1000187.
- Kubbinga, H. (2001). *L'Histoire du concept de 'molécule'*. Paris: Springer-Verlag, France.
- López-Acevedo, V. & de Dios Celada, N. (2012). *Bol. R. Soc. Esp. Hist. Nat. Sec. Geol.* **106**, 1–23.
- Maciá Barber, E. (2010). *Aperiodic Structures in Condensed Matter: Fundamentals and Applications*. Boca Raton: Taylor & Francis Group, LLC.
- Mackay, A. L. (1990). *Nature (London)*, **344**, 21.
- Penrose, R. (1974). *Bull. Inst. Maths. Its Appl.* **10**, 266–271.
- Rao, K. R. M., Rao, P. H. & Chaitany, B. S. K. (2007). *Pramana J. Phys.* **68**, 481–487.
- Romé de L'Isle, J. B. (1783). *Cristallographie, ou Description des formes propres a tous les corps du regne minéral, dans l'état de combinaison saline, pierreuse ou métallique, avec figures & tableaux synoptiques de tous les cristaux connus*. De l'Imprimerie de Monsieur, Paris.
- Schoenflies, A. (1891). *Kristallsysteme und Kristallstruktur*. Leipzig: B. G. Teubner.
- Sequeiros, L. (2002). *Enseñanza de las Ciencias de la Tierra*, **10**, 243–283.

- Shechtman, D., Blech, I., Gratias, D. & Cahn, J. W. (1984). *Phys. Rev. Lett.* **53**, 1951–1953.
- Steno, N. (1669). *De Solido intra Solidum Naturaliter Contento. Dissertationis Prodromus*. 1^a Ed. Sub Signu Stellae. Florencia.
- Torres, M., Pastor, G., Jiménez, I. & Fayos, J. (1989). *Phys. Status Solidi (b)*, **154**, 439–452.
- Tsai, A. P., Inoue, A. & Masumoto, T. (1987). *Jpn. J. Appl. Phys.* **26**, L1505–L1507.
- Van Blaaderen, A. (2009). *Nature (London)*, **461**, 892–893.
- Van Smaalen, S. (1995). *Crystallogr. Rev.* **4**, 79–202.
- Weiss, C. S. (1815). *Übersichtliche Darstellung der verschiedenen natürlichen Abtheilungen der Krystallisations systeme*. Berlin: Akad. der Wiss.
- Werner, A. G. (1774). *Von den äuserlichen Kennzeichen der Fossilien*. Crusius. Leipzig.