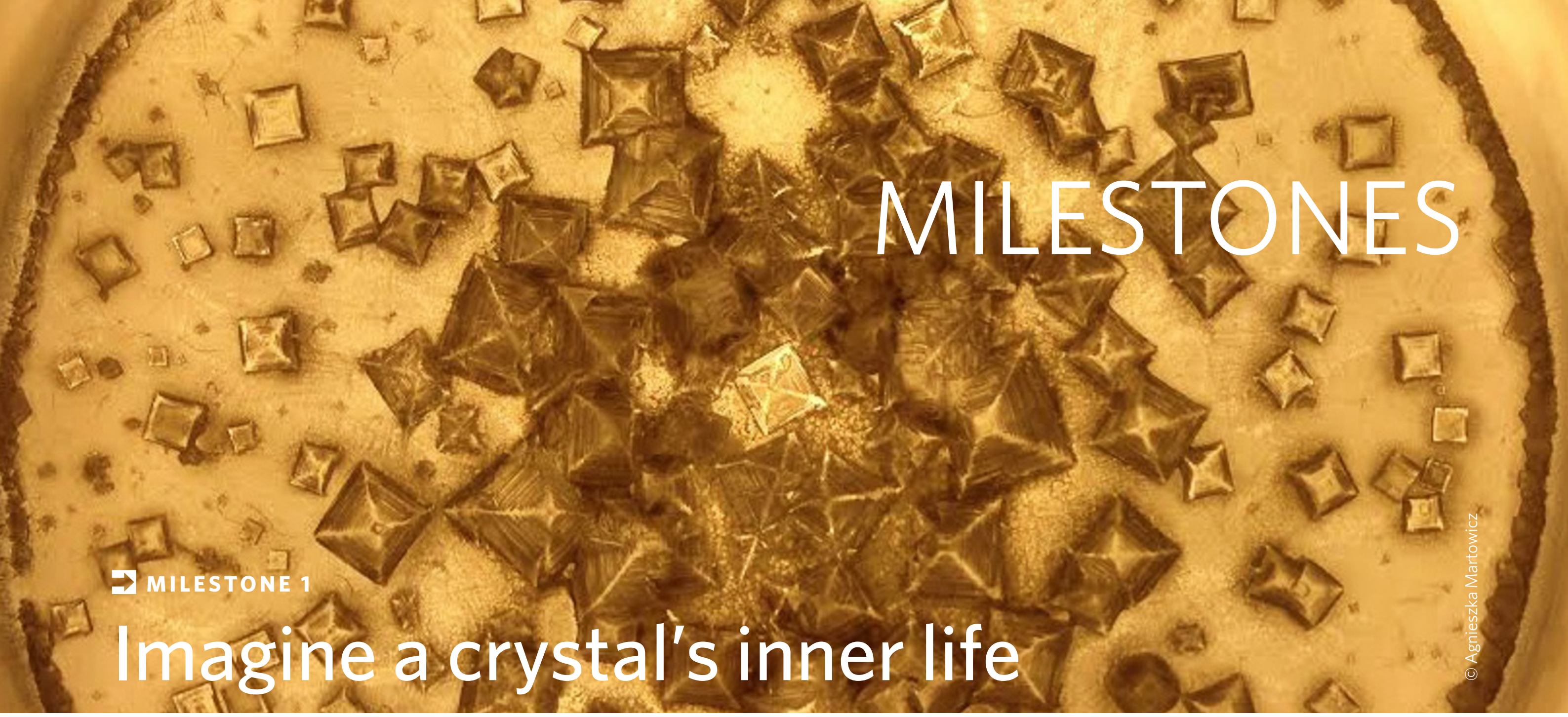


MILESTONES

© Agnieszka Martowicz

MILESTONE 1

Imagine a crystal's inner life

As the story goes, one of the most defining events for crystallography was a mishap. Rene-Just Haüy, a Parisian priest, had been invited to look at a friend's latest acquisition, a beautiful prismatic calcite crystal. In a careless moment, the crystal slipped out of Haüy's hands and shattered on the floor. At this time, in 1781, characterizations of crystals were solely based on their outer morphology. But Haüy's mishap led to a deeper understanding of the essential inner characteristics of the crystalline state of matter: periodicity.

On examination of the crystal's fragments, Haüy noticed that it "had a single fracture along one of the edges of the base… I tried to divide it in other directions and I succeeded, after several attempts, in extracting its rhomboid nucleus." In other words, Haüy realized that crystals always cleave along crystallographic planes. In addition, it was known from previous discoveries that in a given crystal species the interfacial angles always have the same value. Based on these two clues, Haüy concluded that crystals must be periodic and composed of stacks of little polyhedra, which he called *molécules intégrantes*. This theory could conveniently explain why all crystal planes are related by small rational numbers, a principle we nowadays refer to as the law of rational indices.

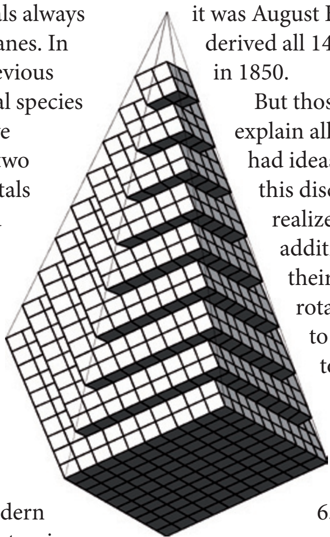
Considering how closely Haüy's theory resembles the modern concept of periodicity, it is a masterpiece of imagination. But it posed two major questions. The first one again relates to outer morphology: What is the complete list of symmetries that a crystal can in principle possess? It was clear that only 2, 3, 4 and 6-fold rotational axes were consistent with Haüy's laws, and eventually Moritz Frankenheim (in 1826) and Johann Hessel (in 1830) concluded that this restriction results in 32 possible crystal classes.

The second question concerns the exact nature of the *molécules intégrantes*, which in Haüy's drawings look like little bricks. But this proved to be incompatible with the observation that crystals are elastic. What was missing was the concept of a space lattice. That a crystal is best described by an array of discrete points generated by defined translational operations was independently devised by Ludwig Seeber in 1824 and Gabriel Delafosse in 1840. And it was August Bravais who then famously derived all 14 possible lattice symmetries in 1850.

But those 14 lattices could not explain all 32 crystal classes. Bravais had ideas about how to reconcile this discrepancy but did not realize his crucial oversight: In addition to pure translations, their combination with rotations and reflections had to be considered. It then took geometrical group theory to elaborate all possible combinations. Leonhard Sohncke took on this task, presenting 65 space groups in 1879, but left out certain symmetry operations. The two scientists who independently sought to extend Sohncke's result were Arthur Shoenflies and Evgraf Fedorov. After learning about each other's work, they started a lively correspondence, eliminating mistakes and finally, in 1891, agreeing on a catalogue of 230 space groups.

Compared with the 32 crystal classes, these concepts seemed like an unnecessary complication. And there was no means of testing the notion of a space lattice or space groups. Consequently, neither of their inventors got due credit at first. "Somehow I did not think that I would live to see the day when the distribution of atoms as I predicted it in my papers would actually be determined," Fedorov commented on the first X-ray diffraction experiments. But thanks to Max von Laue (Milestone 2) and the Braggs (Milestones 3 and 4), the concepts of the space lattice and space groups were verified earlier than Fedorov had ever hoped for.

Leonie Mueck, Associate Editor, Nature



Haüy's concept of periodicity. Construction of a scalenohedron by stacking *molécules intégrantes*. Figure reprinted with permission from A. Authier *Early Days of X-ray Crystallography* p12 (Oxford Univ. Press, 2013).

ORIGINAL RESEARCH PAPERS Haüy, R. J. *Essai d'une Théorie sur la Structure des Crystaux* (Gogué et Née de La Rochelle, 1784) | Hessel, J. F. C. *Kristallometrie oder Kristallonomie und Kristallographie* (E. B. Schwickert, 1830) | Bravais, A. Mémoire sur les systèmes formés par des points distribués regulièrement sur un plan ou dans l'espace. *J. l'Ecole Polytechnique* **19,** 1 (1850) | Fedorov, E. S. Nachala ucheniia o figurakh. *Zap. Min. Obshch.* (The elements of the study of configurations. *Trans. Mineral. Soc.*) **21,** 240 (1885) | Schönflies, A. *Kristallsysteme und Kristallstruktur* (B. G. Teubner, 1891)

FURTHER READING Kunz, G. F. The life and work of Haüy. *Am. Mineral.* **3,** 60–89 (1918) | Whitlock, H. P. Rene-Just Haüy and his influence. *Am. Mineral.* **3,** 92–98 (1918) | Moses, A. J. Haüy's law of rational intercepts. *Am. Mineral.* **3,** 132–133 (1918) | Whitlock, H. P. A century of progress in crystallography. *Am. Mineral.* **19,** 93–100 (1934) | Winkler, H. G. F. Hundert Jahre Bravais Gitter. *Naturwissenschaften* **37,** 385–390 (1950) | Ewald, P. P. (ed.) *50 Years of X-ray Diffraction* (IUCR, Oosthoek, 1962) | Authier, A. *Early Days of X-ray Crystallography* (Oxford Univ. Press, 2013)