





single icosahedral quasi-crystal Ho_{8.7}Mg_{34.6}Zn_{56.8}. Courtesy of I.R. Fisher











B. Le Saffre, J-M. Panel, Colección del museo de Grenoble

Crystals:

- Perennial objects of desire
- Essential for determining how atoms arrange themselves and why materials have the properties they do!
- Numerous applications in materials science, nano-technology, biology/medicine/pharmaceuticals...



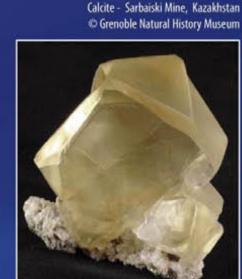




Pyrite or "fools gold" @ Grenoble Natural History Museum

A presentation initially prepared by the French Crystallographic Association for the exhibition "Journey into the Crystal" and modified to celebrate the International Year of Crystallography (IYCr) in 2014





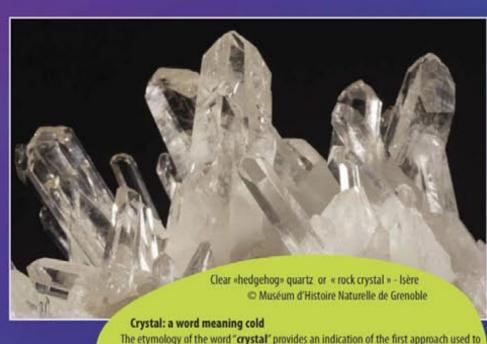


Crystals: Objects of beauty and source of riches

From the earliest times, humans have been aware of rocks/stones emanating from the centre of the earth of an incredible variety of shapes and sizes. Multifaceted crystals, in particular, inspired wonderment. They were called "stars from the centre of the earth".



These "stones" came in a multitude of shapes, sizes and and colours. They sometimes took the form of unusual "angular stones", with flat, smooth sides, as if manufactured. Some of these became known as "Crystal". Their fascinating colours, shapes and sizes naturally attracted mysticism: crystals were talismans of supernatural power supposed to offer healing and protection The colour, transparency, rarity and stability of certain stones made them precious objects used in jewels and gems. They became symbols of power and wealth.

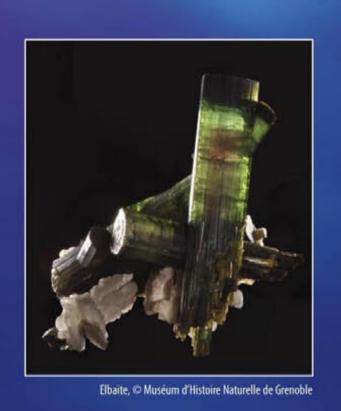


The etymology of the word "crystal" provides an indication of the first approach used to determine the origin of these stones. This word comes from the Greek "krystallos": meaning "ice". Could rock crystal actually be water that has been subjected to such an intense level of freezing that it has been converted into permanent ice? This analogy between rock crystal and other transparent materials can be found in crystal glass... which is truly a glass but not a crystal from a scientist point of view.



Calcite - St Marcellin Isère

Muséum d'Histoire Naturelle de Grenoble





Fluorite Muséum d'Histoire Naturelle de Grenoble

Crystal: a definition that has evolved

In the 18th century the term crystal was used by scientists to describe any angular stone with specifically orientated plane surfaces. In the early 19th century, crystal referred to any homogeneous solid material characterized by

In the 20th and 21st centuries the term crystal refers to any material whose atoms are arranged in an ordered pattern.

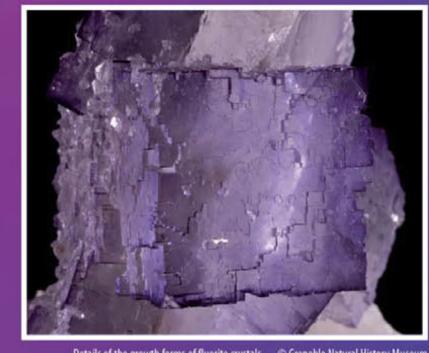


"Angular Stones": The Birth of Crystallography

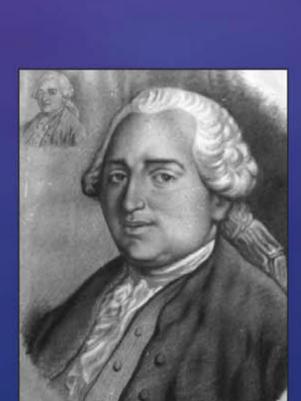
During the Renaissance, a discussion began: do crystals stem from the growth of inert matter or are they somehow sculpted? Using his observations of the shape of quartz crystals, Steno, in the 17th century, was one of the first to imagine crystal growth. It was only during the 18th century, however, that 'crystallographers' formed a picture of the internal structure of crystals by focussing on their external geometry.

It was the discovery of the "constancy of the angles" between the various faces of a given type of crystal, which first drove scientists to suggest that crystals must be made out of a stack of basic building blocks or bricks. This model allowed them to explain crystal faceting. The works of Steno, Romé de L'Isle and Haüy and numerous other scientists thereby gave rise to the new science of "crystallography".

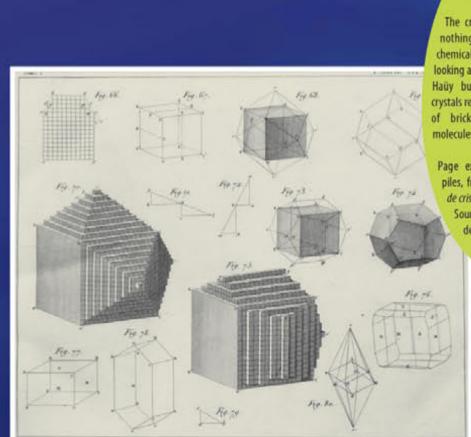
In the 19th century, German and French researchers introduced the concept of symmetry to classify crystals. They used mathematics to formalize their classification theory. Thus, by the beginning of the 20th century, even without being able to "see into" a crystal, crystallographers had developed the notion of atomic order and periodic repetition to understand both the external form of crystals as well as their symmetry.







Romé de l'Isle. Musée Baron Martin



building blocks

Page showing the stacks

The crystalline forms leave nothing to chance, each themical has a specific form, By looking at pieces of broken calcite, Hauy built a model in which crystals resulted from the small pile of bricks he called integral

Page exhibiting examples of piles, from R.J. Haüy Traité de cristallographie (1822). Source : Coll. Minéraux de Jussieu, UPMC



René Just Hauy. © Ecole des Mines de Paris



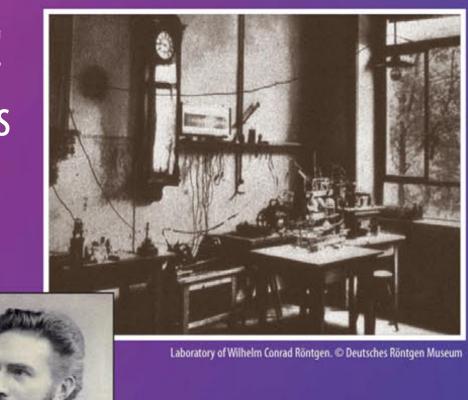


Crystals and X-rays: made for each other! the ideal tool for studying crystalline materials

Insight into the internal structure of crystals initially grew out of using crystals to understand what X-rays were: *insight often comes in unexpected ways!*

X-rays: In 1895, Röntgen discovered a new type of radiation but was unable to determine its precise nature. In the end, he gave up and called them X-rays. Invisible and able to pass through solid matter, these rays were studied by scientists from Australia, Britain and Germany who used crystals to understand their properties. In 1912, von Laue, Friedrich & Knipping exposed a crystal to X-rays. The experiment, now called diffraction, was initially carried out in order to understand the nature of the radiation; instead, its real importance was to reveal the regular order and symmetry of the crystals themselves. This led to the extraordinary possibility of determining the internal atomic arrangement of all crystals.

William Lawrence Bragg and his father, William Henry Bragg, realized that X-rays could be used to understand crystals, to "see" their inner structure and thus developed the new science of X-ray crystallography. WL Bragg is most famous for his law on the diffraction of X-rays by crystals, made during his first year as a research student in 1912. Bragg's law made it possible to calculate the positions of the atoms within a crystal. The "diffraction" of X-rays thus changed from the status of being a physical phenomenon to that of a tool for exploring the arrangement of atoms within crystals. This discovery led to an intense period of research. Most of these pioneering scientists received Nobel prizes, including the first Australian, and the youngest ever, Nobel Prize winner, WL Bragg.

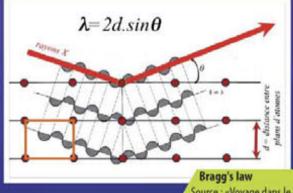


Vilhelm Conrad Röntgen Prix Nobel 1901 © Deutsches Röntgen Museum



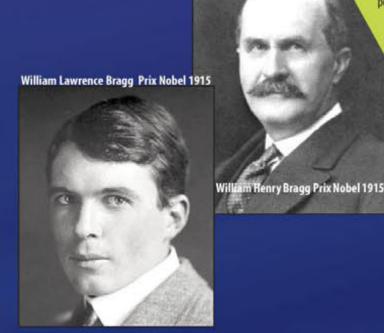
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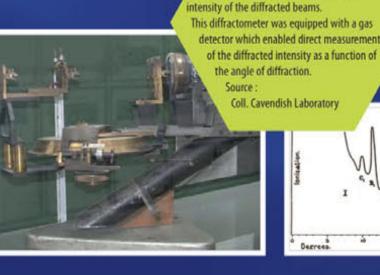
Sim der ersten Inde for der



Source : «Voyage dans le Cristal»

William Henry Bragg, professor of physics, believed that X-rays were particles similar to electrons, but carrying no electric charge. But from the results of Laue, he understood that this experiment showed X-rays were behaving like a wave, like light. His son, then aged 22, was an unconditional supporter of the view taken by his father and in seeking to prove this point he formulated Bragg's law $\lambda = 2 d. \sin \theta$ that connects the deviation of the beam with the distance between the planes formed by the atoms.





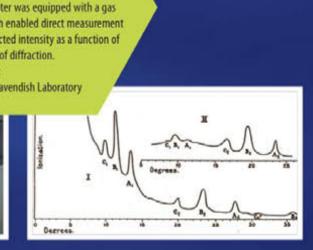
ne diffractometer has

source that radiates at a known

ingle to the surface of a cleaved crystal

and a detector oriented at an angle equal to

he angle of incidence, which registers the





Alice and Joseph in crystal-land

The structure of crystals could not, at the time, be seen directly with a microscope, but had to rely on diffraction. The geometry of the locations of the different diffracted beams/spots allow the structure to be represented in a virtual space which is called "reciprocal space".



A precise mathematical relationship, the "Fourier Transform", exists between the "reciprocal space" observed by diffraction and the real structure of the crystal in "direct space".

In order to 'understand' this relationship, think of Alice (in Wonderland), who has a direct view of the world of the crystal and its atoms, and that of Joseph (Fourier), who can only see those produced by the diffraction spots!

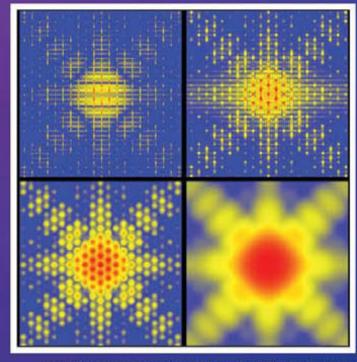
Travelling into "reciprocal space"

The direct observation of "reciprocal space" via symmetry of a crystal, the dimensions of its atoms themselves: the diffraction pattern is a finger print which identifies each crystal.

To understand more...

Diffraction may appear complicated because it provides an inverse image, but this is nothing more than a superposition of sine waves, discovered by Joseph Fourier when he was the state representative "préfet de Grenoble" under Napoleon the First.

diffraction enabled crystallographers to see the building block or "unit cell" and finally to "see" the



Joseph Fourier

the periodic crystals

Egyptologist, scholar and administrator. Prefect of Isere in 1802, he studied the propagation of heat and needed more powerful

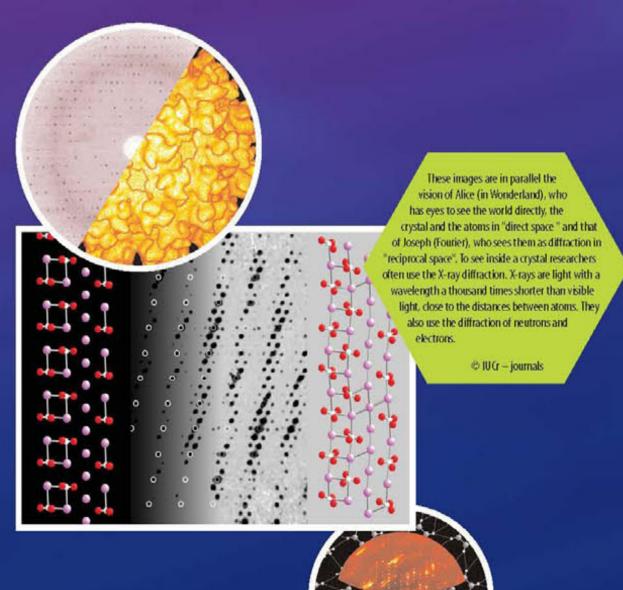
discovered a complex periodic function can be decomposed into a sum of simpler functions (sine wave like), which are now known as Fourier series. This information is

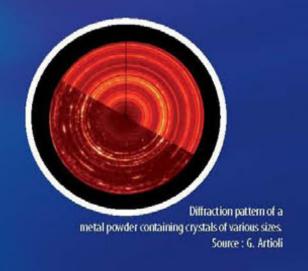
encoded by its Fourier transform. Researchers use the Fourier transform to "see" inside

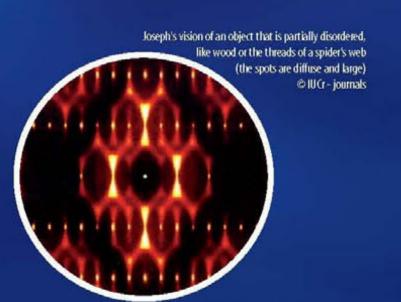
Source: Wikipedia

mathematical tools for these calculations. He

Diffraction patterns obtained from a coherent X-ray diffraction experiment on an artificial crystal of electronic circuit. © IUCr − journals







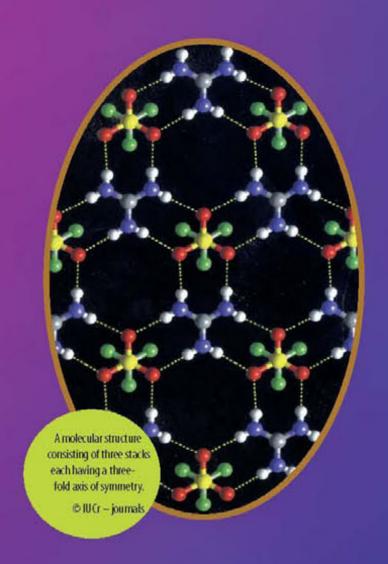


Crystallography

and Crystal Chemistry

Crystals are essential to modern society, their study using X-rays (radio-crystallography) gave birth to crystal chemistry, at the beginning of 20th century.

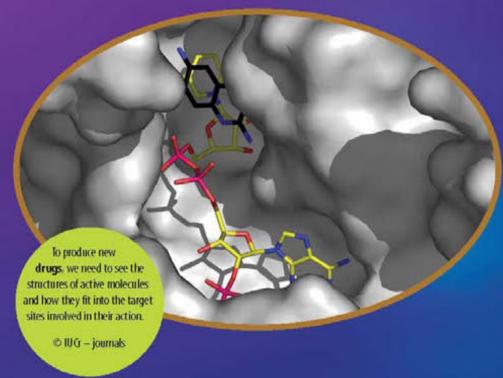
Crystal chemistry's objective is to explain the relationship between the properties, the chemical composition and the arrangement of atoms in crystals.

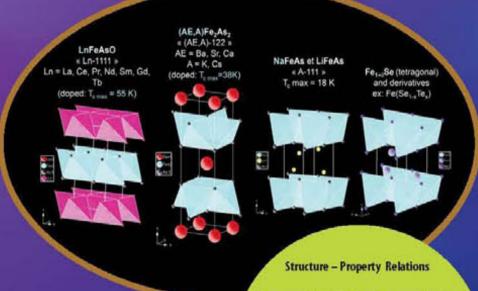


The crystallographic approach

The crystallographic approach to understanding atomic arrangement represented a revolution for science. For the first time, we could directly see the atomic structure and make-up of materials. This enabled scientists to focus on developing strategies for making materials with new and/or improved physical properties e.g. new generation batteries, new materials for hydrogen storage .. etc.

Applications for crystallography today exist not only in **materials science**, but also in the synthesis and structure determination of new molecular materials including the development of new medicines.

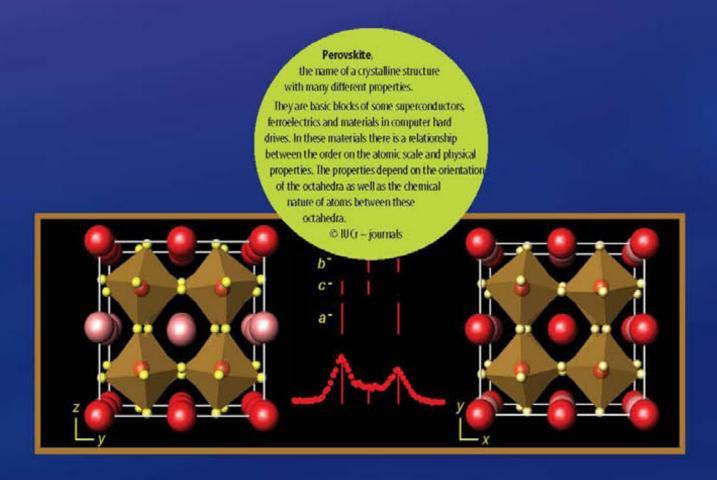


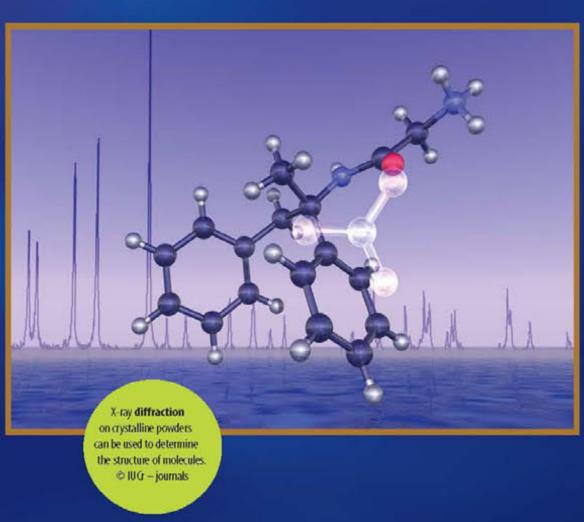


The organization inside a crystal can explain the relationship between structure at the atomic scale and macroscopic properties. With advances in crystallography, chemists can "understand" existing materials and try to design new materials with desirable properties. This has been the case for both "copper oxide superconductors", and more recently iron-based superconductors as well.

source: Institut Néel-CNRS

in principle if a compound or substance can be crystallised its structure can be determined by X-ray crystallography.









Nano-porous Crystals the zeolites

Zeolites seen by
using electron microscopy
O QRFS Photothèque / D.Cot
There are a multitude of zeolites. They
have become indispensable in our daily

lives: used as a softener for household appliances and essential for the petrochemical and even trap odors in the cat's litter tray!

To understand natural crystals, to duplicate them, and then to do better . . . the art of synthesis!

The stone that boils:

an amazing crystal

In 1756, Cronstedt made an astonishing discovery: while heating a sample of the mineral stilbite, it became covered in bubbles at around 150°C, as if the stone were boiling. Hence the name given to this mineral: "**zeolite**", from the Greek zeo (to boil) and lithos (stone).

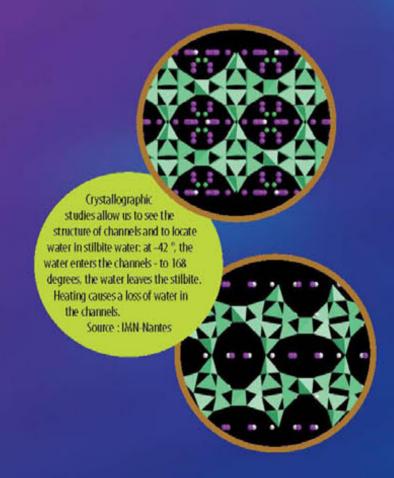
X-rays provide evidence of the nanoporous structure of this crystal

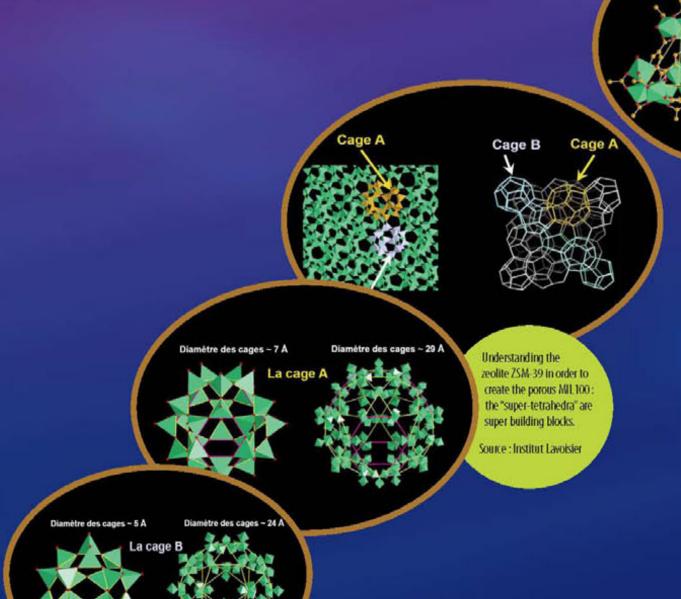
In 1930, Taylor and Pauling used X-ray diffraction to study the first zeolite crystals and revealed that, at an atomic level, these minerals are made up of a nano-porous matrix. Stilbite is a sodium calcium aluminium silicate that can hydrate or dehydrate in a reversible manner, according to the temperature. **Water is trapped** within the cavities of the structure.

There are around 50 natural zeolites and more than 500 artificial zeolites have now been synthesized ...

.. by using the crystallographic approach scientists were able to "visualize" the different atomic arrangements and cavities, enabling them to understand and then create new zeolites.

Zeolites are widely used in industry for water purification, as catalysts, for the preparation of advanced materials and in nuclear reprocessing. They are used to extract nitrogen from air to increase oxygen content for both industrial and medical purposes. Their biggest use is in the production of laundry detergents. They are also used in medicine, in agriculture and in the oil industry.



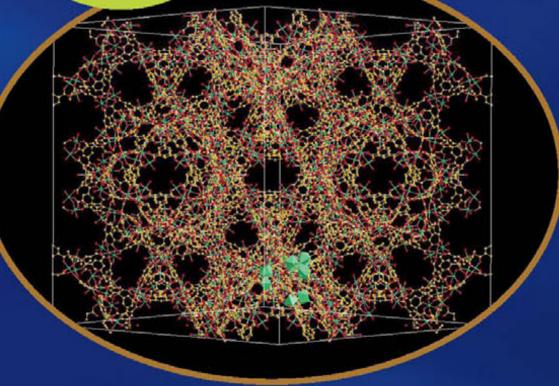


Source : Institut Lavoisier & Gerard Ferey
CNRS 2010 Gold Medal

By combining organic molecules and inorganic bricks
Gerard Ferey and his team at the Institut Lavoisier de
Versailles could create new porous materials like MIL100 and MIL-101 with glant cages, ten to one
hundred times larger than those of zeolites, which
can act as a reservoir for gas, molecules and
even drug molecules.

Spotlight on MIL-100

super - tétraèdres





Crystals, chirality and Pasteur

The concept of chirality is very important in many branches of science. It is responsible for properties such as the direction of rotation of plane polarized light, the taste and smell of chiral compounds and it is fundamental to the chemistry of living organisms.

Chiral comes from the Greek word *chiro* which means 'hand'. When the palms are turned towards the sun, the left hand cannot be superimposed on to the right hand.

The chirality of molecules

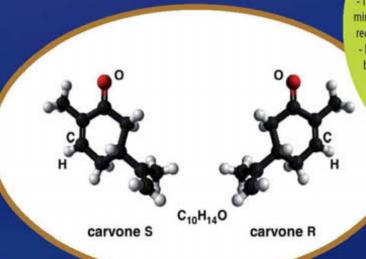
In 1848, Pasteur commented that crystals can have two identical and yet opposing forms, a mirror image of each other. He interpreted it as the existence of two chiral molecules. The chirality of crystals is primarily due to the manner in which the constituent atoms or molecules are arranged. Asymmetric molecules have two chiral forms, generally in nature one of these two forms is dominant.

Our body is made up of basic chiral structures: amino acids, sugars ..

A chiral molecule in one isomer or another will not have the same effect on our bodies. This is the case with many drugs and medicines as well as in the perception of tastes and smells. By examining crystals of
tartaric acid, Louis Pasteur observed
that two crystal forms, images of each other in
a mirror, coexist in the same sample. He separated
the crystals by hand and, by dissolving them separately
in water, he found that the two forms have different
optical properties: one form rotates the polarization plane
of light in the opposite direction to the other. A mixture of
the two solutions does not deviate that light. These two
forms are called enantiomers (Greek enantios
"opposite").

Table from Albert Edelfelt 1885
Coll. Orsay Museum.





Two enantiomers have identical physical properties and share many chemical properties. However, they are perceived differently by living organisms. In other words, depending on whether the molecule is in one form or another it will not have the same effect.

- This explains why a molecule of R-carvone can smell of mint, while that of carvone-5 has a scent of cumin, our olfactory receptors are sensitive to chirality.

- It is the same for the taste: a molecule of asparagine-5 has the

It is the same for the **taste**: a molecule of asparagine-S has the bitter taste of the asparagus while asparagine-R has a sweet taste.

- These differences in properties can be dramatic for drugs: the case of **thalidomide** in one form gives pain relief and the other causes of fetal malformations.

Source : Institut Néel-CNRS





Using crystals to understand living organisms

Biological crystals

Prepared for a diffraction
experiment. © EMBL-Grenoble

The crystals of proteins and other biological
macromolecules are among the most
difficult to obtain and they are never
very large. Those in these photos
are smaller than a millimeter!

At the interface between chemistry and biology: In order to understand the way a living organism functions as well the role of the various proteins involved, scientists have long sought to see their structures. For this, X-ray diffraction has proved to be an extremely powerful technique. It does have one limitation: the proteins must be in a crystalline form.

"Growing" protein crystals ...

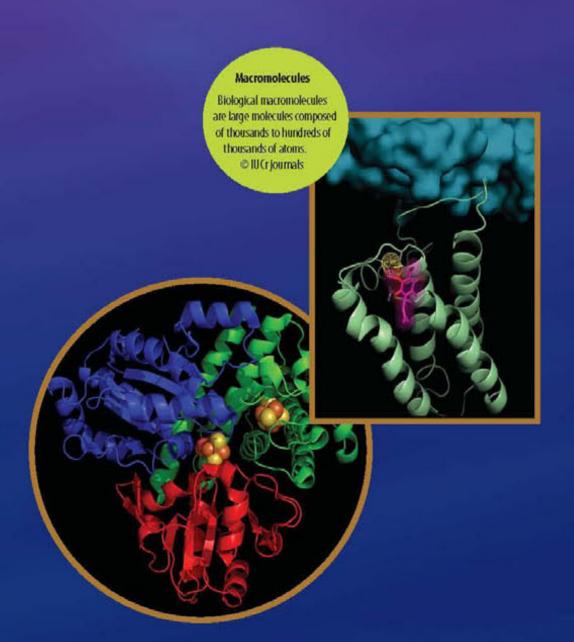
Proteins are very large biological molecules (macromolecules) and essential for life. They are made of amino acids. Each protein has a specific function, directly linked to its three-dimensional structure, i.e. the manner in which the amino acids are laid out, one against the other in space. Proteins do not naturally form crystals, so they have to be grown artifically.

... to study them.

There exists a very strong relationship between the atomic arrangement (the structure) of a biological macromolecule and its function: the precise knowledge acquired about its forms means that a hypothesis can be made regarding its role and the manner in which it carries out its functio Studies relate to both basic research, in order to acquire a precise understanding of the biological processes, and applied research, leading to the synthesis of new medicines.



DNA is present in all living cells. It is the basis of heredity. It consists of two complementary strands formed by two regular sequences of small molecules, a coiled double helix. It can replicate into more molecules identical to each other, the property that is the basis of genetics. This is the image of X-ray diffraction from crystallites in a fiber of DNA, obtained in 1951 by Rosalind Franklin, who help to determine the shape of the molecule.









Egyptian cosmetics .. and crystallography!



Objects found in ancient burial sites are often made up of crystallized chemical materials. These crystals are, for those who know how to 'read them', real archives.

Egyptian make up,

knowledge from crystals

The use of kohl, black eye makeup, is recorded from ancient Egypt. Analysis of cosmetic powders taken from funerary objects preserved in the Louvre Museum, has identified the major component of these old cosmetics as a crystalline lead ore, galena (PbS) but also ... the presence of far rarer crystals ...

The first chemical solution synthesis invented by Man?

Researchers have shown that these crystals are rare chlorinated compounds of lead. The synthesis method (in aqueous media) can be found in Greco-Roman texts. These texts reveal that the artificial white precipitates were highly valued for their medicinal properties, especially for the eyes. The ancient Egyptians were thus the first to use soft chemistry to develop cosmetic products to protect them from eye infections, common in the hot and humid climates along the Nile .. the cradle of their civilization ...

Ancient texts (Discoride, Pliny) describe a method for synthesis of these



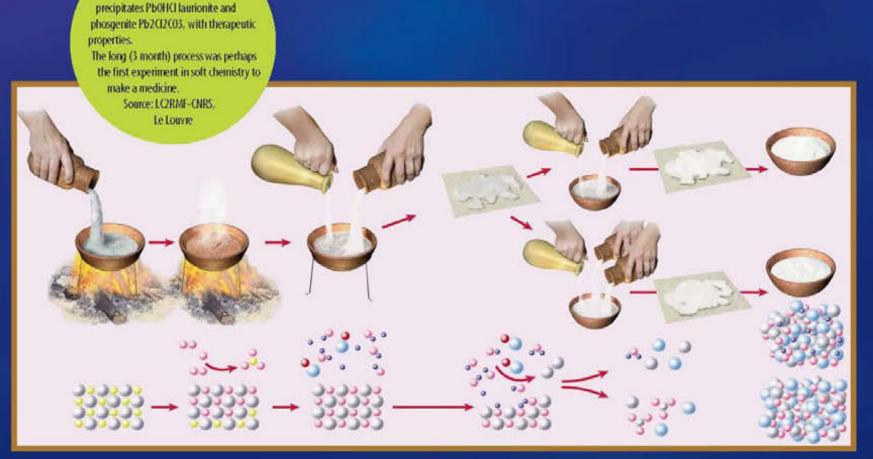


Egyptian woman's bust

Coll. Museum of Grenoble

In the tombs of Egypt from third to fifth centuries BC, grave goods, everyday items and toilettries were found. The materials and their crystals are examined by researchers using beams of light, X rays, neutrons and electrons. These studies together with the evidence and interpretations of the archaeologist, lead to an understanding of their development and purposes.



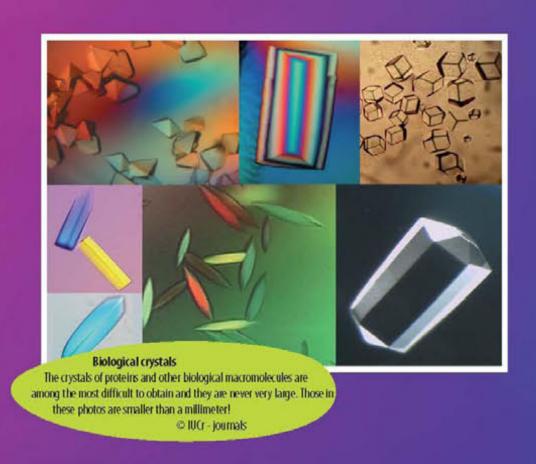


Reconstituted preparation, by using galena (PbS), litharge (PbO), gemmed salt (NaCl) and water (H2O), then by adding natron (Na2CO3) to obtain laurionite (PbOHCl) and phosgenite (Pb2Cl2CO3) © LC2RMF-CNRS Le Louvre.



Growing crystals

The specific properties of crystals make them key materials for a large number of technological fields such as electronics, communications, energy, medicine and defence. For all of these areas, it is of paramount importance to have crystals with the appropriate properties, size and quality. Crystal growth has become a major technological challenge.



Crystallisation

Crystallisation is based on a simple principle: forming a solid object with atoms that are organised in a periodic array. This organisation is spontaneous but **time must be allowed for it to take place** and that time varies according to the crystals you are trying to grow.

Take your time to make large crystals

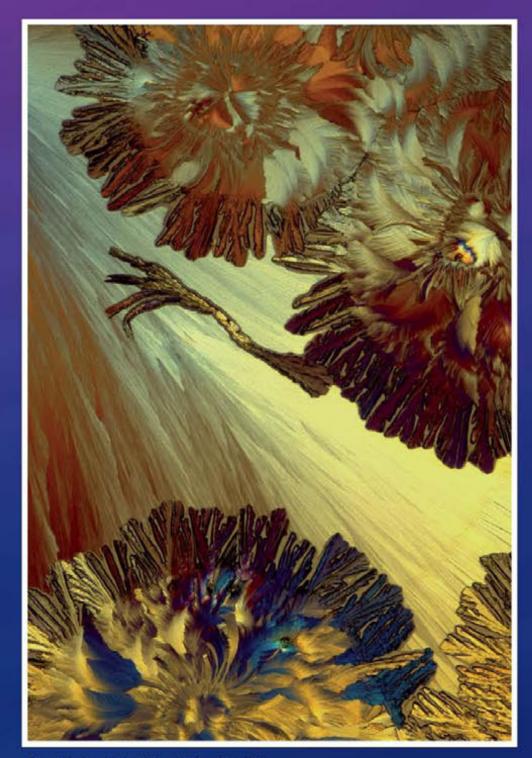
When a molten compound is suddenly cooled (quenched) there is no long-range order of the positions of atoms (amorphous glass) as there was in the molten state. If cooling is sufficiently "slow", then the atoms and molecules have time to move and thus optimise their interactions and compactness. These two factors lead to an atomic order which is regularly repeated, and which will be propagated to new molecules/atoms joining those already solidified. Each atomic "layer" reproduces the order of the inner layer and acts as a model or "pattern" for the following ones.

The period of time may vary considerably according to each material. If you want to grow a few large crystals instead of many small crystals, you'll need more time!





Synthetic quartz crystals. Source : Coll. LMGP-Grenoble-INP



Recrystallization of citric acid viewed under polarized light.

© ONRS Fototeca / A. Jeanne-Michaud







Crystals for bone replacement

Studies of the chemical composition of bones and tooth enamel were quite perplexing for the first researchers. These chemical compounds are very reactive nano-crystals known as apatites. By means of artificial biomineralization, Man has been able to create crystalline prostheses which imitate nature.

Crystals for pharmacetical applications

The same molecule can crystallise in different forms while presenting the same chemical characteristics in solution. This polymorphism results from a different arrangement of molecules. In pharmacy, It is important to control the shape and size of the crystals that contain the active molecule of the medicine, because these parameters may influence the dissolution rate and thus have an effect on the effectiveness of the medicine..

Crystals and their defects

in metallurgy

Metallurgy is the study of metals, intermetallic compounds and mixtures thereof known as alloys. The first evidence of human metallurgy dates from the 5th and 6th centuries BC. They have numerous uses ranging from steel in construction to complex alloys used in modern jet engines to coatings that confer corrosion resistance. It is often the defects in metals and alloys that determine their very useful electrical and mechanical properties.

Liquid crystals!

A liquid crystal is a phase between the liquid and the solid state: it flows like a liquid but has the properties of a solid. The molecules of a liquid crystal are highly elongated and have a tendency to line up like matches in a box. They owe their name to their optical properties which are similar to those of regular crystals.



From the Bronze Age to the "golden" age of steel

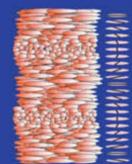
This science seeks to control the chemistry of metals and alloys, it studied their structures and properties, it also refers to the technologies of their manufacture, processing and shaping. The first traces of metallurgy date back to the use of bronze 5000 years ago in the Middle East, Around 1200 BC, it was discovered in Anatolia that when iron is heated with charcoal it becomes harder than bronze. It was not until the early 19th century that new metals such as aluminum were isolated. Many advances in the treatment of ferrous metals made this century the "golden age" of steel that contains iron with some carbon.

Knife Danakil Ethiopia © Coll. Natural History Museum of Grenoble



nématique

smectique



cholestérique

Georges Friedel

1909-1922 studied liquid crystals that can produce stunning images ...

He classified them into three types: Nematic: the molecules are aligned but disorganized, Smectic: The aligned molecules form layers, Cholesteric: the orientation of the molecules form a helix. The orientation of the molecules can be controlled by an electric field. This property is what makes liquid crystals the essential

component of flat screens for moving images and colors. Liquid crystals are also present in nature on the shells

Source: University-IPCMS L. Pasteur -Strasbourg



Hip prosthesis.

© coll. Ecole des Mines de Saint-Etienne

How to mend broken bones? Bone reconstruction in humans is difficult, sometime making use of surgical bone grafts is necessary. However, the difficulties associated with finding grafts from the patient, and the potential risks of viral transmissions raised by foreign transplants (human or animal), lead scientists to consider the creation of synthetic bone substitutes. Recent work shows the importance of biomaterials that influence bone growth and mineralization.



asparagine

Polymorphysm of Asparagine

Polymorphism of crystals gives them distinct properties that may be important in pharmacy:

- Different distributions of faces of the crystals: for example, in the acid L-asparagine, certain solvents influence the formation of polymorphic forms, sticking onto one facet of growth without disrupting the assembly of molecules in the crystal

- Different density and porosity with consequences for the action

- Solubility and dissolution rates modify the bioavailability of the drug with a risk of either under-dosing or

Source: J. Doucet-LPS-Orsay