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..

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.
“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 focusing 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 Hauy 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.
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, Roentgen 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.
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".

Using mathematics to visualise crystals

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 diffraction enabled crystallographers to see the symmetry of a crystal, the dimensions of its building block or "unit cell" and finally to "see" the atoms themselves: the diffraction pattern is a fingerprint 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 "prolet de Grenoble" under Napoleon the First.
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.

in principle if a compound or substance can be crystallised its structure can be determined by X-ray crystallography.
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 nano-porous 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.
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 1846, 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.
Using crystals to understand living organisms

At the interface between chemistry and biology: In order to understand the way a living organism functions as well as 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 artificially.

... 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 function. 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.
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 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 rare 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 ...

Reconstituted preparation, by using galena (PbS), litharge (PbO), gemmed salt (NaI) and water (H2O), then by adding natron (Na2CO3) to obtain laurionite (PbO·2Na2CO3) and phosphates (P2O5·2H2O) © LC2MNF-CHRS 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 crystal 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!
Crystals and their uses

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 biomaterialization, Man has been able to create crystalline prostheses which imitate nature.

Crystals for pharmaceutical applications

The same molecule can crystallize 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 4th 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.

Metallurgy: from the Bronze Age to the "golden" age of steel

This science seeks to control the chemistry of metals and alloys. It studied their structure and properties. It also reflects the techniques of their manufacture, processing and shaping. The first ironworking site dates back to the rise of civilization 3500 years ago in the Middle East, around 1500 BC, thanks to the discovery of asbestos. The other metals came later and were gradually improved. The 18th century brought new steels to use in steel. In 1812, iron was discovered in the manufacture of ferromagnetic wires, which make it an efficient material for the manufacture of various materials.

Geogelina

CaO-FeO-MgO-Al₂O₃-SiO₂

- Low melting point - High resistance - Amorphous structure

Cristobalite

- High melting point - High resistance - Crystalline structure

Chalcedonic

- Intermediate properties - Intermediary structure

Polyphosphates of asparagus

Polyphosphate of asparagus given different properties that may be important in pharmacy. Different distributions of chains of the polyphosphate for example, in the cellulose layers, membranes influence the formation of polyphosphate forms, taking use of the form of crystal without disrupting the anatomy of the crystal. Different density and porosity with consequences for the action of the generating solubility and dissolution will modify the bioavailability of the drug with a scale of other under-diagnosis.

Source: J. Durand (IP-Puy-de-Dôme)