Single crystals—natural and synthetic

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Many natural crystals have great beauty and many great utility. Some have both: diamond is in a class of its own as a gem, yet many industrial processes would be impossible without its unrivalled cutting power. It is these two properties, beauty and utility, that have attracted man's interest in crystals since earliest times.

Mountainous areas are natural places to find crystals. In fact, the rocks of which mountains are made are aggregates of crystals of one or more minerals. Usually, the crystals are only present as small grains and often require a magnifying glass to be seen. Under certain geological conditions, however, quite large crystals are formed—commonly of centimetre dimensions, but on occasion several metres long. The records contain some impressive examples of the size of crystals that have been found. For example, in Iceland a rhombohedral crystal of calcite, the transparent sort which is called 'Iceland Spar', was discovered which measured 6×2 m. A crystal of beryl from Albany, Maine, weighed 18 tons and measured $5{\cdot}5 \times 1{\cdot}2$ m. At Lacy Mine, Ontario, a mica crystal as large as $4{\cdot}2 \times 9$ m and weighing more than 90 tons was found. One frequently sees quite large crystals of quartz in museums, particularly in

43 *Large Single Crystal in a South Dakota quarry* Photo: by permission of the Trustees of the British Museum (Natural History)

mountain areas, but probably not often as large as one weighing about 1400 lb that was found at Hintze in Switzerland. One could go on quoting similar impressive examples. For such large crystals to occur, there must have been not only an ample supply of the constituents, but also constancy of geological conditions for considerable periods. An additionally intriguing fact is that some of the largest crystals found contain some of the less common elements: for example, beryl which contains beryllium.

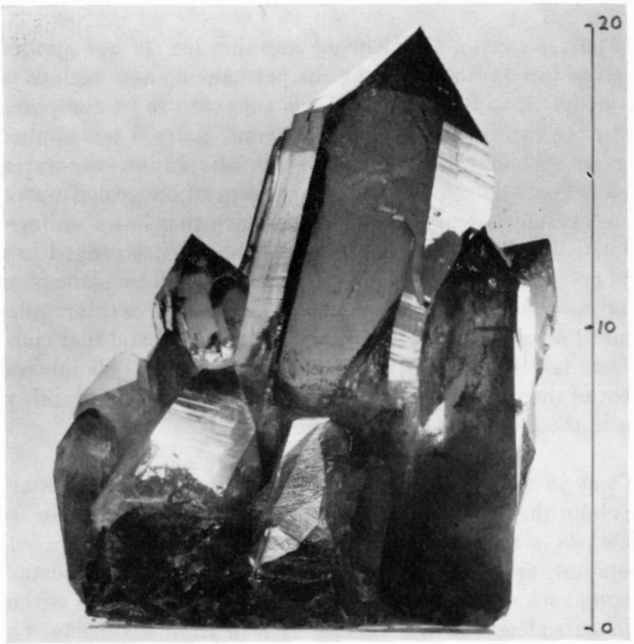
The word 'crystal' derives from a Greek word meaning ice. It was applied to the beautiful lustrous quartz found among the permanent snow regions of the Alps, since this material, as Pliny records, was supposed to be composed of water congealed by the extreme cold of those regions. Later it was applied to the long, slender prisms which are left behind when a salt solution evaporates, and which were also at first thought to be another form of congealed water. Nowadays, the term 'crystal' is reserved for a substance that has a uniform structure throughout, with all the similar atoms composing it arranged in a regular way. Natural crystals, with few exceptions, are bounded by plane faces and present a characteristic form which is an outward expression of this regular internal arrangement of atoms. An interesting example of a crystal that commonly has curved faces is dolomite (in the form of Pearl Spar). This mineral is a major constituent of the rock of the same name of which the type locality, naturally enough, is in the Dolomite Alps of Tyrol.

To understand the way in which natural crystals have grown, it is necessary to know something about the processes by which rocks are formed. There are three broad classifications of rocks based on their mode of formation: igneous, sedimentary and metamorphic. Igneous rocks were formed by the solidification of hot material (magma) which had either been intruded into fissures within the earth's crust, or extruded over the surface as lava from a volcano. On cooling and solidification, crystalline rock forms from the magma: granite is an example. Individual crystals of the three chief constituents of granite (quartz, feldspar and mica) can often be seen with the unaided eye, especially on a freshly broken and unweathered surface. (In towns, quite sizeable crystals can be seen in granite kerb stones, particularly when wet after rain, and on the rock facings of some buildings such as banks.) The larger the crystals, the longer the rock must have taken to cool. Sometimes, gases and liquids become trapped in the solidifying magma, and crystals of such high-temperature minerals as topaz and beryl may be formed, often of gem quality.

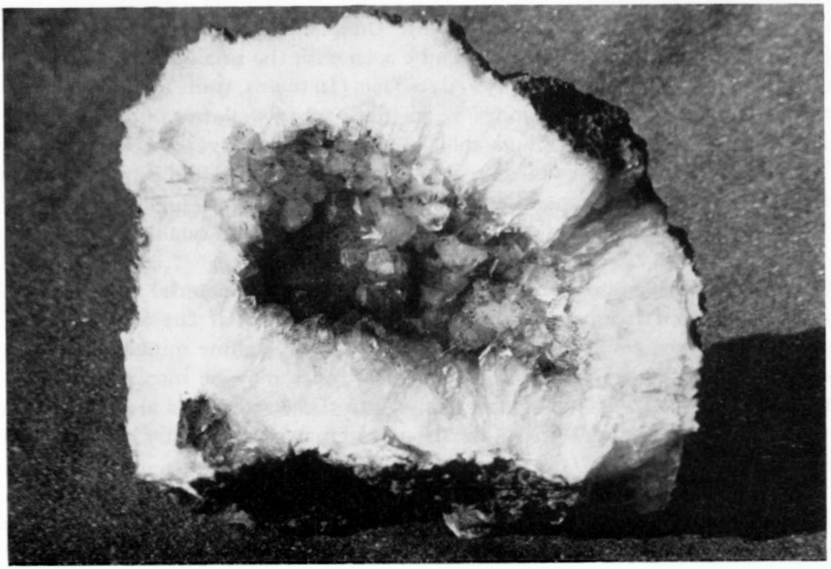
Sedimentary rocks are formed from the deposition of material broken down and transported from other pre-existing rocks. Even if the sedimentation process does not result in the formation of new crystalline minerals, sizeable crystalline fragments from the pre-existing rocks may be incorporated into the sediments, e.g. as a conglomerate. When these sediments are themselves worn away, these crystals may be released and may subsequently be found, for example in river beds.

Metamorphic rocks are produced by heat and pressure acting on igneous or sedimentary rocks to form different rock types. The heat and pressure arise

from the intrusion of magma or while mountains are undergoing folding. During this action any impurities in the original rock may crystallise out as separate minerals which become distributed through the newly formed rock. For example, the ruby and sapphire found in Burma have been produced by metamorphic action on the original ('country') limestone rock. Also, garnet is formed in flaky rock such as schist or slate.



44 *Quartz crystals from the Alps* (*Scale in cms*) Photo: Swiss National Tourist Office



45 *Quartz Geode* (*30 cm across*) This and next photo: J. A. Champion

New rocks may also be formed by the action of reactive vapours such as boron or fluorine on old rocks. Examples of the minerals that can form in this way are tourmaline and topaz in granite.

Some types of crystals are produced from mineral-rich water. Such water, when it flows through cracks and fissures in country rock, may deposit low-temperature minerals. Geodes ('potato stones') are hollow cavities lined with crystals deposited from mineral-rich water which has percolated into steam cavities in lavas, or into cavities in sedimentary rocks, or even into fossils. Such geodes are a common source of crystals of gem quality, particularly various forms of quartz (see Pl 44). Colourless crystalline quartz makes a fine gem, and its name, rock crystal, reflects its origin. Amethyst, whose colour may be due to traces of manganese, is an especially beautiful form of quartz that is frequently found in geodes (see Pl 45).

The list of known minerals increases at a rate of about twenty per year, but only about 2000 distinct species are known: this is much, much smaller than the number of, say, insect species. These different species of minerals can be

Table 1 Crystal systems

System	Number of axes of symmetry[1]	Typical forms	Mineral examples
Cubic	Four, 3-fold	Cube, octahedron, dodecahedron, tetrahedron	Blende, diamond, galena, garnet halite, pyrite
Tetragonal	One, 4-fold	4- or 8-sided prisms and pyramids	Cassiterite, chalcopyrite, rutile, zircon
Hexagonal	One, 6-fold	6- or 12-sided prisms and pyramids	Apatite, beryl, pyrrhotite
Trigonal	One, 3-fold	3- or 6-sided prisms and pyramids	Calcite, quartz, tourmaline
Orthorhombic	Three, 2-fold	Prisms and pyramids with rhomb-shaped cross-section	Andalusite, barytes, olivine, sulphur
Monoclinic	One, 2-fold	Prisms with inclined faces	Augite, gypsum, hornblende, mica, orthoclase
Triclinic	None	2-faced prisms	Kyanite, plagioclase

Note: If a perfect crystal with n-fold axis of symmetry is rotated about that axis, then it presents the same appearance n times in one complete revolution.

classified in various ways, but one which aids their identification is their degree of symmetry. The simplest and most highly symmetric is the cubic system, and fluorite ('Blue John') and diamond are examples of crystals which form in this fashion. The other crystal systems that have various lesser degrees of symmetry are: tetragonal, hexagonal, trigonal, orthorhombic, monoclinic and triclinic. Table 1 lists the typical forms in which crystals from these various systems are found, and examples of the minerals that belong to each. Of course, one generally does not find a complete and perfect crystal displaying a complete set of faces, but often several of the natural faces are evident, and this helps to decide the system to which it belongs and hence is a guide to its identification.

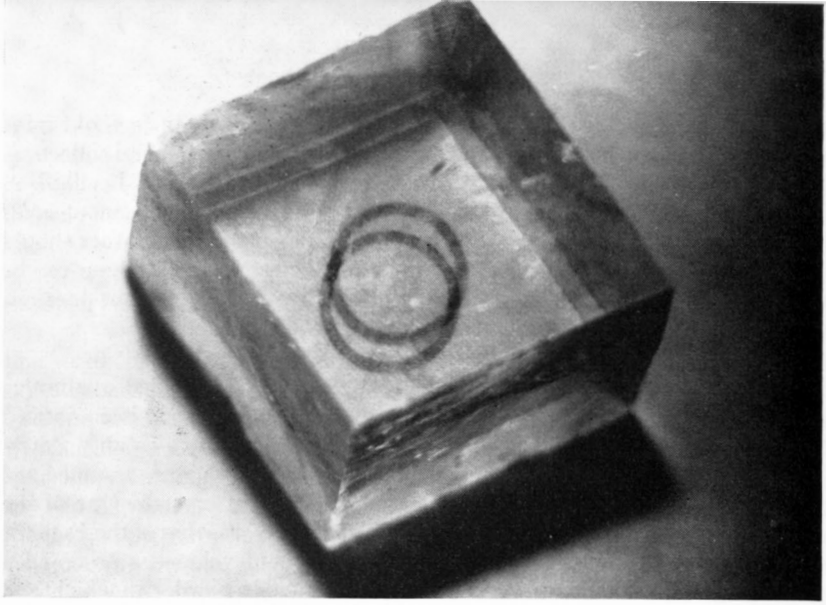
Apart from their form there are other properties of crystals which add to their their beauty, help to identify them, or render them useful for various applications. Colour is one of the first things that one notices about a crystal, but it is only diagnostic in a few instances, e.g. with amethyst. This is because many minerals can show a considerable range of colour due to varying amounts of impurities present. (In fact, the colour of the streak made when a mineral is rubbed on a piece of unglazed porcelain can be more characteristic.)

The hardness of a mineral is one of the properties which help to identify it, and also determine the sort of application it may find industrially. Hardness may be measured in terms of Mohs's scale, which is rather arbitrary and has irregular intervals, but has the advantage that each point on the scale is represented by an actual material (see Table 2). The scale is based on the fact that the mineral

Table 2 Mohs's scale of hardness

Scale No.	Mineral	Remarks
1	Talc	Can be crushed by finger-nail
2	Gypsum	Scratched with finger-nail
3	Calcite	Scratched with iron nail
4	Fluorite	Scratched with glass
5	Apatite	Scratched by penknife
6	Orthoclase	Scratched by quartz
7	Quartz	Scratched by steel file
8	Topaz	Scratched by emerald
9	Corundum	Scratched by diamond
10	Diamond	Only diamond scratches diamond!

with the higher number can scratch anything beneath it, or equal to it, in hardness. Two of the most common crystals one finds in the mountains are quartz and calcite. Both are often colourless, and at first glance appear quite similar. They can easily be distinguished, however, by the fact that calcite can readily be scratched by a penknife, whereas quartz will scratch ordinary steel.



46 *Double refraction in a Calcite crystal*

The way in which a crystal cleaves is often quite characteristic. Mica, for example, splits into thin sheets parallel to the base of the crystal. Calcite can be cleaved fairly easily into perfect rhombs, when the doubly refracting optical properties of this crystal can be seen to good effect (see Pl 46). Galena and fluorite are examples of cubic crystals which show good cleavage. Many crystals do not show any cleavage properties and break in a conchoidal fashion: an example is quartz.

Density is another characteristic which is often a useful guide to the identity of crystals. Although it is not readily measured in the field, some rocks obviously feel heavier than others, and this can be useful in some instances. For example, barytes is the only common white mineral that feels heavy in the hand (compared, say, with a piece of quartz of similar size).

Looking back at the minerals listed in Mohs's scale, it is noticeable that those at the upper end of the range tend to be gem stones. This is scarcely surprising, since one of the essentials of a gem is that it should be durable and hence resistant to damage. Other characteristics of gems include beauty, crystal perfection, colour and, not least, rarity. Fashion also plays its part, since tastes change, and many semi-precious stones which were quite highly regarded 50 years ago or so are thought less of today. The attraction of the more precious stones, such as diamonds and rubies is, however, timeless.

Apart from their aesthetic appeal as gem stones or objects of beauty, many crystals have considerable economic value because of their industrial applications. Diamond, corundum, garnets and quartz are all used for grinding and polishing. Many other natural minerals such as quartz, calcite and fluorite are in demand for their optical or electrical properties. In addition, of course, many minerals, not necessarily in good crystalline form, are mined in order

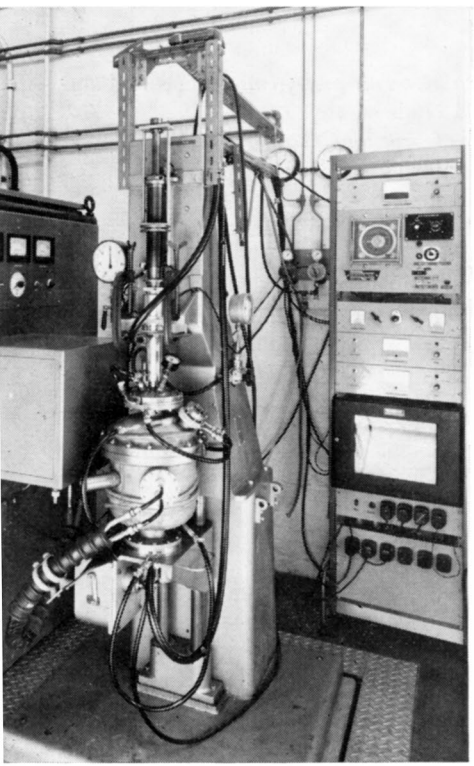
that metals such as lead, tin, and copper can be extracted. In fact, old mine tips provide a useful hunting ground for anyone interested in mineral collecting. In this country the old mines of Cornwall, the Lake District, and Leadhills in Scotland are well-known examples. A glance at a map of mountainous areas here or abroad often reveals the existence of mines, and if the weather should be too bad to prevent one from going up high, many an absorbing hour can be spent picking over an old spoil heap. Somehow, even pouring rain does not seem so bad under such circumstances!

The industrial and commercial value of single crystals provided a stimulus to attempts to copy nature by synthesis in the laboratory. It had been noticed by many investigators that most substances when allowed to solidify slowly from a solution, or from the molten state, or from the vapour, assumed the characteristic form, enclosed by plane surfaces, of most crystals. One of the earliest successful attempts to produce gems artificially was that of the Frenchman, Verneuil, at the beginning of this century; he developed a process for growing synthetic ruby starting from aluminium oxide powder to which had been added a small amount of chromium oxide, which is responsible for the red colour. This starting material is allowed to trickle through an oxy-hydrogen flame where it melts, and falls on to a pedestal. Over the course of a few hours a cylindrical single crystal is built up. The process has changed very little in essence up to the present day, and now very considerable quantities are made on a factory scale, notably in Switzerland, for use in instruments and watches. Mass production has led to cheapness, so that the intrinsic value of the bearings in, say, an 18-jewel watch is measured in pence rather than pounds. An expert can fairly easily distinguish natural from synthetic ruby due to the different nature of the imperfections found in each; and it is these small differences which keep up the value of the natural stones.

Although perhaps the introduction of the Verneuil technique marks the beginning of production of crystals of this type on a factory scale for industrial purposes, this technique is not used for many varieties of crystals. This is because there are many materials of interest which have lower melting points than ruby, or for which suitable solvents can be found, so that they can be grown more controllably by other means. If the material dissolves in water then good-quality crystals can generally be grown from a saturated solution. For example, crystals of ammonium dihydrogen phosphate, which is used for electrical applications, are grown in this way. Some materials while not being readily soluble in water at normal temperatures and pressures will dissolve appreciably if the liquid is enclosed in a suitably strong vessel and heated to several hundred degrees and many hundreds of atmospheres pressure. An example of this is quartz. Considerable quantities of quite large crystals of quartz have been grown artificially in this way and provide an alternative to the natural material, the chief source of which is Brazil, for optical and piezo-electric applications. Unfortunately, few other materials grow hydrothermally as readily as quartz from aqueous solutions. Some crystals, for example garnets, can be grown quite well from solution in various molten oxides and salts. Suitable solvents include molten oxides, fluorides and borates of lead and barium. Although the growth of crystals by this fluxed-melt technique in

some ways resembles crystallisation from molten rock materials under geological conditions, these molten solutions tend to be rather reactive, and generally have to be contained in platinum vessels in the laboratory.

A very useful technique for producing single crystals from those materials that melt at a reasonable temperature and do not sublime or dissociate is that devised by Czochralski. In his technique, the starting material is melted in a suitable crucible. A small seed crystal of the required material is dipped into the melt and slowly withdrawn. If conditions are right, and they can be quite critical, then a single crystal in rod form can be pulled from the melt. Sometimes the seed is rotated to produce more uniform conditions, and often the pulling process is carried out in a vacuum or in an inert atmosphere if oxidation is likely to occur. An example of the type of apparatus used to grow crystals by the Czochralski technique in a research laboratory is shown in Pl 47. The advantage of this method is that conditions can be carefully controlled, as one can see what is going on all the time, and so monitor it continuously.



47 *Czochralski equipment for laboratory growth of single crystals* This and next photo: National Physical Laboratory (Crown Copyright Reserved)

48 *A mass of laboratory grown single crystals of Silicon Carbide*

The above are only a few examples of a great range of techniques which now exist to grow crystals of a great variety of materials. New applications for single crystals are continually being found, frequently in industries such as optics and electronics. The great advantage of growing crystals artificially is that their purity and perfection can be controlled precisely, and that many materials not even found in crystalline form in nature can be produced. Indeed, some crystals which are produced artificially, are formed in such a way that they appear to have been formed by some natural process. An example is the silicon carbide crystals shown in Pl 48. This rather pretty cluster of hexagonal crystals was in fact produced in an open electric furnace charged with a mixture of coal and sand. The process is used commercially to produce silicon carbide (carborundum) in a fairly fine form for use as a grinding powder. Occasionally, however, cavities are formed in the furnace charge as a result of burning and settling, and these large, flat crystals grow inwards from the cavity walls. Thus these crystals are not really the desired end product, but are merely an attractive by-product. In an analogous way, single crystals that form in nature can be looked upon as by-products of the essential geological processes. Thus man as well as nature occasionally produces pleasing results by accident as well as by design.

Suggested books for further reading

Boegel, Hellmuth *A Collector's Guide to Minerals and Gemstones* (edited and revised by John Sinkankas). Thames and Hudson, 1971
Gilman, J. J. (editor) *The Art and Science of Growing Crystals*. John Wiley, 1963
Kirkaldy, J. F. *Minerals and Rocks*. Blandford Press, 1964
Smith, G. F. Herbert *Gemstones*. Methuen, 1958
Zim, H. S. and Shaffer, P. R. *Rocks and Minerals*. Paul Hamlyn, 1965