

Gypsum megacrystals

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is a common mineral in sedimentary environments. The crystal structure of this calcium sulfate dihydrate can be defined as alternating double-sheet layers of sulfates bound covalently by calcium ions and single-sheet layers of water molecules linked by weak hydrogen bonds. The mineral gypsum has several varieties that differ by the shape of the crystals and their textural arrangements. The variety called gypsum alabaster is made of fine-grained crystals and is used for craftworks. The satin spar variety is made of tiny fibrous crystals and has an attractive silky luster. The most famous variety of gypsum is called selenite, which is characterized by colorless and transparent crystals. Large selenite crystals were very valuable in Roman times because they were used for covering windows, in therma (baths) and palaces. Roman stonemasons took advantage of a well-known physical property of transparent selenite crystals, namely cleavage, the ease with which some crystals split along definite planes where the atoms are weakly bonded to the adjacent layers of atoms, thus creating smooth surfaces. In the case of gypsum, that plane is pinacoid (010), which corresponds to the plane parallel to the layers of molecules in the crystal structure. According to Pliny the Elder, the largest, high-quality selenite crystals were found in Segobriga, central Spain. This was the main source of crystals for window coverings until the introduction of the flat glass technology in the Roman Empire at the end of first century A.D. Amazing as these crystals were, they cannot be compared in size or quality with the crystal wonderland recently discovered in Naica, a mining town located 112 km (70 mi) SE of Chihuahua City in Northern Mexico.

Naica crystals. The limestone of the Naica Mountains contains one of the richest lead and silver mines in the world, which has been exploited since the nineteenth century. The ore minerals (silver-lead-zinc sulfides and sulphosalts) formed when the carbonate rocks were intruded by hot, acidic magma about 26 millions years ago. In addition to metal sulfides, the hydrothermal fluid circulation formed the mineral anhydrite (CaSO_4), which occurs massively in Naica at depths below -240 m (-790 ft). The mining district is still under a thermal anomaly that keeps the rocks and ground waters close to 55°C (131°F). The phreatic level (below the water table) is located at a depth of -120 m (-394 ft), so that the main engineering problem for mining and exploration activities in Naica is draining the water from the aquifer. This is achieved by pumping water at average rate of $55\text{ m}^3/\text{min}$ ($14,500\text{ gal}/\text{min}$). Noticeably, the water is slightly supersaturated in calcium sulfate with respect to gypsum and slightly undersaturated with respect to anhydrite.

The underground mine of Naica can be described as a set of exploration and exploitation galleries arising from a central road helicoidally descending toward the mine front, which is currently at -800 m (-2600 ft). During more than 150 years of indus-

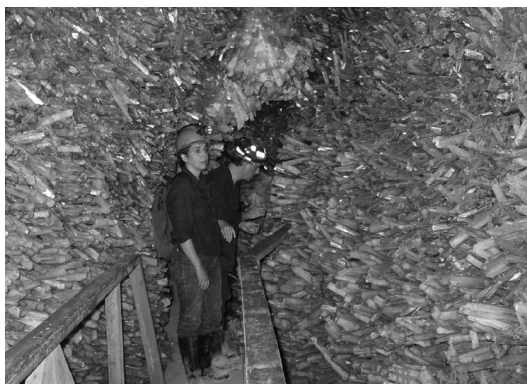


Fig. 1. Cave of the Swords, Naica mine, Mexico. Level = -120 m.

trial mining, cavities containing large gypsum crystals were accidentally discovered. The largest cavities are always close to faults that formed when ore mineralization took place, guiding the main fluid flow in the rocks. The most famous of these cavities, called the Cave of the Swords, was discovered in 1910 at -120 m (-394 ft). It is a 75-m (246-ft) corridor along a fracture covered by flattened crystals of gypsum of a few centimeters long (crystal blades). In addition, the floor is spotted with bunches of meter-size elongate crystals called crystal swords (Fig. 1). In 2000, exploration at -290 m (950 ft) uncovered a few new cavities. The largest of them was called the Cave of Crystals by the miners. The number of crystals per unit volume in this cavity was much smaller than in Cave of the Swords. The floor was covered with stubby crystals of up to 2 m (6 ft) in size but the walls and the ceiling were just spotty with crystals, allowing the walls of limestone to exhibit a red coating containing celestite (strontium sulfate) and iron oxide, among other minerals. Even more amazing, giant elongate gypsum crystals up to 11 m (36 ft) in length, called beams, crossed the cavity from side to side (Fig. 2).

Formation of giant crystals of gypsum. The analysis of the fluids trapped inside has shown that the crystals grew from low-salinity solutions at a temperature of $\sim 54^\circ\text{C}$ (129°F), slightly below the temperature (58°C ; 136°F) at which the solubility of an-



Fig. 2. Cave of the Crystals, Naica mine, Mexico. Level = -290 m. (Photo by Javier Trueba)

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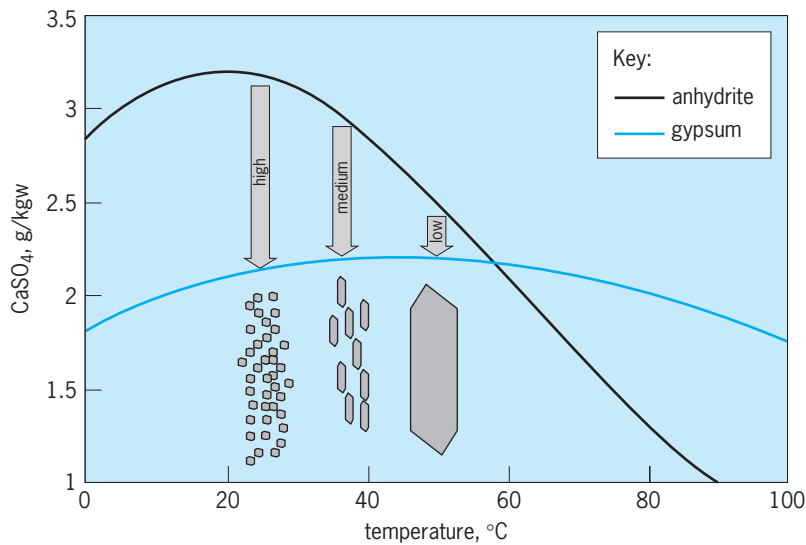


Fig. 3. Variation of solubility of anhydrite and gypsum as a function of temperature. Small differences in undercooling will provoke large changes in nucleation density.

hydrite equals that of gypsum. Sulfur and oxygen isotopic compositions indicate that Naica's gypsum crystals grew from solutions formed by dissolving the anhydrite found in the mine. These and other analyses suggest that the megacrystals formed when the Naica district cooled below 58°C, thus triggering the dissolution of anhydrite and the precipitation of gypsum. The small number of crystals in the caves can only be explained by formation at very low supersaturation. Therefore, the problem is to explain how the required low supersaturation can be sustained for a long time without large fluctuations that would provoke substantial nucleation. **Figure 3** shows the variation of the solubility of anhydrite and gypsum as a function of temperature. Considering that the nucleation flow increases exponentially with supersaturation (or undercooling), for the Cave of the Crystals it is clear that undercooling should never have been very large, keeping the temperature always very close to 58°C. Larger undercooling would have yielded a large number of relatively smaller crystals, as is the case of the shallower (and therefore cooler) Cave of the Swords. A large undercooling would provoke the formation of millions of microcrystals of gypsum. Gypsum nucleation kinetics calculations based on laboratory data show induction times longer than 1 m.y. for the temperature of fluid inclusion (54°C). Therefore, this mechanism can account for the formation of these giant crystals, yet only when operating within the very narrow range of temperature identified by the fluid inclusions. These conditions are very difficult to accomplish, particularly the smooth cooling to keep nucleation flow very low. When all of these conditions take place simultaneously, an extraordinary crystallization phenomenon occurs that creates a mineral wonderland.

Other giant selenite crystals. In addition to Segobriga and Naica, giant gypsum crystals have been found in two other places, both located in mining districts. One of them is the copper mine of El

Teniente, close to Rancagua in the Andes of central Chile. El Teniente is the world's largest underground copper mine. El Teniente is a porphyry Cu-Mo deposit related to calc-alkaline felsic to intermediate intrusions of Miocene and Pliocene age. Most of the ore formed at the late stages of the magmatic episode (5.9–4.9 Ma). The center of this deposit is the so-called Braden Pipe, a massive granitic breccia pipe intruded during a late hydrothermal stage (4.8–4.4 Ma). The Braden breccia presents a system of vertical faults more intense at the boundaries of the intrusion. Several cavities developed in the fault zones containing transparent gypsum crystals of up to 7 m (23 ft) in length and 0.5 m (1.5 ft) thick. The largest cavity is located at level 6 and is about 300 m³ (10,600 ft³) in volume. The fracture seems to extend to other levels with more than 170 m (560 ft) of vertical continuity. The cavity has walls that are covered by centimeter-size euhedral crystals of pyrite and barite and contains elongate gypsum crystals up to 5 m (16 ft) in length (**Fig. 4**). The origin of these crystals is currently under study, but the presence of a large amount of primary igneous anhydrite and the evidence of a cooling thermal history suggest that the mechanism explaining the formation of Naica crystals could also apply for this locality.



Fig. 4. Giant gypsum crystals in El Teniente mine, Chile. (Photo by Javier Trueba)



Fig. 5. Crystal of the giant gypsum geode of Pilar de Jaravia, Spain. (Photo by Javier Trueba)

The second case is an 11-m³ (388-ft³) ovoid geode hosted by carbonates that was discovered by mineral collectors in 1999 at Mina Rica in the extinct iron-lead mining district of Pilar de Jaravia, Almeria, SE Spain. The mineralization occurred when the dolomites of the Alpujarride complex were intruded by Neogene volcanism of Cabo de Gata, and a complex Fe-Pb-Sb-Ag-Ba-Hg mineralization formed within the carbonates due to the hydrothermal fluid circulation. The walls of the geode are covered by stubby gypsum crystals with an average length of 0.5 m (1.6 ft). In the center of the geode there are a couple of elongate crystals up to 2 m (6.6 ft) in length that are similar to the crystal beams found in Naica and El Teniente, which certainly grew later on (Fig. 5). The genesis of these large gypsum crystals in the geode is not yet clear. However, the presence of celestite needles at the base of the gypsum crystals, such as recorded in Naica, suggests that dissolution of preexisting anhydrite, slight supersaturation in gypsum of the solution, and subsequent formation of the crystals could also have taken place.

For the background information see ANHYDRITE; BRECCIA; CRYSTAL STRUCTURE; CRYSTALLIZATION; GEODE; GYPSUM; NUCLEATION in the McGraw-Hill Encyclopedia of Science & Technology.

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