

SPECIAL

Formation of gigantic gypsum crystals

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Fluid inclusions and stable isotopes of giant transparent gypsum crystals in a huge geode recently discovered in Pulpí (SE Spain) are useful tools for explaining its geological formation. Fluid inclusions suggest a mixture of fluids, starting with freshwater and including seawater in more advanced stages of the gypsum crystal growth. The isotopic composition of the hydration water in the gypsum crystals agrees with a meteoric fluid. The gypsum is enriched in ³⁴S, which denotes genetic links with marine sulphates via freshwater dissolution-recrystallization of earlier marine evaporites.

Keywords: gypsum, geodes, fluid inclusions, sulphur isotopes.

Spectacular colour pictures of huge gypsum crystals in a geode from Pulpí (Almería, Spain) were widely publicized in the worldwide media. The impact of these images stems from an exceptional combination of the huge size, transparency and perfection of the crystals in a large rock cavity (Fig. 1). The Pulpí geode is 8 m long, 1.8 m wide and 1.7 m high and is studded with 1 m long gypsum crystals. It is located in the Jaravias Fe–Pb mine (Pulpí, Almería) at about 50 m depth, 3 km from the sea, and 0 m a.s.l. and is hosted by Triassic dolomite of the Betic Cordillera. The gypsum crystallographic lattice has layers of SO₄²⁻ tetrahedra bound together by Ca²⁺ and layers of water molecules, which gives a perfect cleavage parallel to (010). Simple precipitation experiments of Bosbach & Rammensee (1994) demonstrated that speed is constant for crystal growth in different directions and the anisotropy of the crystal habit remain constant during crystal growth. Crystal and dissolution processes on the (010) surface of gypsum is a layer-by-layer process, which is dominated by the movement of [100] and [001]. The large crystal sizes and perfect shape, high transparency and minor solid inclusions, resulting in such clean crystals, must have been produced in a unique environment. A suitable explanation of the geode's origin must address both the cavity formation and fluid characteristics, which produced these exceptional crystals.



Fig. 1. Geode of the Jaravias mine (Pulpí, Almería, SE Spain). Transparent gypsum crystals

Geological setting. The mineralized veins and masses of the Jaravias mine are related to the Miocene volcanic events, and are analogous to those observed in nearby areas (sulphide–sulphate-bearing barite–siderite veins of the Sierra Almagrera (Martinez Frias 1998; Morales 1994); volcano-sedimentary barite, Fe–Mn oxides and marine sediments at Herrerías (Martinez Frias 1998; Morales 1994); dacitic rocks with vertical veins of Fe–Mn oxides and barite at La Serrecica). The geode is hosted by dolomites. The chronological sequence of mineralization is as follows (from host rock to geode core): dolomite host rock, siderite, Fe–Mn oxy-hydroxides and gypsum crystals, which very often included celestine needles.

Experimental procedure. Optical and micro-analytical techniques (petrography, SEM, electron microprobe), micro-thermometry of fluid inclusions and stable isotopes ($\delta^{34}\text{S}$ CDT in sulphides and sulphates; $\delta^{18}\text{O}$ SMOW in sulphates and gypsum hydration water; δD SMOW in gypsum hydration water) have been used to study the gypsum crystals and their host rocks. Transparent gypsum crystals were also analysed by ICP-MS, XRF and AAS. Melting temperatures of the last ice crystal of the fluid inclusions can also be used (Attia *et al.* 1995) to infer the origin of the fluids. This micro-thermometric study was carried out on gypsum chips. $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in gypsum reflect the corresponding values of dissolved SO₄²⁻ in the mineralizing fluid. Data on natural samples and experimental results indicate that isotope ratios of the SO₄²⁻ anion are not significantly affected by dissolution-recrystallization processes at low temperature (Claypool *et al.* 1980; Chiba *et al.* 1981). Analytical results can be obtained from the Society Library or the British Library Document Supply Centre, Boston Spa, Wetherby, West Yorkshire LS23 7BQ, UK as Supplementary Publication No. SUP 18174 (3 pages).

Results and discussion. The transparent gypsum crystals are pure CaSO₄·2H₂O with small and variable Sr (0.02–0.13%) and Hg (0.01–0.23%), and minor amounts of other cations (Zn, Fe, Mg, Mn, Ba). Fluid inclusions (Fig. 2) in the gypsum crystals have polyhedral morphologies (six-sided, trapezoidal, rhomb-shaped, negative crystal shape, etc.); are very large (up to 250 μm), two-phase (liquid + vapour) at room temperature, and have a fairly constant degree of filling (liquid/(liquid + vapour) = 0.85 to 0.95). Petrographic observations have established the presence of two types of fluid inclusions: (a) primary fluid inclusions (PFI), that are generally found isolated and randomly distributed throughout the gypsum crystals and (b)

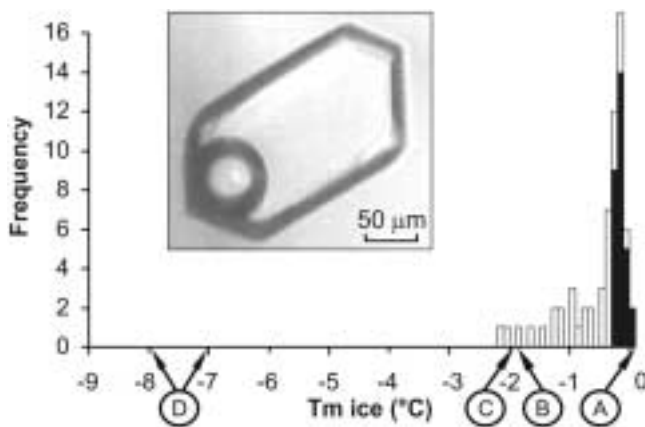


Fig. 2. Fluid inclusion in negative crystal displaying the monoclinic symmetry of gypsum from a (010) section. Frequency histogram of T_{mice} values (melting temperatures of the last ice crystal of the fluid inclusions). Dots (A), (B), (C) and (D) show published T_{mice} values by Attia *et al.* (1995), as follows: (A) Freshwater saturated with gypsum ($T_{mice} = 0.0^\circ\text{C}$); (B) Normal seawater ($T_{mice} = -1.9^\circ\text{C}$); (C) 'Recycled' seawater (seawater saturated with gypsum derived from dissolution) ($T_{mice} = -2.0^\circ\text{C}$) and (D) Seawater evaporated to gypsum saturation point ($T_{mice} = -7.0$ to -8.0°C).

pseudo-secondary fluid inclusions (PSFI), arranged in rows that never cut the crystal boundaries. The presence of both types of fluid inclusion allows characterization of two different fluids during gypsum crystal development, and hence we can describe the evolution of the mineralizing solutions from initial (PFI) to more advanced stages (PSFI). The main results of microthermometric characterization of the fluid inclusions are the following: (a) eutectic temperatures are very similar (from -51 to -38°C) in both PFI and PSFI, suggesting an $\text{H}_2\text{O}-\text{NaCl}-\text{CaCl}_2$ system and (b) melting temperatures of the last ice crystal (T_{mice}) (Fig. 2), in PFI fall in a narrow interval of temperature (between -0.3 and 0.0°C) whereas this interval is broader for values obtained in PSFI (between -2.2 and -0.1°C). Homogenization temperatures could not be determined due to loss of water, and consequent loss of transparency, in gypsum during heating. From microthermometric study, salinity and density of fluid inclusion can be estimated (Potter *et al.* 1978; Shepherd *et al.* 1985). Values of salinity range from 0.0 to 0.5 wt% eq. NaCl for PFI and from 0.2 to 3.7 wt% eq. NaCl for PSFI. Densities are similar for both PFI and PSFI ($0.8-0.9 \text{ gr cm}^{-3}$), suggesting that fluids were always less dense than seawater ($d_{\text{seawater}} = 1.02 \text{ gr cm}^{-3}$).

In view of the fluid inclusion study, a possible direct sedimentary (evaporitic or vadose zone) origin (e.g. Mediterranean Messinian salinity crisis) must be disregarded since the random distribution of the fluid inclusions in the crystals differs significantly from those described in gypsum of evaporitic origin (Attia *et al.* 1995), where fluid inclusions are distributed in bands of uniform salinity, with marked contrast in salinity between bands, and the degree of filling in PFI and PSFI in this study is quite constant (from 0.85 to 0.95), which indicates that gypsum precipitation could not have occurred in a fluid regime typical of the vadose zone (Goldstein & Reynolds 1994). The T_{mice} values of fluid inclusions in Pulpí gypsum (Fig. 2) show a mode near 0°C , which suggests precipitation from non-marine water (i.e., surface water or ground-water) (A in Fig. 2). However, the T_{mice} values have a dispersion range (-0.3 to 0.0°C for PFI and -2.2 to -0.1°C for PSFI, corresponding to respective salinities of up

to 0.5 and 3.7 wt% eq. NaCl). The decrease in T_{mice} values (mainly in PSFI), which reflects an increase in solute content with time, suggests a fluid mixing, starting with freshwater and including a different type of water in more advanced stages of the system. The dispersion of the T_{mice} values to -2.2°C suggests that this later fluid may have been seawater (B in Figure 2) or recycled seawater (C in Fig. 2). All values of T_{mice} are very different from D in Figure 2, which excludes a genesis from evaporated seawater.

The evidence is compelling, therefore, that the area has been exposed to both marine and meteoric environments, thus water of different isotopic composition may have been involved in the formation of the geode gypsum crystals. The crystals are relatively enriched in ^{34}S ($\delta^{34}\text{S} = +18.6\text{‰}$ to $+19.8\text{‰}$, see Fig. 3b), which strongly suggests a genetic link with marine sulphates, probably by means of dissolution-recrystallization of earlier marine evaporites. δD values for the hydration water extracted from the gypsum crystals (ranging from -64.2‰ to -65.4‰ SMOW), however, demand involvement of fresh meteoric waters.

Experiments at temperatures from 17 to 57°C (Fontes & Gonfiantini 1967) have shown that hydrogen isotope fractionation between hydration water of gypsum crystals and the water from which the crystals grow in equilibrium is not temperature dependent; hydration water being 15‰ depleted in D with respect to environmental water. Therefore, an estimated δD value

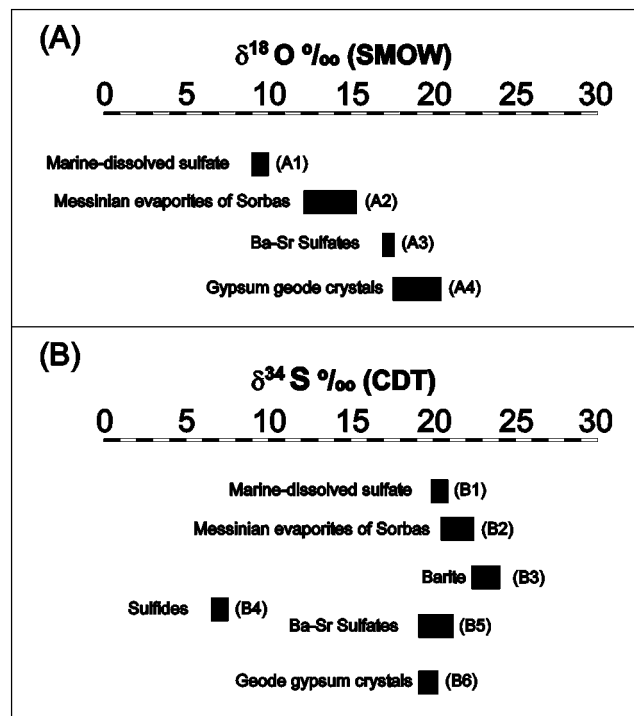


Fig. 3. (a) $\delta^{18}\text{O}$ of gypsum crystals, barite and celestite from Pulpí, compared to marine sulphate and Messinian evaporites. A1 and A2 values from Longinelli & Craig (1967) and Longinelli (1979). A3 and A4 from this study. (b) $\delta^{34}\text{S}$ of gypsum crystals, barite, celestite and sulphides from Pulpí compared to marine sulphate, Messinian evaporites and barite from neighbouring hydrothermal deposits. B1 and B2 values from Claypool *et al.* (1980) and Longinelli (1979) respectively. B3 values from Martinez Frias (1998) and Morales Ruano (1994). B4 to B6 from this study.

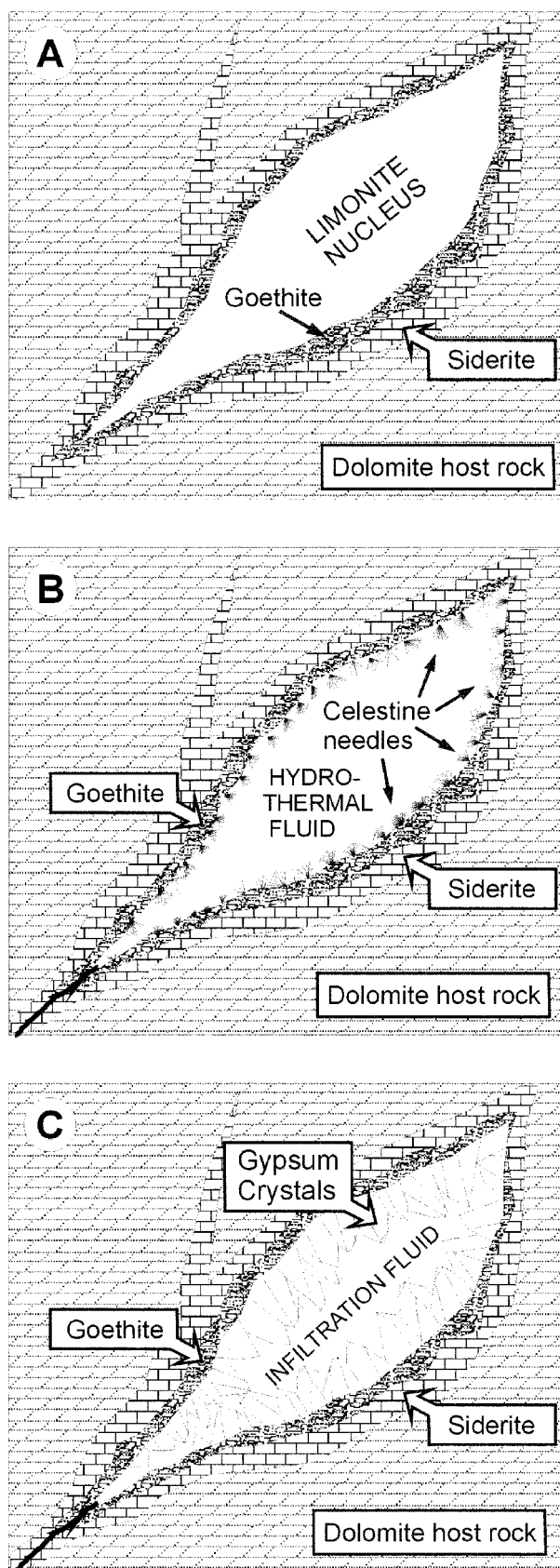


Fig. 4. Simplified sketch of the geode formation: (a) hydrothermal mineralization; (b) karstification and hydrothermal growth of celestine needles; (c) growth of large gypsum crystals.

near -50% (SMOW) can be derived for environmental water from the measured Pulpí values. Moreover, sulphate $\delta^{18}\text{O}$ values ($+17.6\%$ to $+20.3\%$ SMOW) are rather high with respect to present marine sulphate values ($+9.4\%$). These data are inconsistent with direct precipitation of gypsum from dissolved marine sulphate (see Fig. 3a). However, different, repeated low temperature episodes of dissolution-precipitation could explain these values, as kinetic effects during sulphate crystallization can produce a small increase of several units per mil in the $\delta^{18}\text{O}$ values (Longinelli & Craig 1967; Lloyd 1968; Longinelli 1979). This hypothesis of 'inherited-recycled SO_4^{2-} ', agrees with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{18}\text{O}$ data in sulphates and crystallization water of Messinian gypsum, supporting the involvement of meteoric water in the genesis of the evaporitic deposits in the area (Longinelli 1979; Playa *et al.* 2000). These values are also coincident with those of sedimentary gypsum from neighbouring basins where originally marine sulphates, recycled by meteoric waters, present relatively high $\delta^{18}\text{O}$ values (Playa *et al.* 2000), and are consistent with $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the host carbonate (authors' own data), that require interaction with fluids of meteoric derivation.

The chronological sequence of mineralization at Jaravias mine provides a framework for the formation of the cave hosting the geode and its subsequent filling by gypsum mega-crystals, as follows (Fig. 4a, b and c). Alternating hydrothermal-volcanic fluid pulses deposited barite-strontianite (anhydrous Ba-Sr sulphates), sulphides and sulphosalts and Fe-Mn oxy-hydroxides, controlled by discontinuities (fissures, vertical faults and metapelite-dolomite lithologic contacts). The incoming fluid reacted with the dolomite ($\text{CaMg}(\text{CO}_3)_2$) host rock producing siderite (FeCO_3); excess oxy-hydroxides remained in vein cores, e.g. as powdered limonite ($\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$) that can be observed in the nuclei of other stuffed minor geodes. Subsequent karstification processes (favoured by increased acidity caused by H_2SO_4 in solution) dissolved carbonates (dolomite and siderite) from fissures and removed other soluble materials, producing cavities, e.g. the large Pulpí geode cave where some siderite-goethite remains on the internal walls. The final stage was dominated by infiltration of supergene fluids, epsomite- and gypsum-bearing (hydrous Mg-Ca sulphates), from which the gigantic gypsum crystals grew. These crystals enclosed, protected, and thus preserved, the very delicate celestine (SrSO_4) needles that had precipitated at earlier stages.

In summary, the formation of the giant gypsum crystals in the geode may be explained in two steps: (1) formation of the cavity by removal of soluble materials, previously deposited as result of reaction between hydrothermal fluids and the host rock and (2) infiltration of fluid causing the growth of large gypsum crystals. Combined stable isotope and fluid inclusion data indicate that this later fluid varied with time from freshwater in the earlier stages to seawater-like in later stages, most likely as a result of dissolution-recrystallization of earlier marine evaporites.

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