The Formation of Gypsum Megacrystals

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Abstract

Exploration activities in the mine of Naica (Chihuahua, Mexico) recently unveiled several caves containing giant, faceted and transparent single crystals of gypsum ($CaSO_4 \cdot 2H_2O$) up to eleven meters in length. Understanding the formation of giant crystals under natural conditions remains one of the mysteries of mineralogy. The problem lies on the impossibility of reproducing the phenomenon at the laboratory time scale and on the absence of a well-known geological framework for most of the cases reported in the literature. Based on geological and geochemical data, fluid inclusions geothermometry and crystallization studies, we claim that these megacrystals formed by a self-feeding mechanism driven by solution mediated anhydrite-gypsum phase transition. The evidences presented show that this mechanism is the only one that can

account for the formation of these giant crystals, and only when operating within a very narrow range of temperatures, slightly below the one at which solubility of both phases equals. These singular conditions create a mineral wonderland, a site of scientific interest, and an extraordinary phenomenon worthy of preservation.

GEOLOGICAL SETTING

The Naica mine is located on the northern side of the *Sierra de Naica*, 112 km SE of Chihuahua city in Northern Mexico and constitutes one of the most important lead and silver deposit in the world. Geologically, the area is dominated by a domian structure oriented NW-SE of 12 km long and 7 km wide standing out from a very extensive alluvial plain. Naica mining district is entirely formed by sedimentary rocks, consisting in a sequence of Albian limestones with some lutitic interbeddings lying upon an evaporitic sequence of Aptian age, which have been found in the regional surroundings but not in the mining district. The sedimentary rocks are intruded by Tertiary acidic dykes dated 26.2 and 25.9 millions years old (Megaw *et al.,* 1988). The existence of an igneous source located 4 km south of Naica mine at depth between 2 and 5 km has been revealed by magnetometric studies. The hydrothermal fluid circulation associated to the Tertiary dykes formed the Ag-Pb-Zn deposits (Lang, 1995). These deposits—displaying chimney and manto shapes—develop both in the dykes and in the enclosing carbonates, which appear intensively transformed to calcosilicates. The ore assemblage is made up of pyrite-pyrrhotite, sphalerite, galena and chalcopyrite. Late quartz-calcite-anhydrite veins cut the ore (Stone, 1959). Finally, two sets of faults work as the main structural controls of the mineralization, Gibraltar, Montaña and Naica being the most important of them (Fig. 1).

The Peñoles mining company has excavated galleries down to –760 m from the main access gallery (level 0 at 1385 m a.s.l.). This requires an average pumping of 55 m^3/min to create a depression cone of

–580 meters with relation to the phreatic level located at -120 meters, Naica and Gibraltar faults acting as the main drains (Fig. 1). The area is still under a thermal anomaly. Water samples collected at different times and mine locations show that the temperature of the groundwater is around 53°C in the deep levels of the mine although temperatures as high as 59ºC have been measured (Table DR4). As expected from the lithological setting present waters have low salinity, are rich in calcium, sulfate and carbonate, and according to their isotopic values (Table DR3) they have a meteoric origin with more than 50 years of residence time in the aquifer.

GIANT SELENITE CRYSTALS

Since early twentieth century, the excavation of new galleries and tunnels occasionally leads to the discovery of cavities and caves that contain meter-size crystals of selenite, the colorless crystalline variety of gypsum. The caves are always located near fractures and their walls are covered by a red coating made of calcite and celestite with minor amounts of iron oxide, montmorillonite, chlinochlore and illite. The absence of alunite and kaolinite minerals as well as the values of sulfur isotopes discards a sulfuric speleogenesis mechanism (Polyak and Güven, 1996). In 2000, several caves were discovered at level –290 m in secondary faults associated with the Naica fault (Fig. 1). At that depth the impact of oxygen enriched waters is very unlikely and consequently the gypsum crystals contain very few solid inclusions of iron and manganese oxides. One of these caves, named the *Cueva de los Cristales* (Cave of the Crystals), contains selenite crystals up to eleven meters long and one meter thick, i.e., much larger than any gypsum crystal previously reported (Foshag, 1927; García-Guinea *et al.*, 2002; Palache, 1932; Rickwood, 1981). The walls of the cave and particularly the floor are sprinkled with blocky single crystals that in some cases cluster to form parallel aggregates (Fig. DR6). Rather than having the characteristic platy or tabular habit of the gypsum crystals, they are euhedrical displaying well developed {010}, {1k0} and {-111} (Fig. DR2). The {010} pinacoid is less developed than in the usual growth morphology of gypsum crystals. The {1k0} prismatic form appears as striated surface made of

segments of prismatic forms with k = 2, 4 or 6, as shown by laser reflection goniometry and scanning electron microscopy (Fig. DR3, DR4 and Table DR1). The resulting non singular face has an orientation close to {140}. The unusual blocky habit, the development of the more acute prismatic faces {140} and {160} instead of the usual {120} (Simon and Bienfait, 1965) and the alignment of the crystals with the edge [010] vertical, give them an impressive and intimidating sharktooth appearance (Fig. 2 and DR6). From some of these groups of blocky crystals or directly from the floor, grow elongated giant selenite crystals, some of which cross the cave from side to side. Most of these crystals are six meters long and several of them reach ten meters. Consequently, the miners correctly term them *vigas* (beams), not swords. There is only one morphological difference between the beams and the blocky crystals, namely that the pinacoidal cleavage faces {010} disappear in most cases. The crystalline beams are elongated along the zone axis c, defined by huge prismatic {1k0} faces capped by the {-111} prism (Fig. DR5). Finally what makes this a natural scenario of unparallel beauty—and it is critical to explain its formation—is the small number of crystals (Fig. 2) that can only result from extremely low nucleation rates: therefore the value of the driving force for crystal nucleation was kept small (close to equilibrium) for the entire history of the system.

GEOCHEMICAL CONDITIONS

We have measured ice melting temperatures from 33 selected fluid inclusions which were biphasic at room temperature (Fig. DR9 and Table DR2). The range of obtained temperatures indicates low salinity values compatible with today meteoric and mine waters (Bodnar, 1993; Bakker, 2003). That means that the original high-salinity sulfur rich acidic magmatic fluids (Lang, 1995; Erwood *et al.*, 1979) that provoked the skarn formation had practically lost the salinity at the time the gypsum crystals grew. Sulfuric acid formed by oxidation of underlying sulfides deposit reacted with limestone to form calcium sulfate rich waters that precipitated the stable polymorph (anhydrite) during the late

hydrothermal stage. In fact, anhydrite appears massively in Naica at any level below 240 meters. Cooling of the system and contribution of meteoric waters yield sulfate and carbonate rich water with a temperature in the range of 48-59ºC, and a neutral to slightly basic pH (7.0-7.8), like the one today gushed out of the mine. As shown in Fig. 3, the isotopic values of these gypsum crystals are consistent with their formation from waters with dissolved sulfate similar to those found in present day groundwater collected at level -530 (Fig. 3b). The isotopic values of sulfate dissolved in the water can be explained by mixture of sulfates from the dissolution of anhydrite from different locations of the mine, those from the ore deposit area (samples 23, 24, 25 and 34) and those from upper levels in the mine (sample 04 and 21 in Table DR3). This is also confirmed by the presence of celestite, a strontium sulfate found together with clays and iron oxide in a thin layer coating the walls of the Cave of the Crystals. It has been demonstrated that anhydrite structure hosts more strontium than gypsum (Butler, 1973); celestite crystals resulted from the excess of strontium hosted in the dissolving anhydrite with respect to crystallizing gypsum (See table DR4). These data discards the hypothesis of mixing of water of different salinity as the source for the driving force for crystallization and suggest a mechanism for the formation of gypsum crystals based upon Ostwald's law of phase stability.

FORMATION OF MEGACRYSTALS

Gypsum is slightly soluble in water (13.78 10^{-3} mol L^{-1} at 25ºC and atmospheric pressure) (Partridge and White, 1929). Its solubility shows a positive dependence on temperature in cool waters, reaching a maximum at about 58ºC and then decreasing until 107ºC where the solubility is minimum because of the formation of the hemihydrate (Posnjak, 1938). The solubility of gypsum also has a positive variation with salinity but the temperature of maximum solubility does not change significantly,

keeping close to 58ºC. At atmospheric pressure, gypsum becomes unstable at temperatures hotter than 56-58ºC (Hardie, 1967; Blount and Dickson, 1973) while anhydrite becomes unstable with respect to gypsum at temperatures lower than 58°C (Fig. 4a). Therefore, upon cooling of the Naica district, hydrothermal anhydrite associate to the late stage of the formation of the ore deposit became unstable and is dissolved, thus explaining the high content of sulfate anions in the present day waters. The dissolution of anhydrite below 58°C supplies Ca^{2+} and SO_4^{2-} to keep the water slightly supersaturated in gypsum and promoting its precipitation. Examples of this replacement are also observed at microscopic scale in some anhydrite masses close to the cave of the crystals (See Fig. DR11). Actually, supersaturation values ($S = c/c_e$ where c is the actual concentration and c_e is the equilibrium concentration for a given temperature and salinity) calculated for present day waters yields values slightly supersaturated for gypsum and undersaturated for anhydrite. Such a small difference between the solubility of gypsum and anhydrite slightly below 58ºC is a continuous source of calcium and sulfate molecules and also a very stable mechanism to constantly maintain the precipitation system close to equilibrium. The question is how much cooling the system may have undergone to avoid the massive nucleation that would have packed the caves with a large number of small crystals. The nucleation flux is described by the equation:

$$J = A\exp - \frac{16\,\pi\gamma^3 v^2}{3k^3 T^3 ln^2 S}$$

Where γ is the crystal/liquid interfacial tension, v is the molecular volume, k is the Boltzman constant, and T is the absolute temperature. As the nucleation flux J varies with the second power of the logarithm of supersaturation S, low values of J means that supersaturation was kept in the metastable zone and very close to equilibrium for the whole history of crystallization in the cave. The induction time t_{ind} or waiting time for nucleation being inversely proportional to J, the above equation can be written as a linear relationship:

144 $$log t_{ind} \propto \frac{\gamma^3}{T^3 log^2 S}$$

145 Using experimental data available from gypsum nucleation studies (He *et al.*, 1994; Lancia *et al.*, 1999)
146 we have calculated (for both, homogeneous and heterogeneous nucleation) the induction time for three
147 salinities: just calcium, sulfate and water molecules (labeled 0), salinity values (Na, Cl and Mg
148 concentration) identical to those found in Naica waters (labeled 1) and twice these concentrations
149 (labeled 2) (Fig. 4b). For any large geological reservoir where crystallization occurs, heterogeneous
150 nucleation is unavoidable because it requires lower critical supersaturation values to surpass the
151 nucleation barrier. As shown in Figure 4b, the waiting time for heterogeneous nucleation becomes in
152 the order of thousands of years for temperatures of 47-48ºC. For any temperature below 44-45ºC we
153 found a very large probability for a nucleation event in the scale of months or days, which cannot
154 explain the small number of crystals in the caves. We have measured homogenization temperatures
155 (T_h) of 31 fluid inclusions; the data show a distribution with a maximum around 54±1ºC (Fig. 4c, Table
156 DR2). Accordingly with the proposed mechanism, this value indicates that most of the crystallization
157 process took place at a temperature for which t_{ind} is longer than a million years (Fig. 4b). These close to
158 equilibrium conditions were maintained for a long time with some episodes of cessation of growth, as
159 suggested by the occasional solid inclusions of manganese and iron oxi-hydroxides on {1k0} and {-
160 111} growth fronts. Eventually, as indicated by lower values of T_h down to 47ºC, the system cooled
161 down due to a stronger influence of meteoric waters and the probability of nucleation was higher, in the
162 order of thousand of years. Accordingly, with this mechanism, caves such as the Cave of the Swords
163 (Foshag, 1927) that are located closer to the surface undergo lower temperatures and are filled with
164 large number of smaller crystals (Fig. 1 and Fig. DR1).
165
166 The gypsum crystals of Naica are the result of a natural experiment irreproducible at laboratory time
167 scale. Interestingly, these crystals supply information demonstrating the current lack of understanding

of equilibrium crystal morphology, which particularly in the case of gypsum is a long standing problem (Simon and Bienfait, 1965; Weijnen *et al.*, 1987, Heijnen and Hartman, 1991). The morphology of long beams showing the preferential development of non singular {1k0} faces in relation to the cleavage face {010} suggests that ordering at the hydration layer is at least as important as bonding configuration in the three-dimensional structure, a hypothesis suggested by van der Voort and Hartman (1991).

It can be predicted that other caves with similar or even larger selenite crystals can be unseen among the tangle of underground roads drawn in Naica mine for exploration and management of ore minerals. Together they may constitute one of the oddest locations of the mineral world and are worthy of preservation as a geological marvel. Two problems can be envisaged for that task. The cave must be kept wet and hot but equally important is the development of a method to maintain the integrity of the long *vigas* that bend and break once the buoyancy support of the cave water was lost. The second problem is in the long term but more critical: as soon as the mining work is completed, water pumping will stop and the caves will be again flooded to their natural state. According to the proposed mechanism, the selenite crystals will start to grow again but they will be hidden for future generations.

Acknowledgements

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Figure Captions

Figure 1: Geological section of the Naica mine. The mine works a hydrothermal Pb-Zn-Ag deposit with irregular ‘manto’ and ‘pipe’ morphologies entirely enclosed in carbonates (not represented for

193 simplicity). The cavities of gypsum crystals are located in the carbonates close to main and secondary
194 faults. Original and current water level are shown.
195
196 **Figure 2**: A view of the Cave of Crystals showing the characteristic moonlight lustre that name (Selene
197 is the Greek name for the moon) these gypsum crystals. Two crystal morphologies can be observed, the
198 blocky crystals displaying the prisms {1k0} and {-111} and the pinacoid {010} and the beams, which
199 are crystals elongated along the c axis displaying only the prismatic crystal faces. Notice that the
200 population of crystals is much lower in the ceiling of the cave than on the floor. For very large waiting
201 time for nucleation, this gradation is due to a dendity layering of the solution filling the cave (Turner,
202 1985), which increases the probability of nucleation from the solution located in the lower part of the
203 cavern.
204
205 **Figure 3**: Isotope composition of the sulfate molecules in gypsum, anhydrite and water collected at
206 Naica mine. The polygonal surface envelopes the isotope composition of the water from which the
207 gypsum crystals grew.
208
209 **Figure 4**: a) Variation of anhydrite and gypsum solubility with temperature for three different values of
210 salinity: (0) for pure calcium sulphate solutions; (1) for salinity equal and (2) twice the one found in
211 current water collected at Naica mine. Solubility calculated with PHREEQC (Parkhurst, 1980) using
212 the PHREEQC database. b) Waiting time for (homogeneous and heterogeneous) nucleation calculated
213 for supersaturated solutions forming by differences in solubility between anhydrite and gypsum at
214 different temperatures. c) Homogenization temperatures of 31 fluid inclusions showing the actual
215 temperature of growth. The heating rate was of 2°C/min, and the precision of the measurement is
216 estimated to be ±1°C. From the geological setting no correction due to confinement pressure is
217 required, and this temperature range can be considered the actual temperature of crystal growth.

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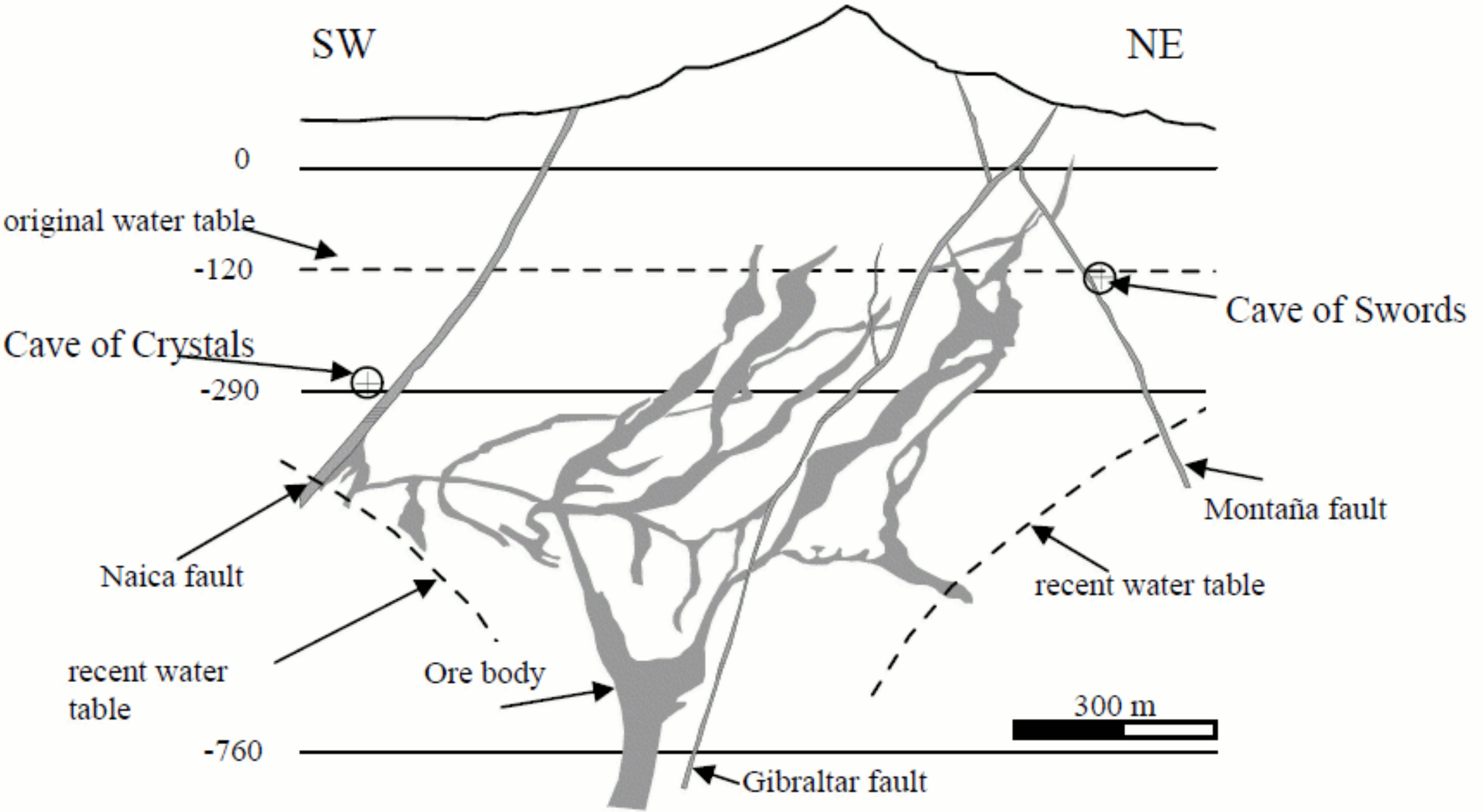

Fig. 1. García-Ruiz, Villasuso, Ayora, Canals & Otálora. (GIF)

Fig. 2. García-Ruiz, Villasuso, Ayora, Canals & Otalora (GIF)

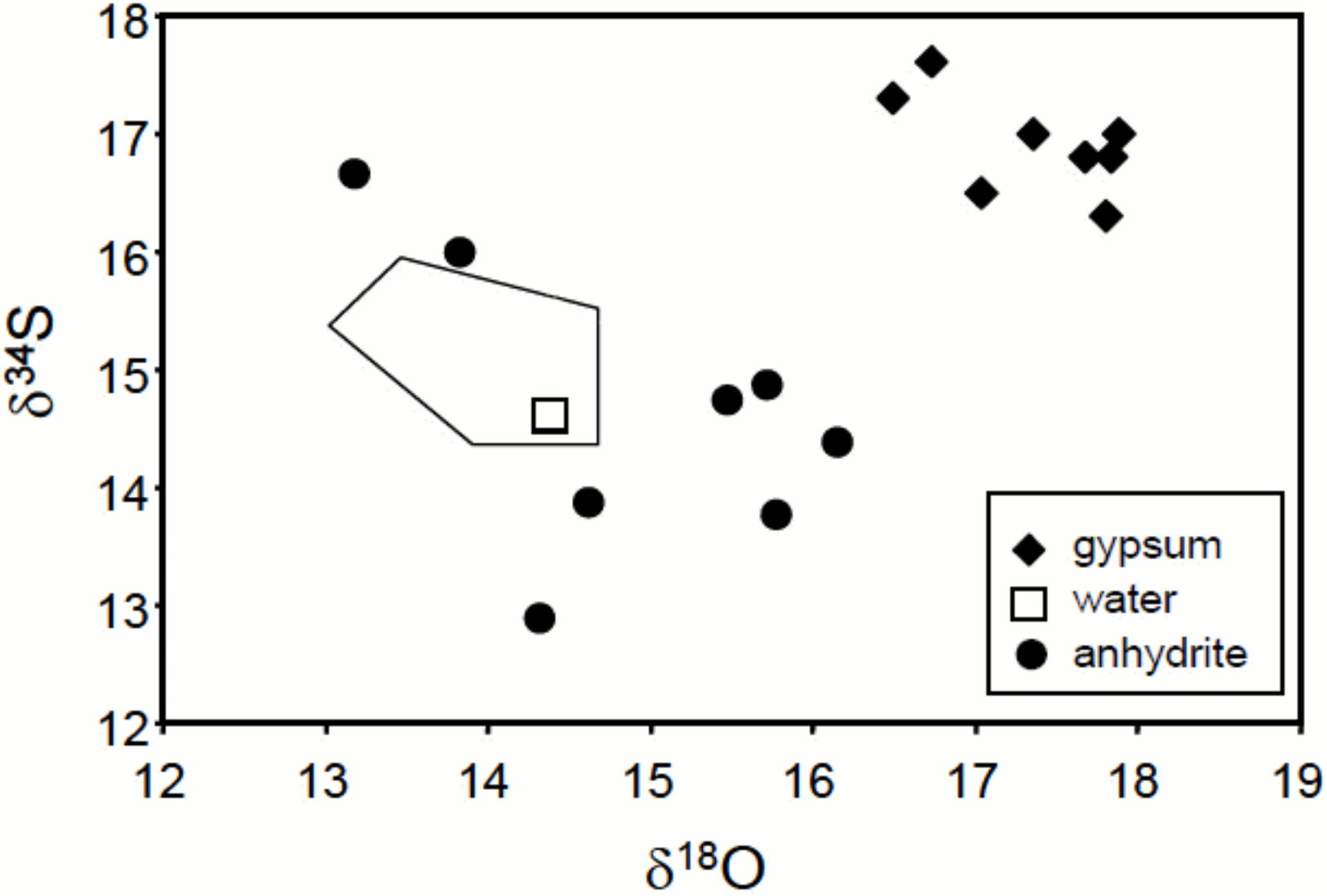

Fig. 3. García-Ruiz, Villasuso, Ayora, Canals & Otálora. (GIF)

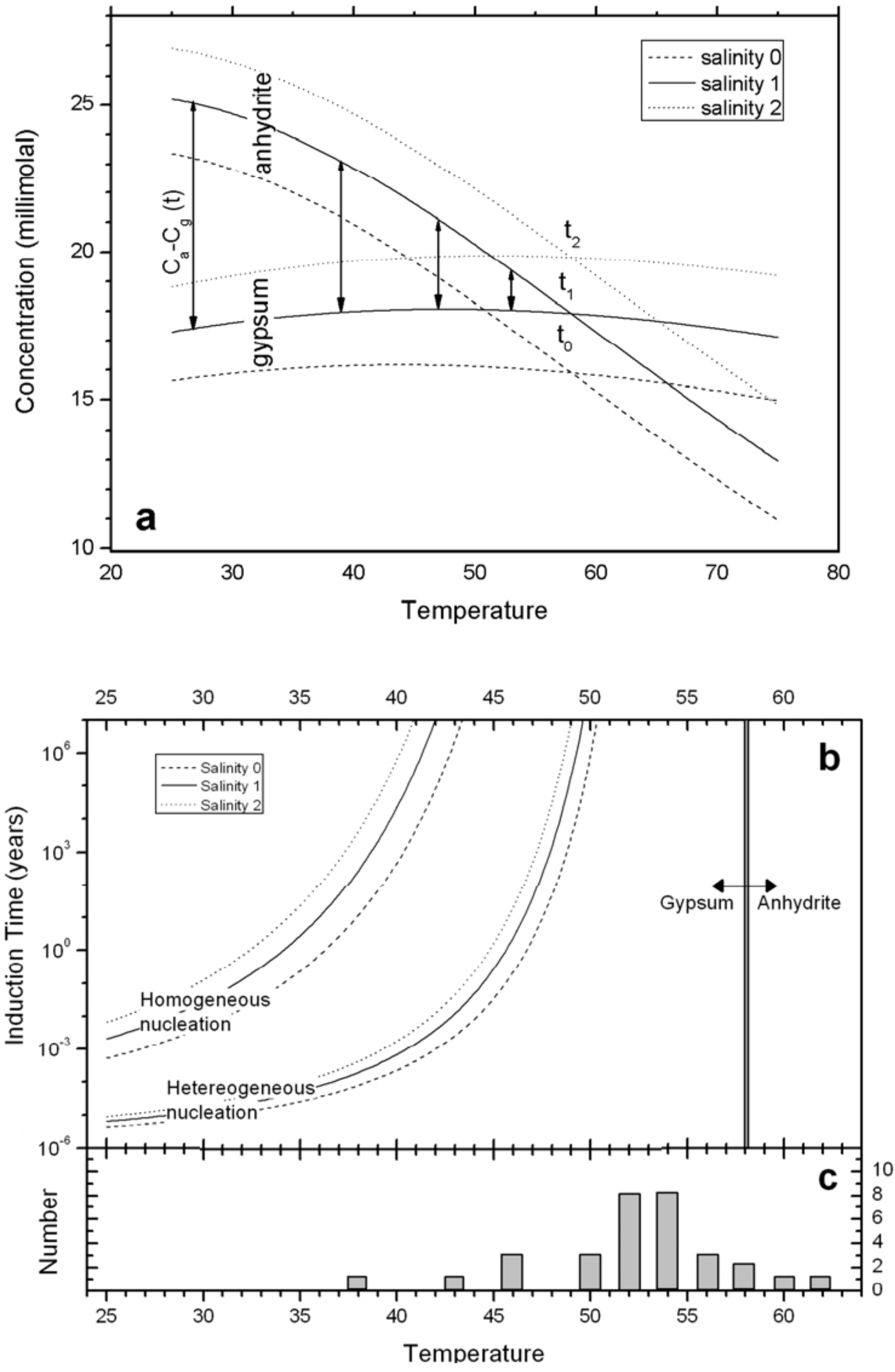

Fig. 4. García-Ruiz, Villasuso, Ayora, Canals & Otálora. (GIF)