Beams and Blocky Crystals: Another Challenge from the Naica Giant Gypsum Crystals

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INTRODUCCIÓN

The giant gypsum crystals discovered in 2000 in Naica (Mexico) have been since them a source of deep fascination not only because of their look, but also due to the wealth of scientific information that the mineralogical/crystallographic community can get from them. The first report explaining the extremely unusual size of these crystals (García-Ruiz et al. 2007) showed that they are only compatible with very low nucleation and growth rates under extremely steady conditions very close to equilibrium. These results lead to a deeper understanding of the nucleation and growth processes at very low supersaturation and to the definition of geological settings where nucleation and growth of giant crystals is plausible. Further advances trying to understand the chemistry of solutions producing these crystals (Krüger et al. 2013) also improved the instrumentation and knowledge available to study fluid inclusions in minerals. The obvious next question for these extremely slow growing crystals was about their age, which promoted demanding studies of isotopic dating (Sanna et al. 2010) and growth rate at very low supersaturation (Van Driessche et al. 2011) at the frontier of currently available experimental techniques and basic knowledge. Even the state of the art of our knowledge concerning the equilibrium morphology of gypsum was challenged (Massaro et al. 2010) by these unique crystals growing in conditions very close to equilibrium, where no experiments can be performed in the laboratory.

After 14 years of study, (see Otálora and García-Ruiz, 2013 for a review) one question was still missing in this list of scientific advances triggered by the giant Naica crystals. The presence of two clearly distinct crystal habits for gypsum in Naica was reported, but left unexplained, from the first studies. Crystals in the Cave of Crystals are always huge, but they are either bulky crystals with a morphology close to the equilibrium one (Massaro et al. 2010) or much longer crystals, called "beams", up to 11 meters long. The coexistence of two habits so widely different can only arise from two distinct nucleation and growth events or from two different growth mechanisms. The first option is incompatible with the mechanisms proposed in García-Ruiz et al,. 2007, while the operation of two different growth mechanisms is very unlike in conditions that are extremely steady and close to equilibrium... Except if the source of growth steps is different in both types of crystals.

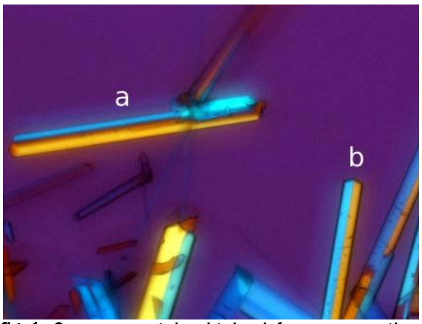

fig 1. Gypsum crystals obtained from evaporating seawater. Crystals labeled a and b are shown in figs 3-5.

LOW SUPERSATURATION GROWTH

The commonly assumed source of growth steps in crystals growing at low supersaturation are screw dislocations. These have been seldomly observed in the giant gypsum crystals, and always in the <010> directions, which are perpendicular to the elongation of beams so this mechanism is unlike to be the origin of elongation. Long gypsum crystals, even needles, have been reported in crystal growth experiments by chemical mixing or solution evaporation. An evaporating seawater experiment is shown in figure 1. All crystals in the picture are elongated and most of them are twinned (100 contact twin law). These twinned crystals are frequent in Naica, where virtually all beams (fig. 2a) display 100 contact twins (fig. 2b). Blocky crystals are single crystals (fig. 2c) showing a morphology close to the equilibrium one. The twinned crystals feature a reentrant angle where four {111} faces (two from each individual) meet. These reentrant angles are known to be a source of steps under some circumstances (Hartman, 1956). It is also known that reentrant twin angles often produce elongated morphologies at low supersaturation in crystals containing few or no screw dislocations, resulting in crystals that grow much larger than the coexisting single crystals (Kitamura et al. 1979). The reason for all these features, that giant beams display, is a growth rate enhancement because the surface at the atomic scale shows positions similar to growth steps in the reentrant corner. These positions operate as a source of growth steps additional to any other mechanism. This extraordinary source of steps changes the relative growth rate, accelerating the growth of the faces meeting at the reentrant angle and modifying the habit of the twinned crystal. To check for this mechanism as the origin of the elongation of gypsum beams we must check that the growth rate of the {111} faces at the convex and concave ends of the crystal is different.

TWINS AND GROWTH RATE

Figure 3 shows six consecutive stages during growth of the crystals labeled a and b in fig. 1. The twinned crystal is bound by {010} faces (parallel to the image), {120} faces (top and bottom of the images) and {111} faces (left and right ends). The twin produces a reentrant (concave) angle in the left side. The crystal grows mostly by elongation along the c axis by growth of

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the {111} faces and, more surprisingly, the growth rate of the left side is much larger than that of the right side. The enhanced growth rate of the side displaying a reentrant angle in more than one order of magnitude lager than the other, although the crystal faces shaping both ends are symmetrically equivalent. This proves the role of the reentrant twin angle as a source of steps controlling the overall kinetics of crystal growth.

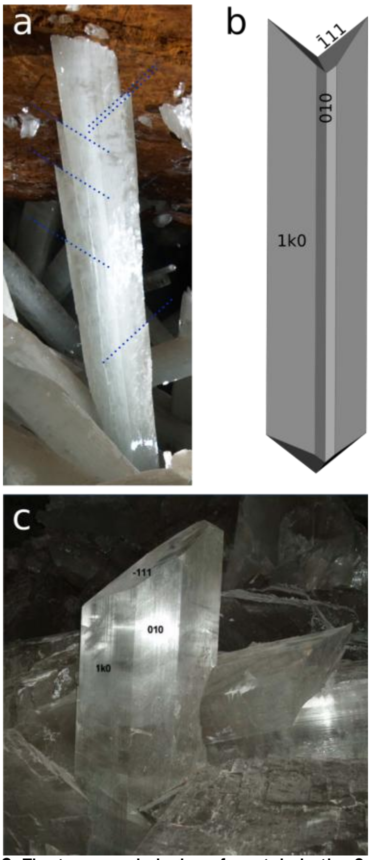

fig 2. The two morphologies of crystals in the Cave of Crystals in Naica. From top to bottom, blocky crystals, equilibrium habit of gypsum, a twinned beam and a sketch of the two individuals making the crystal.

Figure 4, shows a series of 915 profiles along the crystal in figure 3. Time is represented in the vertical axis. The time-series shows that, after the first third of the experiment, the growth rate of the left side starts to decrease and, after a transient period, it ends up being similar to that of the right side. This change of growth rate happens between pictures 3d and 3e, where a destabilization of the left growth front is evident and the reentrant angle disappear because the steps coming from the angle bunch giving rise to new {011} faces that end-up shaping the left side and filling the reentrant angle.

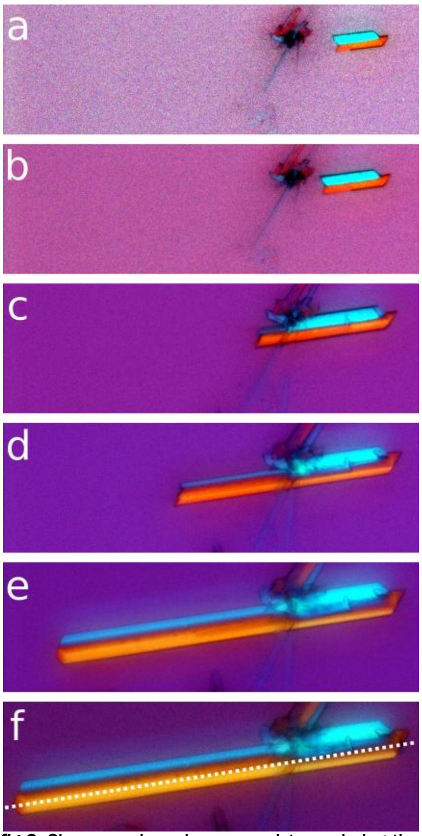

fig 3. Six successive microscopy pictures during the growth of crystal labeled a in figure 1. Picture f shows (dotted line) the profile used in figure 4 for growth rate measurement.

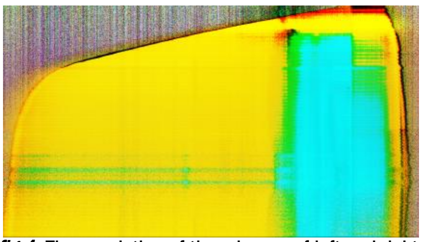

fig 4. Time evolution of the advance of left and right ends of the crystal shown in figure 3. The vertical axis is time (increasing from top to bottom). The x-axis is the distance along the line shown in figure 3f.

This process is quite frequent in these experiments. Most crystals in figure 1 are elongated twins repeating the same growth history. Figure 5 shows a detail of the destabilization of the reentrant angle in the crystal labeled b in figure 1.

This behavior of 100 contact twinned gypsum explains the two different crystal habits observed in the Cave of Crystals and let us conclude that the giant beams making so spectacular the site are the crystals that, among many others, developed 100 contact twins and happen to have the reentrant twin angle upwards. The destabilization process described is due to step bunching, so it should be much less important in the Naica crystals growing at very low supersaturation. Some morphological features of Naica Crystals can be attributed to this destabilization due to step bunching, but (fortunately) they were insufficient to stop the growth of the magnificent giant beams.

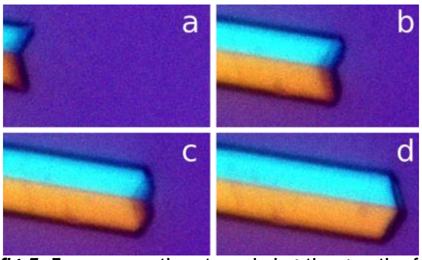

fig 5. Four consecutive steps during the growth of crystal labeled b in figure 1. The sequence shows the destabilization of the reentrant twin angle due to step bunching and the development of {011} faces.

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