Gypsum Twin Laws and habits

An unexplored tool as a proxy for the chemistry of the original brine

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Depending on the depositional environment, gypsum exhibits different idiomorphic single and twinned crystal habits. In soils (Jafarzadeh & Burnham, 1992), desert regions (Shahid & Abdelfattah, 2009) and salt lakes (Warren, 1982; Mees et al., 2012), acicular, tabular-prismatic, lenticular, and twinned crystals are observed. In marine evaporites, mostly twinned and tabular gypsum crystals are found (Ortí, 2010). In caves and in Badenian evaporitic gypsum deposits, distinctive curved crystal structures (the so-called ram's horn and sabre gypsum) are observed (Wenrich & Sutphin, 1994; Panczner, 2013; Bąbel et al., 2015), whereas the most spectacular habits are related to the prismatic meter-sized single crystals and twins of Naica Mine (Mexico) (García-Ruiz et al., 2007) and in the Geode of Pulpì (Almería, Spain) (Canals et al., 2019), which grew by an anhydrite-gypsum thermally driven transformation by a self-feeding mechanism at low supersaturation values (Fig. 1).

These different gypsum habits were believed to reflect peculiar growth conditions (Lacroix, 1897). A better understanding of the environmental factors responsible for different gypsum crystal habits could have crucial implications for interpreting the origin of gypsum deposits formed in the geological past (Van Driessche et al., 2019). Consequently, many crystal growth laboratory experiments have been performed to establish which conditions favour specific gypsum habits. The acicular habit developed along [001] is the most common and representative of gypsum habit in a pure system (Craker & Schiller, 1962; Rinaudo et al., 1985), whereas tabular-prismatic and lenticular habits are promoted by different chemical composition of the mother solution (Cody, 1979; Rabizadeh et al., 2017; Reiss et al., 2019). Overall, saline waters with Na^+, K^+, $Mg^{2+,}$ Sr^{2+}, Cl^-, and Br^- ions in solution reduce the [001] elongation of gypsum single crystals switching from acicular to tabular habit (Reiss et al., 2019), and organic molecules from green plants' decomposition promote the lenticular habit (Cody, 1979). Remarkably, twinned gypsum crystals have often been observed both in natural environments (Warren, 1982; Shahid & Abdelfattah, 2009; Ortí, 2010) and by crystal growth laboratory experiments (Simon, 1968; Cody & Cody, 1989). However, twinned crystals have often been defined as "swallowtail" twins, avoiding their twinning law identification. Limited knowledge of the morphological, crystallographic, and optical characteristics of the twinning laws of gypsum was at the origin of this missed identification. Consequently, relatively little has been done to understand which impurities exert a critical role in the selection of different twinning laws and how this may impact our awareness of their occurrence in nature. Hopefully, to date, the crystallographic growth directions of the twinning laws of gypsum have been described, and their twinning energies have been determined (Follner et al., 2002; Rubbo et al., 2012a, 2012b). Only five different twinning laws are possible for gypsum structure, and each twinning law is described by a contact and a penetration twin; hence, at least ten different twinned habits are possible (Fig. 2). Therefore, in this PhD thesis, which largely represents the results described in Cotellucci et al. (2023a) and Cotellucci et al. (2023b), we provided new and useful tools to recognize the different twinning laws of gypsum univocally (Cotellucci et al., 2023a): the re-entrant angle value (θ), the extinction angle (Δ) formed between the two sub-crystals composing the twin, and the orientations of the primary fluid inclusions of the negative crystal shape (FIs) with respect to the twin plane (Fig. 2).

Despite this theoretical morphological variability, to date the 100 contact twinning law is the only well recognized gypsum twinning law occurring in natural environments (Ortí, 2010), whereas it has never been observed by laboratory experiments. Noteworthy, we suggested that the 101 contact twinning law occurs in geological evaporitic environments and has been confused with the most widespread 100 contact twin, up to date (Cotellucci et al., 2023a) (Fig. 3). Both 100 and 101 twinning laws show the same re-entrant angle value. However, the

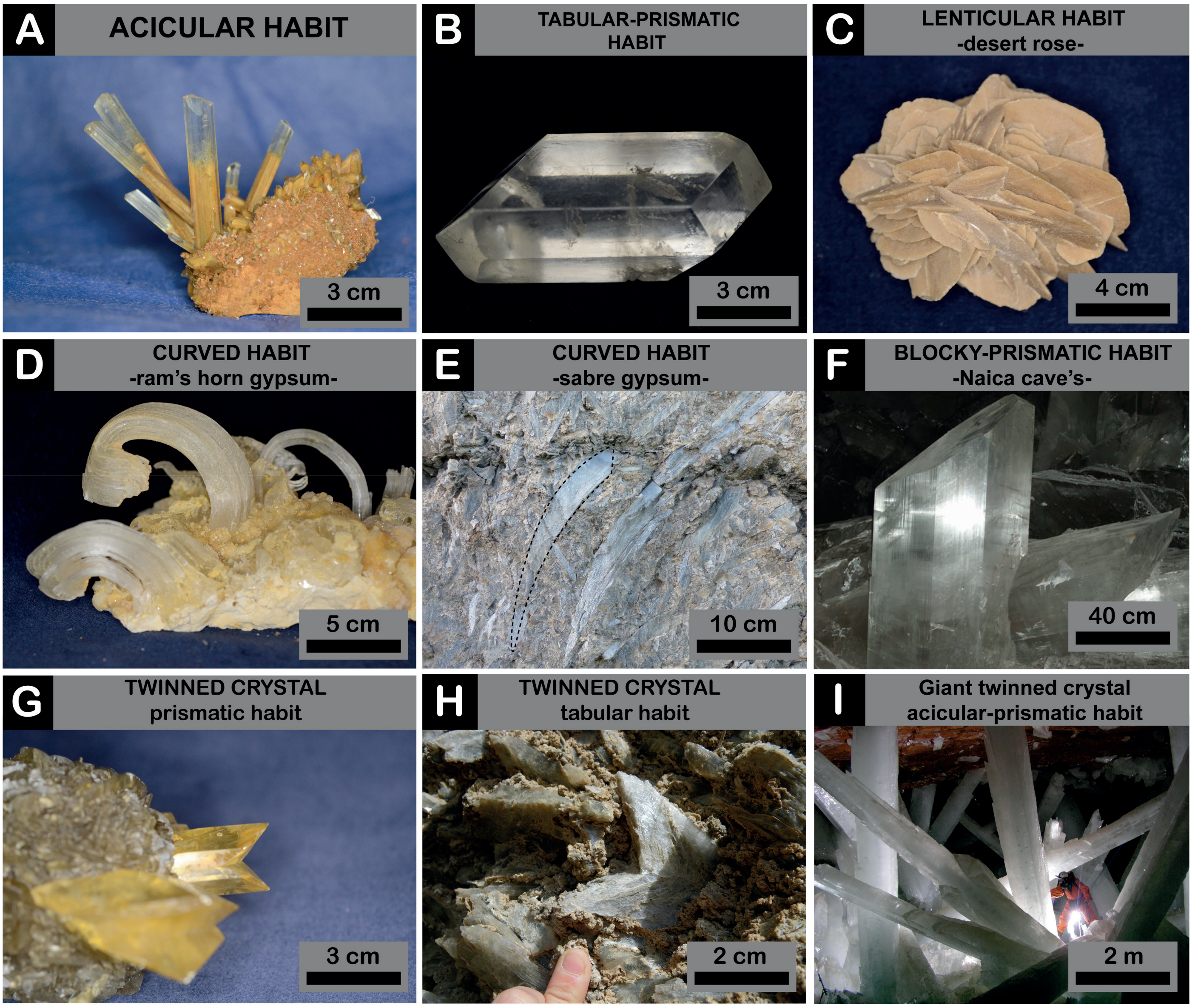

Figure 1 ***a)*** *Acicular habit from Mexico, Naica (collection of the Turin Natural Science Regional Museum).* ***b)*** *Tabular-prismatic habit from Chaine Lake, Alberta, Canada (collection of the Turin Natural Science Regional Museum).* ***c)*** *Lenticular crystals aggregated together to form the well-known "desert rose" (from Tunisia; collection of the Turin Natural Science Regional Museum).* ***d)*** *Ram's horn gypsum from Sicily, Cava di Rocca Chi Parra (collection of the Turin Natural Science Regional Museum).* ***e)*** *Curved gypsum crystals (sabre gypsum) from the Badenian succession of Poland.* ***f)*** *Blocky-prismatic single crystal from Mexico, Naica (ph. Juan-Manuel Garcia-Ruiz).* ***g)*** *Prismatic twinned crystal from Red River Floodway, Winnipeg, Manitoba, Canada (collection of the Turin Natural Science Regional Museum).* ***h)*** *Prismatic twinned crystal from Spain, Sorbas (ph. Laura Sanna).* ***i)*** *Giant acicular-prismatic twinned crystals from Mexico, Naica (ph. Laura Sanna - LaVenta archive).*

sub-crystals composing 100 twins grow parallel to the twinning plane (Otálora & García-Ruiz, 2014), whereas we demonstrated that in 101 twinning law the main elongation of subcrystals is oriented obliquely with respect to the twinning plane (Fig. 3). Therefore, we also propose that the main elongation of the sub-crystals forming the twin with respect to the twinning plane is a useful tool to distinguish between 100 and 101 twinning laws, especially for natural samples whose optical extinction angles can often be difficult to measure.

Furthermore, we re-investigated gypsum habits in an impurity-free system by the evaporation of a solution saturated in $CaSO_4{\cdot}2H_2O$, focusing on the identification of twinning laws and their habit description (Cotellucci et al., 2023b): depending on the evaporation rates, acicular crystals, curved ones, 100 penetration twinning law, and 101 penetration twinning law can be observed.

Finally, the last chapter of the thesis analyzes the different gypsum habits observed both in presence and absence of sulfide oxidation. The preliminary results suggest that H_2S, along with its oxidation products, may promote the precipitation of 100 gypsum contact twin, and the possible geological implications of these laboratory experiments are discussed.

To summarize, in this thesis, *i)* we described which among the twinning laws of gypsum are possible in a pure solution and, for the first time, established a correlation between different gypsum habits and evaporation rates, so contributing to a better understanding of gypsum habits in evaporitic environments; *ii)* we provided new insights into the mineralogical implications of twinned gypsum crystals and their potential use as a tool for a deeper comprehension of the natural gypsum deposits; *iii)* we contributed to the debate on the origin

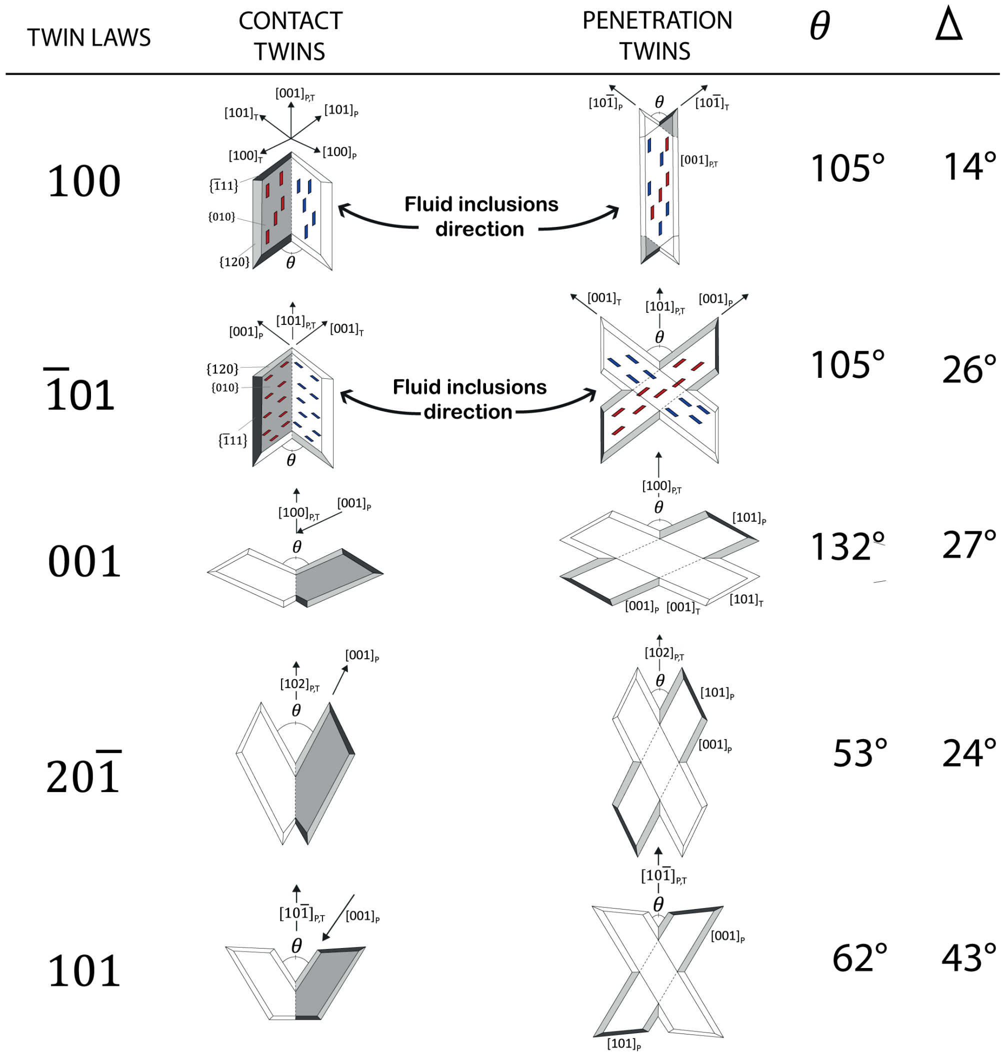

Figure 2 Geometrically, each twinning law is characterized by a specific re-entrant angle. By measuring its value, we can identify the twinning law. However, the 100 and $\bar{1}01$ twinning laws have the same re-entrant angle (i.e., 105°). Thus, goniometry cannot distinguish these twins and the formal way to correctly identify the 100 and $\bar{1}01$ twinning laws requires the measurement of the extinction angle (Δ) formed between the two individuals, by means of optical microscopy in crossed polarizers. This angle is 14° and 26° for 100 and $\bar{1}01$ twinning laws, respectively. Moreover, FIs in 100 twinning law are elongated along [001] oriented parallel with respect to the twinning plane, whereas FIs in $\bar{1}01$ twinning law are always elongated along [001] but oriented obliquely with respect to the twinning plane. Consequently, the orientations of FIs with respect to the twinning plane is a fast and useful method to distinguish between the 100 and $\bar{1}01$ twinning laws. Modified from Cotellucci et al. (2023a).

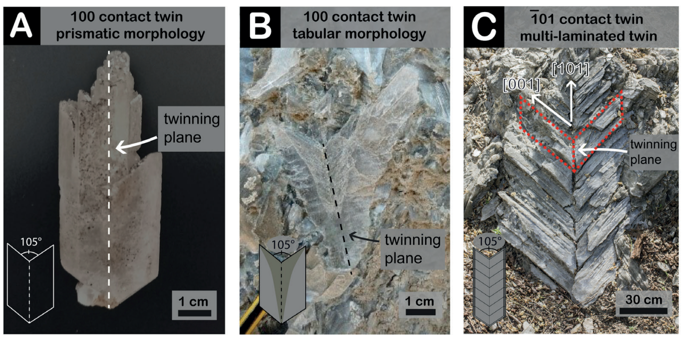

Figure 3 Examples of natural gypsum contact twins in modern and ancient evaporitic environments. ***a)*** Centimeter-sized gypsum twin from the Atacama Desert, Chile. ***b)*** Centimeter-sized Messinian selenitic gypsum from Piedmont basin, Italy (photograph courtesy of Marcello Natalicchio). ***c)*** Meter-sized Messinian selenitic gypsum from 'Vena del Gesso Romagnola', Italy, composed of many sub-crystals obliquely elongated with respect to the twin plane (photograph courtesy of Piero Lucci). Credits by Cotellucci et al. (2023a).

of ancient Salt giants, where 100 gypsum contact twins constitute a typical mineral component, providing new experimental data and stimulating further research in the field of the sulfur cycle in sedimentary environments. Our results improve the knowledge of the influences of variations in solution composition on the habits of gypsum crystals. This may aid in understanding the chemistry of the original brine in ancient sedimentary successions depending on the twinning laws of gypsum observed and their habits.

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