



Amorphous carbonates as precursors of dolomite and magnesite in caves

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ARTICLE INFO

Associate editor: Adrian Immenhauser

Keywords:

Amorphouscalcium-magnesium carbonate
Amorphous magnesium carbonate
Dolomite
Magnesite
Low temperature
Non-classical crystallization

ABSTRACT

Low-temperature (*T*) dolomite (and magnesite) formation remains a longstanding, strongly debated problem in carbonate geochemistry. It has been recently proposed that protodolomite (at low-*T*) and ordered dolomite (at high-*T*) can form via a non-classical route involving an amorphous calcium-magnesium carbonate (ACMC) precursor. Although this crystallization pathway has been observed in the laboratory using abiotic and microbially mediated routes, its occurrence in natural environments has not yet been documented. Here we show the formation of poorly ordered dolomite (protodolomite) and ordered dolomite, along with magnesite, in close association with ACMC and amorphous magnesium carbonate (AMC) in the moonmilk deposits from Nerja Cave (Spain). Our results suggest that these amorphous carbonate phases are crucial precursors in the formation of dolomite and magnesite in this environment, after the initial precipitation of huntite that acts as a Mg²⁺-rich carbonate reservoir. We show that the crystallization of dolomite and magnesite is governed by a dynamic interplay between fluctuating drip water chemistry, cyclic precipitation-dissolution of huntite, and the stabilization and subsequent crystallization of amorphous carbonate phases mediated by dissolved silica and microbially-derived organic compounds. These findings provide mechanistic insights into low-*T* dolomite and magnesite formation in cave systems and shed light on their nucleation barrier in Earth's surface environments.

1. Introduction

Understanding how anhydrous Mg²⁺-bearing carbonates form at Earth surface conditions represents a key and long-standing challenge in geology and modern geochemistry, with major implications for paleo-environmental reconstructions, hydrocarbon reservoir characterization, carbon capture technologies, and biomineralization research (Warren, 2000; Power et al., 2019; Fang et al., 2023; Santos et al., 2023). While carbonate precipitation in surface environments typically involves calcite and aragonite, the limited occurrence of dolomite (and magnesite) in modern settings in contrast with its abundance in the ancient sedimentary record, combined with the difficulties to replicate ordered dolomite crystallization in the laboratory at near-surface temperatures, represent some of the key issues in the so-called ‘dolomite (and magnesite) problem’ (Warren, 2000; Frisia et al., 2018; Raudsepp et al., 2024).

Recently, Pina et al. (2022) highlighted that the scarcity of modern dolomites rather than an inability of dolomite to form is due to kinetic barriers as extended timescales are required to achieve the high degree of cation ordering characteristic of well-crystallized dolomite. Therefore, the so-called ‘dolomite problem’ is mostly a matter of understanding the environmental conditions and temporal scales that govern both mineral formation and the progressive ordering of cations in natural settings. Furthermore, both classical and non-classical processes have been proposed as mechanisms involved in the formation of dolomite and other carbonates in cave speleothems (Frisia et al., 2018; Frisia et al., 2022) and other Earth's surface settings (Raudsepp et al., 2022). Therefore, although there has been an extensive debate about the mechanisms, processes, and environmental factors governing the low-*T* formation of dolomite and magnesite in nature, our understanding of the physicochemical processes and mechanisms involved is still limited.

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<https://doi.org/10.1016/j.gca.2026.07.016>

Received 23 April 2026; Accepted 10 July 2026

Available online 24 July 2026

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Magnesite reportedly forms at nearsurface temperature (T) in different lacustrine and playa systems (Power et al., 2019). This low- T formation process has gained attention for its potential significance toward large-scale carbon sequestration applications (Santos et al., 2023). Similarly, recent dolomite formation has been reported in specific superficial environments associated with anoxic or sulfate-rich marine settings, where the kinetic barriers to its formation are thought to be overcome by factors such as the presence of silica, saturation fluctuations (Frisia and Wenk, 1993; Wenk et al., 1993; Deelman, 1999; Meister and Frisia, 2019; Kim et al., 2023) and/or microbial activity (Petrash et al., 2017; Chen et al., 2024). Yet most recent ‘dolomites’, unlike their ancient counterparts, are typically poorly ordered, being considered not ‘true dolomites’ but very high Mg^{2+} -calcites or disordered dolomites (protodolomites) (Gregg et al., 2015; Pina et al., 2022).

Cave systems represent distinctive sedimentary environments in which Mg^{2+} -rich carbonates can form under low- T , oxic, and near-neutral pH conditions that are generally considered unfavorable for anhydrous magnesium carbonate precipitation. The occurrence of dolomite at around 17 °C in vadose cave environments, such as Castañar Cave (Spain), has highlighted the existence of alternative formation pathways (Alonso-Zarza and Martín-Pérez, 2008; Martín-Pérez et al., 2021). In caves, Mg^{2+} and Mg^{2+} - Ca^{2+} -carbonates commonly occur as speleothems and moonmilk deposits precipitated from drip waters that have interacted with dolostones and dolomitic marbles (Martín-Pérez et al., 2021; Martín-Pérez et al., 2015). These deposits form through complex interactions between host rock dissolution, groundwater chemistry, and environmental conditions that create favorable micro-environments for magnesium-rich carbonate phases nucleation and growth (Jones, 2010). Microorganisms are frequently present in these settings and have been suggested to influence low- T dolomite formation, although their precise role remains debated (Jones, 2010; Petrash et al., 2017; Mather et al., 2023). Despite these advances, the mechanisms, rates, and controls governing Mg^{2+} -rich carbonate formation in caves are still poorly constrained.

Importantly, non-classical crystallization from a transient amorphous precursor is common in both abiotic and microbially-induced calcium carbonate precipitation in laboratory settings (Hu et al., 2012; Rodríguez-Navarro et al., 2015) and has been suggested for the formation of natural carbonates in many different sedimentary environments (Wang et al., 2012; Raudsepp et al., 2024; Dietzel and Boch, 2024). Amorphous calcium-magnesium carbonate (ACMC) and amorphous magnesium carbonate (AMC) phases have been identified under laboratory conditions as metastable precursors that transform into low- T high-magnesium calcite/protodolomite/disordered dolomite, and high- T ordered dolomite (Oomori et al., 1983; Rodríguez-Blanco et al., 2015; Liu et al., 2019; Purgstaller et al., 2021). However, although this non-classical crystallization pathway could be a potential route to overcome the kinetic barriers to dolomite and magnesite precipitation (Hardie, 1987; Gregg et al., 2015), and thus, help to explain the distinctive nanoscale features (e.g., nanoglobules or nanogranules) observed in modern and ancient dolomites and magnesites (Frisia et al., 2018; Raudsepp et al., 2024), the occurrence of ACMC and AMC in natural environments (hereafter referred to as A(C)MC when we denote both phases) has not yet been demonstrated. This challenges the models suggesting that these Mg^{2+} -carbonate phases form via a non-classical route in sedimentary environments. Moreover, the mechanistic details facilitating the amorphous to dolomite (or magnesite) transformation remain uncertain.

To elucidate the pathways and mechanisms governing low- T dolomite and magnesite formation in cave environments, we conducted a comprehensive characterization during a seasonal period to follow the crystallization in the moonmilk deposits from Nerja Cave (Málaga, Spain) (Supplementary Fig. S1) using a multi-analytical approach. This work increases our current understanding of the complex mechanisms that enable the formation of magnesite and dolomite in cave systems, providing new perspectives on long-standing questions in carbonate

geochemistry and the role of amorphous precursors in the low- T formation of Mg^{2+} - and $\text{Mg}^{2+}/\text{Ca}^{2+}$ -carbonates in nature.

2. Site description

Nerja Cave is located in the Internal Zone of the Betic Cordillera in southern Spain (see Supplementary Fig. S1). Geologically, the cave developed within fissured and karstified Triassic marbles belonging to the Alpujarride complex of the Internal Zones of the Betic Cordillera. They are medium-coarse-grained recrystallized dolomitic marbles that contain trace amounts of quartz, phlogopite and chlorite (López Sánchez-Vizcaíno and Gómez-Pugnaire, 1993). They are 400–500 m thick, affected by open folds and low penetrative cleavage, with 10°–20° S average dip regional bedding (Martínez-Moreno et al., 2021). These marbles show little edaphic development. In situ weathering of the dolomitic marbles has resulted in brecciation, rock disintegration, and the production of dolomitic sands (>97% dolomite), together with the development of a variety of secondary carbonate deposits, including calcretes and speleothems (Aranburu et al., 2018). Based on micro-texture and colour, Aranburu et al. (2018) distinguished two types of calcretes: (i) biogenic laminated red calcretes containing pisolitic layers, glaeboles, and detrital silicate minerals (muscovite, vermiculite, and quartz), interpreted as having formed in surface soil environments; and (ii) laminated beige micritic calcretes composed of floating dolomite crystals dispersed within a carbonate mud matrix and lacking phyllosilicates. The carbonate formation is underlain by a thick sequence of mostly Palaeozoic schists and Permian-Triassic phyllites, at least 1 km thick (Martínez-Moreno et al., 2021). Above the Alpujarride units, Neogene-Quaternary sediments lie in stratigraphic unconformity. The Pliocene deposits rest unconformably on the Alpujarride metamorphic basement. Quaternary deposits rest unconformably on both Pliocene units and on the Alpujarride basement (Guerra-Merchán et al., 2004).

The cave system extends approximately 5 km horizontally, with elevations ranging from 123 to 191 m above sea level. It has a vertical height of 68 m, covers an area of 35,000 m², and has a volume of approximately 300,000 m³. The cave is divided into two main sectors (Fig. S1): the tourist galleries and the non-tourist sector. The tourist galleries, which are open to visitors, occupy a volume of 106,285 m³ and cover an area of 9,371 m². This sector includes the *Vestíbulo*, *Belén*, *Cascada*, *Fantasmas*, and *Cataclismo* chambers. The non-tourist sector, not open to public visit, comprises the Upper Galleries, which contain the *Hércules* and *Inmensidad* chambers, and the New Galleries, which include the *Lanza* and *Montaña* chambers.

The climate in the study area is coastal Mediterranean, with an average historic annual rainfall (1969/70 to 2003/04) of 490 mm (Andreo and Carrasco, 1993; Liñán et al., 2007). Rainfall occurs predominantly in autumn and winter and less frequently in springtime (Andreo et al., 2018). For the period 1992 to 2025 the monthly average temperature ranged from 13.5 °C in February to 26.1 °C in August, with a mean annual temperature of 18.70 °C (C. Liñán, personal communication). The mean annual cave air temperature is 18.82 °C in the tourist galleries and 19.86 °C in the non-tourist galleries.

In the Nerja cave, drip water flows are generally very low. In the tourist area, under normal rainfall conditions, maximum drip flow rates are recorded during the summer and autumn (66 ml/day, mean value from June to October), whilst minimum flow rates are observed in winter and spring (38 ml/day, mean value from December to March). This general time lag (6 to 8 months according to Liñán et al., 1999; Liñán et al., 2002) reflects the inertial behavior of the cave and the great capacity of the vadose zone in which the cave is located to modulate the input signal (Carrasco et al., 2006). After exceptional rain events, the time lag is reduced to 1–2 months (Mudry et al., 2008; Batiot et al., 2003; Liñán et al., 1999; Liñán et al., 2002; Andreo et al., 2002). The natural ventilation of the cave is determined by variations in the density differences between the external and internal air (Liñán et al., 2018; Liñán et al., 2020). In winter, the natural ventilation is maximum, and

the external air enters the Nerja cave and moves from the tourist to the non-tourist sector. The strong ventilation regime during this period contributes to the entry of atmospheric air and promotes evaporation and subsequent carbonate precipitation, particularly in the chambers of the tourist sector, nearest the entrance, and where the air is dryer than in the non-tourist sector, where the air relative humidity was > 95% during all the studied period (Liñán et al., 2018; Liñán et al., 2020).

3. Moonmilk deposits

Moonmilk is a type of speleothem or endokarstic deposit of chemical and/or biochemical origin, characterized by its distinctive physical properties and its soft and creamy appearance when wet, and crumbly, powdery texture when dry. It is composed of a variety of mineralogical species, whose composition and relative abundance may vary depending on environmental conditions and formation processes (Hill and Forti, 1997). The genesis of moonmilk remains debated, and its formation has been attributed to abiotic, biotic, and combined physicochemical–biological processes (Smith, 2024). Abiotic mechanisms include direct carbonate precipitation from supersaturated solutions, dissolution and recrystallization of limestone or pre-existing speleothems, and, in some cases, freezing-related processes (Hill and Forti, 1997; Aranburu et al., 2010; Borsato et al., 2000; Casas et al., 2001; Forti, 2001). Crystal growth driven by slow CO₂ degassing and capillary water flow under conditions of high relative humidity has also been proposed as a key mechanism for calcite moonmilk formation (Borsato et al., 2000). Biotic models suggest that microorganisms, including bacteria, fungi, algae, and archaea, contribute to moonmilk formation either by inducing carbonate precipitation or by providing nucleation sites for mineral growth (Jones and Kahle, 1993; Northup and Lavoie, 2001; Blyth and Frisia, 2008). Microbial activity may also enhance bedrock dissolution through the production of organic acids, increasing calcium availability for subsequent carbonate precipitation (Forti, 2009). Although microbial communities are commonly found in moonmilk deposits and have been linked to calcification processes (Gradziński et al., 1997), many deposits show no clear microbial association, indicating that physicochemical processes alone may also account for their formation (Borsato et al., 2000; Northup and Lavoie, 2001). Consequently, moonmilk is generally considered to result from varying contributions of biological and abiotic factors depending on the cave environment (Hill and Forti, 1997; Forti, 2009).

Two types of moonmilk have been reported in the Nerja cave: calcium-rich and magnesium-rich (Casas et al., 2001; Delgado et al., 2024). Drip water precipitates are primarily calcite, occasionally accompanied by aragonite (Liñán et al., 2023). In this study, four moonmilk samples were collected from the cave floor of a relatively extensive outcrop in the *Cataclismo* chamber within the tourist sector. The material was characterized by a dry, crumbly, and powdery appearance. In the non-tourist sector, two additional moonmilk samples were collected from the cave floor of the *Inmensidad* chamber, where the deposit exhibited a comparable crumbly and powdery texture, although with greater moisture content. The differences in water content observed among the moonmilk samples are consistent with the increase in cave-air relative humidity from the tourist sector (89%) to the non-tourist sector (96–100%) (Liñán et al., 2020; Delgado et al., 2024). In both sectors, moonmilk occurs as irregular meter-scale masses developed on the cave floor.

The deposits are considered to result from the direct precipitation of mineral phases from groundwater under cave environmental conditions (Casas et al., 2001). However, mineral precipitation in the Nerja cave does not occur under constant conditions over time. Active drip sites in Nerja cave are fed by groundwater that percolates through overlying dolomitic marbles, supplying Mg²⁺, Ca²⁺, carbonate, and bicarbonate ions, and through poorly developed clay-rich soils that represent a source of dissolved silica. Episodic events of continuous, slow infiltration may be followed by short episodes of rapid infiltration and fast drip

flow rates, when intense Mediterranean rainfall events occur (Carrasco et al., 2006).

Previous mineralogical characterization of the moonmilk deposits from Nerja cave (Casas et al., 2001) have shown that they are composed exclusively of carbonate minerals. Huntite and dolomite constitute the predominant phases, with huntite generally being more abundant. Minor amounts of calcite (both stoichiometric and Mg²⁺-rich) and magnesite are also present, whereas aragonite occurs only rarely and in trace proportions. Hydromagnesite has been also identified in the moonmilk deposits of the *Cataclismo* chamber (Casas et al., 2002). Recently, Delgado et al. (2024) first reported hydrated phosphates (wicksite, iangreyite), sulfates (langbeinite) and witzkeite (nitrate-sulphate mineral) in the moonmilk deposits from the Nerja cave although in much smaller proportions than carbonate minerals.

Speleothems spanning a wide range of ages have been dated in Nerja cave, from older than 800 ka BP to younger than 20 ka BP (Durán, 1996; Arrese, 2009; Aranburu et al., 2026). However, none of these absolute ages corresponds to moonmilk deposits. The only chronological constraint currently available for the moonmilk investigated in this study comes from the *Cataclismo* chamber. Medina-Alcaide et al. (2019) reported the occurrence of a charcoal layer from a prehistoric hearth directly overlying the surface of the moonmilk deposit, which yielded a radiocarbon age of 28,155–27,730 cal BP (AMS ¹⁴C). Consequently, the moonmilk deposit must predate this archaeological horizon, indicating a minimum age of approximately 28 ka cal BP. This chronological constraint is consistent with the observations of Durán et al. (2001), who suggested that some Spanish moonmilk deposits may have formed during the Late Pleistocene and have remained stable under present cave environmental conditions. Although the precise onset and duration of moonmilk formation remain unknown, these observations indicate that the deposits represent long-lived mineral accumulations that developed over extended timescales rather than ephemeral precipitates.

4. Material and methods

4.1. Drip water characterization

Temperature, pH, and electrical conductivity of the drip water were measured in situ, using a WTW conductivity and pH-meter. In the laboratory, the alkalinity (HCO₃⁻) was measured by volumetry with H₂SO₄, and Ca²⁺ and Mg²⁺ by complexometry with EDTA, the same day when sampled. Major components were analyzed: Cl⁻ by argentometry, SO₄²⁻ by gravimetry, SiO₂ and NO₃⁻ by spectrophotometry, and Na⁺ and K⁺ by flame photometry. The most recent samples were analyzed by liquid ion chromatography using a DIONEX instrument from Centro de Instrumentación Científica of the University of Granada (Spain) and CEHUMA of the University of Málaga (Spain). Drip water chemical composition data (samples collected at a point considered representative of the touristic area of the cave over 10 years, from April 1991 to August 2001) were used to determine the speciation and the saturation indexes (SI, SI = Log(IAP/Ksp)), where IAP is the ion activity product and Ksp is the solubility product of a particular phase) with respect to potential relevant phases using the code PHREEQC (Parkhurst and Appelo, 2013). For the calculations the PHREEQC thermodynamic database (phreeqc.dat) was expanded with additional data from the MINTEQ and WATEQ databases for huntite and magnesite, respectively. Solubility data for ACMC and AMC were incorporated from Purgstaller et al. (2019) and the value for amorphous sepiolite was taken from Wollast et al. (1968).

The hydrochemical dataset used for PHREEQC modeling was collected between 1991 and 2001 because it represents the most comprehensive and internally consistent hydrochemical monitoring available for Nerja cave, including the complete suite of parameters required to calculate mineral saturation indices. Although the moonmilk samples investigated in this study were collected between 2023 and 2025 (see below), both the hydrogeological framework and the cave

microclimate controlling groundwater evolution and carbonate precipitation have remained essentially unchanged over this period.

Groundwater continues to percolate through the same Triassic dolomitic marbles and the overlying clay-rich soils, so the dominant water–rock interaction processes supplying Mg^{2+} , Ca^{2+} , dissolved inorganic carbon and silica are expected to remain stable through time. Likewise, the seasonal cave ventilation regime, which largely controls cave-air $p\text{CO}_2$ and consequently the saturation state of drip waters with respect to carbonate minerals, has remained remarkably consistent according to long-term monitoring.

As discussed in Section 2, the Nerja karst system behaves as a highly buffered vadose aquifer with long groundwater residence times and a delayed response to rainfall. Under normal conditions, drip water discharge typically lags precipitation by 6–8 months, although exceptionally intense rainfall events can shorten this response time to 1–2 months. As a result of these seasonal hydrological variations, hydrochemistry also follows a recurrent seasonal pattern. During summer, drip waters display their highest conductivity, alkalinity, Ca^{2+} and Mg^{2+} concentrations, together with elevated cave-air $p\text{CO}_2$, resulting in lower supersaturation with respect to calcite. From autumn onwards, conductivity progressively decreases, reaching minimum values during winter, when enhanced cave ventilation lowers cave-air $p\text{CO}_2$, promotes CO_2 degassing, increases calcite supersaturation, and favours carbonate precipitation (Andreó et al., 2002; Batiot et al., 2003). Long-term cave monitoring indicates that these seasonal relationships between cave-air $p\text{CO}_2$, drip water electrical conductivity, and carbonate precipitation remain unchanged under present-day conditions.

Therefore, temporal variability mainly affects the magnitude of drip water discharge rather than the fundamental hydrogeochemical processes controlling carbonate precipitation. The long-term hydrochemical dataset thus captures the natural seasonal variability of the system and remains representative for evaluating the saturation state of Mg-bearing carbonate phases and the hydrogeochemical conditions responsible for moonmilk formation.

4.2. Moonmilk sample collection

Moonmilk samples were collected during different periods of the year: September 2023, May 2024, and March and June 2025. These sampling campaigns were designed to reflect the contrasting seasonal hydrological conditions within the cave. As described above, rainfall in the region occurs predominantly during autumn and winter, whereas precipitation is less frequent in spring. In the tourist sector, under normal rainfall conditions, drip flow rates are highest during summer and autumn (June–October) and lowest during winter and early spring (December–March). Consequently, the selected sampling periods include both low-flow conditions (March and May) and high-flow conditions (June and September), allowing the assessment of potential seasonal variations in moonmilk geochemistry associated with changes in water availability and recharge dynamics. As detailed in section 3, the samples were collected from the cave floor of two locations within Nerja cave (see details in Supplementary Material): 1) the touristic sector, specifically of the *Cataclismo* chamber; and 2) the non-touristic sector, the cross-passage between the *Immensidad-Lanza* chambers. After collection, the samples were dried at room T under vacuum for 24 h in the laboratory and later they were kept in a desiccator at 10% relative humidity prior to analysis.

4.3. Solids characterization

Samples were analyzed by means of Fourier transform infrared spectroscopy (FTIR) with a JASCO FTIR 6600 from Department of Mineralogy and Petrology, University of Granada (Spain). The measurement was performed in the 400 to 4000 cm^{-1} spectral range, with a 2 cm^{-1} resolution, and equipped with an attenuated total reflection (ATR) device. For each measurement (samples and background) a total

of 64 scans were averaged. Prior to ATR-FTIR analysis, the spectra were normalized to the most intense absorption band, corresponding to CO_3^{2-} at $\sim 1400 \text{ cm}^{-1}$. The absorbance of this band was set to 1.0, and the entire spectrum was scaled accordingly.

Additionally, X-ray diffraction (XRD) analysis was performed using a PANalytical X'Pert Pro X-ray diffractometer from Department of Mineralogy and Petrology, University of Granada (Spain) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Data were collected from 3 to $70^\circ 2\theta$ at a scanning rate of $0.11^\circ 2\theta \text{ s}^{-1}$. For the complete characterization of the clays in the samples, oriented aggregates (OA) were prepared. The samples underwent a three-step acetic acid treatment to eliminate the carbonates. First, the samples were exposed to a solution of 5 mL of acetic acid per 1 L of water for 8 h, and the supernatant was discarded. Then, a second and third treatment were performed, each with 10 mL of acetic acid per liter of water for 8 h. Once the carbonates were removed, the remaining solids were rinsed thoroughly with deionized (DI) water. The resulting dispersions were deposited on glass slides. After complete air drying, the oriented aggregates were subjected to XRD analysis.

High-resolution X-ray diffraction (HRXRD) analyses were performed at the CRISTAL beamline of the SOLEIL Synchrotron (Paris, France) and at the BL04-MSPD beamline of the ALBA Synchrotron (Barcelona, Spain). Measurements were carried out using wavelengths of $\lambda = 0.67157 \text{ \AA}$ (18 keV) at SOLEIL and $\lambda = 0.7083 \text{ \AA}$ (17.5 keV) at ALBA, both selected using double-crystal Si (111) monochromators. The beamlines are equipped with position-sensitive MYTHEN detectors, particularly suited for time-resolved experiments.

Powder samples were loaded into 0.7 mm diameter borosilicate glass capillaries and continuously rotated during data acquisition to improve diffracting particle statistics. Data acquisition times were 3 min per pattern at SOLEIL and 5 min per pattern at ALBA, with two iterations per measurement to improve the signal-to-noise ratio. Instrument calibration and determination of the instrumental resolution function were performed using LaB6 (NIST-SRM660) and $\text{Na}_2\text{Al}_2\text{Ca}_3\text{F}_{14}$ (NAC) standards at SOLEIL and ALBA, respectively. Under these acquisition conditions, the angular resolution ranged from 0.02° to 0.04° full width at half maximum (FWHM) at SOLEIL and reached 0.01° to 0.04° FWHM at ALBA. As opposed to conventional XRD, synchrotron powder HRXRD analysis is accurate enough to detect peak shifts and broadening induced by small lattice strains ($<10^{-4}$) associated with the presence of intracrystalline organics, which upon thermal decomposition result in lattice strain relaxation (Rodríguez-Navarro et al., 2024). Isochronous annealing ($10^\circ \text{C min}^{-1}$; 30s stabilization time at target T , tolerance $\pm 5^\circ \text{C}$) was performed using a Cyberstar hot gas blower with a Eurotherm T controller (Eurotherm, Worthing, UK), collecting diffraction data each 50 $^\circ \text{C}$ during the heating ramps (50° to 400°C). Once the maximum T was reached, the samples were cooled to room T , and a final measurement was taken. X-ray diffraction data were processed and analyzed using HighScore (PANalytical) for phase identification, TOPAS 5 (Bruker) for unit cell refinement, and OriginPro 2019b for data visualization and plotting.

Transmission electron microscopy (TEM) data were acquired using a TALOS F200X and a TALOS S200 (Thermo Fisher) operated at an acceleration voltage of 200 kV from Centro de Instrumentación Científica of the University of Granada, and Centro de Investigación, Tecnología e Innovación of the University of Sevilla, respectively. Prior to analysis, the powder samples were dispersed in ethanol, sonicated for 60 s, and deposited on carbon-coated copper grids or Formvar-coated grids. TEM observations were performed using a 40 μm objective aperture. Selected area electron diffraction (SAED) patterns were collected using a 10 μm aperture, which allowed diffraction data to be collected from a circular area with a diameter of 0.5 μm . Z-contrast imaging was performed using a high angle annular dark field detector (HAADF) and energy dispersive X-ray spectroscopy (EDS) microanalysis was performed in scanning-TEM (STEM) mode. Thermogravimetric (TG) analyses were performed on a METTLER TOLEDO STARe TGA/DSC 3 + equipment from Unidad de Excelencia “Carbonatos” of the University of Granada (Spain), using

the following settings: flowing air atmosphere (100 cm³/min), heating from 25 to 950 °C at a rate of 20 °C/min. The shape, size, morphology, composition, and microstructure of the reactant and product phases were analyzed using scanning electron microscopy (SEM) coupled with EDS for microanalysis. Samples (in powder form) were placed onto carbon-coated sticky stubs and carbon-coated. Observation was performed on a high-resolution AURIGA SEM from Carl Zeiss SMT, and an ultra-high-resolution JMS-IT800 SHL SEM from JEOL Ltd. both from the Centro de Instrumentación Científica of the University of Granada (Spain).

Solid-state nuclear magnetic resonance (NMR) analyses were performed using a Bruker spectrometer equipped with a magic angle spinning (MAS) probe from Centro de Instrumentación Científica Técnica at the University of Jaén (Spain). The NMR measurements were acquired on a 11.75 T magnet with a ¹H frequency of 299.673 MHz and a ¹³C frequency of 500.130 MHz with a commercial MAS 4 mm BB/¹H probe. The powdered samples were packed into zirconia rotors of 50 µL capacity. ¹³C{¹H} static NMR spectra were acquired with 14 k scans and a recycle delay of 5 s was used between successive scans by a Waltz-16 sequence with decoupling during acquisition, using a $\pi/2$ pulse length of 5.2 µs. ¹³C{¹H} CPMAS (cross-polarization magic angle spinning) spectra were acquired with a spinning speed of 5 kHz at the magic angle (54.7°), with 13 k scans and 5 s between scans by a TPPM-15 sequence with decoupling during acquisition. Cross-polarization dynamics were acquired using a contact time (tcp) of 100 µs with a 1H amplitude ramp during the spin-lock period, following initial excitation with a ¹H $\pi/2$ pulse of 5 µs. Chemical shifts were referenced to adamantane at 29.45 ppm. The isotropic chemical shifts for the spectra were assigned via peak fitting. For the ¹H NMR experiments, the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence was employed. Zirconia rotors of 12 µL were used. MAS spinning speed of 13 kHz was applied under a field strength of 4.743 T. A total of 256 scans were accumulated, with a 3 s recycle delay between each scan. The echo time was 1 ms. Gaussian peak deconvolution of the ¹H and ¹³C NMR spectra was performed using OriginPro. The spectra were fitted directly without explicit baseline correction, as the spectral background was stable in the region of interest. Overlapping resonances were modeled as a sum of Gaussian functions using nonlinear least-squares optimization. Fit quality was assessed by residual analysis.

5. Results

5.1. Characterization of moonmilk deposits

Synchrotron HRXRD analyses revealed that, consistent with previous works (Casas et al., 2001; Borsato et al., 2000), the studied moonmilk deposits from Nerja cave are predominantly composed of huntite and dolomite (showing superstructure Bragg reflections), with minor amounts of calcite and magnesite (Supplementary Table S1; Fig. 1a–b). The HRXRD pattern of the dolomitic marble host rock showed that it is composed predominantly of dolomite (95.7%) and calcite (4.3%), consistent with the SAED and fast Fourier transform (FFT) of TEM and EDS microanalysis (see Supplementary Fig. S2). HRXRD analysis showed that dolomites in the moonmilk samples have a marked peak broadening as compared with the highly crystalline dolomite standard from Eugui (Navarra, Spain) (Fig. 1b). By applying the Turpin et al. (2012) method to the HRXRD data, the composition of dolomite was found to be 50.5 mol% Ca²⁺/49.6 mol% Mg²⁺, 51.5 mol% Ca²⁺/48.5 mol% Mg²⁺ and 52.9 mol% Ca²⁺/47.1 mol% Mg²⁺ for the Eugui dolomite and the dolomite present in the dolomitic marbles of the outcropping area of Mijas (Málaga, Spain) and the host rock, respectively (Table 1). The stoichiometry of Eugui dolomite is in excellent agreement with reported values (Turpin et al., 2012). Dolomites in *Immensidad* and *Cataclismo* moonmilk samples are nearly stoichiometric (54.2 and 55.1 mol % Ca²⁺ and 45.9 and 45.0 mol% Mg²⁺), consistent with the Mg²⁺:Ca²⁺ ratio determined by TEM-EDS microanalysis and the observed

elemental profile composition (Fig. 1c–n).

The Mg²⁺-Ca²⁺ ordering of the dolomites was determined using the intensity ratio of the 015 and 110 Bragg peaks (I₀₁₅/I₁₁₀) (McKenzie, 1981; Pina et al., 2020; Zvir et al., 2021; Kaczmarek and Sibley, 2011). This ratio was 0.19 ± 0.04 for *Cataclismo* sample. In contrast, the *Immensidad* value was 0.41 ± 0.10, the host rock was 0.59 ± 0.13, the reference Eugui dolomite was 0.55 ± 0.03, and the Mijas dolomite (near Nerja) was 0.59 ± 0.02. Values between 0 and 0.39 are typical of disordered dolomites (i.e., protodolomite), while values above 0.4 (up to 0.88) are found in ordered dolomites (Kaczmarek and Sibley, 2011; Pina et al., 2020; Pina et al., 2022; Zvir et al., 2021). Dolomite crystallite size (*D*, nm) was determined using the Scherrer equation (for the 104 Bragg peak). Results showed values above 120 nm for the Eugui, Mijas and host rock dolomites, whereas values of 85 nm and 71 nm were observed in *Immensidad* and *Cataclismo* (proto)dolomite, respectively (Table 1), consistent with the ordering degree of the Mg²⁺-Ca²⁺ carbonate phases.

TEM-EDS analysis (Fig. 1c–n) revealed Mg²⁺-Ca²⁺ ratios ranging from 1:0, 1:1, and 3:1 corresponding to magnesite, dolomite and huntite, respectively (Fig. 1f, n). The presence of these phases was confirmed by SAED and FFT of high-resolution TEM (HRTEM) images (Fig. 1d, h, l). The edges of dolomite crystals showed high Si concentrations as seen in compositional line profiles (Fig. 1j). TEM and HAADF-EDS analyses of huntite and dolomite are shown on Fig. 2. Huntite typically exhibited euhedral crystals with corroded edges (Fig. 2a, c) and thin amorphous rims, clearly visible in HRTEM images (Fig. 2d), which contrast to dolomite (Fig. 1c, g and 2b) and magnesite (Fig. 1k) that showed a markedly different nanogranular texture. Both ACMC and AMC nanogranular precipitates were found closely associated with corroded huntite crystals (Fig. 2a), as well as dolomite and magnesite particles (Fig. 2b). Additionally, HRTEM images of *Cataclismo* and *Immensidad* samples and the FFT patterns of selected areas from the images showed the existence of amorphous areas (i.e. showing no lattice fringes) within the huntite (Fig. 2d), dolomite and magnesite lattices (Fig. 1h, l, respectively).

Mg²⁺-Si⁴⁺ rich fibers were detected closely associated with huntite and were ubiquitous in the moonmilk samples (Fig. 2a, and Fig. 3). These fibers were found to be amorphous to poorly crystalline, as revealed by their SAED patterns (insets in Fig. 3a, d). Although important Si concentrations were systematically detected in the amorphous Mg²⁺ and Mg²⁺-Ca²⁺ carbonates, the Mg²⁺:Si⁴⁺ ratio in the amorphous carbonates was higher than in the amorphous magnesium silicate fibers (Fig. 3c, f). The fibers were also found alongside ACMC and dolomite (Fig. 2e). XRD analyses of oriented-aggregates (Fig. 3g, h) confirmed the presence of sepiolite in the *Immensidad* sample (March 2025), whereas the *Cataclismo* sample (June 2025) contained an amorphous Mg²⁺-silicate phase, which is consistent with the FTIR spectra (Supplementary Fig. S3, S4).

SEM-EDS characterization of the moonmilk samples (Fig. 4a) and correlative TEM observations and SAED patterns (Fig. 4b–d) confirmed the presence of amorphous nanoparticles (see SAED pattern shown in Fig. 4b and 4d). According to their Mg²⁺:Ca²⁺ ratio (1:0 and 1:1), two different A(C)MC phases formed (Fig. 4c and 4e), both containing significant amounts of Si (between 6% and 64% of atomic fraction according to the semiquantitative analysis). SEM revealed that the moonmilk samples (Fig. 5a, b) are also composed of faceted, rhombohedral Mg²⁺-Ca²⁺ carbonate crystals with nanoglobular, rough surfaces formed by irregularly shaped aggregates of nanoparticles < 100 nm in size. This size matched that of the ACMC and AMC nanoparticles observed under the TEM. Additionally, it was confirmed the presence of Mg²⁺-Si⁴⁺ rich fibers (Fig. 5c), together with bacterial cells forming filamentous structures and exopolymeric substances (EPS) (Fig. 5d–f), associated with the Ca²⁺-Mg²⁺ carbonates.

The FTIR spectra of moonmilk samples (Supplementary Figs. S3–S5) were dominated by CO₃²⁻ vibrations with diagnostic ν_4 bands at 680–730 cm⁻¹ and ν_2 bands at 860–890 cm⁻¹, allowing the identification of Mg-rich carbonates, including magnesite (~879 cm⁻¹) (Lafuente et al.,

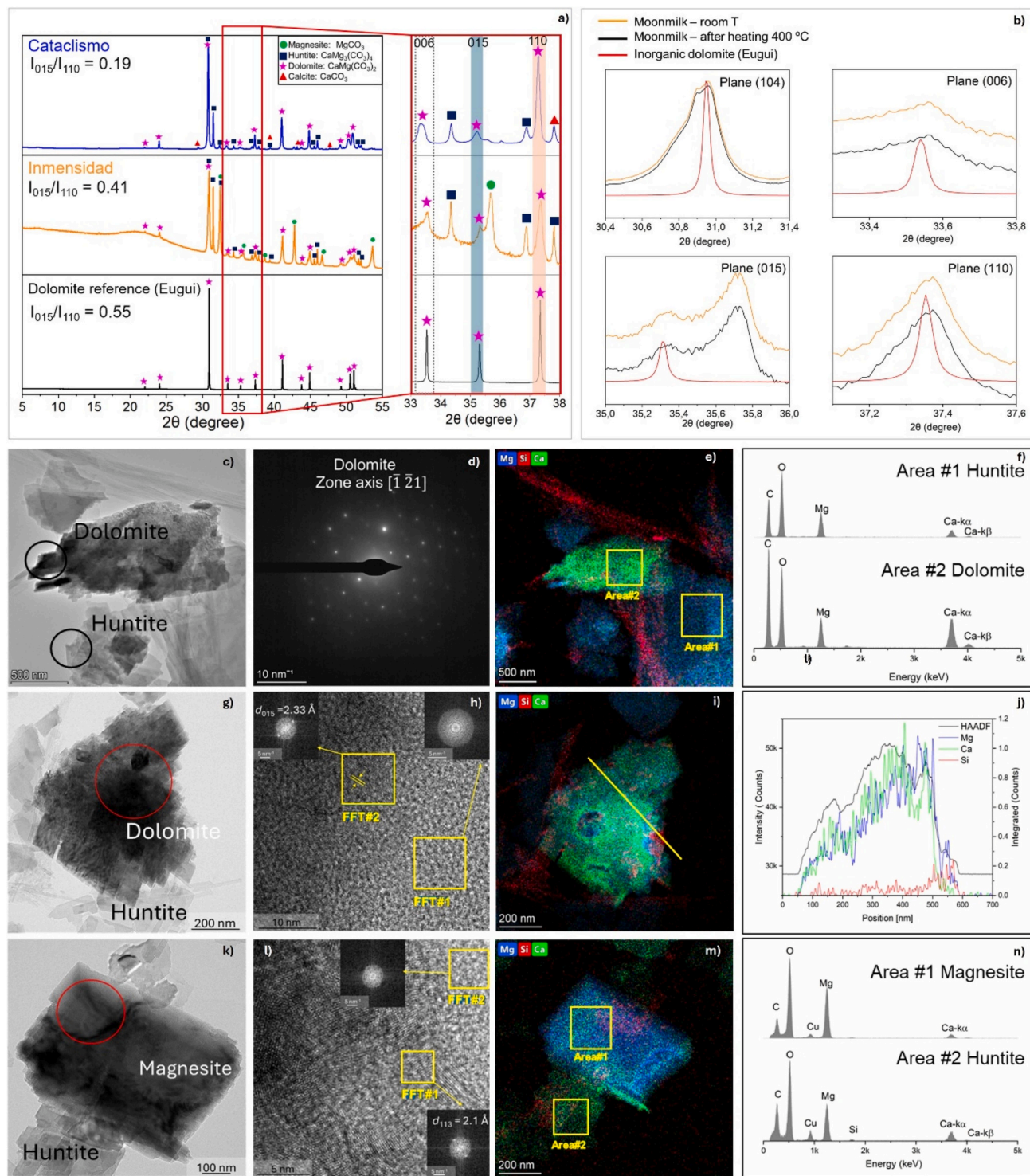


Fig. 1. Analysis of moonmilk samples. a) High-resolution synchrotron X-ray diffraction patterns showing distinct Bragg peaks corresponding to dolomite, with main reflections indexed. b) Comparison of the main Bragg peaks of dolomite, corresponding to the (104) plane at $\sim 31^\circ$, (006) at $\sim 33.5^\circ$, (015) at $\sim 35.3^\circ$, and (110) at $\sim 37.3^\circ$ 2θ (converted to $\lambda = 1.5406 \text{ \AA}$ of $\text{CuK}\alpha$), in the inorganic dolomite standard (Eugui) and Nerja's cave moonmilk samples. The continuous red trace corresponds to Eugui dolomite, the orange trace to *Inmensidad* sample at room temperature and the black trace after heating this sample at 400°C and cooling to room T. c) TEM images and d) corresponding selected area electron diffraction (SAED) patterns of (proto)dolomite (area marked by the black circle in (c)) in *Cataclismo* sample. e) EDS elemental map of the area depicted in (c), and f) spectra of the areas marked by yellow squares in (e) showing compositions corresponding to huntite and (proto)dolomite. g) TEM image and h) HRTEM and FFT patterns of dolomite (area marked by the red circle) present in the *Cataclismo* sample. Note that there are amorphous areas (showing no lattice fringes) within the dolomite lattice. i) EDS elemental map of the area depicted in (g); and j) elemental composition of the profile marked by the yellow line in (i), showing compositions corresponding to dolomite with (adsorbed) silica. k) TEM image and l) HRTEM image and FFT patterns of magnesite (area marked by the red circle) present in the *Cataclismo* sample. m) EDS elemental map of the area shown in (k), and n) EDS spectra of the areas marked in (m).

Table 1
Crystallite size (D, nm, for 104 Bragg peak), dolomite ordering (expressed as I_{015}/I_{110} intensity ratio and used to distinguish dolomite from protodolomite), and stoichiometry calculated using the Turpin et al. 2012 method based on a- and c-parameters obtained from unit cell refinement of dolomite and magnesite, for different Mg-Ca-carbonate samples.

Sample	Peak 104 D (nm)			Dolomite ordering I_{015}/I_{110}			Phase	Stoichiometry N CaCO_3 (mol%)	N MgCO_3 (mol%)	Phase
<i>Eugui</i>	171	±	31	0.55	±	0.03	Dolomite	50.5	49.6	Dolomite
<i>Mijas</i>	185	±	16	0.59	±	0.02	Dolomite	51.5	48.5	Dolomite
<i>Inmensidad</i>	85	±	46	0.41	±	0.10	Dolomite	55.1	45.0	Dolomite
								9.0	91.0	Magnesite
<i>Cataclismo</i>	71	±	20	0.19	±	0.04	Protodolomite	54.2	45.8	Protodolomite
								6.3	93.7	Magnesite
<i>Host Rock</i>	120	±	5	0.59	±	0.13	Dolomite	52.9	47.1	Dolomite

± shows standard deviation (1σ).

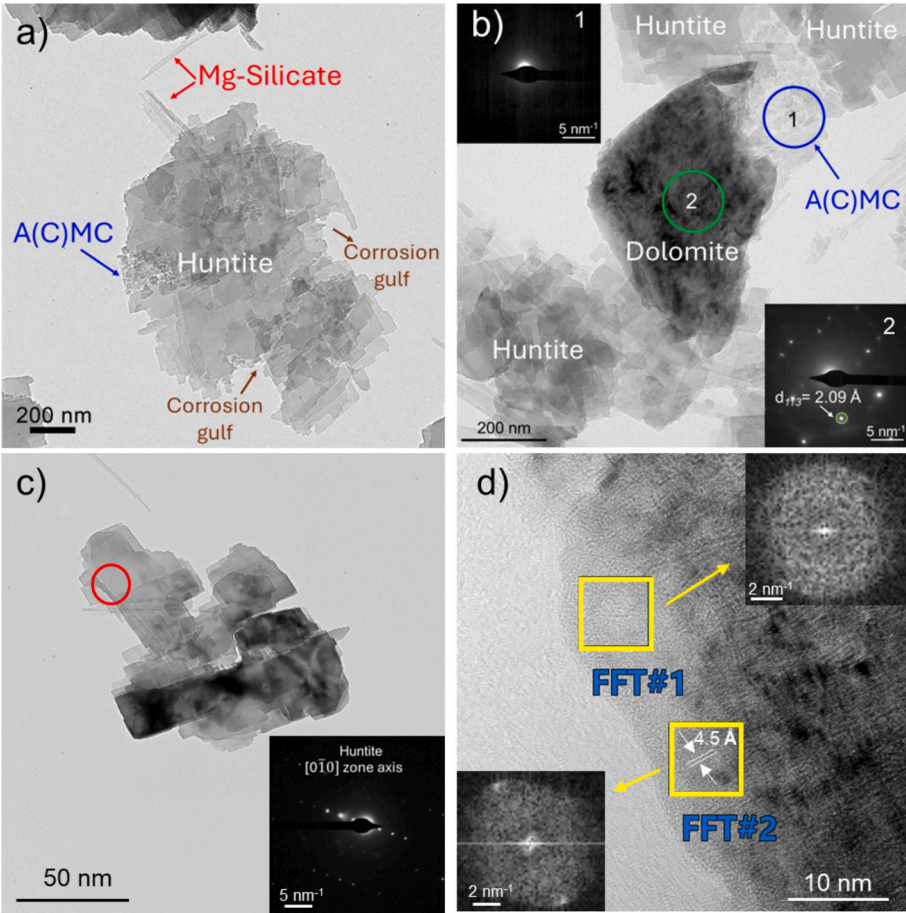


Fig. 2. TEM and HAADF-EDS analysis of huntite and dolomite. a) TEM image showing the lamellar-acicular morphology of the amorphous Mg-silicate aggregates, the nanogranular aggregates of A(C)MC and AMC, and the huntite crystals (some of them showing corrosion gulfs) in *Inmensidad* sample collected in May 2024. b) The TEM image shows the association between A(C)MC and dolomite, as well as the morphology of the dolomite, which is formed by aggregation of nanoparticles in *Cataclismo* sample from September 2023. In contrast, the huntite has euhedral crystals. c) Representative TEM image of *Inmensidad* sample collected in May 2024 showing huntite crystals (SAED pattern of the area marked by a red circle in the inset). d) HRTEM image of the circled area in (c) revealing lattice fringes corresponding to huntite, and fast Fourier transform (FFT) patterns (insets) of the areas marked by yellow squares, corresponding to amorphous calcium magnesium carbonate (A(C)MC, FFT1) and huntite (FFT2).

2015; RUFF ID: R050676.1), huntite (bands approximately at 866, 877, and 890 cm^{-1}), dolomite ($\sim 883 \text{ cm}^{-1}$), and amorphous Mg-(Ca) carbonates (858–863 cm^{-1}) (see also [Supplementary Fig. S6](#) for reference spectra). The ν_3 mode (C–O stretching) typical of Mg-carbonates appeared at $\sim 1500 \text{ cm}^{-1}$ and 1437 cm^{-1} . A broad band at 950–1100 cm^{-1} indicated the presence of O–Si–O bonds in the samples (i.e., amorphous silica and other silicate phases, see below). Broad O–H stretching bands at 3000–4000 cm^{-1} revealed the presence of water in *Cataclismo* samples from May 2024 and March 2025 ([Supplementary](#)

[Fig. S3](#)). FTIR spectra of *Cataclismo* moonmilk samples from September 2023 showed a broadening of the band at 860–890 cm^{-1} , consistent with the presence of amorphous phases including A(C)MC ($\sim 867 \text{ cm}^{-1}$), whereas *Cataclismo* samples from May 2024, March 2025, and June 2025 and *Inmensidad* from May 2024 and June 2025 displayed the characteristic huntite bands (at around 865–868, 877, 889 cm^{-1}). All samples exhibited a small IR-active ν_1 band of carbonate groups at $\sim 1080\text{--}1082 \text{ cm}^{-1}$ ([Supplementary Figs. S3,S4,S6](#)) further confirming the presence of A(C)MC phases in the moonmilk deposits.

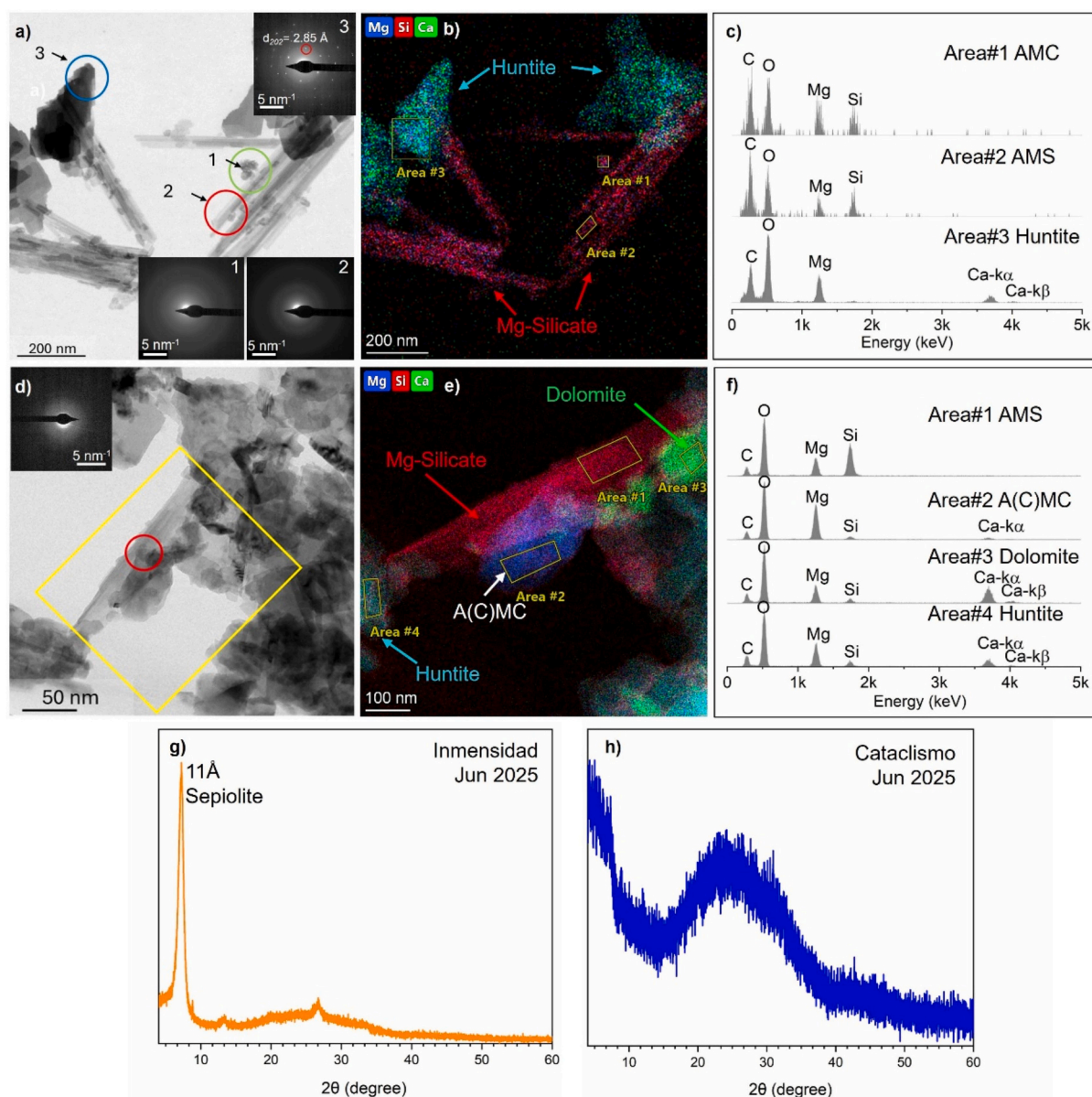


Fig. 3. Carbonate and silicate amorphous phases in moonmilk samples. (a, d) TEM images and SAED patterns (insets) of the areas marked by circles showing the fibrous- and foil-like morphology of the clays, as well as their amorphous character (AMS) in (a) *Cataclismo* and (d) *Inmensidad* samples collected in September 2023 and May 2024, respectively. b, e) EDS elemental maps, and (c, f) spectra of selected areas showing Si- and Mg-rich composition of the fibers. The EDS map in (e) corresponds to the area marked by a yellow square in (d). g, h) XRD patterns of oriented aggregates (OA) of (g) *Inmensidad* and (h) *Cataclismo* samples. The magnesium silicate in *Cataclismo* sample is amorphous, while the *Inmensidad* sample shows diffraction peaks corresponding to sepiolite.

Most moonmilk samples showed a small doublet at 2800–3000 cm⁻¹ (Supplementary Fig. S5) corresponding to the C–H stretching of organic compounds (e.g., carbohydrates), consistent with the observation of biofilms in the SEM.

TG and first derivative of the TG (DTG) curves of the samples and standards are shown in Fig. 6. The results revealed distinct thermal profiles of the carbonate standards (Fig. 6a, c) and the cave moonmilk samples (Fig. 6b, d), with variations in the position of the thermal events, reflecting differences in mineralogical composition and crystallinity (Supplementary Table S2). Most phases used as reference exhibited a characteristic multi-step decomposition. Dolomite showed two primary weight loss events at 800 °C and 850 °C, while huntite decomposed in two steps at 600 °C and 765 °C (Ozao and Otsuka, 1985). In both cases, the lower *T* event corresponds to structural breakdown and CO₂ release forming MgO and CaCO₃, while the higher *T* event marks CaCO₃ decomposition (Rodríguez-Navarro et al., 2012).

Magnesite decarbonated in a single step at 634 °C (Ozao and Otsuka, 1985) which partially overlaps with the first decomposition of huntite. Synthetic AMC decarbonated at significantly lower temperatures (390 °C), and structural water loss started at 94 °C. The decarbonation of synthetic ACMC with Mg²⁺:Ca²⁺ ratios of 75:25 and 50:50 was similar to that of pure AMC but had a second decarbonation step at 700 °C.

Regarding the natural samples (Fig. 6b, d), the decomposition of *Cataclismo* moonmilk collected in September 2023 showed two main thermal events, reaching maximum weight losses at 555 °C (i.e., presence of huntite) and 845 °C (i.e., presence of dolomite). In contrast, the *Cataclismo* samples collected in 2024 and 2025 showed significant differences. The broad band observed in the DTG plot (Fig. 6d) at approximately 445 °C is attributed to A(C)MC decarbonation, but it is shifted by about 55 °C toward higher temperatures compared to synthetic ACMC, likely due to stabilization of natural amorphous A(C)MC phases by organic matter and/or silica (see Discussion). A second

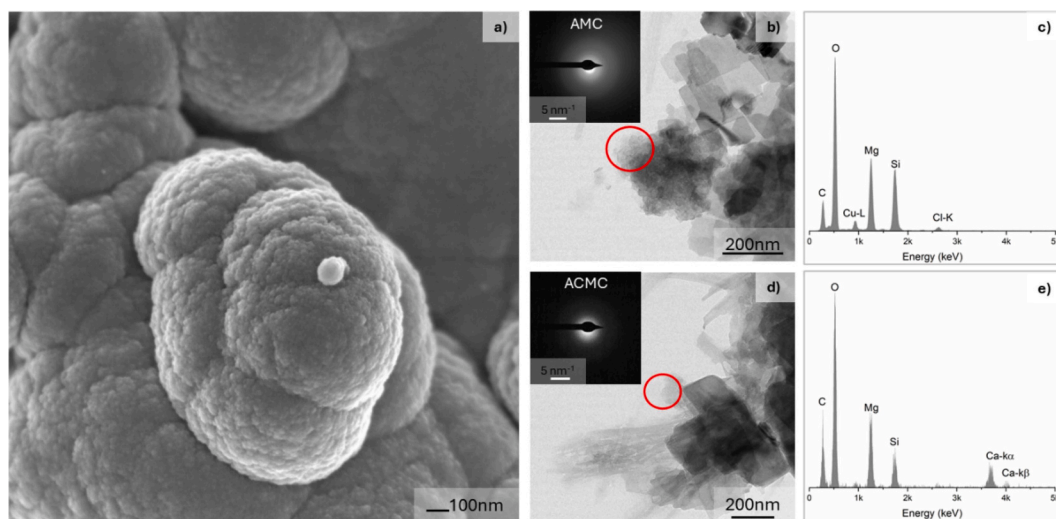


Fig. 4. Analysis of amorphous precursors. a) SEM image of amorphous magnesium carbonate (AMC) in *Cataclismo* sample. b) TEM image and SAED pattern –inset– of the area marked by a red circle in (b) and EDS spectrum (c) of AMC in *Cataclismo* sample collected in September 2023. d) TEM image and SAED pattern –inset– of the area marked by a red circle in (d) and EDS spectrum (e) of ACMC in *Inmensidad* sample collected in May 2024.

asymmetric broad band at 800 °C, observed in both *Inmensidad* and *Cataclismo* samples, corresponds to dolomite decomposition. In this case, the two-step decomposition typical of standard dolomite, merged into a single broad event, probably due to the poor crystallinity of the samples. In addition, all moonmilk samples displayed a small peak at approximately 85 °C, corresponding to A(C)MC dehydration. The *Inmensidad* sample collected in May 2024 showed three bands at 605, 755, and 800 °C, corresponding to the decarbonation of huntite and dolomite, with dolomite decomposing in a single step, as observed in the *Cataclismo* sample. In contrast, the sample from June 2025 only showed a single broad band at 800 °C. Overall, the *Inmensidad* samples showed narrower peaks than the *Cataclismo* samples, indicating a higher degree of crystallinity of their mineral phases, especially the May 2024 *Inmensidad* sample. Also, the dolomitic host rock displayed peaks shifted to higher temperatures compared to the moonmilk samples, consistent with its higher crystallinity and calcite content.

5.2. Structure of moonmilk Mg^{2+} -carbonates

The internal structure of the carbonate phases in the moonmilk samples was studied by solid-state NMR spectroscopy. The direct ^{13}C NMR spectra of the *Cataclismo* and *Inmensidad* samples are shown in Fig. 7 compared to those of abiotic huntite, dolomite, and synthetic AMC. All samples showed only carbonate peaks in the 160–169 ppm range. Synthetic AMC exhibited a single ^{13}C NMR resonance at 166.3 ppm (Fig. 7a), in agreement with published data (Chang et al., 2021) (166.2 ppm), and upfield or shielded with respect to that of amorphous calcium carbonate (Nebel et al., 2008) (168.0 ppm). Synthetic huntite displayed very narrow NMR peaks (pointing to a high crystallinity), with ^{13}C chemical shifts of 165.4 (width 1 ppm) and 164.2 ppm (width 1 ppm) (Fig. 7b). This is due to the existence of two crystallographically inequivalent carbons in the structure of huntite (Graf and Bradley, 1962). Eugui dolomite showed a single, broad, ^{13}C NMR resonance at 166.9 ppm (width 9 ppm) (Fig. 7c). This agrees well with published values (Papenguth et al., 1989) (ancient “saddle” dolomite: chemical shift 167.7 ppm, width 5 ppm; modern disordered dolomite: chemical shift 168 ppm, width 2.1 ppm). For magnesite, one single ^{13}C resonance has been reported (Papenguth et al., 1989) (chemical shift 170 ppm), and a chemical shift of 160 ppm has been suggested for bicarbonate ions (Huang et al., 2021).

In the $^{13}C\{^1H\}$ CPMAS spectra, only ^{13}C atoms in proximity to proton-containing moieties are detectable. Consequently, no signal was

observed for Eugui dolomite (Fig. 7c). However, huntite contained traces of water, which appeared in the CPMAS spectrum as weak peaks barely distinguishable from the background. The asymmetric line shape of the peak in the 163–169 ppm region of the moonmilk sample from *Cataclismo* collected in September 2024 indicated that there are several spectral components. The spectrum was deconvoluted into four components positioned at 167.4, 166.1, 165.2 and 164.2 ppm (Fig. 7d), which agree well with the ^{13}C chemical shifts of dolomite (166.9 ppm), A(C)MC (166.3 ppm), huntite (165.4 and 164.2 ppm), and magnesite (170 ppm) phases which were identified by HRXRD, TEM, as well as FTIR (see Supplementary Table S1). The ^{13}C resonance of A(C)MC was shifted downfield by approximately 3 ppm in the ^{13}C CPMAS spectra, although no additional peaks were detected. This spectral feature confirms that ACMC and AMC include structural water.

The $^{13}C\{^1H\}$ CPMAS spectrum of the *Cataclismo* sample collected in May 2024 exhibited an asymmetric peak, which could be deconvoluted into four components located at 168.4, 166.1, 164.7, and 163.4 ppm (Fig. 7e), corresponding to the chemical shifts of dolomite, A(C)MC, and huntite. In this spectrum, the main peak was broader, possibly reflecting an increased contribution of A(C)MC to the ^{13}C signal than in the direct polarization spectrum. This is consistent with the hydrated nature of A(C)MC, which contains more protons in proximity to its carbon atoms than other carbonate phases present in the sample, which are essentially anhydrous. The fact that a dolomite component was detected in the main resonance of the moonmilk $^{13}C\{^1H\}$ CPMAS spectrum is likely related to the presence of hydrogen atoms from organic compounds near carbon atoms. It could be argued, however, that this observation is related to the possible presence of protodolomite, which can be hydrated (Zheng et al., 2021). The latter is consistent with the relatively low I_{015}/I_{110} ratio (0.19) of this sample. Additionally, a relatively minor peak at around 160.5 ppm was observed and attributed to HCO_3^- . The bicarbonate ions are likely included in the A(C)MC phase (Huang et al., 2021; Yang et al., 2016). This finding is not unexpected, as bicarbonate ions are a major species in the solution of the low-pH drip water from which moonmilk precipitates. For the *Inmensidad* sample, the $^{13}C\{^1H\}$ CPMAS spectrum (Fig. 7f) showed four partially overlapping components at chemical shifts of 168.9, 167.2, 166.1, 163.2, and 160.5 ppm. These corresponded, respectively, to dolomite/magnesite, dolomite, A(C)MC, huntite, and bicarbonate species. The overall signal was narrower and more symmetric than that of the *Cataclismo* samples, suggesting a lower amount of hydrated A(C)MC and a greater contribution of more crystalline carbonate phases.

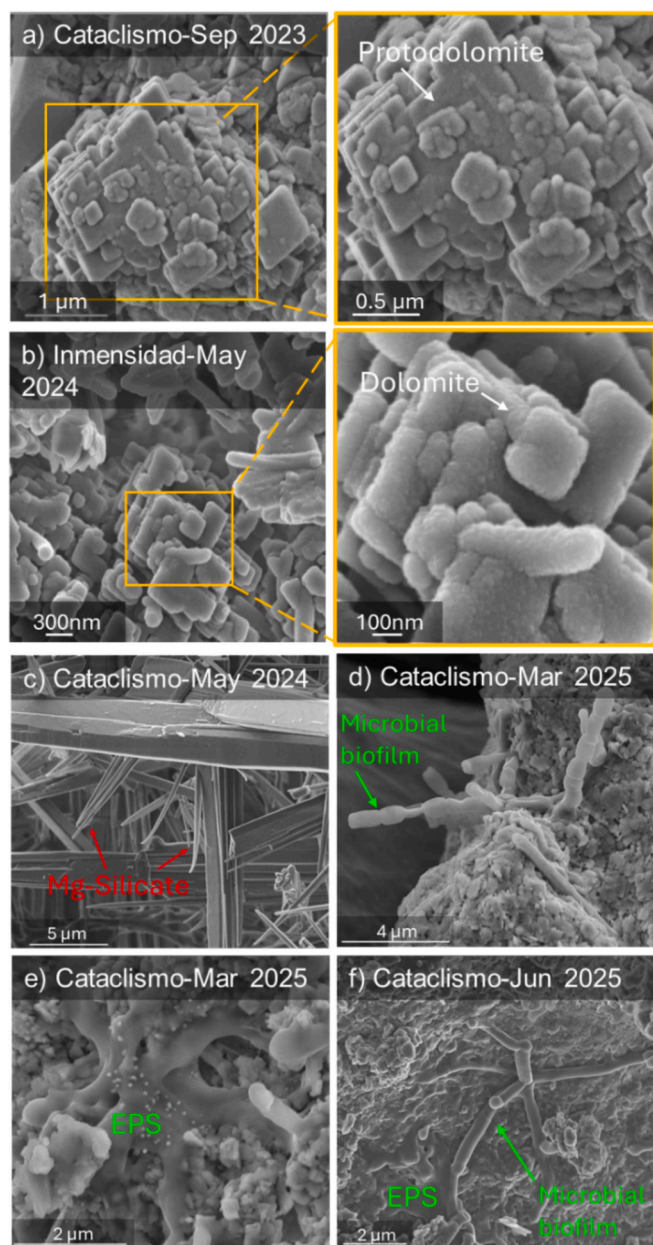


Fig. 5. SEM images of moonmilk samples. SEM images showing the texture of (proto)dolomite in the *Cataclismo* sample (a) and dolomite in the *Inmensidad* sample (b). The orange boxes of panels (a) and (b) correspond to the magnified areas shown on the right, where the nanogranular features of the (proto) dolomite are observed. c) Fiber-like Mg-silicates in *Cataclismo* sample collected in May 2024. d) *Cataclismo* sample (March 2025) showing the presence of microbial biofilm. Note the fibrous-like characteristics of the structures, suggesting the presence of strings of bacteria cells in the sample. e-f) Detail of EPS and microbial biofilm.

The directly detected ^1H NMR spectrum (Fig. 7g) of synthetic AMC and moonmilk samples showed resonances only in the 0–6 ppm range. Superimposed on a broad central peak (ranging from 0.5 to 3.5 ppm), several sharp resonances appeared, most likely arising from hydroxide species involved in fast exchange dynamics with mobile water. The variability in chemical shifts could reflect distinct coordination environments of hydroxyl groups within the mineral structure, which give rise to localized differences in basicity (Huang et al., 2021; Yang et al., 2016; Gindele et al., 2024). Additionally, the moonmilk spectrum exhibits a dominant sharp peak at ~ 5 ppm corresponding to water molecules, which appears as a very weak doublet in the A(C)MC sample.

The ^1H spectra indicates that hydrogen in moonmilk samples occurs mainly with H bond strengths typical of H_2O and OH^- in hydrated carbonate minerals, while in the case of synthetic AMC, it occurs mainly in the form of $-\text{OH}$. Interestingly, the moonmilk spectrum showed two additional low-intensity, broad signals in the 3.2–3.8 ppm region, not observed in synthetic AMC, which can be attributed to methylene protons in $\text{O}-\text{CH}_2$ and $\text{N}-\text{CH}_2$ groups (Farmer et al., 2024), an indication of the presence of organic compounds (e.g., oligo and polysaccharides (Furevi et al., 2022), in the moonmilk samples. This is further evidence of the incorporation of biopolymers such as polysaccharides, proteins, or other organic materials commonly found in microbial extracellular substances and biofilms.

5.3. Organic-mineral interactions

To investigate the possible mechanisms of organics incorporation from microbial origin whose presence was inferred by NMR, FTIR and SEM analysis of the moonmilk samples, we performed HRXRD analyses involving isochronous heating (annealing) (Fig. 1b). (Proto)dolomite in the moonmilk sample from the *Cataclismo* chamber did not show any shift in the 104, 006, 015, and 110 Bragg peak positions as compared with inorganic dolomite (from Eugui), before, during, or after heating up to 400°C , and then cooling down to room T . No additional broadening was observed after the heating/cooling run. This suggests that the organics are not incorporated into lattice planes (i.e., as intracrystalline solutes). However, the observed broadening and associated low crystallite size are compatible with the incorporation of organics between nanodomains in the moonmilk dolomite, thereby not causing any anisotropic lattice strain (Kim et al., 2016) yet being consistent with the NMR results.

5.4. Cave drip water

To determine the solution conditions under which the precipitation of the Mg^{2+} -rich carbonates occur in the Nerja cave moonmilk, we performed PHREEQC speciation-solubility calculations based on drip water compositional data collected from April 1991 to August 2001 (Fig. 8). These calculations indicated that drip waters are constantly supersaturated with respect to dolomite, calcite, aragonite, and magnesite crystalline phases and undersaturated with respect to the amorphous phases (ACMC, AMC, and amorphous sepiolite-like phyllosilicates). In contrast, drip waters exhibit alternating periods of supersaturation and undersaturation with respect to huntite and sepiolite during the sampling period.

6. Discussion

6.1. Pathways for dolomite and magnesite formation in moonmilk

Understanding the pathways leading to dolomite and magnesite formation in moonmilk and other speleothems is essential to interpret the formation of cave carbonates. Previous studies have proposed that carbonate precipitation sequences in caves are primarily controlled by the progressive removal of Ca^{2+} from solution through calcite and aragonite precipitation, which increases the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio, consequently promoting the formation of more Mg^{2+} -rich minerals, such as huntite, dolomite, and magnesite (Deelman, 1999; Ford and Williams, 2007). While the formation of anhydrous Mg^{2+} -carbonates is generally considered to be kinetically hindered due to the difficulty of Mg^{2+} dehydration, the relatively open crystal lattice of huntite may allow partial Mg^{2+} dehydration at lower energy levels, promoting its formation under cave conditions over dolomite or magnesite (Lippmann, 1973). Indeed, huntite is ubiquitous in the Nerja moonmilk samples analyzed in this study (Figs. 1–3). We propose that huntite precipitation is the first step in the formation of dolomite and magnesite in cave moonmilk and that it can form directly from drip water via a classical

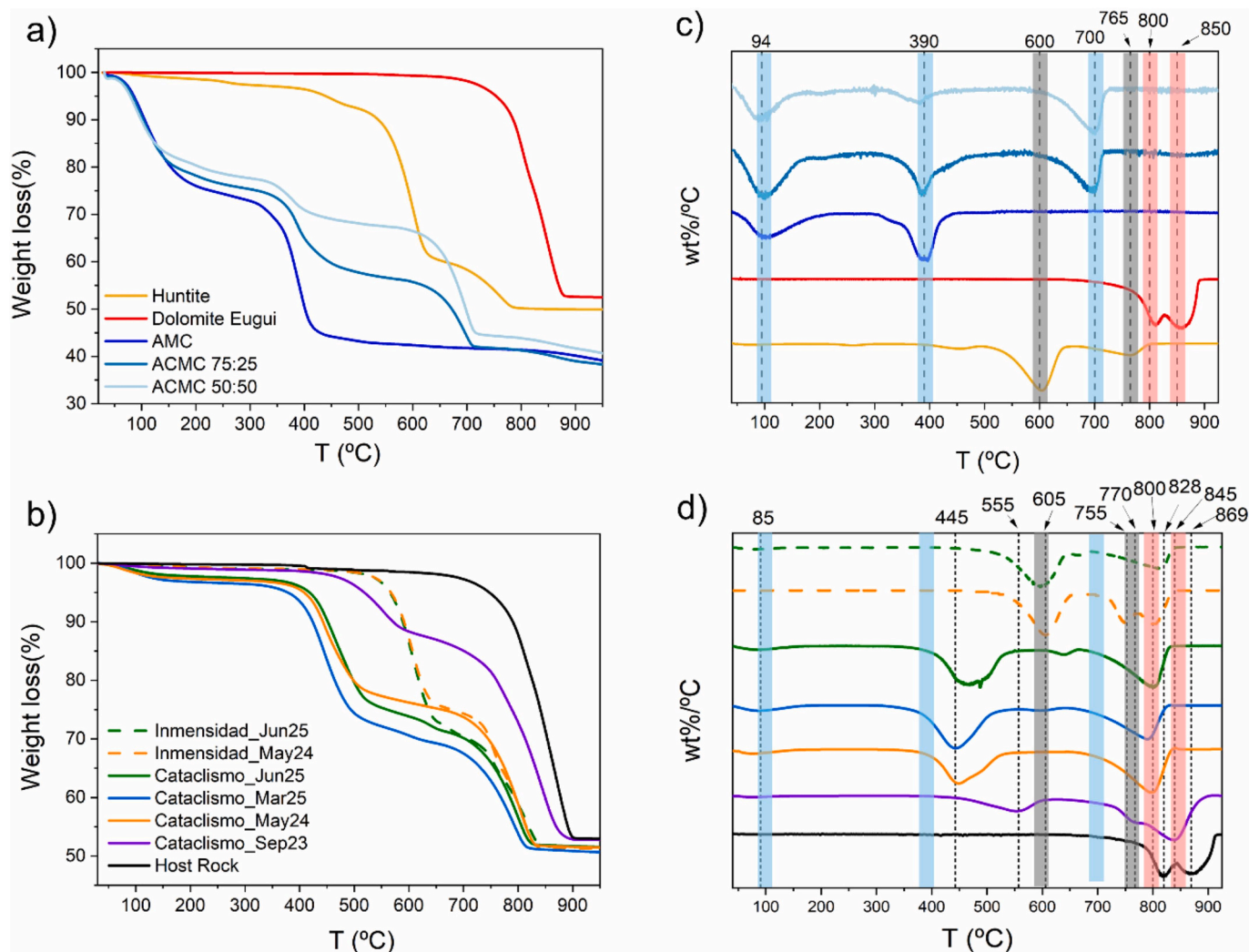


Fig. 6. TG and first derivative TG (DTG) curves of inorganic references and moonmilk samples: a) TG and c) DTG traces of inorganic references: AMC, ACMC with different Mg: Ca ratios, huntite, dolomite (Eugui). b) TG and d) DTG traces of moonmilk samples collected at different times of the year (September 2023, May 2024, March and June 2025), and host rock from Nerja. Blue shaded areas highlight AMC decomposition steps, with dehydration occurring at 94 °C and decarbonation at 390 °C. Grey shaded areas correspond to huntite decomposition, with a first step at 600 °C ($\text{Mg}_3\text{Ca}(\text{CO}_3)_4 \rightarrow \text{CaCO}_3 + 3\text{MgO} + 3\text{CO}_2$) and a second step at 785 °C ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$). Red shaded areas mark the two-steps decomposition of dolomite, taking place between 800 and 850 °C ($\text{MgCa}(\text{CO}_3)_2 \rightarrow \text{CaCO}_3 + \text{MgO} + \text{CO}_2$ and $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$).

precipitation pathway under conditions of seasonal supersaturation with respect to this phase, as suggested by the presence of euhedral huntite crystals with well-defined faces observed by TEM (Fig. 2). Sepiolite-like, poorly crystalline fibers, observed here in close association with huntite (Figs. 2 and 3), may facilitate the initial formation of huntite by providing nucleation sites for the heterogeneous nucleation of this phase. Previous works have identified huntite (Lippmann, 1973) and hydrated calcium and magnesium carbonates (Kelleher and Redfern, 2002; Santos et al., 2023) as potential precursors to abiogenic dolomite. For example, Alonso-Zarza and Martín-Pérez (2008) and Martín-Pérez et al. (2021) proposed that huntite may act as a dolomite precursor in oxidizing, non-sulphatic environments such as caves. This mechanism is supported by the occurrence of huntite relicts preserved within dolomite, as well as by textural evidence showing dolomite directly replacing and corroding huntite and by a compositional zoning, where dolomite closest to the huntite/aragonite substrate is Ca-rich while outer bands approach stoichiometric dolomite, reflecting progressive transformation over time. However, no huntite relicts within dolomite were identified in our samples, nor did we observe the compositional zoning described by these authors as evidence of progressive huntite to dolomite transformation. Instead, our observations,

such as corroded edges and amorphous rims in huntite crystals and the presence of localized amorphous domains in dolomite, suggest that dolomite does not form through the direct transformation of huntite; instead, the process occurs through an intermediate step which includes the formation of A(C)MC. This is a key finding of this study, since, to the best of our knowledge A(C)MC phases as dolomite or magnesite precursors have not been documented in nature. Here we provide ample evidence of amorphous nanoparticles appearing frequently in contact with corroded huntite and newly-formed dolomite crystals (Figs. 2, 3). Seasonal hydrological variations drive recurrent changes in hydrochemistry and, consequently, induce fluctuations in the supersaturation of solutions with respect to different mineral phases within Nerja cave, as evidenced by our PHREEQC speciation-solubility calculations (Fig. 8). Solutions display alternating periods of supersaturation and undersaturation with respect to huntite, experiencing cyclic crystallization-dissolution processes as confirmed by our TEM observations showing eroded edges of the huntite crystals (Fig. 2). Huntite dissolution results in a local enrichment of the solution in carbonate and magnesium, promoting supersaturation and precipitation of A(C)MC, which explains the occurrence of these amorphous phases in close contact with huntite (Fig. 2a, b), even though the bulk solution is

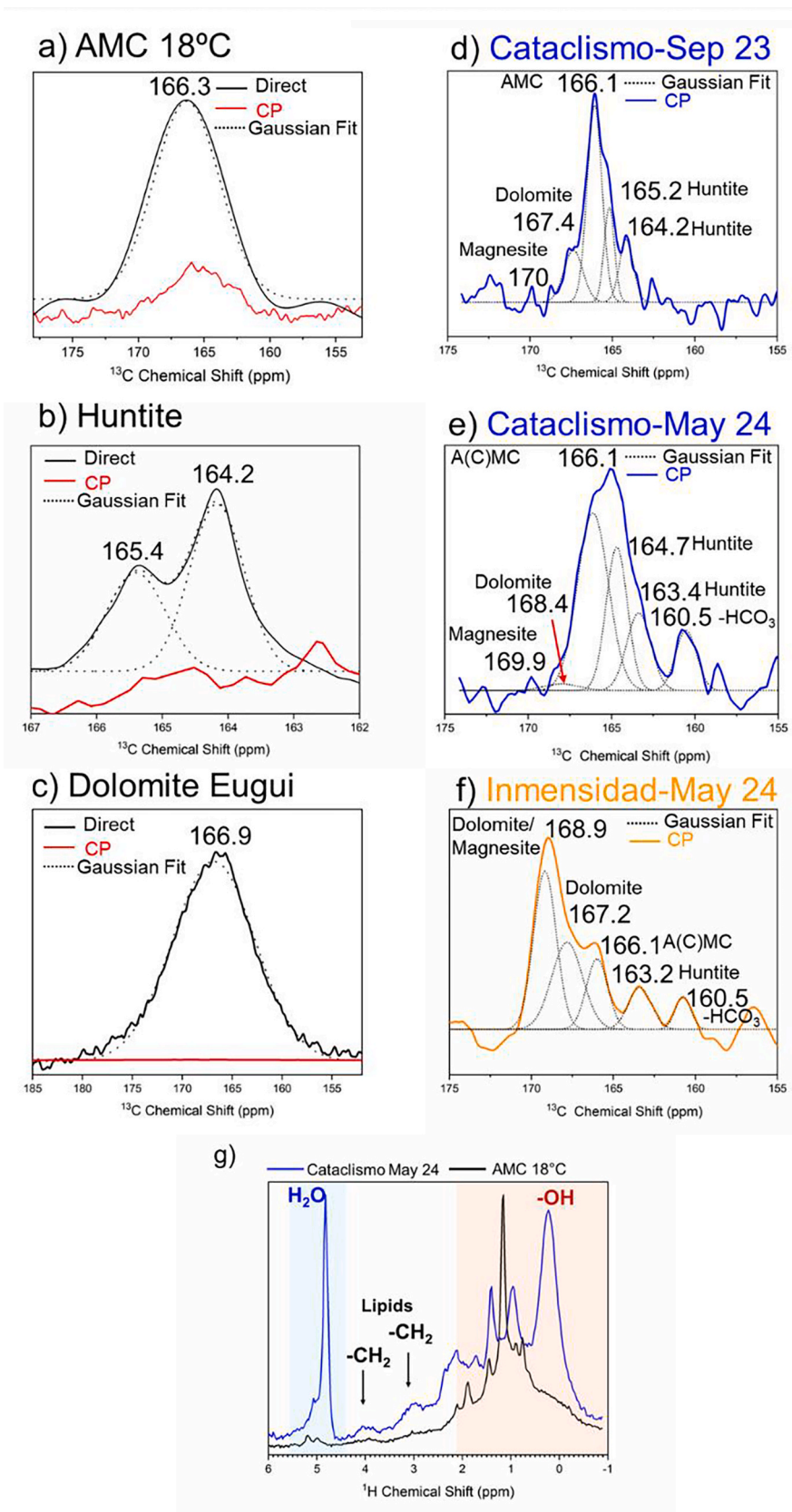


Fig. 7. ^{13}C and ^1H NMR spectra of moonmilk samples and standards. a-c) Raw direct (black curve) ^{13}C , cross-polarization $^{13}\text{C}\{^1\text{H}\}$ (red curve) MAS spectra and gaussian fits of AMC, huntite, and Eugui dolomite standards; d-f) Raw and gaussian fitted cross-polarization $^{13}\text{C}\{^1\text{H}\}$ MAS spectra of Nerja cave moonmilk samples; g) ^1H NMR spectra of *Cataclismo* sample. Water is present as molecular water and $-\text{OH}$ (as in AMC).

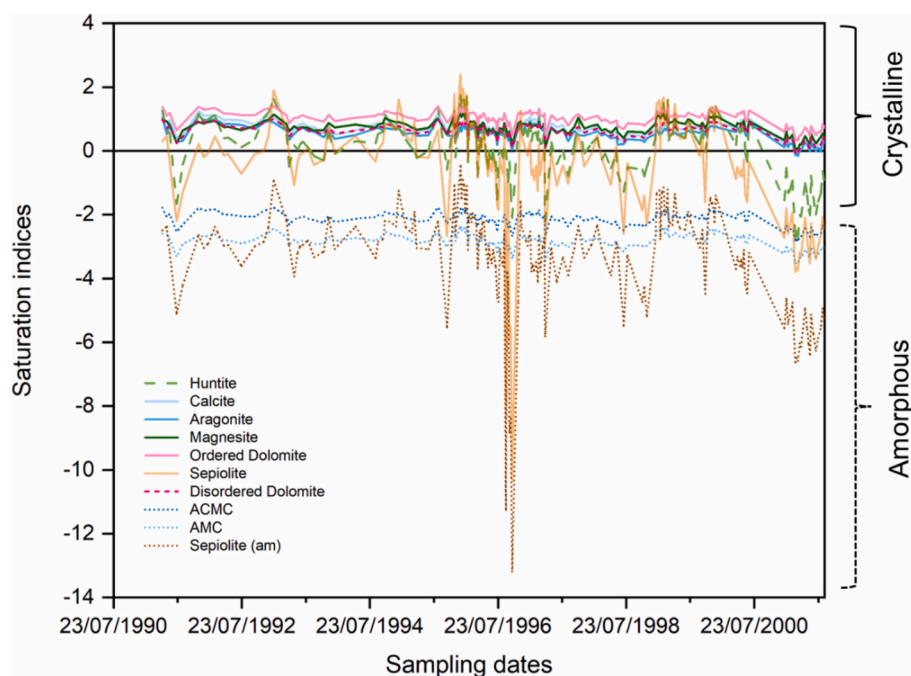


Fig. 8. Time evolution of saturation indices with respect to relevant crystalline and amorphous phases in the cave system. Note: sepiolite (am) corresponds to amorphous sepiolite.

undersaturated with respect to any amorphous carbonate phase (Fig. 8). The $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio during huntite dissolution likely governs the composition of the resulting A(C)MC and AMC phases detected, and finally the crystalline phase formed (dolomite or magnesite, respectively).

It could be argued that host rock-derived nano/micrometer sized dolomite particles could be transported and deposited in the speleothems as detrital grains (Frisia et al. 2000), acting as seeds for the formation of the moderately ordered dolomite in *Inmensidad* samples (Bragg-Williams cation order parameter (S) $\approx 0.41 \pm 0.10$). However, in this setting, the host rock only contains dolomite and calcite, so this mechanism could not explain how magnesite forms in our system. Moreover, the dolomite in the host rock shows a significantly higher Mg-Ca ordering (0.59 ± 0.03) than that determined for any of the moonmilk samples analyzed here, thus suggesting that the dolomite in the host rock is not the seed for that found in the moonmilk. This hypothesis is not consistent either with the fact that we observed an A(C)MC precursor for (proto)dolomite. If colloidal nanosized (ordered) dolomite strained from the host rock would be responsible for the formation of the more ordered cave dolomite observed here, the formation of an amorphous precursor should be bypassed as it would be more energetically favorable the re-growth of the ordered nanodolomite coming from the host rock than the precipitation of A(C)MC and its subsequent transformation into protodolomite and moderately ordered dolomite.

6.2. Prevalence of A(C)MC in cave environments and transformation into dolomite and magnesite

Regarding A(C)MC and its transformation into dolomite and magnesite, earlier studies have shown that, under laboratory conditions, Mg^{2+} -ACC transforms into dolomite through: (i) recrystallization of protodolomite formed during the dehydration of the amorphous phase at temperatures between 60 and 220 °C (Rodríguez-Blanco et al., 2015), or (ii) via solid-state transformation at 450 °C in the presence of organic polymers, such as polydimethylsiloxane and poly(acrylic acid) (Zhang et al., 2022). Magnesite formation appears to follow comparable pathways. It has been observed to initiate through amorphous calcium-magnesium carbonate (AMC) at approximately 50 °C, which

subsequently transforms into hydromagnesite and ultimately into magnesite (Chen et al., 2024). Other experiments indicate that magnesite may form via the dehydration and transformation of intermediate hydrated magnesium carbonates, such as hydromagnesite and nesquehonite (Qafoku et al., 2015). The absence of these intermediate, hydrated crystalline phases in the natural cave samples studied here further supports the key role of amorphous precursors in magnesite formation at low- T .

However, experimental results from our group (Bonilla-Correa et al., 2025) demonstrate that synthetic AMC becomes unstable below pH 10.5, rapidly recrystallizing into hydrated MgCO_3 phases such as nesquehonite. Thus, A(C)MC phases should not be preserved in moonmilk deposits, given that drip waters have near-neutral pH, unless these phases are effectively stabilized. Organic molecules, including small anions and bacterial EPS, as well as the presence of dissolved silica, may be responsible for the stabilization of amorphous carbonate phases in our moonmilk samples (Santoro De Vico et al., 2024; Zhang et al., 2024; Kellermeier et al., 2010). Note that microbial films and EPS were found associated with A(C)MC phases (Fig. 5e,f), and that these amorphous phases systematically show high Si contents (i.e., 6–64 at %), much higher than the crystalline phases (i.e., 0.8–13.3 at %) (see for example the microanalysis of dolomite in Fig. 1j and that of A(C)MC phases in Figs. 3 and 4).

Drip waters and carbonate precipitates in Nerja cave host diverse microbial communities, including *Proteobacteria*, as the dominant phylum, together with *Actinobacteria*, and cyanobacteria assemblages, which are potential sources of organic compounds such as EPS (Jurado et al., 2022). Although the precise role of microorganisms in carbonate mineralization remains incompletely understood, they are known by their ability to induce the formation and stabilization of mineral phases, including carbonates and silicates (Enyedi et al., 2020; Popović et al., 2019). Also, experimental evidence shows that when abiotically precipitated A(C)MC is stabilized by bacterial organics, Mg^{2+} release to the solution is retarded, enabling protodolomite formation (Liu et al., 2024). In contrast, rapid dissolution of unstable A(C)MC in the absence of organics promotes Mg^{2+} -calcite and aragonite precipitation.

Additionally, dissolved silica has been shown to play a key role in dolomite formation by facilitating Mg^{2+} dehydration through its low

dipole moment (Fang and Xu, 2022), although the exact mechanism remains unclear. The frequent natural co-occurrence of dolomite and Mg^{2+} -rich clay minerals including palygorskite, sepiolite, and smectites, as well as kerolite (Cuadros, 2017; Yenyol, 2014) supports silica's role in promoting dolomite crystallization (Mather et al., 2023; Fang et al., 2023). In cave environments, Martín-Pérez et al. (2021) showed that Mg^{2+} -silicate phases such as kerolite and sepiolite appear to play an important role in carbonate mineralization rather than forming as isolated, independent precipitates. According to these authors, in Castañar cave (Cáceres, Spain), the Mg^{2+} -clays and the associated Mg^{2+} -rich carbonates (dolomite, huntite and magnesite) are co-genetic products of the same evolving water chemistry, controlled by evaporation and CO_2 degassing of slow-moving drip and capillary waters. As Ca^{2+} is progressively removed through calcite/aragonite precipitation, the rising $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio, pH and dissolved Si^{4+} promote both the sequential precipitation of Mg^{2+} -carbonates and the neoformation of kerolite and sepiolite from an amorphous Mg^{2+} - Si^{4+} gel precursor. Because this sequence is often disrupted by changes in water supply, Mg^{2+} -silicates can precipitate over any carbonate phase at the microscale, and diagenetic transformations among carbonates (e.g., huntite to dolomite) may release additional Mg^{2+} , sustaining further clay formation. Overall, these authors highlighted that Mg^{2+} -silicate and carbonate formation are closely linked processes in the Mg^{2+} -rich speleothems in this cave (moonmilk, crusts and dolomite coatings).

Laboratory studies have also shown that disordered dolomite precipitates surrounded by a Mg^{2+} -silica gel, a precursor to Mg^{2+} -clays (Fang and Xu, 2022). Moreover, amorphous Mg^{2+} -silicate phases are frequently associated with recent sedimentary protodolomite and dolomite deposits (Fang et al., 2023). Recently, under laboratory conditions, Chen et al. (2024) reported the formation of a sepiolite-like amorphous Mg^{2+} -silicate prior to protodolomite, with and without bacterial activity, suggesting that dissolved silica promotes Mg^{2+} dehydration and its incorporation into an ACMC precursor with stoichiometry close to that of dolomite. Furthermore, they suggested that such sepiolite-like phase could function as a template for protodolomite formation (i.e., heterogeneous nucleation). As stated above, in our system, the sepiolite-like, poorly crystalline fibers may aid in the precipitation of huntite; additionally, these fibers could act as a silica source that stabilizes A(C)MC, and also promotes its heterogeneous nucleation. Silica is also known to facilitate the formation and stabilization of other amorphous carbonate phases, such as amorphous calcium carbonate (ACC) (Kellermeier et al., 2010; Gal et al., 2010). Due to the fluctuating chemistry of the drip water (see above), the dissolution of Mg-Si fibers is expected to occur alongside the dissolution of huntite. This releases silica along with Mg^{2+} ions, which facilitates the formation of A(C)MC and enhances its stabilization. The association of both phases has been shown by our TEM HAADF-EDS analyses (Fig. 3).

In the Nerja moonmilk deposits, silica and organics jointly stabilized amorphous precursors, thereby facilitating their subsequent transformation into (initially) disordered dolomite and magnesite under the low- T cave conditions, which preserved a nanogranular texture inherited from the amorphous precursors (Fig. 5). This texture, common in both recent (Kaczmarek and Sibley, 2011) and ancient dolomites (Meister and Frisia, 2019), supports a formation mechanism involving aggregation of the A(C)MC nanoparticles followed by their amorphous-to-crystalline conversion via an interface-coupled dissolution-precipitation mechanism that produces a pseudomorphic replacement of the original nanoparticulated aggregates (Rodríguez-Navarro et al., 2016), consistent with observations in biotic and abiotic systems (De Yoreo et al., 2015). The nanogranular texture preserved within the faceted crystals likely results from the presence of organic compounds within the nanoparticles during their amorphous-to-crystalline transformation. Indeed, the observation of areas with no lattice fringe in the HRTEM images of dolomite and magnesite crystals (Fig. 1h, l) could correspond either to areas where the amorphous precursor remains untransformed or to organic compounds that, as shown above, are occluded in the

crystals.

Overall, our results provide evidence of the incorporation of microbial organic substances and silica in the amorphous phases favoring the stabilization and preservation of A(C)MC in the cave. Semi-quantitative analyses revealed silica contents of 6–64 at % in the amorphous phases, whereas the abundance of organic matter could not be determined with the analytical techniques used in this study, this (semi)quantification will be considered in future works.

7. Geological implications

The evidence presented here indicates that the formation of transient amorphous phases is key for the subsequent formation of dolomite or magnesite under Earth's surface conditions: upon their dissolution, high supersaturation with respect to the crystalline Mg^{2+} - Ca^{2+} phases may be locally reached in the fluid close to the A(C)MC surface, enough to overcome the kinetic barrier for dolomite and magnesite precipitation at low- T . A simplified model of the processes is shown in Fig. 9. This crystallization pathway through nanoparticle aggregation, previously suggested to explain nanogranular features in ancient dolomites (Frisia et al., 2018; Raudsepp et al., 2024), together with the features of subsequent classical crystallization, prevails in both ancient and recent cases. Although previous studies did not demonstrate the existence of amorphous precursors, they provided indirect evidence for their role in dolomite (and magnesite) formation, suggesting that this may be a common pathway in natural environments (Chen et al., 2024; Wenk et al., 1993; Meister and Frisia, 2019).

Here, we provide the first direct evidence that, in cave environments, dolomite and magnesite formation proceeds through nanoparticle aggregation with A(C)MC as a transient phase stabilized by (microbially derived) organics and silica. This evidence includes (i) corroded edges and amorphous rims in huntite crystals, (ii) amorphous domains within huntite, dolomite, and magnesite lattices, and (iii) the occurrence of Si-rich fibers and exopolymeric substances intimately associated with Mg^{2+} - Ca^{2+} carbonates observed by HRTEM.

Although dolomite and magnesite formation in cave environments represents a relatively minor process within the sedimentary record and may not be directly translated to the case of recent marine and saline lakes dolomites or the case of many ancient (diagenetic/replacement) dolomites, the mechanisms identified in this study provide new insights into the non-classical crystallization of Mg^{2+} -rich carbonates at low- T . Our results demonstrate the formation of amorphous precursors (ACMC and AMC) prior to the precipitation of protodolomite, ordered dolomite, and magnesite, and suggest that the combined influence of amorphous magnesium silicates and microbially derived organic matter may facilitate the formation of these minerals. These findings support the hypothesis that non-classical crystallization through amorphous precursors constitutes an important pathway for low- T dolomite and magnesite formation. Furthermore, this study provides direct evidence for the formation of A(C)MC prior to the precipitation of (proto)dolomite and magnesite in nature, a process that has largely been inferred rather than directly observed. Given the complexity of the “dolomite (and magnesite) problem”, further investigations are needed to assess whether the formation model proposed here for cave environments can be extended to other sedimentary settings where recent dolomite and magnesite occur. Nevertheless, the results presented here contribute to a broader understanding of the mechanisms controlling dolomite (and magnesite) nucleation barrier in Earth's surface.

8. Conclusions

Low- T dolomite and magnesite formation in cave moonmilk deposits is governed by dynamic, non-classical processes rather than traditional crystallization pathways, involving the precipitation of key precursors such as A(C)MC, which are essential for the formation of dolomite and magnesite within the cave system. Interaction of these amorphous

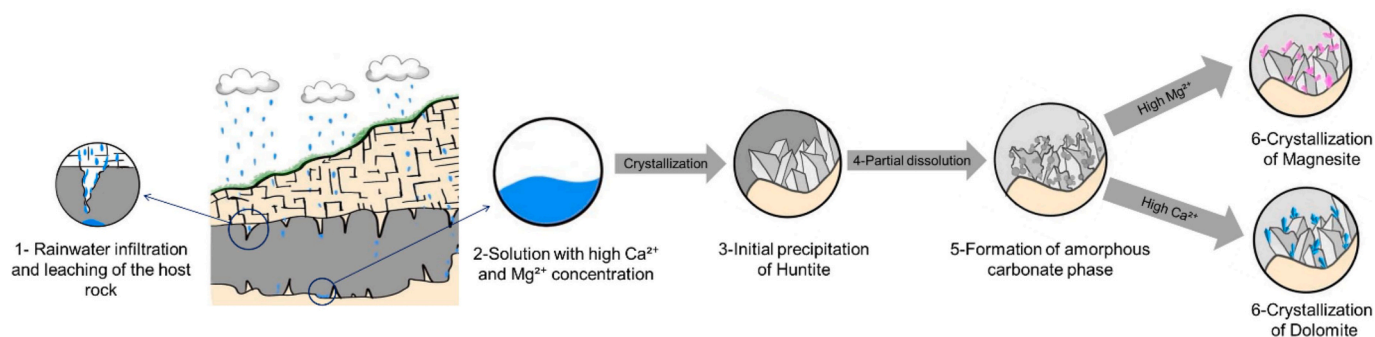


Fig. 9. Conceptual model of the crystallization processes in Nerja cave. (1) Dissolution of the dolomitic host rock. (2) Solutions enriched in Ca^{2+} and Mg^{2+} (and HCO_3^- and CO_3^{2-}). (3) Initial precipitation of huntite. (4) Dissolution of huntite driven by changes in the dripping flow regime and the evolving geochemical conditions of the environment. (5) Formation of amorphous (magnesium and calcium) carbonate phases from the interfacial solution in contact with the huntite crystals. (6) Transformation/crystallization of A(C)MC into magnesite and/or dolomite, followed by progressive increase in crystallinity and cation ordering caused by successive dissolution-reprecipitation cycles.

precursors with Ca^{2+} -rich fluids favors the formation of (proto)dolomite, whereas Mg^{2+} -rich fluids promote magnesite crystallization. It is important to note that, although numerous studies in caves, lakes, and evaporite deposits provide strong indirect evidence for the formation of dolomite and magnesite via AMC and APMC phases (Petrash et al., 2017; Raudsepp et al., 2022; Raudsepp et al., 2024), to the best of the authors' knowledge, this study provides the first direct evidence of magnesium and calcium-magnesium amorphous phases occurrence and transformation in a natural setting, offering new insights into alternative low- T formation pathways for dolomite and magnesite in sedimentary environments.

Data availability

Data are available through University of Granada repository (Digital) at <https://hdl.handle.net/10481/112972>.

CRediT authorship contribution statement

Sarah Bonilla-Correa: Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. **Encarnación Ruiz-Agudo:** Writing – review & editing, Writing – original draft, Funding acquisition, Formal analysis, Conceptualization. **Concepción Jiménez de Cisneros:** Writing – review & editing, Resources. **Cristina Liñán Baena:** Writing – review & editing. **Isabel Sánchez-Almazo:** Writing – review & editing. **Carlos Rodríguez-Navarro:** Writing – review & editing, Funding acquisition, Conceptualization. **Maria P. Asta:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This study was supported by the grants DOLOMYSTERY (CNS2024-154148), PRECURSOREFFECT (PID2024-157386NB-I00), CARMIN (PID2024-161146OB-C-21), and PID2021-125619OB-C22 funded by MICIU/AEI/10.13039/501100011033 and European Union NextGenerationEU/PRTR, by the Junta de Andalucía research group RNM-179 and University of Granada Unidad Científica de Excelencia UCE-PP2016-05. HRXRD experiments were performed at the CRISTAL beamline of SOLEIL Synchrotron (France) and at the BL04-MSPD beamline of the ALBA Synchrotron (Spain) (proposal 20250370193) with the excellent support and expertise of the beamline staff (Erik

Elkaim of Soleil and Dimitrios Chatzogiannakis of Alba). Funding for open access charge: Universidad de Granada/CBUA. We thank Luis Monasterio, Julia Atiénzar, Aurélie Pace, and Núria Pujol for their help with HRXRD analysis of moonmilk samples. We also acknowledge the analytical support in TEM provided by Josefa Pedrajas at the Centro de Instrumentación Científica, University of Granada (Spain), and Francisco Varela Feria at the Centro de Investigación, Tecnología e Innovación, University of Sevilla (Spain). Oscar del Pico performed NMR analyses at the Centro de Instrumentación Científica Técnica at the University of Jaén. We thank Samantha Bonilla for designing the conceptual model. Finally, we thank the Nerja Cave Foundation for the moonmilk samples, collected as part of the Nerja Cave Interdisciplinary Research Project, authorized by the Consejería de Cultura (Junta de Andalucía). We also gratefully acknowledge the helpful comments and valuable suggestions made by Dr. Daniel Petrash, one anonymous reviewer, and associate editor Dr. Adrian Immenhauser.

Appendix A. Supplementary material

Supplementary material to this article can be found online at <https://doi.org/10.1016/j.gca.2026.07.016>.

Additional figures showing the study site location, the analysis of the host rock, the ATR-FTIR absorption bands of *Cataclismo* and *Immensidad* samples and reference phases and two tables with the dates of sample collection, the mineralogy and the temperatures of dehydration and decarbonation of inorganic standards and Nerja samples are provided as Supplementary Data 1.

The chemistry of the drip waters can be found in an excel file as Supplementary Data 2.

The PHREEQC input file is presented as Supplementary Data 3.

References

- Alonso-Zarza, A.M., Martín-Pérez, A., 2008. Dolomite in caves: recent dolomite formation in oxic, non-sulfate environments. Castañar Cave, Spain. *Sediment. Geol.* 205, 160–164.
- Andreo, B., Barberá, J.A., Mudarra, M., Marín, A.I., García-Orellana, J., Rodellas, V., Pérez, I., 2018. A multi-method approach for groundwater resource assessment in coastal carbonate (karst) aquifers: the case study of Sierra Almajara (southern Spain). *Hydrogeol. J.* 26, 41–56.
- Andreo B. and Carrasco F. (1993) Estudio hidrogeológico del entorno de la Cueva de Nerja. *Geología de la Cueva de Nerja. Trabajos sobre la Cueva de Nerja* (eds. Carrasco F.) 3, 163–187.
- Andreo B., Carrasco F., Linán C. and Vadillo I. (2002) Epigenic CO_2 controlling the drip water chemistry and speleothem growth in a Mediterranean karst area (Nerja Cave, southern Spain). In: *Karst processes and the Carbon cycle* (eds. Y. Daoxian, and Z. Cheng), 51–64.
- Aranburu A., Vadillo Pérez I., Damas Mollá L., García-Garmilla P., Iridoy P., Arriolabengoa M., Berreteaga A. and Olaetxea C. (2010) Degradación de los espeleotemas de la Cueva de Praileaitz I (Deba, Guipúzcoa). In *Cuevas: Patrimonio, Naturaleza, Cultura y Turismo* (eds. J. J. Durán and F. Carrasco). Asociación de Cuevas Turísticas Españolas, Madrid. pp. 435–450.

- Aranburu, A., Arriolabengoa, Z.M., Bodego, A.A., Álvarez, G.I., Bilbao, L.P., Yusta, A.I., Liñán, B.C., 2018. Meteorización de mármoles dolomíticos y su relación con la arena dolomítica de la Cueva de Nerja (Málaga, España). *Geogaceta* 64, 123–126.
- Aranburu, A., Damas-Mollá, L., Bodego, A., Álvarez, I., Madarieta-Txurruka, A., Liñán, C., Iriarte, E., 2026. Nuevos avances en la reconstrucción de la historia geológica de la Cueva de Nerja (Málaga). I Encuentro De Geología Subterránea Cueva De Nerja, Trabajos Del Instituto De Investigación De La Cueva De Nerja 3, 54–62.
- Arrese B. (2009) Geomorfología, evolución geológica y condiciones ambientales actuales de la Cueva de Nerja, Málaga. Ph.D. thesis, Universidad Autónoma de Madrid.
- Batiot, C., Liñán, C., Andreo, B., Emblanch, C., Carrasco, F., Blavoux, B., 2003. Use of Total Organic Carbon (TOC) as tracer of diffuse infiltration in a dolomitic karstic system: the Nerja Cave (Andalusia, southern Spain). *Geophys. Res. Lett.* 30, 2179.
- Blyth, A.J., Frisia, S., 2008. Molecular evidence for bacterial mediation of calcite formation in cold high-altitude caves. *Geomicrobiol. J.* 25, 101–111.
- Bonilla-Correa S., Ruiz-Agudo C., Asta M. P., Huber L., Rodríguez-Navarro C. and Ruiz-Agudo E. (2025) Stability of Amorphous Magnesium Carbonate at Low T and Variable pH Conditions. *Goldschmidt 2025 Conference Abstract*.
- Borsato, A., Frisia, S., Jones, B., Van Der Borg, K., 2000. Calcite moonmilk: crystal morphology and environment of formation in caves in the Italian Alps. *J. Sediment. Res.* 70, 1171–1182.
- Carrasco, F., Andreo, B., Liñán, C., Mudry, J., 2006. Contribution of stable isotopes to the understanding of the unsaturated zone of a carbonate aquifer (Nerja Cave, southern Spain). *Comptes Rendus. Géoscience* 338, 1203–1212.
- Casas J., Martín de Vidales J. L., Durán Valsero J. J., López-Martínez J. and Barea J. (2001) Mineralogía de depósitos de tipo moonmilk en la Cueva de Nerja. *Geogaceta* 29, 29–32.
- Casas, J., Martín de Vidales, J.L., Durán, J.J., López-Martínez, J. y Barea, J., 2002. Presencia y mineralogía de depósitos de tipo moonmilk en la Cueva de Nerja (Málaga). En Carrasco, F., Durán, J.J. y Andreo, B. (Eds.). *Karst and Environment*, 485–489. Fundación Cueva de Nerja. Málaga.
- Chang, C., Yang, S., Chan, J.C., 2021. Solubility product of amorphous magnesium carbonate. *J. Chin. Chem. Soc.* 68, 476–481.
- Chen, T., Qiu, X., Liu, D., Papineau, D., Wang, H., Dai, Z., Bontognali, T.R., Benzerara, K., 2024. Dissolved silicon as a beneficial factor for biomineralization of disordered dolomite by a halophilic cyanobacterium. *Chem. Geol.* 670, 122435.
- Cuadros, J., 2017. Clay minerals interaction with microorganisms: a review. *Clay Miner.* 52, 235–261.
- De Yoreo, J.J., Gilbert, P.U., Sommerdijk, N.A., Penn, R.L., Whitlam, S., Joester, D., Zhang, H., Rimer, J.D., Navrotsky, A., Banfield, J.F., 2015. Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science* 349, 6760.
- Deelman, J.C., 1999. Low-temperature nucleation of magnesite and dolomite. *Neues Jahrb. Mineral. Monatsh.* 7, 289–302.
- Delgado, T., García-Gómez, L., Fortes, F.J., Cabalín, L.M., Liñán, C., Vadillo, I., Jiménez-Gavilán, P., Ojeda, L., Laserna, J.J., 2024. Discriminating organic carbon from endokarstic moonmilk-type deposits by LIBS. The case of a natural carbonated Martian analogue. *Talanta* 271, 125639.
- Dietzel, M., Boch, R., 2024. Precipitation of CaCO₃ in natural and man-made aquatic environments-mechanisms, analogues, and proxies. *Geochemistry* 84, 126206.
- Durán J. J. (1996) Los sistemas kársticos de la provincia de Málaga y su evolución: contribución al conocimiento paleoclimático del Cuaternario en el Mediterráneo Occidental. Ph.D. thesis, Universidad Complutense de Madrid.
- Durán, J.J., López-Martínez, J., de Vidales, J.M., Casas, J., Barea, J., 2001. El moonmilk, un depósito endokárstico singular. Presencia En Cavidades Españolas. *Geogaceta* 29, 43–46.
- Northrup, D.E., Lavoie, K.H., 2001. Geomicrobiology of caves: a review. *Geomicrobiol. J.* 18, 199–222.
- Enyedi, N.T., Makk, J., Kótai, L., Berényi, B., Klébert, S., Sebestyén, Z., Molnár, Z., Borsodi, A.K., Leél-Össy, S., Demény, A., 2020. Cave bacteria-induced amorphous calcium carbonate formation. *Sci. Rep.* 10, 8696.
- Fang, Y., Hobbs, F., Yang, Y., Xu, H., 2023. Dissolved silica-driven dolomite precipitation in the Great Salt Lake, Utah, and its implication for dolomite formation environments. *Sedimentology* 70, 1328–1347.
- Fang, Y., Xu, H., 2022. Dissolved silica-catalyzed disordered dolomite precipitation. *Am. Mineral.* 107, 443–452.
- Farmer S., Kennepohl D., Soderberg T. and Reutenauer L. (2024) 13.3: Chemical Shifts in ¹H NMR Spectroscopy. *Organic Chemistry (Morsch et al.) Structure Determination: Nuclear Magnetic Resonance Spectroscopy*.
- Ford D. and Williams P. D. (2007) *Karst hydrogeology and geomorphology*. John Wiley & Sons.
- Forti P. (2009) Speleothems and living organisms: What kind of relationship? 2009 ICS Proceedings - 15th International Congress of Speleology 741–747.
- Forti, P., 2001. Biogenic speleothems: an overview. *Int. J. Speleol.* 30, 39–56.
- Frisia, S., Wenk, H., 1993. TEM and AEM study of pervasive, multi-step dolomitization of the Upper Triassic Dolomia Principale (Northern Italy). *J. Sediment. Res.* 63, 1049–1058.
- Frisia, S., Borsato, A., Fairchild, I.J., McDermott, F., 2000. Calcite fabrics, growth mechanisms, and environments of formation in speleothems from the Italian Alps and southwestern Ireland. *J. Sediment. Res.* 70, 1183–1196.
- Frisia, S., Borsato, A., Hellstrom, J., 2018. High spatial resolution investigation of nucleation, growth and early diagenesis in speleothems as exemplar for sedimentary carbonates. *Earth Sci. Rev.* 178, 68–91.
- Frisia, S., Borsato, A., Hartland, A., Faraji, M., Demeny, A., Drysdale, R.N., Marjo, C.E., 2022. Crystallization pathways, fabrics and the capture of climate proxies in speleothems: examples from the tropics. *Quat. Sci. Rev.* 297, 107833.
- Furevi, A., Ruda, A., d'Ortoli, T.A., Mobarak, H., Ståhle, J., Hamark, C., Fontana, C., Engström, O., Apostolica, P., Widmalm, G., 2022. Complete ¹H and ¹³C NMR chemical shift assignments of mono- to tetrasaccharides as basis for NMR chemical shift predictions of oligo- and polysaccharides using the computer program CASPER. *Carbohydr. Res.* 513, 108528.
- Gal, A., Weiner, S., Addadi, L., 2010. The stabilizing effect of silicate on biogenic and synthetic amorphous calcium carbonate. *J. Am. Chem. Soc.* 132, 13208–13211.
- Gindele, M.B., Vinod-Kumar, S., Rochau, J., Boemke, D., Groß, E., Redrouth, V.S., Gebauer, D., Mathies, G., 2024. Colloidal pathways of amorphous calcium carbonate formation lead to distinct water environments and conductivity. *Nat. Comm.* 15, 80.
- Gradziński, M., Respondek, M., Szulc, J., 1997. Microbial agents of moonmilk calcification. 12th International Congress of Speleology, Swiss Speleological Society, Proceedings 1, 275–278.
- Graf, D.L., Bradley, W.F., 1962. The crystal structure of huntite, Mg₃Ca (CO₃)₄. *Acta Crystallogr.* 15, 238–242.
- Gregg, J.M., Bish, D.L., Kaczmarek, S.E., Machel, H.G., 2015. Mineralogy, nucleation and growth of dolomite in the laboratory and sedimentary environment: a review. *Sedimentology* 62, 1749–1769.
- Guerra-Merchán, A., Serrano, F., Ramallo, D., 2004. Geomorph and sedimentary Plio-Pleistocene evolution of the Nerja area (northern Alboran basin, Spain). *Geomorphology* 60, 89–105.
- Hardie, L.A., 1987. Dolomitization; a critical view of some current views. *J. Sediment. Res.* 57, 166–183.
- Hill C. and Forti P. (1997) *Cave minerals of the world*. 2nd edition, National Speleological Society, Huntsville, Alabama.
- Hu, Q., Nielsen, M.H., Freeman, C.L., Hamm, L.M., Tao, J., Lee, J.R.I., Han, T.Y.J., Becker, U., Harding, J.H., Dove, P.M., De Yoreo, J.J., 2012. The thermodynamics of calcite nucleation at organic interfaces: classical vs. non-classical pathways. *Faraday Discuss.* 159, 509–523.
- Huang, Y., Rao, A., Huang, S., Chang, C., Drechsler, M., Knaus, J., Chan, J.C.C., Raiteri, P., Gale, J.D., Gebauer, D., 2021. Uncovering the role of bicarbonate in calcium carbonate formation at near-neutral pH. *Angew. Chem. Int. Ed.* 60, 16707–16713.
- Jones, B., 2010. The preferential association of dolomite with microbes in stalactites from Cayman Brac, British West Indies. *Sed. Geol.* 226, 94–109.
- Jones, B., Kahle, C.F., 1993. Morphology, relationship, and origin of fiber and dendrite calcite crystals. *J. Sediment. Res.* 63, 1018–1031.
- Jurado, V., Del Rosal, Y., de Cisneros, C.J., Liñán, C., Martín-Pozas, T., Gonzalez-Pimentel, J.L., Hermosin, B., Saiz-Jimenez, C., 2022. Microbial communities in carbonate precipitates from drip waters in Nerja Cave, Spain. *PeerJ* 10, e13399.
- Kaczmarek, S.E., Sibley, D.F., 2011. On the evolution of dolomite stoichiometry and cation order during high-temperature synthesis experiments: an alternative model for the geochemical evolution of natural dolomites. *Sed. Geol.* 240, 30–40.
- Kelleher, L.J., Redfern, S.A., 2002. Hydrous calcium magnesium carbonate, a possible precursor to the formation of sedimentary dolomite. *Mol. Simul.* 28, 557–572.
- Kellermeier, M., Melero-García, E., Glaab, F., Klein, R., Drechsler, M., Rachel, R., García-Ruiz, J.M., Kunz, W., 2010. Stabilization of amorphous calcium carbonate in inorganic silica-rich environments. *J. Am. Chem. Soc.* 132, 17859–17866.
- Kim, J., Kimura, Y., Puchala, B., Yamazaki, T., Becker, U., Sun, W., 2023. Dissolution enables dolomite crystal growth near ambient conditions. *Science* 382, 915–920.
- Kim, Y., Semsarilar, M., Carloni, J.D., Cho, K.R., Kulak, A.N., Polishchuk, I., Hendley IV, C.T., Smeets, P.J., Fielding, L.A., Pokroy, B., 2016. Structure and properties of nanocomposites formed by the occlusion of block copolymer worms and vesicles within calcite crystals. *Adv. Funct. Mater.* 26, 1382–1392.
- Lafuente B., Downs R. T., Yang H. and Stone N. (2015) The power of databases: the RUFF project. In *Highlights in Mineralogical Crystallography* (eds. T. Armbruster and R. M. Danisi). W. De Gruyter, Berlin, pp. 1–30.
- Liñán C., Andreo B., Carrasco F. and Vadillo I. (1999) Hidrodinámica e hidroquímica de las aguas de goteo de la Cueva de Nerja. In: *Contribución del estudio científico de las cavidades kársticas al conocimiento geológico*. B. Andreo, F. Carrasco y J.J. Durán (Eds), pp. 393–402. Patronato de la Cueva de Nerja, 1999, Nerja (Málaga).
- Liñán C., Carrasco F., Andreo B., Jiménez de Cisneros C. and Caballero E. (2002) Caracterización isotópica de las aguas de goteo de la Cueva de Nerja y de su entorno hidrogeológico (Málaga, Sur de España). *Karst and environment. Málaga: Fundación Cueva de Nerja* 243–249.
- Liñán, C., de Cisneros, C.J., Benavente, J., Vadillo, I., Del Rosal, Y., Ojeda, L., 2023. Coronavirus pandemic: an opportunity to study the anthropogenic impact on microclimate conditions and CaCO₃ crystal morphology in the Nerja Cave (SE Spain). *Sci. Total Environ.* 883, 163693.
- Liñán, C., Del Rosal, Y., Carrasco, F., Vadillo, I., Benavente, J., Ojeda, L., 2018. Highlighting the importance of transitional ventilation regimes in the management of Mediterranean show caves (Nerja-Pintada system, southern Spain). *Sci. Total Environ.* 631, 1268–1278.
- Liñán, C., Simón, M.D., del Rosal, Y., Garrido, A., 2007. Estudio preliminar del clima en el entorno de la Cueva de Nerja (Andalucía, provincia de Málaga). *Cuevas Turísticas: Aportación Al Desarrollo Sostenible* 24, 159–168.
- Liñán, C., Ojeda, L., Benavente, J., del Rosal, Y., Vadillo, I., Carrasco, F., 2020. Coupling air temperature records and gravimetric data to interpret ventilation patterns in a Mediterranean karstic system (Nerja-Pintada caves, southern Spain). *Sci. Total Environ.* 730, 139147.
- Lippmann, F., 1973. Crystal chemistry of sedimentary carbonate minerals. In *Sedimentary Carbonate Minerals*. Springer 5–96.
- Liu, D., Chen, T., Dai, Z., Papineau, D., Qiu, X., Wang, H., Benzerara, K., 2024. A non-classical crystallization mechanism of microbially-induced disordered dolomite. *Geochim. Cosmochim. Acta* 381, 198–209.

- Liu, D., Xu, Y., Papineau, D., Yu, N., Fan, Q., Qiu, X., Wang, H., 2019. Experimental evidence for abiotic formation of low-temperature proto-dolomite facilitated by clay minerals. *Geochim. Cosmochim. Acta* 247, 83–95.
- López Sánchez-Vizcaíno, Gómez-Pugnaire, M.T., 1993. Introducción a la petrología de los mármoles de la Cueva de Nerja y materiales asociados. *Geología De La Cueva De Nerja* 3, 189–229.
- Martínez-Moreno, F.J., Galindo-Zaldívar, J., Baena, C.L., González-Castillo, L., Herrera, J.B., Martínez-Martos, M., Padial, Y.D.R., Rodríguez, L.F., Tenders-Salmerón, V., Madarieta-Txurruka, A., 2021. Development and collapse of karstic cavities in folded marbles: geomorphological and geophysical evidences in Nerja Cave (southern Spain). *J. Appl. Geophys.* 187, 104287.
- Martín-Pérez, A., Košir, A., Otonicar, B., 2015. Dolomite in speleothems of Snežna Jama cave, Slovenia. *Acta Carsologica* 44, 81–100.
- Martín-Pérez, A., La Iglesia, Á., Almendros, G., González-Pérez, J.A., Alonso-Zarza, A.M., 2021. Precipitation of kerolite and sepiolite associated with Mg-rich carbonates in a cave environment. *Sed. Geol.* 411, 105793.
- Mather, C.C., Lampinen, H.M., Tucker, M., Leopold, M., Dogramaci, S., Raven, M., Gilkes, R.J., 2023. Microbial influence on dolomite and authigenic clay mineralisation in dolomite profiles of NW Australia. *Geobiology* 21, 644–670.
- McKenzie, J.A., 1981. Holocene dolomitization of calcium carbonate sediments from the coastal sabkhas of Abu Dhabi, UAE: a stable isotope study. *J. Geol.* 89, 185–198.
- Medina-Alcaide, M.A., Cabalín, L.M., Laserna, J., Sanchidrián, J.L., Torres, A.J., Intxaurbe, I., Romero, A., 2019. Multianalytical and multiproxy approach to the characterization of a Paleolithic lamp. An example in Nerja cave (Southern Iberian Peninsula). *J. Archaeol. Sci. Rep.* 28, 102021.
- Meister, P., Frisia, S., 2019. Dolomite formation by nanocrystal aggregation in the Dolomia Principale of the Brenta Dolomites (northern Italy). *Riv. Ital. Paleontol. Stratigr.* 125, 183–196.
- Mudry, J., Andreo, B., Charmoille, A., Liñán, C., Carrasco, F., 2008. Some applications of geochemical and isotopic techniques to hydrogeology of the caves after research in two sites (Nerja Cave-Spain and Fourbanne system-French Jura). *Int. J. Speleol.* 37, 6.
- Nebel, H., Neumann, M., Mayer, C., Eppe, M., 2008. On the structure of amorphous calcium carbonate—a detailed study by solid-state NMR spectroscopy. *Inorg. Chem.* 47, 7874–7879.
- Oomori, T., Kaneshima, K., Taira, T., Kitano, Y., 1983. Synthetic studies of protodolomite from brine waters. *Geochem. J.* 17, 147–152.
- Ozao R. and Otsuka R. (1985) Thermoanalytical investigation of huntite. *Thermochimica acta* 86, 45–58.
- Papenguth, H.W., Kirkpatrick, R.J., Montez, B., Sandberg, P.A., 1989. ¹³C MAS NMR spectroscopy of inorganic and biogenic carbonates. *Am. Mineral.* 74, 1152–1158.
- Parkhurst, D.L., Appelo, C., 2013. Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *US Geological Survey Techniques and Methods* 6 (A43), 497.
- Petrash, D.A., Bialik, O.M., Bontognali, T.R., Vasconcelos, C., Roberts, J.A., McKenzie, J. A., Konhauser, K.O., 2017. Microbially catalyzed dolomite formation: from near-surface to burial. *Earth Sci. Rev.* 171, 558–582.
- Pina, C.M., Pimentel, C., Crespo, A., 2022. The dolomite problem: a matter of time. *ACS Earth Space Chem.* 6, 1468–1471.
- Pina, C.M., Pimentel, C., Crespo, A., 2020. Dolomite cation order in the geological record. *Chem. Geol.* 547, 119667.
- Popović, S., Nikolić, N., Jovanović, J., Predojević, D., Trbojević, I., Manić, L., Subakov-Simić, G., 2019. Cyanobacterial and algal abundance and biomass in cave biofilms and relation to environmental and biofilm parameters. *Int. J. Speleol.* 48, 49–61.
- Power, I.M., Harrison, A.L., Dipple, G.M., Wilson, S., Barker, S.L., Fallon, S.J., 2019. Magnesite formation in playa environments near Atlin, British Columbia, Canada. *Geochim. Cosmochim. Acta* 255, 1–24.
- Purgstaller, B., Goetschl, K.E., Mavromatis, V., Dietzel, M., 2019. Solubility investigations in the amorphous calcium magnesium carbonate system. *Cryst. Eng. Comm.* 21, 155–164.
- Purgstaller, B., Mavromatis, V., Goetschl, K.E., Steindl, F.R., Dietzel, M., 2021. Effect of temperature on the transformation of amorphous calcium magnesium carbonate with near-dolomite stoichiometry into high Mg-calcite. *Cryst. Eng. Comm.* 23, 1969–1981.
- Qafoku, O., Dixon, D.A., Rosso, K.M., Schaeff, H.T., Bowden, M.E., Arey, B.W., Felmy, A. R., 2015. Dynamics of magnesite formation at low temperature and high pCO₂ in aqueous solution. *Environ. Sci. Technol.* 49, 10736–10744.
- Raudsepp, M.J., Wilson, S., Morgan, B., Patel, A., Johnston, S.G., Gagen, E.J., Fallon, S.J., 2022. Non-classical crystallization of very high magnesium calcite and magnesite in the Coorong Lakes, Australia. *Sedimentology* 69, 2246–2266.
- Raudsepp, M.J., Wilson, S., Zeyen, N., Arizaleta, M.L., Power, I.M., 2024. Magnesite everywhere: formation of carbonates in the alkaline lakes and playas of the Cariboo Plateau, British Columbia, Canada. *Chem. Geol.* 648, 121951.
- Rodríguez-Blanco, J.D., Shaw, S., Benning, L.G., 2015. A route for the direct crystallization of dolomite. *Am. Mineral.* 100, 1172–1181.
- Rodríguez-Navarro, A.B., Domínguez-Gasca, N., Athanasiadou, D., Le Roy, N., González-Segura, A., Reznikov, N., Hincke, M.T., McKee, M.D., Checa, A.G., Nys, Y., 2024. Guinea fowl eggshell structural analysis at different scales reveals how organic matrix induces microstructural shifts that enhance its mechanical properties. *Acta Biomater.* 178, 244–256.
- Rodríguez-Navarro, C., Kudlacz, K., Ruiz-Agudo, E., 2012. The mechanism of thermal decomposition of dolomite: new insights from 2D-XRD and TEM analyses. *Am. Mineral.* 97, 38–51.
- Rodríguez-Navarro, C., Kudlacz, K., Cizer, Ö., Ruiz-Agudo, E., 2015. Formation of amorphous calcium carbonate and its transformation into mesostructured calcite. *Cryst. Eng. Comm.* 17, 58–72.
- Rodríguez-Navarro, C., Burgos, C.A., Elert, K., Putnis, C.V., Ruiz-Agudo, E., 2016. Direct nanoscale imaging reveals the growth of calcite crystals via amorphous nanoparticles. *Cryst. Growth Des.* 16, 1850–1860.
- Santoro De Vico F., Bonilla-Correa S., Pelayo Punzano G., Elert K., Rodríguez Navarro C. M. and Ruiz Agudo E. (2024) Additive impact on early-stage magnesium carbonate mineralisation. *Geochem. Persp. Lett.* 32, 46–51.
- Santos, H.S., Nguyen, H., Venâncio, F., Ramteke, D., Zevenhoven, R., Kinnunen, P., 2023. Mechanisms of Mg carbonates precipitation and implications for CO₂ capture and utilization/storage. *Inorg. Chem. Front.* 10, 2507–2546.
- Smith, G.K., 2024. Moonmilk: sample analysis and review of the literature. *Helvite* 49, 11–18.
- Turpin, M., Nader, F.H., Kohler, E., 2012. Empirical calibration for dolomite stoichiometry calculation: application on Triassic Muschelkalk-Lettenkohl carbonates (French Jura). *Oil Gas Sci. Technol. – Rev. IFP Energies Nouvelles* 67, 77–95.
- Wang, D., Hamm, L.M., Giuffrè, A.J., Echigo, T., Rimstidt, J.D., Yoreo, J.J., De, G.J., Dove, P.M., 2012. Revisiting geochemical controls on patterns of carbonate deposition through the lens of multiple pathways to mineralization. *Faraday Discuss.* 159, 371–386.
- Warren, J., 2000. Dolomite: occurrence, evolution and economically important associations. *Earth Sci. Rev.* 52, 1–81.
- Wenk, H., Hu, M., Frisia, S., 1993. Partially disordered dolomite: microstructural characterization of Abu Dhabi sabkha carbonates. *Am. Mineral.* 78, 769–774.
- Wollast, R., Mackenzie, F.T., Bricker, O.P., 1968. Experimental precipitation and genesis of sepiolite at earth-surface conditions. *Am. Mineral.* 53, 1645–1662.
- Yang, S., Chang, H., Lin, C., Huang, S., Chan, J.C., 2016. Is Mg-stabilized amorphous calcium carbonate a homogeneous mixture of amorphous magnesium carbonate and amorphous calcium carbonate? *Chem. Commun.* 52, 11527–11530.
- Yeniyol, M., 2014. Characterization of two forms of sepiolite and related Mg-rich clay minerals from Yenidoğ an (Sivrihisar, Turkey). *Clay Miner.* 49, 91–108.
- Zhang, C., Yang, K., Li, F., Zhou, J., 2024. The roles of amorphous phase on Ca–Mg carbonate mineralization under the action of bacteria and EPS. *J. Cryst. Growth* 644, 127841.
- Zhang, S., Nahi, O., Chen, L., Aslam, Z., Kapur, N., Kim, Y., Meldrum, F.C., 2022. Magnesium ions direct the solid-state transformation of amorphous calcium carbonate thin films to aragonite, magnesite-calcite, or dolomite. *Adv. Funct. Mater.* 32, 2201394.
- Zheng, W., Liu, D., Yang, S., Fan, Q., Papineau, D., Wang, H., Qiu, X., Chang, B., She, Z., 2021. Transformation of protodolomite to dolomite proceeds under dry-heating conditions. *Earth Planet. Sci. Lett.* 576, 117249.
- Zvir, Y., Pimentel, C., Pina, C.M., 2021. The effect of stoichiometry, Mg–Ca distribution, and iron, manganese, and zinc impurities on the dolomite order degree: a theoretical study. *Minerals* 11, 702.