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Do magnesian clays play a role in dolomite formation in alkaline environments? An example from Castañar Cave, Cáceres (Spain)

¿Cuál es el papel de las arcillas magnesianas en la formación de dolomita en ambientes alcalinos? Un ejemplo de la cueva de Castañar, Cáceres (España)

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ABSTRACT

The speleothems of Castañar Cave are made of a complex mineralogical association including aragonite, dolomite, huntite, hydromagnesite and a small proportion of Mg-rich clays whose mineralogy is difficult to determine. These clays appear as thin mats composed by fibres that are commonly associated to dolomite. The composition of cave waters and the textural relationship between the minerals indicate that in these alkaline environments there are several possible evaporation/concentration stages (with waters with pH > 8) followed by other stages characterized by freshwater entrances. All this result in complex precipitation sequences in which Ca and Mg are always available, and then it is silica content the main factor driving Mg-clay formation. The high Mg/Ca ratios drive initial aragonite precipitation, which contributes to an additional increase in this ratio enabling precipitation of huntite and Mg-clays (if silica is available). The following stage is dolomite formation either by replacement of metastable huntite or by direct precipitation on the Mg-clays that act as templates.

Key-words: *Dolomite, Mg clays, huntite, speleothem.*

RESUMEN

Los espelotemas de la cueva de Castañar, Cáceres, están formados por una asociación mineralógica compleja que incluye aragonito, dolomita, huntita, magnesita e hidromagnesita y pequeñas proporciones de arcillas magnesianas, cuya mineralogía es muy difícil de determinar. Estas arcillas aparecen como películas formadas por finos entramados de fibras, íntimamente relacionadas con la dolomita. La composición de las aguas de la cueva y relaciones texturales sugieren que en estos ambientes alcalinos hay numerosas etapas de evaporación/concentración, con aguas con pH superiores a 8, seguidas de otras etapas en las que hay entrada de agua dulce. Ello da lugar a secuencias de precipitación complejas y teniendo en cuenta que el aporte de Ca y Mg está garantizado, la disponibilidad de sílice va a ejercer un papel prioritario en la formación de las arcillas magnesianas. Las altas relaciones Mg/Ca condicionan la precipitación inicial de aragonito, lo que hace aumentar aún más esa relación y favorecen la precipitación de huntita y arcillas magnesianas (si hay sílice disponible). A partir de este momento la dolomita puede formarse bien por reemplazamiento de la huntita metaestable o por precipitación directa sobre las arcillas magnesianas que actúan como "template".

Palabras clave: *Dolomita, arcillas magnesianas, huntita, espeleotema.*

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Introduction

Mg-rich clays are common components of saline and alkaline lake deposits (Pozo and Casas, 1999; Deocampo, 2005). Although less frequent, they have also been described forming part of speleothems, such as the kerolite found in lava tubes of Hawai (Léveillé *et al*., 2002) or the trioctahedral smectite associated with dolomite and huntite in crusts and moonmilk of caves of Guadalupe Mountains (Polyak and Güven, 2000). These clays occur in small quantities, forming mats, so their precise identification is not easy and in many cases they can be misinterpreted as organic films (Alonso-Zarza *et al*., 2005). The close relationships of dolomite with these Mg-rich clays in speleothems may point out to their common origin in some particular environments.

The Castañar Cave in Cáceres (Fig. 1) has been the aim of a number of studies focused on the controls on its formation (Alonso-Zarza *et al*., 2011), the characterization of its speleothems and their diagenetic processes (Martín-García *et al*., 2009; Martín-Pérez *et al*., 2012), the study of its environmental conditions (Fernández-Cortés *et al*., 2009, 2010) or the origin of high amounts of radon in the cave air, related to uranyl-silica complexes of the host rock (Garcia-Guinea *et al*., 2013). All the studies highlight the special characteristics of the cave, which formed by dissolution of dolostones and magnesites (Herrero *et al*., 2011) interbedded with shales. The host rock controls the Mg-rich character of the dripping waters and the presence of silica (Garcia-Guinea *et al*., 2013). The evolution

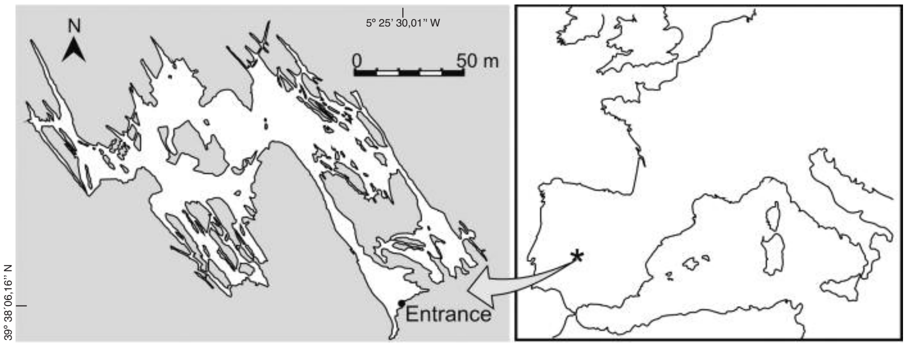

Fig. 1.- Castañar cave map and location of Castañar in Iberian Peninsula.

Fig. 1.- Mapa de la cueva de Castañar y su localización en la península Ibérica.

of the waters within the cave due to evaporation and/or degasing results in the formation of a complex mineral association including aragonite, calcite, Mg-rich clays, dolomite and huntite as main minerals.

Methods

Thin sections of speleothems, which due to their fragility were previously embedded in resin, were examined by petrographic microscopy. Scanning electron microscopy was performed on gold-coated samples using a JEOL 6400 working at 20 kV and with a resolution of 35 Å. Secondary electron and backscatter detectors (BSE) were used together with an X-ray detection system (XDS) to obtain semiquantitative compositions. Mineralogical characterization was done by X-ray diffraction (XRD) using a Philips PW-1710 XRD system operating at 40 kV and 30 mA, at 2°/min, with monochromated CuK radiation. XRD spectra were obtained from 2 to 66° 2θ.

Cave microclimatic conditions and water geochemistry

Microclimatic parameters of Castañar cave are very stable throughout the year. The mean temperature is 16,95ºC with maximum oscillations of 0,15ºC and the mean value of CO_2 air concentration is 3685 ppm, with annual amplitudes of 1300 ppm and lower values reached during the summer. The values of humidity are close to saturation (> 99,5%) and very stable throughout the year (Fernández-Cortés *et al.*, 2010). The water of Castañar cave has a moderate to high mineralization of calcium-magnesium type. Data on mineral saturation state and CO_2 partial pressure suggest that analysed samples of Castañar cave are close to saturation (± 0,25) in aragonite, or oversaturated (> 0,25) with respect to calcite and dolomite (Sánchez-Moral *et al.*, 2006; Fernández-Cortés *et al.*, 2010). The Si concentration in solution is relatively low but could be adequate to precipitate silica speleothems (Garcia-Guinea *et al.*, 2013).

Dolomite speleothems

Detailed descriptions of speleothems can be found in Martín-Pérez (2012) and Martín-García (2012), amongst many others. Here we will describe only the common speleothem type containing the most complex mineral association. Mg-rich minerals mostly occur forming part of coatings over aragonite frostwork, moonmilk and crusts (Fig. 2).

Aragonite forms as acicular transparent crystals about 10-200 µm wide and up to 5 cm long. Most of the crystals show a radial arrangement from a central point to form fans that overlap each other constituting the different speleothems. Aragonite speleothems have undergone a variety of diagenetic processes such a as transformation to calcite, micritization or dissolution (Martín-García, 2012) and dolomitization, a process that has been rarely described in speleothems (Martín-Pérez, 2012; Alonso-Zarza and Martín-Pérez, 2008).

Huntite ($Mg_3Ca(CO_3)_4$) is the main component of moonmilk, a white, pasty, microcrystalline deposit with high amounts of intercrystalline water. It appears under the microscope as brownish micritic masses composed of randomly oriented flakes less than 5 µm across.

Magnesite and hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \times 4(H_2O)$) also form part of moonmilk speleothems and occur as small crystals (< 10 µm) with rhombohedral or plate morphology respectively.

Dolomite appears as white to beige opaque coatings over huntite and magnesite globules in moonmilk or over aragonite crystals in frostwork and crusts. It forms spheroids and dumbbells 50–300 m across in a fibrous-radial pattern with concentric bands (Fig. 3). Dolomite spheroids may be observed between aragonite crystals, coalescing to form mosaics or replacing aragonite. Dolomite spheroids show different shapes of crystal subunits, varying from rounded to rhombohedral morphologies (Fig. 4A) commonly associated with huntite flakes and fibrous Mg-clays.

Mg clays

Microscopic observations of moonmilk and crusts have shown the ubiquitous presence of Mg-Si fibres and laths associated

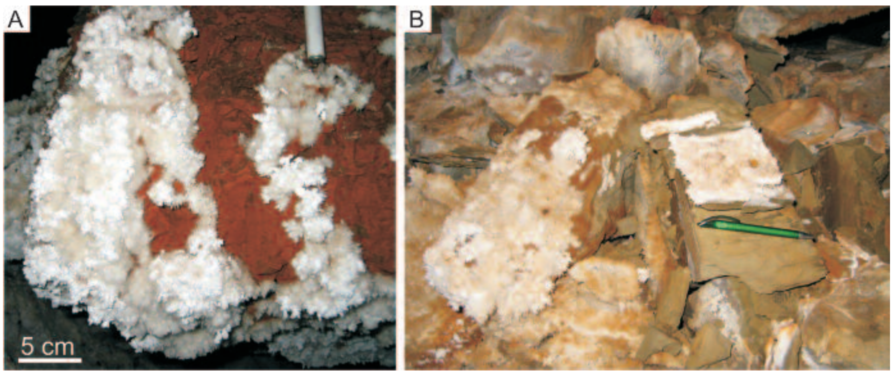

Fig. 2.- Speleothems containing Mg minerals. A) Moonmilk globules covering aragonite frostworks that nucleate on red soil of the cave. B) Polymineral crust speleothems covering fragments of shales.

Fig. 2.- Espeleotemas que contienen minerales magnésicos. A) Glóbulos de moonmilk cubriendo cristales de aragonito formando "frostwork" que nuclean en arcillas rojas. B) Costras poliminerales que cubren fragmentos de pizarra.

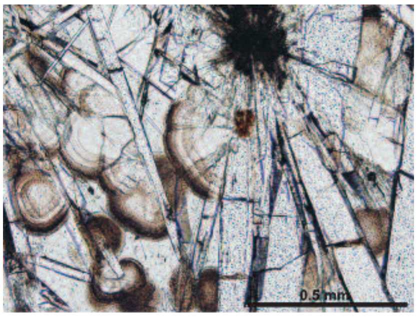

Fig. 3.- Microscope image of dolomite spheroids growing between aragonite crystals. The outer darker band of the spheroid is rich in Mg clays.

Fig. 3.- Imagen de microscopía de esferoides de dolomita creciendo entre cristales de aragonito. La banda oscura externa de los esferoides es rica en arcillas magnesianas.

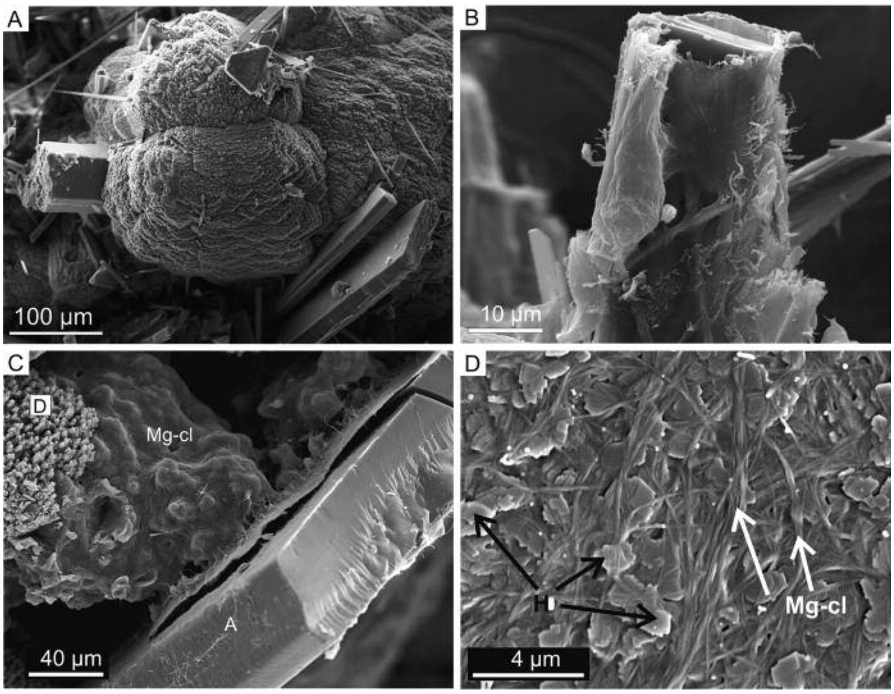

Fig. 4.- A) Dolomite spheroid growing over aragonite fibres. B) Aragonite crystal covered by a mat composed of intertwined Mg-clay fibres. C) Mat formed by Mg-clays (Mg-cl) covering an aragonite crystal (A) and dolomite spheroid (D). D) Fibres of Mg-clay (white arrows) intertwined with huntite flakes (black arrows).

Fig. 4.- A) Esferoide de dolomita creciendo sobre fibras de aragonito. B) Cristal de aragonito cubierto por una malla de fibras de arcillas. C) Malla de fibras de arcillas magnesianas (Mg-cl) que recubre un cristal de aragonito (A) y un glóbulo de dolomita (D). D) Arcillas magnesianas fibrosas intercreciendo con copos de huntita.

with all the minerals described above (Fig. 4B-D). They have been interpreted as Mg clays, specifically sepiolite, based on their morphology and EDS chemical composition, but their precise identification was difficult due to their small size and their small quantities in comparison with carbonates, what makes XRD identification difficult. On-going further XRD and TEM studies suggest the presence of kerolite, stevensite and sepiolite (Martin-Pérez *et al*., 2014) but this mineralogy still needs to be confirmed. Mg clays occur as flexible fibres between 1 and few tens of microns long and between 50 and 200 nm wide. They appear as individual fibres surrounding dolomite crystal subunits of dolomite spheroids and intergrowing with huntite flakes (Fig. 4D) or tightly interwoven forming mats. These mats can form irregular flakes, honeycomb structures, wrinkled planar structures, or coatings that tightly cover the surface of all carbonate crystals (Fig. 4B, C).

Discussion

Several factors have to be considered when interpreting the primary/diagenetic mineral association in the speleothems of Castañar Cave. The first factor, common to most caves, is that the supply of water is not continuous along time. Thus, water geochemistry continuously evolves, and diagenetic trends can be modified by the entrance of fresher and more diluted meteoric waters to the cave. This results in complex mineralogical sequences that overlap and may interrupt each other. The second factor is the fact that siliceous rocks (shales, greywackes and sandstones) are interbedded with the carbonates of the host rock. In Castañar Cave Mg and Ca are constantly supplied to cave waters due to the dissolution of dolostones and magnesites, and the weathering of shales and greywackes, mostly through hydrolysis (Martín-García *et al*., 2011) provide silica to the cave waters.

Mg rich minerals of Castañar Cave form by sequence precipitation due to progressive increase in the Mg/Ca ratio and CO_2 loss (Hill and Forti, 1997; Polyak and Güven, 2000; Alonso-Zarza and Martín-Pérez, 2008). The initial high Mg/Ca of the waters favours aragonite precipitation instead of calcite (Martín-García, 2012), which removes Ca from solution resulting in an increase of Mg/Ca ratios in the residual water. This increase, plus the progressive CO_2 degassing allow the precipitation of huntite, and eventually, when Ca is removed from solution, hydromagnesite and magnesite (Fig. 5). In this Mg-rich, alkaline conditions, and provided that the cave waters contain dissolved silica, Mg-rich clays can precipitate (Polyak and Güven, 2000) contemporarily to all the other minerals (Fig. 5).

The exact mechanisms of dolomite formation are not well understood yet, but two main processes are possible: 1) Transformation of the metastable huntite, which will also releases Mg for clay formation (Lippmann, 1973; Alonso-Zarza and Martín-Pérez, 2008). 2) Direct precipitation of dolomite on the Mg-clays mats. Such process has been identified in some Miocene alkaline soils (Casado *et al*., 2014) and in microbial dolomites of Abu Dhabi sabhka, where Mg-Si phases act as intermediates between exopolymeric microbial substances (EPS) and spheroidal dolomite (Bontognali *et al*., 2010). Mg clays can transform into dolomite and silica in lake systems (Wright, 2012) and they can also have an influence in dolomite formation in soils, because they promote the incorporation of Mg^{2+} in the structure of the dolomite (Díaz-Hernández *et al*., 2013). The influence of microbial biofilms in Castañar cave cannot be totally discarded, as their EPS would do the same effect that the inorganic mats. However, their presence in the speleothems is very small in comparison with the Mg-rich clay mats, and so far no other indication of organic influence has been found (Martín-Pérez, 2012).

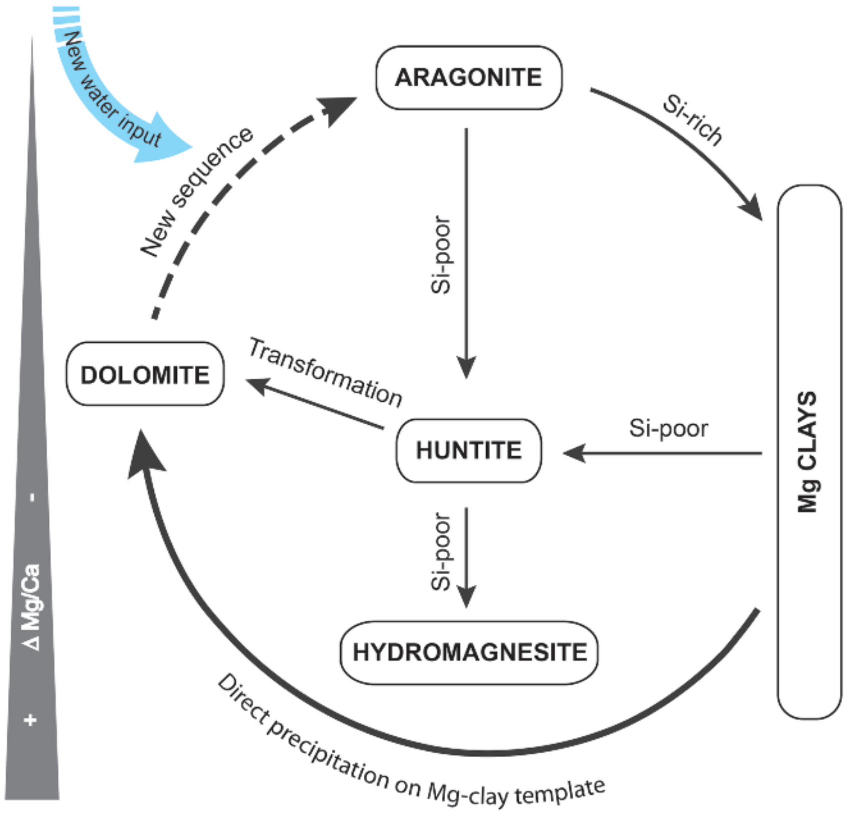

Fig. 5.- Sketch illustrating sequence precipitation of Mg-minerals and diagenetic relationships in Castañar cave.

Fig. 5.- Esquema de las secuencias de precipitación mineral y los procesos diagenéticos que intervienen en la formación de los minerales magnésicos de la cueva de Castañar.

Conclusions

The complex mineralogical association of Castañar Cave is the result of the evolution of Mg-rich water containing silica in alkaline environments. The discontinuous renovation of waters results in the overlapping of different primary-diagenetic processes making it difficult to provide a simple paragenetic sequence. Tentatively, the more simple sequence would include the formation of aragonite –huntite– dolomite. After aragonite formation, if Ca is consumed magnesite and hydromagnesite may form. A more complex and common sequence is produced in waters containing silica, which will allow the precipitation of Mg-rich clays at any stage. These clays can then serve as templates for direct dolomite precipitation.

Although more work is still needed to better characterize the Mg-rich clays, their presence in these alkaline environments is significant because they may provide a new and easy mechanism for dolomite formation at ambient temperatures.

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