Dolomite in caves: Recent dolomite formation in oxic, non-sulfate environments. Castañar Cave, Spain

Ana M. Alonso-Zarza *, Andrea Martín-Pérez

Dpto. de Petrología y Geoquímica, Fac. CC. Geológicas—Instituto de Geología Económica, Universidad Complutense-CSIC, 28040 Madrid, Spain

1. Introduction

Dolomite is a common mineral in the rock record but rare in recent superficial environments. Where it does occur, it is related to anoxic, sulfate-rich environments and microbial activity. The occurrence of some dolomite deposits in caves, however, indicates that dolomite formation is also possible in oxic, non-sulfate settings. Dolomite is forming at 17 °C and in oxic-vadose conditions on the host rocks and aragonite speleothems of the Castañar Cave, Cáceres, Spain. It appears as spheroids and dumbbells 50–300 μm in diameter that internally consist of micron-sized rhombic to rounded crystals. Initially this dolomite is Ca-rich, non-stoichiometric and poorly ordered. Mg-rich solutions allow the precipitation of metastable Mg-rich carbonates, such as huntite. This soon transforms into this Ca-rich dolomite, which later "ages" to form a more stoichiometric dolomite. These dolomites show similarities to those grown under anoxic, sulfate-rich conditions and their presence in caves provides a different setting that may contribute to the understanding of the "dolomite problem", including their initial formation and later recrystallization processes.

2. Geological setting and mineral associations in the cave

Castañar Cave is situated in Cáceres, Spain. It is hosted in Neoproterozoic rocks that form the core of the Ibor Anticline (Fig. 1). These rocks are shales and greywackes with interbedded dolostones and magnesites (Alonso Zarza et al., 2005a). Dissolution of the dolomitic beds and the extensive weathering of the shales and greywackes favor collapses which create and enlarge the cavities. This dissolution also determines the composition of the cave waters, which are rich in Mg. The waters show Ca/Mg ratios of 0.5–1.0 and are usually saturated in calcite, dolomite and aragonite (Sánchez-Moral et al., 2006). The mean temperature of the cave is 17 °C (very constant year round); the relative humidity of the air is close to 100% (Sánchez-Moral et al., 2006).

In the Castañar Cave, in Cáceres, Spain, dolomite occurs as a minor component of speleothems. Mineral precipitation in the cave follows the classic sequence. In this sequence as a result of the precipitation of calcite and aragonite, drip waters become relatively enriched in Mg, favoring the precipitation of hydromagnesite (Self and Hill, 2003). In Castañar, huntite globules or rosettes composed of platelets are commonly formed instead of hydromagnesite (Alonso Zarza et al., 2005b). Dolomite is common in moonmilk deposits together with huntite when drip water dries.

3. Methods and materials

The mineralogy of 33 samples from the Castañar Cave was studied using a Philips PW-1710 XRD system operating at 40 kV and 30 mA and with monochromated CuKα radiation. XRD spectra were obtained from 2 to 66° 2θ. The degree of ordering of the samples was determined from diffraction patterns obtained at a velocity of 0.5°/min over the range 31–39° 2θ. In order to check if composition and relative degree of order show some correlation, the ratio between the intensity of d015...
(superstructure peak) and d110, was measured according to standard procedures (Hardy and Tucker, 1988). Sixty nine samples were subjected to conventional optical petrographic analysis. Due to the fragility of the samples these were previously submerged in a resin containing Epofer EX 401 and Epofer E 432 in a vacuum system. In all cases the obtained thin sections were polished on both sides to favor their study with an electronic microprobe. Scanning electron microscopy was performed on 43 gold-coated samples. Observations were made using a JEOL 6400 working at 20 kV and with a resolution of 35 Å; secondary electron and backscattering detectors (BSE) were used together with an X-ray detection system (XDS) to obtain semi-quantitative compositions. Mg/Ca ratios of the dolomites were obtained using an electronic microprobe (JEOL JXA 8900 M) operating at 15Kv and 20 nA and with an electron beam of 5 μ diameter.

4. Dolomite features in the Castañar Cave

Macroscopically, the dolomite in the Castañar Cave occurs as an opaque white to orange precipitate (Fig. 2). This dolomite is found: 1) as scattered spheroids on the host rock shales; 2) growing on fibrous aragonite crystals (Fig. 3A and B) which it etches, corrodes and may completely replace; 3) nucleating on huntite CaMg3 (CO3)4 globules to form spheroids of dolomite that include relics of huntite and sepiolite; and 4) replacing huntite globules and fibrous aragonite crystals on which huntite had previously formed.

The dolomite in the cave is found as dumbbells (Fig. 3C) or spheroids (Fig. 3D) 50–300 μm across. The dumbbells are composite crystals that consist of fibrousradial aggregates that internally are formed by individual rhombic dolomite crystals (1 μm wide). The spheroids represent an advanced stage of growth of these dumbbells, in which the crystals are aligned along all the axes of the sphere to produce a radial, fibrous structure. Similar development has been recorded in the experimental growth of Ca–Mg carbonates (Castanier et al., 1989; Rivadeneyra et al., 2006). The individual dolomite crystals vary in shape from rhombohedral to rounded. Both the dumbbells and spheroids can be found isolated or coalescing to form coatings on the growth surfaces (host rocks, aragonite or huntite). Huntite coats some aragonite crystals. It occurs as white and fine precipitated that form globules. The globules consist of platelet crystals, ~1 μm long. Relics of huntite platelets are commonly found in the dolomite dumbbells and spheroids.

In some cases, dolomite totally replaces the aragonite or huntite to form a coarse mosaic of dolomite crystals (Fig. 3E). Dolomite mosaics are formed by rounded to euhedral crystals about 0.2 mm across; relics of huntite and aragonite are in cases preserved within them (Fig. 3F). Some of these mosaics serve as nucleation sites for new aragonite fans and huntite, although they can also be used as nuclei for the growth of further dolomite with no inclusions and no precursors.

The dolomite in this cave is poorly ordered. The degree of order varies from 0 (without superstructure peak d015) to 0.86. Fig. 4 shows the high degree of order of the host-rock dolomite and the variation of order of different samples from the cave dolomite. Analyses performed on individual crystals indicate Ca-rich dolomite in most of the cases. The values vary between 62.5% to 50% mol CaCO3, with a mean value of 56.5% mol CaCO3 (mean Mg/Ca ratio 0.77), which defines high-Ca calcian dolomites (Jones and Luth, 2002). Experiments on Ca–Mg carbonate formation at low temperatures (Fritz and Smith, 1970) have shown the dolomite produced to be disordered, and the Mg/Ca ratio to be around 0.6–0.7. Superstructure peaks were also lacking in the dolomite formed in these experiments; the authors considered this phase to be a precursor mineral for dolomite formation.

In the coarse dolomite mosaics in the Castañar Cave, the degree of ordering is higher and the mineral approaches stoichiometric composition. The Ca-richer dolomites show less ordering. Microprobe images in backscatter mode show the different composition of the dolomites from the closest areas to the aragonite fibers to the outer part. The dolomite that surrounds the aragonite is lighter indicating...
higher Ca content whereas the outermost and darker areas are closer to the stoichiometric composition of dolomite (Fig. 3F).

5. Discussion

In the Castañar Cave, Mg–Ca carbonates are forming as the final products of precipitation from water that becomes relatively enriched with respect to Mg due to the initial precipitation of aragonite and calcite. In Mg-rich solutions such as those found in this cave (Sánchez-Moral et al., 2006), the precipitation of aragonite is favored, whereas calcite growth is kinetically and thermodynamically inhibited due to the poisoning effect of partially dehydrated Mg (Berner, 1975). The latter attaches to the surfaces of incipient calcite nuclei, inhibiting their growth and favoring the formation of aragonite (Lippmann, 1973; Raz et al., 2000), which contains no Mg. Thus, the solution becomes relatively enriched in Mg, and can become saturated in Ca–Mg phases such as magnesite, huntite (Deelman, 2003) or hydromagnesite in addition to dolomite (Sánchez-Moral et al., 2006). Huntite can form at low temperature surface or near-surface conditions; either by direct precipitation from Mg-rich solutions or by interaction of the Mg-rich water with precursor carbonate minerals (Dollase and Reeder, 1986). It is commonly recognized in moonmilk deposits in caves (together with
magnesite and dolomite) (Polyak and Güven, 2000), in which the sequence of mineral precipitation due to the progressive increase in the Mg/Ca ratio and CO$_2$ loss is: calcite, aragonite, dolomite, huntite and magnesite (Casas et al., 2001). This sequence, however, does not take into account the possible transformation of metastable minerals into more stable forms. Experimental studies (Davies et al., 1977) have shown that huntite always precipitates before dolomite, the main factor controlling the formation of both being the increase/maintenance of the CO$_3^{2-}$ concentration. Huntite grows before dolomite since its more open structure allows Mg dehydration more readily (Lippmann, 1973). The necessary increase/maintenance of CO$_3^{2-}$ can be obtained either by dissolution of previous hydrous Mg carbonates (Kinsman, 1967) or by photosynthetic activity (Davies et al., 1977), although in the cave the latter is impossible due to the lack of light.

The possibility that huntite might be a precursor of dolomite has been proposed (Lippmann, 1973), but this transformation has rarely been taken into account, even when considering solutions to the “dolomite problem”. After 31 years of continued experiments, dolomite has never been found to form inorganically at 25 °C (Land, 1998). There is agreement that dolomite formation is rare under environmental conditions due to thermodynamic constraints (Machel and Mountjoy, 1986). However, some catalysts (Land, 1998) might allow for the easy low temperature laboratory synthesis of dolomite. In recent years it has been shown that, in anaerobic environments, sulfate-reducing bacteria can induce the low temperature formation of Ca-rich dolomite and Mg-rich calcite, both in natural environments and under experimental conditions (Vasconcelos and McKenzie, 1997; Van Lith et al., 2003). Bacteria play a passive role in this dolomite formation; precipitation is induced simply because of the modification of the microenvironment around the bacterial cells (Vasconcelos et al., 2005). Huntite itself (Lippmann, 1973) or hydrous calcium magnesium carbonates (Kelleher and Redfern, 2002; Schmidt et al., 2005) may also act as catalysts or precursors, as shown by the experimental synthesis of dolomite in the latter is impossible due to the lack of light.

In Castañar Cave, the common association of huntite and dolomite and the presence of huntite relics in some of the dolomite mosaics, strongly indicate that dolomite is formed by the transformation or replacement of huntite. At present no clear conclusions can be drawn on possible organic influences for two reasons: i) laboratory-produced organic (Castañier et al., 1989; González-Muñoz et al., 2000; Van Lith et al., 2003) and inorganic (Fernández-Díaz et al., 1996) crystalline habits and morphological sequences are the same as those seen in the dolomites in the Castañar Cave, and ii) organic morphologies (such as fungal filaments or spheres of possible bacteria) are very rare and were found only on the surface of the dolomites (never inside), suggesting that either the organic structures are lost once the crystals are formed, or that they do not play a role in the formation of dolomite. In any event, candidate microbes ought not be light-dependant since the cave is a dark (as well as oxic and sulfate-poor) environment. Further studies are needed to determine the influence of microbes in the formation of this dolomite.

In the Castañar Cave, the dolomite-type mineral that initially forms is Ca-rich dolomite. In recent sedimentary environments it is very rare; where it does occur it is often related to anoxic, sulfate-rich environments. The Ostwald ripening process (Ostwald, 1900), in which surface recrystallization is due to the growth of large crystals at the expense of smaller ones. There is no change of volume but the number of crystals per unit volume decreases. Equilibrium is reached with the formation of a final single crystal or when all the crystals are of the same size, which in the Castañar Cave occurs in the mosaics formed by the largest dolomite crystals. Texturally this transformation is seen as a loss of the radial fibrous structure (of both the dumbbells and spheroids), to form single crystals with an undulate to straight extinction pattern, which are more ordered dolomites.

6. Conclusions

Dolomite formation in Castañar Cave was favored because the cave forms by dissolution of dolomites and magnesites. Prior precipitation of calcite and aragonite favors the enrichment of the vadose waters with Mg, in which huntite precipitates before dolomite because of its more open structure. However it transforms to poorly ordered Ca-rich dolomite later ages to more ordered dolomite, forming coarse crystalline mosaics. The initial dolomite shows dumbbell and spheroid morphologies similar to natural dolomites formed in the presence of bacteria and to experimentally grown “organic” and “inorganic” dolomites.

Dolomite is a common mineral in ancient marine and terrestrial deposits. In recent sedimentary environments it is very rare; where it does occur it is often related to anoxic, sulfate-rich environments. It seems, however, to be present in small quantities in several vadose
caves, where it forms in oxic, sulfate-poor environments and at low temperatures. Recently formed cave dolomites may be more abundant than presently believed, and further studies are needed to determine their exact mechanism of formation and to clarify the possible influence of microbes. Caves may be important, natural, low temperature environments for dolomite formation; such dolomite may provide new information that could help solve the “dolomite problem”.

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