Barite replacement boxwork in the Frasassi caves (Italy)

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Abstract: The Frasassi caves, located in the Sentino River Gorge in Ancona Province (Marche, Italy), contains boxwork in a small zone in the inner part of the cave system where it is closely associated with subaqueous corrosion produced by sulfuric acid speleogenesis. The boxwork consists of barite that replaces calcite spar-filled veins and limestone porosity and projects from the corroded cave walls. The replacement involved only the calcite that protrudes from the rock surfaces, indicating that the process took place in the cave environment, and therefore the boxwork is not simply a product of differential corrosion. I hypothesize that the boxwork formed in nearly stagnant bodies of sulfidic water as a consequence of lateral recharge of O₂-rich bicarbonate water moving upward along the walls because of its lower density. The acidity produced by the oxidation of H₂S enhanced limestone corrosion and incision of rills and channels, while also releasing sulfate ions that induced the precipitation of barite. This sulfuric acid process was sufficiently slow to dissolve the micritic bedrock and replace spar with barite, preserving the shape of the network of fissures and pores formerly filled by calcite.

Keywords: boxwork, karst, sulfuric acid speleogenesis, barite, Frasassi caves

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INTRODUCTION

Boxwork is a solutional cave feature consisting of thin veins that protrude from bedrock walls, speleothems and clay deposits. Boxwork is typically composed of calcite, but it can be made of many different minerals. It primarily develops from differential erosion between a network of resistant material and the surrounding rock, but it can also be created through other processes (Hill & Forti, 1997, and references therein). The Frasassi boxwork was first reported by Galdenzi (1990), who initially identified it as protruding sheets of calcite based on morphology and a misleading field test with HCl.

This research analyzes the distribution and characteristics of boxwork along with related morphologies and mineral deposits and provides a first tentative hypothesis on their development. For each studied feature, the elevation was determined with a hydraulic digital level, connected to a pre-existing tachometric traverse, and standardized with respect to a height zero reference located in the main spring at the cave entrance. Mineralogical and isotopic analyses were conducted on the most significant samples. Analytical methods are described in the [Supplementary file](#).

GENERAL CAVE SETTING

The Frasassi cave system (43°24'N, 12°57'E) is located in the Sentino River gorge in Ancona Province, Marche, Italy (Fig. 1), and is one of the most studied hypogene caves in Italy (Galdenzi & Jones, 2017, with references therein). Sulfuric acid speleogenesis is still active in the lower sulfidic passages.

The Frasassi caves consist mainly of sub-horizontal passages that are organized into superimposed, interconnected levels related to deepening of the river valley. The lower levels develop close to the local base level, and include two main levels at ~225 and 250 m asl. Dissolution occurred in the shallow phreatic zone due to the oxidation of sulfide (Galdenzi, 1990). Patchy replacement gypsum as well as corrosion pockets from subsequent gypsum removal demonstrate the contribution of H₂S oxidation to subaerial corrosion above the paleo water table (Galdenzi, 1990; Galdenzi & Maruoka, 2003).

The hydrology and chemistry of the cave water are well known (Galdenzi et al., 2008). Groundwater in the shallow phreatic zone is a mixture of meteoric bicarbonate water and rising mineralized water. In many stagnant pools, groundwater stratification is common. The surface layer can vary from purely

Fig. 1. A) Plan of the cave system, with location of the boxwork area (BX); s: sulfidic spring; e: cave entrance. B) Profile of the Budellone Basso di Sala della Neve, projected on the main trend of the passage (drawn based on the survey of E. Sbaffi & G.G. Recanati).

bicarbonate to intermediate between seepage and mineralized water, typically with some dissolved O_2 and without measurable H_2S . The thickness of these surface layers ranges from a few cm to 5 m (Galdenzi et al., 2008). The sulfidic groundwater is cold (about $13^\circ C$), and salinity (mainly sodium and chloride) approaches 2 gL^{-1} . The water also contains up to 20 mgL^{-1} sulfide, up to 220 mgL^{-1} sulfate and minor ions such as Ba^{2+} , Sr^{2+} , Li^+ , and F^- , which are almost absent in the infiltration water. Dissolved salts likely originate in the underlying Triassic evaporitic formation (Anidridi di Burano), composed by alternation of dolostone, anhydrite and minor halite and known in the area only from deep wells (Anelli et al., 1994). The presence of barium in the sulfidic water was initially reported by Bertolani et al. (1977). Concentrations range from 0.11 to 0.19 mgL^{-1} in samples collected in a variety of locations (Macalady, personal communication). Based on the measured ion concentration, the sulfidic water is oversaturated with barium sulfate. Oversaturation of barium sulfate is common in sulfidic groundwater in Central Italy (Baldi et al., 1973), with barium sourced by underlying Triassic evaporitic strata. In certain locations, rising sulfidic water produced economic barite-celestite deposits (Barbieri & Masi, 1978).

THE BOXWORK ZONE

The studied boxwork is located in the Budellone Basso di Sala della Neve, a passage remote from the Sentino River in the southwestern sector of the cave (Fig. 1A). The Budellone is the main feeder to a large horizontal passage at 225 m asl , 26 m above the emergence of sulfidic water. Below the steeply inclined entrance the Budellone is a system of small, inclined or sub-horizontal, commonly anastomosing tubes. These passages have an irregular profile with many loops, and original phreatic features are excellently preserved (Fig. 1B). Deposits of subaerial replacement gypsum are lacking, with only a few remains found at the top of the entrance ramp. Aluminosilicate-rich clay deposits, which are widespread in the rest of the cave, are absent in this zone. Dripstone and vadose speleothems are also rare, in contrast to the rest of the cave, as this zone underlies a marly unit and receives little percolating water. Inside the Budellone, the water table can be reached in many places at 2.5 m above the spring, generally at the bottom of steeply

dipping passages. A layer of oxygen-rich bicarbonate water floats above the sulfidic water, with a thickness that can range from a few to tens of centimetres. This thin bicarbonate layer prevents the release of H_2S into the cave atmosphere.

Widespread boxwork highlights the well-developed network of veins and pores filled by spar in the limestone (Fig. 2A, B). The boxwork generally protrudes several centimeters from the walls, exceeding 10 cm in a few places. It is composed of barite that replaced the original calcite spar. Cross sections of rock samples verified that only the portion of the veins that protrudes from the wall surface is replaced by barite, leaving the veins in the bedrock unaltered. The boxwork is commonly covered by a thin carbonate coating and generally has a reddish or brownish colour.

The boxwork zone is characterized by many different types of corrosional rills and channels that formed on the walls and ceilings by ascending fluids, likely water, that moved upward due to their lower density.

Most of the rills are a few millimeters wide and deep and extend for several decimeters. They begin either from half-cupolas or directly from injection points on the cave walls (Fig. 2C, D). Larger channels emerge from minor passages or niches in the walls. These channels can be over 10 cm wide and several centimeters deep. Their sections are generally rectangular, with clean, flat upper surfaces and steep, sub-vertical walls (Fig. 2E). Some of these wall channels reach the passage ceiling where they become inclined roof channels.

Incision of the rills and wall channels coincided with boxwork growth, as demonstrated by the presence of boxwork inside the niches and in some channels. On the ceilings, small flat cupolas likely represent former air bells that were rich in acidic gases (H_2S and CO_2) capable of contributing to the dissolution.

In most passages, the floor is covered by a thin layer of whitish mud that is weakly cohesive, is $94.5\text{--}97.5\%$ carbonate composition and is commonly cracked by shrinkage structures. Detached boxwork lies on the whitish mud on the floor, indicating that the mud was deposited before the boxwork collapsed. White calcite rafts are abundant in places, hence the name of the cave passage ('neve' is Italian for snow). Rafts form small masses on the floor and walls and can overlie the boxwork.

Boxwork formed up to 15 m above the spring level, but an upper limit of distribution on the cave walls

Fig. 2. A) General view of a cave wall covered by boxwork; B) Detail of boxwork; C) Ascending corrosion rills from a half-cupola; D) Details of rills from injection points; E) Co-existence of boxwork and an ascending channel rising from a tributary passage.

cannot be clearly defined. Below this height, wall features record changes that occurred during or after boxwork formation. The walls may be bare at different heights due to the destruction or detachment of the boxwork, and corrosional notches may mark previous chemoclines between different bodies of water. Subaqueous calcitic coatings are common at various heights and encrust the boxwork (Fig. 3A). These depositional events must have co-existed or alternated with corrosion by ascending fluids, as corrosion rills commonly incise calcite coatings on boxwork (Fig. 3B, C). The vertical distribution of these horizontal

paleolevels is strongly influenced by local conditions, and in most examples, they do not extend into nearby passages.

GEOCHEMISTRY

Carbonates

The isotopic composition of the inorganic carbon in the cave water was monitored from 2008-2010 (unpublished data). The average $\delta^{13}\text{C}$ value was -10.5‰ for the seepage water, -8.9‰ for the sulfidic groundwater, and -8.6‰ for the less diluted sulfidic water rising from the aquifer's deep zones. The $\delta^{13}\text{C}$ of bicarbonate water at the surface of stratified lakes varied from -7.8‰ to -5.6‰ . Detailed measurements from a stalagmite revealed that the $\delta^{13}\text{C}$ values ranged between -10 and -5‰ during the last 13 ka (Tuccimei et al., 2003). A similar range of $\delta^{13}\text{C}$ values was obtained from scattered samples of dripstones. In the limestone bedrock, the $\delta^{13}\text{C}$ values were about $+2\text{‰}$. All the samples from the boxwork study area had high $\delta^{13}\text{C}$ values, compared to cave water and calcite speleothems (Table 1). The whitish carbonate mud on the floor and the limestone bedrock had similar $\delta^{13}\text{C}$ values. The $\delta^{13}\text{C}$ values of calcite rafts and crystals on the floors and walls ranged between -1.4 and -4.8‰ .

Sulfur

The $\delta^{34}\text{S}$ measured in barite samples ranged between $+15.3$ and $+17.3\text{‰}$ (Table 1). These values can be compared to those of the sulfur species dissolved in the sulfidic groundwater

Fig. 3. Co-existence of depositional and corrosional features. A) Coating of subaqueous calcite crystals over the boxwork; B) Ascending channels carved in bedrock and calcite coating; note the hole in the rock created by the channel; C) Detail of the calcite coating corroded by a rill from an injection point. (Photos by A. Gianangeli).

(Galdenzi & Maruoka, 2003; unpublished data of 2008–2010 monitoring). In the water, the $\delta^{34}\text{S}$ varied between -18 and -13‰ for dissolved sulfide and between +19 and +22‰ for dissolved sulfate. Sulfate $\delta^{34}\text{S}$ values decreased up to +13‰ during periods of high freshwater dilution.

Table 1. Isotopic composition of the cave samples. In brackets the sampling sites of Fig. 1.

Calcite samples		$\delta^{13}\text{C}$ ‰ PDB	$\delta^{18}\text{O}$ ‰ SMOW
B03	limestone	-1.7	-4.6
B22 (5)	spar vein	0.9	-5.7
B24 (7)	spar vein	0.3	-5.2
F57 (5)	whitish mud	1.8	-3.3
F62 (3)	whitish mud	1.2	-4.4
F58 (5)	raft	-1.4	-7.1
F61 (6)	raft	-2.5	-7.7
B21 (5)	wall paleolevel	-3.9	-6.5
B23 (8)	crystals on boxwork	-2.9	-6.9
F60 (7)	crystals on boxwork	-4.8	-7.5
Barite samples		$\delta^{34}\text{S}$ ‰ V-CDT	
B40 (7)	boxwork	16.7	
B48 (2)	boxwork	16.6	
B59 (7)	boxwork	16.9	
B62 (7)	boxwork	15.7	
B25 (4)	boxwork	15.3	
B39 (7)	boxwork	16.4	
B53 (6)	dark boxwork	16.9	
B54 (6)	reddish boxwork	15.9	
F59 (8)	boxwork	16.6	
F60 (8)	boxwork	17.3	
Gypsum samples			
B46 (1)	replacement gypsum	-16.9	
B47 (1)	replacement gypsum	-17.4	

DISCUSSION

Frasassi boxwork is distinct from boxwork found in other caves because it is not a simple product of differential corrosion between veins and the surrounding rock. It is the result of a specific cave process that coupled micrite corrosion and the replacement of calcite spar by barite. The barite replacement only affects the protruding parts of the calcite veins, and does not penetrate into the limestone, where the veins maintain their original composition.

Barite replacement boxwork occurs in a phreatic zone that fed a wide water table passage of the cave tier at +26 m (Fig. 1B). It is a rare phenomenon in the cave system due to local conditions that did not occur anywhere else. Barite-replaced boxwork developed under subaqueous conditions when the passages had almost reached their final shape, in locations that probably were cut off from the cave atmosphere (Fig. 1B). These passages were still filled by sulfidic water, which was the source of barium and sulfate ions implicated in the replacement process (Fig. 4).

These bodies of sulfidic water were stagnant or had little movement, and water inflow from the walls produced limestone corrosion and a diffuse incision of ascending rills. The inflowing fluid likely was vadose bicarbonate water, which would have moved up the walls towards the groundwater surface due to its lower density. Bicarbonate water is derived from surface infiltration, and could have descended below groundwater level because of the hydraulic head in fissures inside the limestone.

The inflowing fluid generated the acidity responsible for the observed bedrock corrosion (Fig. 4). The oxygen carried from the surface by vadose water could have promoted the oxidation of H_2S to sulfuric acid, which is considered to be the main cave-forming process in the cave (Galdenzi, 1990), and is associated with the release of bicarbonate ions derived from limestone dissolution. The process was sufficiently slow to result in the complete removal of micrite, while spar was replaced by barite, setting into relief the network of fissures and pores.

The inflow of oxygenated, bicarbonate water could not directly produce barite precipitation. Barite is poorly soluble, but vadose water has a low sulfate content with only trace amounts of barium (Bertolani et al., 1977). Furthermore, barite solubility is only slightly affected by pH, Ca^{2+} , Mg^{2+} , and Sr^{2+} (Zhen-Wu et al., 2016), and therefore the acidity produced by sulfide oxidation should not influence barite precipitation. Barite precipitation might have been induced by the release of sulfate ions in the oxidation process, which produced a local increase in the SO_4^{2-} concentration sufficient to precipitate barite. However, it is important to note that sulfate derived from H_2S oxidation was not directly involved in the replacement process. Barite $\delta^{34}\text{S}$ values (+15.3 to +17.3‰) are dramatically different from the negative values of

Fig. 4. Schematic model of the replacement process in sulfidic groundwater. Note that the $\delta^{34}\text{S}$ values of barite are less high than the present $\delta^{34}\text{S}$ of water sulfate, suggesting a contribution of sulfate ions produced by H_2S oxidation.

dissolved sulfide (-18 to -13‰) and are close to the present $\delta^{34}\text{S}$ of dissolved sulfate, which normally ranges between +19 and +22‰. On the contrary the $\delta^{34}\text{S}$ barite values are compatible with an increase in dissolved sulfate due to H_2S oxidation.

After the main phase of boxwork growth, the water table progressively fell, until the whole zone was exposed to the cave atmosphere. This process was not continuous, because the groundwater level is dependent on erosion or sedimentation processes in the Sentino River valley. Changes in the elevation of the water table would have produced significant changes in the groundwater drainage in each passage.

The lowering of the water table facilitated gas exchange with the cave air, and the resulting CO_2 degassing favored carbonate oversaturation in the groundwater. During this period, the boxwork was coated with subaqueous calcite, as indicated by crystalline coatings and overlying rafts. The carbon in these carbonate deposits has higher $\delta^{13}\text{C}$ values than present cave waters, both sulphidic and vadose. It has values consistent with carbonate derived from limestone bedrock dissolution rather than atmospheric CO_2 or decaying organic matter.

In the boxwork zone, the coexistence of corrosional rills and channels with calcite coatings and the evidence of crystal re-corrosion due to ascending water demonstrate that lateral freshwater recharge responsible for the corrosion was occurring. Alternating calcite corrosion and precipitation in the same passage was probably caused by changes in the elevation of the chemocline, amount of recharge, and also by variation of degassing towards the cave atmosphere. These processes resulted in boxwork that is well preserved over large areas, some coated with calcite and some not, at various elevations within the cave passages.

Close relationships between boxwork, corrosion rills and channels, and the process of calcite deposition/corrosion in the same body of water highlight the complexity of the chemical processes involved in speleogenesis in the shallow phreatic zone at Frasassi.

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METHODS

Analytical methods

X-ray diffraction

X-ray diffraction of the boxwork samples was performed using a Rigaku Miniflex 200sc101 powder X-ray diffractometer, CuK α radiation, kV = 30, Ma = 15 at Hartwick College, Oneonta, New York, U.S.A.

Carbon-13 and Oxygen-18 analysis of carbonate samples

The carbonate samples were analyzed in duplicate by Iso-Analytical Limited (United Kingdom). The average value is reported in delta notation. Two milligrams of fine dry powder of each sample was placed in clean glass septum capped vials. The vials were then sealed and their headspaces flushed with pure helium (99.995%). After flushing, ~0.5 mL of pure phosphoric acid, prepared according to Coplen et al. (1983), was injected into the vials and mixed with the sample powder. The samples were left to react for a period of not less than 36 hours to ensure complete conversion of carbonate to carbon dioxide for analysis. Standard reference materials were prepared in the same manner as the samples.

The CO $_2$ gas was then analyzed by continuous flow isotope ratio mass spectrometry. The CO $_2$ is flushed from the septum vial using a double holed needle and resolved on a packed column gas chromatograph. The carbon dioxide then enters the ion source of a Europa Scientific 20-20 IRMS and is ionized and accelerated. Here, gas species of different mass are separated in a magnetic field then simultaneously measured using a Faraday cup collector array at m/z 44, 45, and 46.

The reference material used for this analysis was the laboratory's calcium carbonate standard IA-R022 ($\delta^{13}\text{C}_{\text{V-PDB}}$ -28.63‰ and $\delta^{18}\text{O}_{\text{V-PDB}}$ -22.69‰), which is traceable to NBS-19 Limestone ($\delta^{13}\text{C}_{\text{V-PDB}}$ +1.95‰ and $\delta^{18}\text{O}_{\text{V-PDB}}$ -2.2‰). During analysis, NBS-18 calcite ($\delta^{13}\text{C}_{\text{V-PDB}}$ -5.00‰ and $\delta^{18}\text{O}_{\text{V-PDB}}$ -23.00‰), NBS-

19 limestone and IA-R022 were analyzed as check samples.

Sulphur-34 analysis of sulfate samples

Sulfur isotopic compositions in cave samples were determined by a helium gas continuous flow isotope ratio mass spectrometer (CF-IR-MS; ISOPRIME-EA; Isoprime Ltd., UK) at the University of Tsukuba (Ikehata and Maruoka, 2016). The sulfur isotopic compositions are expressed in terms of $\delta^{34}\text{S}$ (‰) relative to the V-CDT (Vienna-Canyon-Diablo-Troilite) standard. The results of three IAEA (International Atomic Energy Agency) silver sulfide standards (IAEA-S-1, -0.3‰; IAEA-S-2, +21.80‰; IAEA-S-3, -31.95‰; Mayer and Krouse, 2004) were compared to constrain the $\delta^{34}\text{S}$ values. The isotopic compositions of sulfur were determined to a precision of $\pm 0.1\text{‰}$ (1 σ), the precision being reached by combining the standard deviations for repeated analyses of samples and standards (Maruoka et al., 2003).

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