

SPELEOTHEMS IN CAVITIES DEVELOPED IN MAGMATIC ROCKS

Juan Ramón Vidal-Romani ⁽¹⁾; Jorge Sanjurjo-Sánchez ⁽¹⁾; Marcos Vaqueiro-Rodríguez ⁽¹⁾; Laura González-López ⁽¹⁾ and María José López-Galindo ⁽¹⁾

(1) University Institute of Geology, Campus de Elviña s/n 15071 – Coruña, Spain, e-mail: juan.vidal.romani@udc.es

Abstract Four types of natural cavities in magmatic rocks are known: (1) developed along fracture planes, (2) associated with residual block fields, (3) tafone, and (4) lava tube. Due to the low permeability of the rock, these openings are the only access for the runoff, always in water flows of low velocity (trickles) toward inside the rocky massif that will be weathered forming small fissural regoliths that are moved by the water and then deposited, giving rise to granular detrital accumulations (primary speleothems) of openwork texture always. The porous system of these sediments is the temporal refuge for different microorganisms (bacteria, algae, fungi, testate amoebae, spores, diatoms, collembola and mites, etc.) which inhabit the cavity during the humid stage. Their organic activity provides the water with metabolic compounds able to solubilise ions, mainly Si, of the rock without changes in pH which in the dry stage will precipitate by oversaturation as opal-A and other authigenic minerals that will not only contribute to cement the primary speleothems but also to form the secondary speleothems. The shape of the speleothems, either cylindrical or planar, is mainly defined by the way of the water circulation at low velocity by dripping, capillarity, foam-drops like textures or by laminar flow. The relationship between the microbiological activity and the processes of weathering, dissolution and sedimentation justifies their name as biospeleothems.

1. Introduction

The speleothems studied in this paper are formed during the water circulation at low velocity (trickles) through the fissural system of massifs of igneous rocks. In the water/rock contact the physical weathering of the rock produces a heterometric detrital aggregate of mineral grains which are first moved by the water as a hydro-suspension (slurry) and then deposited on the walls, floor or ceiling of the cave. These types of speleothems may be considered as residual materials because they derive from the rocky substratum of the cavity, but other authigenic species are associated with them, i.e., generated in the same cave at room temperature as amorphous opal, evansite, bolivarite, struvite, pigotite, taranakite, allophane, hematite, goethite. The most common mineral species of all of them is the amorphous opal (called coralloid in the old works (Caldcleugh 1829; Swarzew and Keller 1937), though here the term opal-A is used (Vidal Romani et al. 2010 a and b). An additional feature of the silica hydrogel from which the opal-A speleothems are formed is that it may be the base for the formation of new authigenic mineral species called whiskers (Twidale and Vidal Romani 2005). They are twined crystalline aggregates of mineral species as halite, gypsum, siderite, cerusite, plumbean aragonite, malachite, etc., though this list is growing every day more. However, in the caves developed in basic igneous rocks (gabbros, diorites, peridotites, basalts), the amorphous opal speleothems are not very frequent, being habitual other minerals, also authigenic, as the carbonates of Ca, Mg, Fe, Pb, etc. All these minerals were described in caves of very different rock types and varied geographic-climatic environments: temperate humid, arid to cold regions (Spain, Portugal, Açores Islands, United Kingdom, Germany, Poland, Czech Republic, Sweden, Finland, Corea), tropical (Brazil, Venezuela, Madagascar), arid (South Australia, Argentina, Nigeria, Botswana, Mexico, U.S.A., etc) (Willems et al., 1998, 2002; Twidale and Vidal Romani

2005; Vidal Romani et al. 2010).

2. Morphological features of the speleothems

Speleothems are not only differentiated by their mineralogical composition but also by their morphology. For example, carbonates or whiskers associated with the amorphous opal speleothems are always presented as crystals of high idiomorphy in spite of their small size. On the contrary, the amorphous mineral species are adapted to the relief of the surface on which they deposit, and their morphology is related to the features of the dynamics of the fluid which originates the speleothem.

Types of speleothems of cavities in magmatic rocks.

The following types are distinguished:

2.1.- Cylindrical speleothems.

They are associated with water movement either by dripping or capillarity. There are different types as follows:

Stalactites s.s.: they are formed on the upper part of rock fissures (the ceiling or eaves of cavities) when the weight of the drop overcomes the superficial stress (then dripping is produced).

Grass-shaped speleothems: multiple associations of very thin (maximum 1 mm) cylindrical forms and associated with the ceiling, walls or floor of cavities. These speleothems grow by deposition associated with capillary movements of the water through the agglomerate mass of clastic accumulations of angular grains soaked in water.

Anti-stalactites: These individual speleothems (Vidal Romani and Vilaplana 1984) grow by capillary movements of the water from a clast grain mineral

agglomerate soaked in water. They are usually thicker (up to 4 mm of diameter) and reach longitudinal developments between 4 and 10 mm.

Stalagmites s.s.: these speleothems are infrequent in the igneous rock caves. They are formed by the precipitation of the substances dissolved or dragged by the water which fall from the stalactites s.s..

Club-like stromatolites s.l.: they are formed by the growth of biofilms of blue-green algae while there is humidity inside the cave. When the environment dries, the algae transform into the substratum of the new generation of algae which will grow in the following humid stage.

2.2.- Planar speleothems.

They may normally appear associated on any flat, low relief surface (either ceiling or floor) but even in subvertical surfaces as far as they do not overpass the threshold of dripping which is given by the stress adherence of the water to the cave rocky surfaces. Different types of planar speleothems are distinguished:

Flowstone, rimstones and microgours: they are continuous covers of the cave rocky surface with variable thicknesses and may also hide the rock micro rugosity. They are disordered accumulations of mineral clasts pushed by the water layer during the humid phases marked by lineal accumulations with sinuous shape behind the ones that may even hold water temporarily. Flowstones, rimstones and associated pool (microgour) are associated with flat (either ceiling or floor), gentle-sloped and inclined or even subvertical surfaces when the flow speed does not overpass the threshold of water-rock superficial adherence in the trickles.

Water drop structures: they are similar to the foam-like structures formed on the upper part of the beach when an advance front of the water layer is individualized into small drops. They are associated with the ceiling of the cavity where the water is divided into small drops which, by superficial stress, attract a thin coat of clasts of minerals that the water evaporation will cement as opal-A allowing the conservation of the morphology of the drop.

3. Methods

Different analytical techniques have been used to study these speleothems: ICP Masses, XR.D., XE.F. and mainly S.E.M.; all of them, but the last, are destructive analytical methods. Though S.E.M. gives morphological information (texture, structure, morphometry of grains), it also gives data of elemental composition with the backscattered X-R. From the first works (Caldcleugh, 1829) these speleothems were considered to be formed by water dripping ignoring the existence of other types of speleothems. In this work, the information obtained by Stereoscopic Microscopy is included, allowing to establishing the complete sequence of formation of speleothems.

4. Results and discussion

The following stages are distinguished in the formation of speleothems: (1) accumulation of the granular material coming from the fissure regolith and transported by water; (2) first colonisation by microorganisms as bacteria, algae, fungi, amoebae, collembola and mites; (3) formation, dissolution and precipitation of amorphous opal; and (4) formation of whiskers from the silica hydrogel. The activity of the microorganisms that inhabit the cavities promote the dissolution of Si, mainly, enhanced by biochemical weathering (Ehrlich 1996) when contributing to the sedimentary environment with low molecular weight organic acids (mainly oxalates) with chelant ability determinative in the biochemical weathering without pH changes (McMahon and Capelle 1991; Baker et al. 1997). Later, the dissolved Si precipitates as amorphous opal $\text{SiO}_2 \cdot 1.5(\text{H}_2\text{O})$, 100 times more soluble in water converting the generation of speleothems into a continuous process always depending on the water circulation through the fissure system. Each time it rains again, the re-circulation of water through the fissural system of the rocky massif produces the re-dissolution of the amorphous opal and its later re-precipitation. This phase in the evolution of the speleothem is favourable for the growth of authigenic minerals of small size, whiskers, which are located on the points where water accumulates, for the cylindrical speleothems on their final edge and for the planar speleothems or flowstone in the places where the water accumulates as the depressions of the microgour or pool. The mineralogy of these whiskers is very varied: gypsum, carbonates, halides, though the most common is gypsum ($\text{SO}_4\text{Ca} \cdot 2\text{H}_2\text{O}$). In some cases, whiskers appear as isolated individuals or in little quantities except for gypsum which always gives well twined crystalline associations and of varied idiomorphy in physical continuity, though not crystallographic, with deposits of opal-A. Some authors attribute the presence of S necessary for the formation of gypsum to the activity of microorganisms (Franklin et al. 1994; Welch and Ullman 1996) which are able to produce sulphate oxides from oxidation of organic matter, this latter invariably associated with the zones where the speleothems are observed (Vidal Romani et al. 2003). Some authors (García Ruíz and Miguez 1982) achieved to reproduce the process in laboratory using a silica hydrogel base to obtain the growth of crystals of different substances in very low concentrations. In the cavities of igneous rocks, gypsum whiskers are normally found, but also, in accordance with our own observations, whiskers of calcite, aragonite, plumboaragonite and phosphates. Some authors (Van Rosmalen and Marchéé 1976) explain the diverse morphology of the gypsum whiskers formed from silica hydrogel by the presence of different additives or impurities. The lowest abundance of opal-A speleothems is symptomatic in cavities (e.g. lava tube) (Woo, Choi and Lee 2008) developed in basic igneous rocks (syenites, granodiorites, diabases, etc.) and their physical association with calcite crystals obviously formed (Beinlich and Austrheim 2012) by combination of CO_2 dissolved in water with brucite or other carbonates existing in the rock. At pressure and room temperature, Si does not form stable crystalline structures but minerals of low temperature (opal-A) that with the time evolve toward more stable polymorphs of silica as opal-CT (Bustillo 1995). Notwithstanding, the first essays to date opal-A speleothems by O.S.L. (Sanjurjo and Vidal Romani 2011)

seem to indicate that at least in some climatic environments the transition Opal-A to Opal-CT may be delayed many thousands of years.

These types of microenvironments developed in the porous system of the cylindrical speleothems or the opal clasts mantles that form flowstones and their small gours where water is kept temporarily and considering the great quantity of different biological remains found in them seems to be a very suitable environment for the development of microorganisms which develop their vital cycle while water remains. Their disappearance by evaporation during the dry stages causes the precipitation of amorphous opal dissolved in it fossilizing the

microorganisms or their remains that are immediately coated by opal-A. Each time the rain provides the fissural system with water, life regenerates, at least partially, in the speleothem producing the germination of the latent or resistance forms developed in diatoms, spores, algae, amoebae, testate, etc, which live and develop in the micro speleological system. At the same time, other organisms (mites and collembola) use the speleothem as physical support to move and feed on organic matter. The growth processes of the speleothems are superposed to the ones of the development of microorganisms in these cavities causing subtle differences between life and sedimentation, justifying the name of biospeleothems given to these deposits.

5. Conclusions

The partially open fissure systems of granitic massifs through which water circulates at very slow speed (trickles) are natural environments with which different types of neomineralizations are associated: opal-A, gypsum, the most frequent. These biominerals or biospeleothems are formed due to microbiological processes indirectly (as consequence of reactions produced by the metabolic products derived from the organic activity). Si and Al are the most abundant elements in the granitic rocks and thus mainly prevail in the infiltration water. The oversaturation by water evaporation or/and the pH changes cause the precipitation of the elements and solubilised compounds originating the speleothems of granite systems. Opal-A (Si) is the most important type of

speleothem quantitatively and the most diversified morphologically. The organisms (bacteria, algae, fungi) that live and are developed in these speleothems are active while the speleothem is wet. When water flow diminishes or evaporates, the organisms react developing resistance spores staying until the next humid period when they germinate again. Mites and collembola also have activity in the speleothem using the content in organic matter of the same speleothem for their subsistence. The last stage in the speleothem development is where S of organic origin is combined with the Ca of the plagioclases, and using the substratum of amorphous silica (silica gel) gypsum crystals develop with an excellent idiomorphy and are present widely in the opal-A.

Acknowledgments

This paper is a contribution to the Research Project BTE-CGL-2006-08996 of the Ministry of Education and Science of Spain. We thanks Ana Martelli for the

translation and help to eliminate many errors and inconsistencies.

References

- Barker WW, Welch SA, Banfield JF, 1997. Biogeochemical weathering of silicate minerals. In: Geomicrobiology: interactions between microbes and minerals, (Banfield, J. F. and Nealson KH, eds.). Washington: Mineralogical Society of America. 391-428.
- Bennett PC, 1991. Quartz dissolution in an organic-rich aqueous system. *Geochimica et Cosmochimica Acta*, 55, 1781-1797.
- Blyth, AJ, Baker, A, Collins, MJ, Penkman, KEH, Gilmour, MA, Moss, J S, Genty, D, Drysdale, RN, 2008. Molecular organic matter in speleothems and its potential as an environmental proxy. *Quaternary Science Reviews* 27, 905-921.
- Brady PV, Walther JV, 1990. Kinetics of quartz dissolution at low temperatures. *Chemical Geology*, 82: 253-264.
- Bustillo MA, 1995. Una nueva ultraestructura de ópalo CT en silcretas. Posible indicador de influencia bacteriana. *Estudios Geológicos*, 51: 3-8.
- Caldcleugh A, 1829. On the geology of Rio de Janeiro. *Transactions of the Geological Society*, 2: 69-72.
- Cañaveras JC, Sánchez-Moral S, Soler V, Saiz-Jiménez C, 2001. Microorganisms and microbially induced fabrics in cave walls. *Geomicrobiology Journal*, 18: 223-240.
- Ehrlich H L, 1996. *Geomicrobiology*. 3rd edition. Marcel Dekker, Inc., New York, 719 pp.
- Franklin SP, Ajas AJR, Dewers, TA, Tieh T.T, 1994. The role of carboxylic acids in albite and quartz dissolution: An experimental study under diagenetic conditions. *Geochimica et Cosmochimica Acta*, 58(20), 4259-4279.
- García-Ruiz, JM, Miguez, F, 1982. Condiciones de formación del primer precipitado en la técnica del gel de sílice. *Estudios Geológicos*, 38, 3-14.
- Kröger N, Deutzmann R, Sumper M, 1999. Polycationic peptides from diatom biosilica that direct silica nanosphere formation. *Science*, 286, 1129-1131.
- McMahon PB, Chappelle FH, 1991 - Microbial production of organic acids in aquifer sediments and its role in aquifer geochemistry. *Nature*, 349: 233-235.
- Sanjurjo Sánchez, J, Vidal Romani JR, 2011. Luminescence dating of pseudokarst speleothems: a first approach. 2nd Conference on Micro-Raman and luminescence studies in the Earth and Planetary Sciences (CORALS II). May 18-21,

Madrid, Spain.

Swarzlow CI, Keller WD, 1937. Coralloid Opal. *Journal of Geology*, 45, pp.101-108.

Twidale CR, Vidal Romani JR, 2005. Landforms and geology of granite terrains. Balkema, London, 351 pp.

Van Rosmalen GM, Marcheée WGH, 1976. A comparison of gypsum crystals grown in silica gel and agar in the presence of additives. *Journal of Crystal Growth* 35, 169-176.

Vidal Romani JR, Bourne, J A, Twidale CR, Campbell EM, 2003. Siliceous cylindrical speleothems in granitoids in warm semiarid and humid climates. *Zeitschrift für Geomorphologie*, 47(4): 417-437.

Vidal Romani JR, Vilaplana JM, 1984. Datos preliminares para el estudio de espeleotemas en cavidades graníticas. *Cadernos do Laboratorio Xeolóxico de Laxe*, 7: 305-324.

Vidal Romani JR, Sanjurjo J, Vaqueiro, M, Fernández Mosquera D, 2010. Speleothem development and biological activity in granite cavities. *Geomorphologie: relief, processus, environment*, 4, 337-346.

Vidal Romani, JR, Bourne, JA, Twidale, CR, Campbell, EM, 2003. Siliceous cylindrical speleothems in granitoids in warm semiarid and humid climates. *Zeitschrift für Geomorphologie* 47, 417-437.

Welch SA, Ullman WJ, 1996. Feldspar dissolution in acidic and organic solutions: Compositional and pH dependence of dissolution rate. *Geochimica et Cosmochimica Acta*, 60(16), 2939-2948.

Willems L, Compere P, Sponholz B, 1998. Study of siliceous karst genesis in eastern Niger: microscopy and X-ray microanalysis of speleothems. *Zeitschrift für Geomorphologie*, 42(2), 129-142.

Willems L, Compère P, Hatert F, Pouclet A, Vicat JP, Ek C, Boulvain F, 2002. Karst in granitic rocks, South Cameroon: cave genesis and silica and taranakite speleothems. *Terra Nova*, 14: 355-362.

Woo, KS, Choi DW, Lee KC, 2008. Silicification of cave corals from some lava tube caves in the Jeju Island, Korea: Implications for speleogenesis and a proxy for paleoenvironmental change during the Late Quaternary Quaternary