

Speleothem development and biological activity in granite cavities

Développement de spéléothèmes et activité biologique dans les cavités granitiques

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Abstract

Water trickling through the discontinuities of granitic massifs causes a slow chemical and physical weathering of the rock related to biological activity. The weathered materials are first eroded and later deposited in either the same fissures or the water output of fissures. The formed deposits are considered speleothems due to their morphology, genesis and association with rock fissure systems. They are comparable to their congeners in karstic systems *s.s.* though they are always smaller in size and volume. Speleothems of granite caves are a suitable microenvironment for the settlement and development of microorganisms as bacteria, fungi, algae, diatoms, polychetes, mites, etc., which at least develop part, if not all, of their vital cycle in the speleothem. The biological activity is responsible for the formation of the speleothem because it promotes the weathering of the rock contributing to the generation of new minerals (pigotite, evansite-bolivarite, opal-A) which may be called biominerals due to their relationship with the organic activity and also acting as sedimentation trap of the resulting materials.

Key words: granite cavities, speleothems, opal-A, pigotite, evansite, bioweathering.

Résumé

Les suintements de l'eau à travers les discontinuités des massifs granitiques provoquent une météorisation chimique et physique de la roche en relation avec l'activité biologique. Les matériaux altérés sont prélevés puis redéposés aussi bien dans les fissures qu'à l'exutoire de celles-ci. Ces dépôts néoformés sont des spéléothèmes de par leur morphologie, leur genèse et leur association avec l'eau et les systèmes de fissures. Ils sont comparables avec leurs congénères des systèmes karstiques bien que, usuellement, plus petits en taille et en volume. Les spéléothèmes des grottes granitiques se caractérisent par un micro-environnement apte à l'établissement et au développement de microorganismes tels que les bactéries, les champignons, les algues, les diatomées, les polychètes, les acariens, etc., qui développent, en partie ou complètement, leur cycle vital dans le spéléothème. L'activité biologique est responsable de la morphologie du spéléothème car elle promeut la météorisation de la roche en contribuant à la génération de nouveaux matériaux (pigotite, evansite-bolivarite, opale A), pouvant être nommés biominéraux dus à leur genèse en étroite relation avec l'activité organique. Ils agissent également comme des pièges sédimentaires pour les matériaux néoformés.

Mots clés : cavités granitiques, spéléothèmes, opale-A, pigotite, evansite, bioaltération.

Version française abrégée

Cet article décrit les effets de la circulation phréatique au sein de massifs granitiques fracturés. L'étude des effets de la circulation de l'eau dans les systèmes fissuraux partiellement ouverts des massifs granitiques – et leurs spécificités

lorsque la vitesse de percolation est lente – est un aspect pratiquement inédit dans la littérature, bien que d'un grand intérêt puisque, dans ce cas, l'altération chimique prédomine sur l'érosion mécanique (Wray, 1997). Les néoformations minérales qui en résultent dans les cavités granitiques ont un aspect comparable à celles des systèmes karstiques

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et restent des objets peu connus de cette morphodynamique, bien qu'elles aient été décrites très tôt mais selon une terminologie présentant peu d'intérêt scientifique (Caldcleugh, 1829; Swarzlów et Keller, 1937). Pourtant, la circulation de l'eau dans les systèmes rocheux granitiques produit des dépôts dont l'appellation « spéléothèmes » se justifie en raison de leur genèse, leur morphologie, leur structure et leur texture analogues aux stalagmites, stalagmites et draperies (flowstone) des milieux calcaires (Finlayson et Webb, 1985; Kashima, 1987; Vidal Romani et al., 2003). Ce travail est donc une synthèse des données existantes sur des spéléothèmes de milieux granitiques variés, étudiés sous différents régimes climatiques, en Europe, en Argentine et en Australie. Les spéléothèmes ont été classés selon leurs compositions chimique et minéralogique et leurs morphologies respectives. Bien qu'ils soient monominéraux, ces dépôts présentent une composition très variée. Dans cette étude, les types les plus fréquents sont analysés : pigotite, evansite-bolivariite et opale amorphe (opale-A). Dans les trois cas, il s'agit de minéraux amorphes qui ont été caractérisés en utilisant différentes techniques analytiques (Fluorescence RX, DRX et, plus spécialement, MEB). La composition chimique des spéléothèmes est en rapport direct avec celle de l'encaissant : les éléments majeurs des minéraux entrant dans composition des granites (Si, Al et, de manière moins importante, d'autres éléments issus de la roche-mère : Fe, Mg, K, Na, etc.) y prédominent. D'autres éléments chimiques ont également été identifiés : C, S, P et, dans tous les cas, le H₂O d'hydratation, ce qui est logique puisqu'il s'agit de l'agent de transport. L'origine de ces derniers éléments est externe à la roche-mère granitique. L'origine du C est organique et entre en rapport avec l'activité métabolique de différents microorganismes qui résident dans les cavités granitiques : bactéries, champignons, algues, diatomées, acariens, polychètes. D'autres composés organiques (acides organiques et phosphates) identifiés dans ces spéléothèmes sont associés à l'activité biologique développée dans les protosols qui couvrent les massifs granitiques.

Tous les éléments et composés, aussi bien d'origine minérale (granite), que d'origine organique, ont été transportés en dissolution et finalement déposés par l'eau qui circule à travers les discontinuités du système pseudo-karstique granitique. L'étude de ces spéléothèmes au MEB révèle que l'activité des microorganismes via la production de composés métaboliques a un rôle décisif dans l'altération de la roche quand les conditions du pH de l'eau sont modifiées, ce qui permet la dissolution de la roche. Postérieurement, l'évaporation de l'eau et, de nouveau, les variations du pH, induisent la formation des spéléothèmes. De même, les microorganismes, qui développent partiellement ou totalement leur cycle de vie à l'intérieur des systèmes pseudo-karstiques granitiques, ont une grande influence sur le développement des spéléothèmes en agissant comme un piège sédimentaire.

Introduction

Most of the water runoff in continental zones is produced superficially and only a smaller fraction through the discon-

tinuities of rocky massifs. The water movement through the massifs of soluble rocks (carbonates and evaporite rocks) is well-known but less for non-soluble rocks (granites, quartzite, etc.). This paper describes the effects of water circulation in closed regime through the discontinuities of granitic rock massifs.

When the water movement is slow (water trickling), chemical weathering associated with slight mechanical or physical erosion will occur (Wray, 1997). In the case of granites, the rock chemical weathering will be enhanced by the activity of microorganisms living in the rock fissures. The mobilisation of ions from the rock minerals dramatically depends on the water pH that is affected in turn by such microbiological activity (as stated below). The chemical elements of the granitic rock minerals are first mobilised in solution by water. Finally, they will precipitate as deposits whose composition will vary according to the parent rock composition. In felsic and intermediate granites (from granite to granodiorite), Si is the most abundant element (between 80% and 60%), followed by Al (14%) and the other elements (Na, K, Ca, etc.) in minor proportion. The chemical analyses of the speleothems found in the granite caves described in this paper show a very varied composition though the prevailing elements are Si and Al, coming from the original rock, and C, P and S due to the organic activity developed in the fissure system. The minerals formed by all these elements will be deposited as a specific type of sediment called speleothem due to either its position within the fissure system of the rocky massif and/or its genesis and morphology. Early descriptive reports (Caldcleugh, 1829; Swarzlów and Keller, 1937) called these deposits as coralloids, crusts, speleothems, etc., a terminology without scientific value because it only considers the external aspect. Later, by analogy with calcareous speleothems (Finlayson and Webb, 1985; Kashima, 1987) the preferred nomenclature was stalactites for deposits associated with a punctual output of the water on the ceiling of the rocky cavity, stalagmites for the ones due to the dripping on the ground of the cavity and flowstones for the ones formed by laminar water flow (Vidal Romani et al., 2003).

Aim of the work and methods

This paper consists of a synthesis of existing data about the types of speleothems found in cavities and fissure systems of granitic rocks. From the compilation of data, a systematisation was carried out to classify these deposits according to the mineralogical and morphological characteristics in order to elucidate the processes that originate their formation. First, the existing references of studies on these types of deposits were compiled. Also, samples of speleothems were taken in different zones of Australia, Argentina and Europe (Spain, Portugal, France, Germany) during several years in order to compare their compositions and morphological features in granitic rocks of variable composition and under different climatic conditions. Based on this information, the speleothems were classified according to chemical and mineralogical composition and morphologic features. For the study of these spe-

leothems all the samples were analysed by X-Ray Fluorescence (XRF) to know the major elements, and examined under Scanning Electron Microscopy (SEM) equipped with an Energy Dispersive Spectroscopy analysis (EDS). Also, there were carried out elemental analyses of some of the samples to establish their content in C, P and S (of organic origin). Some of the speleothems were dated by AMS ^{14}C in order to know their age and growth speed.

Results

Mineralogy and genesis of speleothems

The mineralogy of the speleothems described for granitic cavities is very varied. Up to now, the following types of minerals have been mentioned in the literature: opal-A, evansite, bolivarite, struvite, pigotite, taranakite, allophane, hematite, goethite, etc. (Webb, 1976; Macías *et al.*, 1979, 1980; Hill and Forti, 1995). All these minerals were described in very different rock types and geographic-climatic environments: temperate humid (Northern Spain and Portugal, United Kingdom, Germany, Poland, Czech Republic), tropical (Brazil, Venezuela, Madagascar), arid (South Australia, Argentina, Nigeria, Mexico, U.S.A., etc.; Willems *et al.*, 1998, 2002; Twidale and Vidal Romaní, 2005). This geographic-climatic ubiquity seems to show that their formation, though always associated with water circulation and sedimentation, is independent from climate (fig. 1). So far, the prevailing mineralogies of the speleothems associated with granitic rocks are three from greater to minor frequency according to their citations in the literature: opal-A, pigotite and evansite-bolivarite.

Opal-A speleothems [$\text{SiO}_2 \cdot 1.5(\text{H}_2\text{O})$]. These types of speleothems show a great morphologic variability (stalactites, stalagmites and flowstone) and were characterised by different analytical techniques: elemental chemical analysis, XRD, XRF and DTA-GTA (Vidal Romaní, 1983). Such speleothem is mainly a quartz polymorph (Vidal Romaní *et al.*, 1998) formed by Si, H_2O and other minor elements (Ca, Na, K, etc.) typical from the parent granite, and others (S) alien to it (tab. 1). The formation of opal-A needs the dissolution of Si, which is very low in the water pH ranges typical of the natural granite environments (pH~5; Welch and Ullman, 1993). However, the granite forming silicates are easily etched and ions mobilised by biochemical weathering due to the activity of bacteria, algae, fungi and lichens (Ehrlich, 1996). The dissolution by the chelant ability of low molecular weight organic acids (mainly oxalates) is determinative in the biochemical weathering of the granite minerals (McMahon and Chapelle, 1991; Barker *et al.*, 1997). In the pH range between 2.0 and 8.5 (Brady and Walther, 1990; Bennett, 1991), such dissolution is produced by an increase of the solubility even of the crystalline quartz, remarked in the pH range 5.5-7 (fig. 2). Also, some of the mentioned organisms (Franklin *et al.*, 1994; Welch and Ullman, 1996) are able to produce sulphate oxides from oxidation of organic matter. The formation of gypsum crystals ($\text{SO}_4\text{Ca} \cdot 2\text{H}_2\text{O}$; fig. 3A) associated with final growth stages of opal-A speleothems (Vidal Romaní *et al.*, 2003) is due to the combination of SO_2 of organic origin with the Ca of the plagioclases and shows a change in the pH of the water that circulates through the speleothem from acid (~5) in the first stage to alkaline (~10) in the final growth stage. This change coincides with a decrease in the infiltration water contributions (end of the rainy period and relative increase of the evapo-

Fig. 1 – Pictures of biospeleothems. A: Granite tafone from Los Gigantes, Sierra Grande de Córdoba, Argentina: the gray and black dots are the water outputs where the speleothems are formed; B: Pigotite column covered by gour dam, 3000 years old from Trapa Cave, Galiñeiro, Galicia Spain; C: Evansite deposits associated to planar fissure, Monte Costa Grande, Muros, Coruña Spain; D: Cross-section of a pigotite speleothem formed by rhythmic accretion, with dark and light layers.

Fig. 1 – Photographies de bio-spéléothèmes. A : Taffoni granitique de Los Gigantes, Sierra Grande de Córdoba, Argentine : les points noirs et blancs (flèches) sont des sorties d'eau où se forment les spéléothèmes ; B : colonne de pigotite, recouverte de structures « gour dam », âgée de 3 000 ans, Grotte de Trapa, Galiñeiro, Galice, Espagne ; C : dépôts d'évansite associés à une fissure plane, Monte Costa Grande, Muros, Galice, Espagne ; D : section transversale d'un spéléothème de pigotite formé par accréation rythmique, à couches foncées et claires.

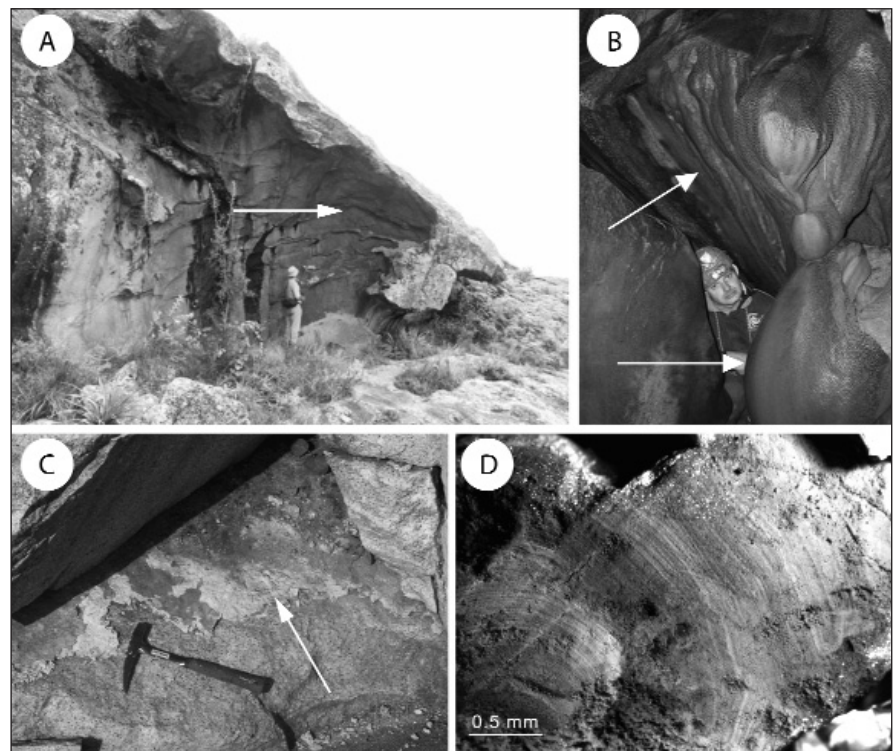
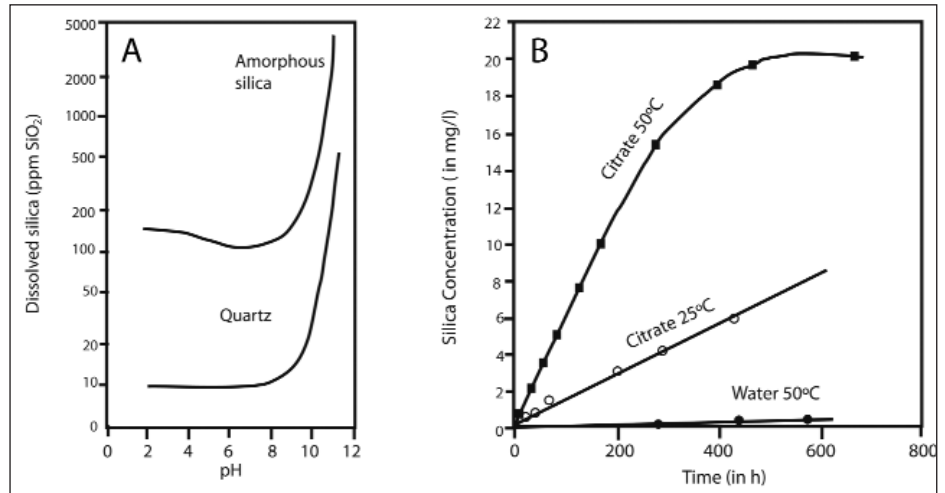


Fig. 2 – **Quartz solubility.** A: Solubility of silica at 25°C (modified from Kraskopf, 1967); B: Quartz dissolution in a K-citrate solution 0.02 M at 25°C and 50°C time function (modified from Bennett, 1991).

Fig. 2 – **Solubilité du quartz.** A : solubilité de la silice à 25°C (modifié de Kraskopf 1967) ; B : dissolution du quartz dans une solution de 0.02 M de K-citrate à 25°C et 50°C, en fonction du temps (modifié de Bennett, 1991).



ration) and with a decrease of the microbiological activity as proved by the development of resistance forms (spores, schists) or the burial of the microorganisms in opal. The precipitation of Si from the water that circulates by the speleothem is due to two effects mainly: chemical (oversaturation by evaporation) carried out at alkaline and biological pH (passive, precipitating the Si over the same microorganism or incorporating the Si to their organic structure (Kröger *et al.*, 1999).

Pigotite speleothems [Al₄C₆H₅O₁₀.13H₂O or 4Al₂O₃.C₁₂H₁₀O₈.27H₂O]. This is a salt composed of alumina and

organic acids (tab. 2 to tab. 4) formed on the surface of the granite and typically found in granitic cavities. It forms incrustations on the walls of granitic fissures and caverns (fig. 1B). This mineral was early described by Mr. Pigot in marine caves from Cornwall (United Kingdom) and was called pigotite by mineralogists. J.F.W. Johnston (1840) considered it as an organic substance derived from the decay of moist moorlands above the cave which he calls mudescous acid, combined with Al (dominant) and Fe (secondary). Due to its amorphous character, the information given by the existing bibliography is not very precise when trying

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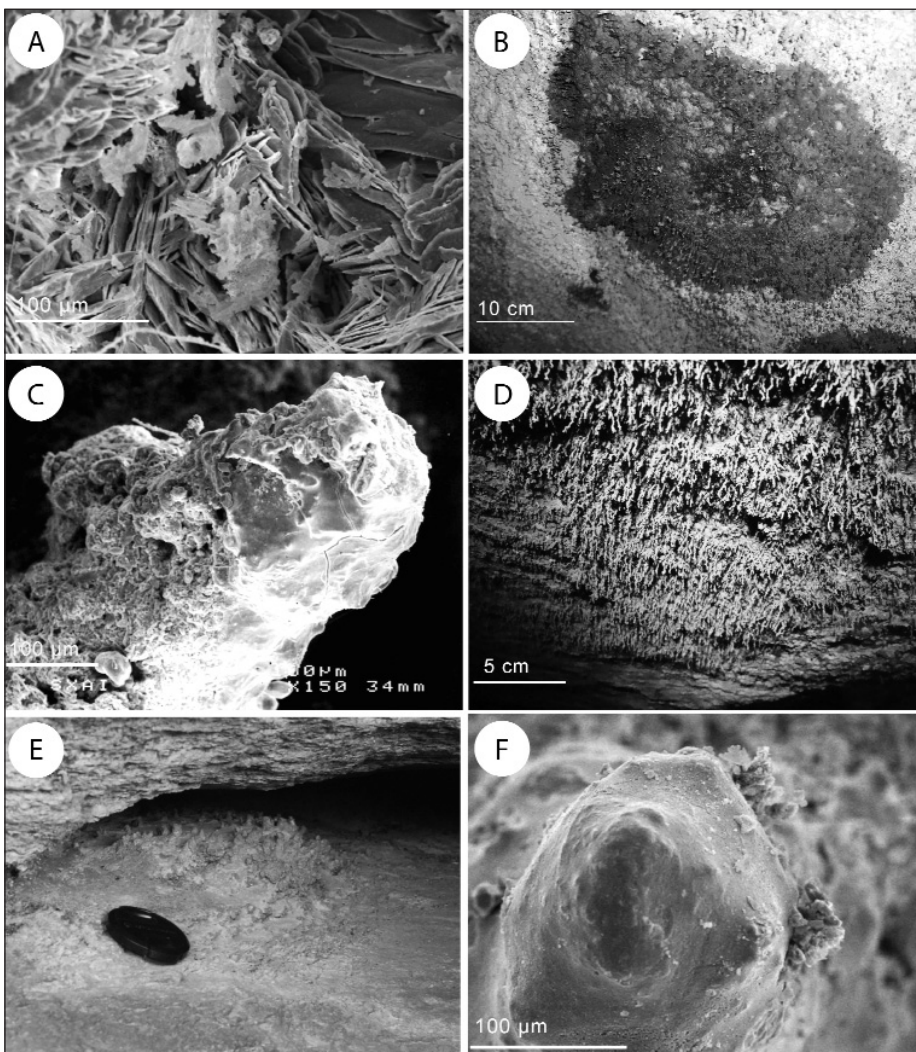


Fig. 3 – **Opal A speleothems.** A: Gypsum twin formed by planar crystals on the tip of a speleothem, Ávila, Central Spain; B: Output of water in the roof of a granite cave with associated opal A stalactites; C: Opal A coats the porous texture near the tip of speleothem from the Traba Mountains, Northern Galicia, Spain; D: Opal A grass shaped stalactites on the roof of a granite cave, Cova do Demo, Vigo, Spain; E: Opal A antistalactites from Mina Clavero, Córdoba, Argentina; F: Opal A stalagmite from Colegio Liqueño, Pampa de Achala, Córdoba, Argentina.

Fig. 3 – **Spéléothèmes d'opale-A.** A : Macles de gypse formées par des cristaux planaires dans l'extrême libre d'un spéléothème, Ávila, Centre de l'Espagne ; B : sortie d'eau au plafond d'une grotte granitique avec stalactites d'opale-A associées ; C : l'opale-A recouvre la texture poreuse d'un spéléothème proche à son extrémité, Montagnes de Traba, Nord de la Galice, Espagne ; D : stalactites d'opale-A en gazon dans le plafond d'une grotte granitique, Cova do Demo, Vigo, Espagne ; E : antistalactites d'opale-A de Mina Clavero, Córdoba, Argentine ; F : stalagmite d'opale-A de Colegio Liqueño, Pampa de Achala, Córdoba, Argentine.

Area	Place	Morphology	Texture	Elemental Composition (in %)															
				C	O	Mg	Al	Si	P	K	S	Ca	Fe	Na	Ti	Cl			
Argentina	Pampa Achala	Flowstone	Compact	22.78	34.39	0.69	4.96	47.38			3.01		4.98	3.85	0.73				
			Semi-porous	27.34	46.4	0.54	2.99	18.02	1.63	5	1.54	1.11							
	Cerro Blancos	Mini-gour dam	Compact	20.18	38.5	1	7.03	27.14			1.24		0.69	2.93	0.3				
			Semi-porous	46.12	45.64		4.65	22.9	0.26		0.96	0.64							0.31
Spain	Pampa Blanca	Cylindrical stalactite	Porous	27.34	50.35	1	6.76	32.09			2.26	1.3	1.3	4.54	1.15		0.55		
			Compact	13.96	43.32		13.7	36.64	1.55		6.34						0.94		
			Porous	7.59	50.93		7.32	22.08	3.24		3.22								
			Compact	27.34	44.31		11.22	29.82			3.82								
	V. Señor Peña	Grass-shaped stalagmite	Compact	20.18	38.5	1	7.03	27.14			1.24		0.69	2.93	0.3				
			Semi-porous	46.12	45.64		4.65	22.9	0.91		1.31	0.43							
			Compact	15.92	54.73	0.49	10.05	30.63	1.75		1.46	0.7							
			Porous	27.34	50.09	0.7	3.58	24.8	2.83		0.93								
	Pindo, Coruña	Grass-shaped stalagmite	Semiporosa	44.32	45.33	0.85	4.94	41.49			1.92		1.76	2.81	0.51				
			Compact	49.66	44.32	0.69	4.16	45.6	2.92		1.67	0.66							0.46
			Porous	13.16	49.66	1.12	5.64	35.59			0.67	3.36							
			Semi-porous	18.33	41.47		3.98	35.5	1.32		4.64								
S. Gardunha	Cylindrical stalactite	Semi-porous	37.35	38.16	2.8	3.32	28.66			1.08		1.23	2.52	0.39					
		Compact	12.78	44.06	0.77	3.91	29.48			1.6									
		Anti-stalactite	18.12	52.98	0.64	3.64	20.74			0.55									
		Rims	37.93	37.93		6.89	55.17			1.48									
Portugal	Mini gour	Compact	13.86	36.24		1.78	48.11												
		Flowstone																	

Tab. 1 – Summary of elemental composition of opal-A speleothems obtained by EDS coupled to SEM, from samples of diverse provenance.

Tab. 1 – Résumé de la composition élémentaire des spéléothèmes d'opale-A, obtenue par EDS couplé au MEB, à partir d'échantillons d'origines diverses.

to define the chemical and mineralogical composition. Pigotite is presented as stalactites, stalagmites, columns and flowstone covering from horizontal surfaces to very stepped walls, even vertical. Up to now, the biggest pigotite speleothem was located in Serra do Galiñeiro, Galicia, NW Spain and is formed by the union of a stalactite and a stalagmite in a column of more than 1 m long. A cross or longitudinal section of that sample shows a rhythmic accretion structure in concentric layers as it occurs in calcite speleothems (fig. 1D). The different layers alternatively show light (Al prevails; cream) and dark colours (Fe prevails; reddish chestnut) that seem to correspond to seasonal stages (winter-summer) similar to the varves of lake deposits (tab. 5). On surface the aspect of these pigotite deposits is slightly different presenting a crenulated morphology due to the development of mini gour with dimensions from millimetres to some micras. There do not exist many data in the literature on the age and velocity of formation of these types of speleothems. For the speleothems described in Galicia, NW Spain, the radiocarbon dating of some samples gave an age ranging from 1500 years B.P. (O Folón System, Galicia, Spain) to 3000 years B.P. (Trapa cave system, Galiñeiro Sierra, Galicia, Spain) which confirms a great continuity and quickly growth in the deposition process even when compared to calcium carbonate speleothems (tab. 6). The quantity of water present in this mineral is highly variable, but always important in natural conditions. Once a sample is taken from the cave, the dehydration transforms the mineral into a powdered mass with very little cohesion in a short time.

	Evansite Costa Grande-1	Pigotite Trapa-1	Pigotite Baiona-Red layer-1	Pigotite Baiona-Black layer-1
SiO ₂ (in %)	1.11	4.91	9.05	12.45
Al ₂ O ₃ (in %)	36	29.4	33.5	33.9
Fe ₂ O ₃ (in %)	0.14	0.17	0.42	0.21
CaO (in %)	0.05	0.03	0.02	0.02
MgO (in %)	0.01	0.01	0.01	0.01
Na ₂ O (in %)	0.01	< 0.01	0.02	0.01
K ₂ O (in %)	< 0.01	< 0.01	0.05	0.01
Cr ₂ O ₃ (in %)	< 0.01	< 0.01	< 0.01	< 0.01
TiO ₂ (in %)	< 0.01	0.01	0.01	< 0.01
MnO (in %)	< 0.01	< 0.01	0.15	0.01
P ₂ O ₅ (in %)	23.8	2.45	7.66	5.11
SrO (in %)	< 0.01	< 0.01	< 0.01	< 0.01
BaO (in %)	< 0.01	< 0.01	< 0.01	< 0.01
LOI (in %)	38.4	61.4	48.6	46.4
Total	99.5	98.4	99.5	98.1

Tab. 2 – Elemental composition of major components of pigotite and evansite speleothems obtained by XRF, from samples collected in Galicia, Spain.

Tab. 2 – Composition élémentaire des principaux éléments des spéléothèmes de pigotite et evansite, obtenus par FRX à partir d'échantillons recueillis en Galice, Espagne.

	Sample weight (in mg)	N (in %)	C (in %)	H (in %)	S (in %)
Pigotite	5.181	0.34	10.56	5.61	0.35
Evansite	5.141	< 0.05	0.49	4.57	0.17

Tab. 3 – Content in C, N, H and S of a pigotite sample (from Trapa Cave, Monte Galiñeiro, Galicia, Spain) and an evansite sample (from Monte Costa Grande, Muros, Galicia, Spain).

Tab. 3 – Contenu en C, H, H et S d'un échantillon de pigotite (grotte de Trapa, Monte Galiñeiro, Galice, Espagne) et d'un autre d'évansite (Monte Costa Grande, Muros, Galice, Espagne).

Total organic carbon (T.O.C)	Sample weight (in mg)	T.O.C. (in %)
Pigotite	10.080	6.88
	9.935	7.77
Evansite	14.944	0.44
	15.015	0.45

Tab. 4 – Content in total organic carbon in samples of pigotite (from Trapa Cave, Monte Galiñeiro, Galicia, Spain) and evansite (Monte Costa Grande, Muros, Galicia, Spain).

Tab. 4 – Contenu en carbone organique total des échantillons de pigotite (Traba Cave, Monte Galiñeiro, Galice, Espagne) et d'évansite (Monte Costa Grande, Muros, Galice, Espagne).

Evansite-bolivarite. [Al₃(PO₄)(OH)₆.6(H₂O)-Al₂(PO₄)(OH)₃.4-5(H₂O)]. These speleothems are frequently found in well diaclased rocky massifs with development of sheet structure (fig. 1C). All these types of speleothems display a typical structure in rhythmic layers or layered sequences (flows-tone), some centimetres thick covering surfaces of various square metres. The colour of evansite is yellow to yellowish brown to reddish. Evansite is amorphous and massive with a morphology in botryoidal or reniform coatings, concen-

Tab. 5 – Summary of elemental composition of evansite and pigotite speleothems obtained by EDS coupled to SEM, from samples of Spain.

Tab. 5 – Résumé de la composition élémentaire de spéléothèmes d'évansite et pigotite, obtenue par EDS couplé au MEB, à partir d'échantillons de Galice, Espagne.

Mineralogy	Sample	Morphology	Texture	Elemental Composition (in %)													
				C	O	Mg	Al	Si	P	K	S	Ca	Fe	Na	Ti	Cl	
Evansite	MCG-1	Light layer Dark layer	Compact	20.45	53.74		14.79	2.41	6.31	0.18	0.4		1.72				
	MCG-2			9.14	57.8		20.1	1.86	9.98			1.12					
Pigotite	ETP-1		Layered	23.98	31.91		30.25	13.86					2.49				
				22.65	39.26		26.27	9.32									

Sample	Code number	$\delta^{13}\text{C}$ (in ‰)	^{14}C Age (a BP)	Calibrated Age (95.4%; a BP)
Stalactite Trapa-1 (inside)	Ua-38467	-28.1	2884 ± 119	3410-2810
Stalagmite Trapa-1 (inside)	Ua-38468	-28.8	3131 ± 147	3760-2960
Stalactite Trapa-1 (outside)	Ua-38469	-28.7	2277 ± 86	2750-2050
Flowstone -1 (top)	Ua-34282	-26.5	1755 ± 40	2140-2400

Tab. 6 – ^{14}C AMS ages obtained from pigotite speleothems from Trapa and O Folón caves, Vigo, Spain.Tab. 6 – Âges obtenus par ^{14}C AMS de spéléothèmes de pigotite dans les grottes de Trapa et Folón, Vigo, Espagne.

tric, colloform structure at times, opaline, stalactitic. They are very frequent in Galicia, NW Spain, but also in other parts of the World (Mt. Zeleznik, Gomor, Slovakia). A mineral species related to evansite and also amorphous is the bolivarite defined for the first time in Campo Lameiro, Pontevedra, Spain (Navarro and Barea, 1921), which is shown to have physical and optical properties similar to those of evansite. Both minerals are X-Ray amorphous. According to previous literature (García-Guinea *et al.*, 1995), DTA spectra of both minerals show a strong endothermic effect at 120°C and a weaker one at 399°C. IR spectra show absorption peaks at 3500, 1600 and 100 cm (super -1), which are attributed to OH, H₂O and PO₄, respectively. NMR spectra give a P signal centered at -10.7 ppm, typical of amorphous phosphates, and an Al signal centered at -4.2 ppm, which is typical of Al in octahedral coordination. Chemical analyses give the empirical formula Al₂(PO₄)(sub 0.92)(OH) (sub 3.25).4.03H₂O for bolivarite and Al₃(PO₄)(sub 1.09)(OH) (sub 5.73).7.77H₂O for evansite. The results of analyses of specimens of hydrous aluminium phosphates from Costa Grande (Galicia, Spain) indicate a range of Al:P atomic ratios varying between 2 and 3.58 (tab. 2 to tab. 5). Because of the amorphous nature of these materials, it is difficult to know if these analytical data pertain to mixtures of hydrous aluminium phosphates or if bolivarite and evansite represent intermediate members of a wide solid-solution series in which PO₄ radicals are replaced by 3(OH). Some authors (Martín Cardoso and Parga Pondal, 1935; García-Guinea *et al.*, 1995) believe that under the name of evansite-bolivarite there may be represented transition terms between alumina silicates and alumina phosphates where the phosphorous that appears in them increases progressively as Si diminishes till substituting it completely.

Morphologic-genetic characterisation of the speleothems

The following morphological types of speleothems are distinguished: cylindrical and in crusts or sheets.

Cylindrical speleothems. They are associated with water circulation by external dripping (fig. 3B) or internal movements by capillarity. It is used the same nomenclature as for their congeners in karstic environments *s.s.* These types of forms have been described only for two of the normal mineralogies in granitic cavities: opal-A and pigotite.

- Stalactites *s.s.*: formed (fig. 3C) on the high part of rock fissures or the ceiling or eaves of cavities when the weight of the drop overcomes the superficial stress (then dripping is produced). They usually develop as individual forms with gypsum whiskers on their ends, in case of opal-A mineralogies.

- Grass-shaped stalactites: multiple associations of very thin cylindrical forms (maximum 1 mm) and associated with the ceiling, walls or floor of cavities (fig. 3D). These speleothems grow by capillary movements of the water through the clast agglomerate mass of amorphous silica soaked in water. Like the previous ones, they have gypsum whiskers on their ends. They are exclusive of opal-A mineralogies.

- Anti-stalactites: these individual speleothems (Vidal Romaní and Vilaplana, 1984) are exclusive of the opal-A mineralogy (fig. 3E). The speleothems grow by capillary circulation of the water from a clast agglomerate mass of amorphous silica soaked in water. They are usually thicker (up to 4 mm of diameter) and reach longitudinal developments between 4 and 10 mm. They may develop very big whiskers on their ends with cauliflower or mushroom morphology of up to 4 mm wide. They are exclusive of opal-A mineralogies.

- Stalagmites: these speleothems (fig. 3F) are very little frequent in granitic caves. They are formed as their congeners in karstic environments *s.s.* by the precipitation of the substances dissolved or dragged by the water which fall from the growing points of stalactites *s.s.* They have been only observed for the case of speleothems of pigotite and opal-A.

Planar speleothems. They are common microforms for the 3 types of mineralogies described herein: pigotite, evansite and opal-A and are produced as consequence of the water circulation in laminar regime. They may appear on any flat or little-sloped surface (the limit is given by the adherence of the water to the surface) either on the ceiling, floor or base of the cavity walls. 2 types of speleothems are distinguished (Vidal Romaní *et al.*, 1998):

- Flowstone: they are continuous covers of the rocky surface (fig. 4A) with variable thicknesses and may also hide the rock micro rugosity. The mineralogies in which these speleothems appear are the main three ones: pigotite, opal-A and evansite-bolivarite.

- Micro gourds: they are accumulations of opal-A clasts with lineal and sinuous development that may hold water temporarily contributing to the opal precipitation in the maximum

Fig. 4 – **Opal A speleothems**. A: Opal A flowstone from Estancia de las Piedras, Pampa de Achala, Córdoba Argentina; B: Opal A gour dam defining a small pool with a mite, Cerros Blancos, Pampa de Achala, Córdoba, Argentina; C: Mini-Gour dam filled by opal A showing the progressive desiccation lines. Cerros Blancos, Pampa de Achala, Córdoba, Argentina; D: Opal A clasts trapped by fungi hyphae in speleothems from Colegio Liqueño, Córdoba, Argentina.

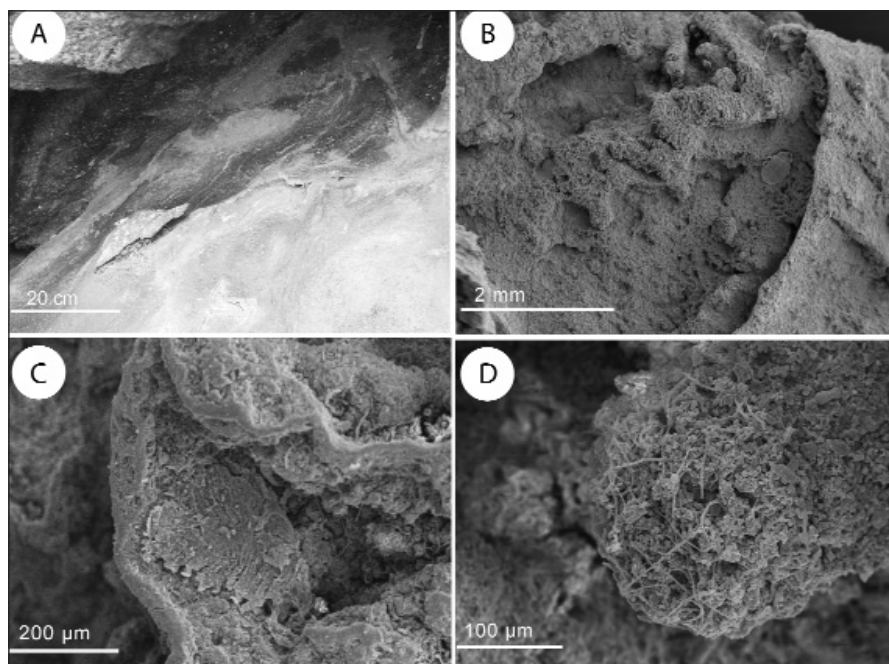


Fig. 4 – **Spéléothèmes d'opale A** : « Flowstone » d'opale-A de Estancia de las Piedras, Pampa de Achala, Córdoba, Argentine ; B : « Gour dam » d'opale-A avec un acarien, Cerros Blancos, Pampa de Achala, Argentine ; C : Mini-gour remplis d'opale-A qui présente des lignes de desiccation successifs, Cerros Blancos, Pampa de Achala, Córdoba, Argentine ; D : Clastes d'opale-A attrapés par des hyphes de champignons en spéléothèmes, de Colegio Liqueño, Córdoba, Argentine.

overspill rim (fig. 4 B and C). They are normally associated with flat or little-sloped surfaces that ensure a slow circulation. However, they may be also found in more sloped or even subvertical surfaces when the flow speed does not go beyond the forces of the water adherence to the sliding surface of the water. The mineralogies of the three main speleothems are: pigotite, opal-A and evansite-bolivarite.

Discussion

The biological activity has an important role in the rock weathering in the fissure systems of granitic massifs; it is essentially produced first by the dissolution of the rock in water and then by the precipitation of the dissolved materials. In both processes, dissolution and precipitation, not only the water influences but also the changes in the pH related to the microbiological activity (Barker *et al.*, 1997; Cañaveras *et al.*, 2001). The chemical elements of the rock minerals are mobilised in a different rate along with their original abundance; Si and Al are the most abundant and, therefore, mainly contribute to the formation of new minerals. The 3 species of minerals described in this paper (pigotite, evansite-bolivarite and opal-A) have a different relationship with the microbiological activity developed in the fissure system. Pigotite will be mainly formed by the water infiltration through the peat bogs which allow to incorporating organic acids and carrying out the chelation of ions of the underlying rock. In this case, the organic acids are the only relationship between microbiological activity and weathering of the rock. The formation of pigotite speleothems (stalactites, stalagmites and flowstone) is due to the loss of transport capacity of the water when the flow stops at the end of a rainfall event and the water evaporation prevails. The changes in the regime of water contribution may be reasonably due to seasonality as suggested by the internal structure of the speleothem of rhythmic accretion

with alternation of light layers (prevalence of Al), which correspond to summer periods when the water flow diminishes, and dark layers (prevalence of Fe) which correspond to the greater contributions and lower temperature (winter). The evansite-bolivarite is the second type of biomineral formed in the granitic cavities. Its relationship with the organic activity is recognised in this case by the presence of phosphates, of organic origin, which is combined with the elements coming from the rock, essentially Al and Si. In this case, the relationship between microbiological activity, rock weathering and formation of speleothems is again due to the loss of the transport capacity because of reduction of water flow and prevalence of evaporation. The third type of biomineral, speleothems of opal-A, is the one that shows a clearer and more direct relationship with the microbiological activity. Again, the effect of organic acids in the water solution causes the dissolution of rock minerals and the formation of the opal-A speleothem with the water evaporation at the end of the rainy period. Here the changes in the water pH are the triggering factors, first the solution of Si (acid pH) then, in the final stage (alkaline pH), the precipitation of opal-A and finally, the growth of gypsum crystals in continuity with the opal-A substratum. From the microbiological point of view, the speleothem may be considered a tiny ecosystem where it is produced a substitution of different microorganisms related to the presence and circulation of water through the speleothem. Considering the short period of water permanence in the pseudokarstic microsystem, while the contributions of rain water to the fissural phreatic of the massif continue, the process goes on at least for some days and is reproduced unceasingly after each rainy period. At first, the bacterial activity weathers the quartz and the other silicates; a silica gel is formed and when it desiccates, it will give rise to opal clasts that form open work accumulations where water eventually accumulates and is the basis for the development of bacteria, fungi and algae which alter-

natively germinate in the humid stage or form spores in the dry stages and may be even covered or buried by the precipitation of opal-A (fig. 4D). The opal gel dissolved in the water is mainly used by the diatoms incorporating it to their organic structures. Some author (Kashima, 1987) considers that the diatoms are allochthonous and have been dragged by the water from outside the system when it is proved that they have a complete development inside the speleothem (fig. 5A and B). In the last stage, when the speleothem is already formed, mites (fig. 5C) and polychetes (fig. 5D) take advantage of the organic material and residual humidity to live temporarily in the external part of the speleothem. In this last stage, the S produced by microorganisms originates sulphates by oxidation of organic matter (bacteria, fungi). Then the growth of gypsum crystals ($\text{SO}_4\text{Ca}\cdot 2\text{H}_2\text{O}$) will take place: Ca comes from the alteration of the plagioclases while S is of biological origin (Twidale and Vidal Romaní, 2005). This phase is called azoic (Vidal Romaní *et al.*, 1998) due to the absence of life forms justified by the drastic change of the pH from acid (when the Si dissolves) to basic when amorphous opal precipitates and gypsum grows (García Ruíz *et al.*, 1981; García Ruíz and Miguez, 1982). Generally, whiskers are calcium sulphate crystals though in some cases (Vidal Romaní, 1983) calcium carbonates and calcium phosphates have been found (though these latter do not present a idiomorphism comparable to the two aforesaid mineral species).

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 neo-mineralisations are associated: opal-A, pigotite and evansite-bolivarite, the most frequent. These biominerals or biospeleothems (Forti, 2001) 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 causes 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

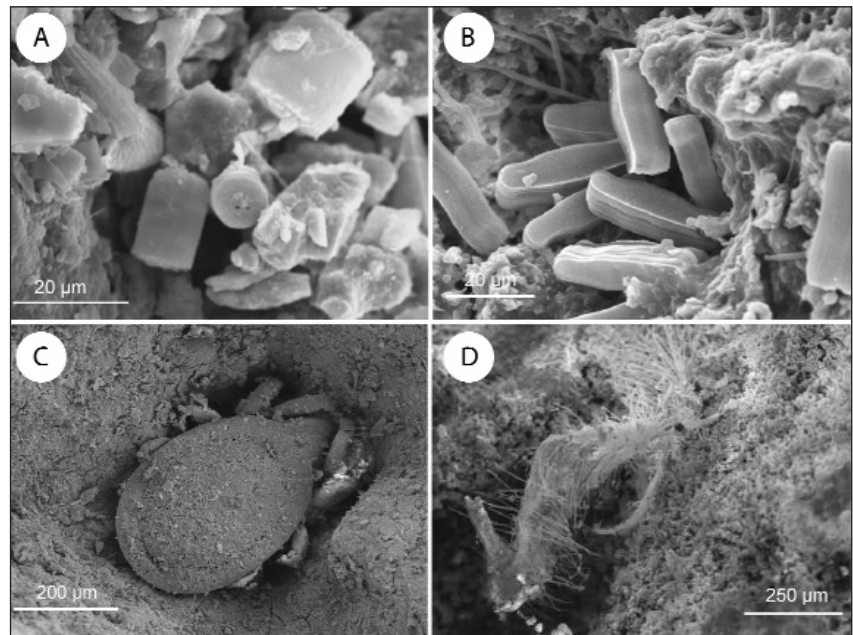


Fig. 5 – **Organisms found in opal-A speleothems.** A: Centric diatoms in opal-A speleothems from Pampa de Achala, Argentina; B: Pennate diatoms in opal-A speleothems from Pampa de Achala, Argentina; C: Mite trapped in a gour dam of opal-A, from Cerros Blancos, Pampa de Achala, Córdoba, Argentina; D: Polychete on the surface of an opal-A speleothem from Eyre Peninsula, South Australia.

Fig. 5 – **Organismes observés dans les spéléothèmes d'opale-A.** A : Diatomées centrales dans des spéléothèmes d'opale-A de Pampa de Achala, Argentine ; B : diatomées pennées dans des spéléothèmes d'opale-A de Pampa de Achala, Argentine ; C : acarien piégé dans un mini-gour d'opale-A de Cerros Blancos, Pampa de Achala, Argentine ; D : polychète observé à la surface d'un spéléothème d'opale-A de la Péninsule d'Eyre, Sud de l'Australie.

humid period when they germinate again. Mites and polychetes 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 the so-called azoic stage 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 idiomorphism and are present widely in the opal-A.

Acknowledgements

This paper is a contribution to the Research Project BTE-CGL-2006-08996 of the Ministry of Education and Science of Spain. We thank Dr Yves Perette and an anonymous reviewer for the insightful comments on an earlier version of this manuscript. We also thank Ana Martelli for the translation and help to eliminate many errors and inconsistencies.

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Article soumis le 6 janvier 2010, accepté le 24 août 2010.