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SULFATE AND PHOSPHATE SPELEOTHEMS AT JENOLAN CAVES, NEW SOUTH WALES, AUSTRALIA

SULFATNA IN FOSFATNA SIGA V JAMI JENOLAN CAVES, NOVI JUŽNI WALES, AVSTRALIJA

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Ross E. Pogson, R. Armstrong L. Osborne, David M. Colchester & Dioni I. Cendón: Sulfate and Phosphate Speleothems at Jenolan Caves, New South Wales, Australia

Sulfate and phosphate deposits at Jenolan Caves occur in a variety of forms and compositions including crusts, 'flowers' and fibrous masses of gypsum (selenite), and clusters of boss-like speleothems (potatoes) of ardealite (calcium sulphate, phosphate hydrate) with associated gypsum. This boss-like morphology of ardealite does not appear to have been previously described in the literature and this is the first report of ardealite in New South Wales. Gypsum var. selenite occurs in close association with pyrite-bearing palaeokarst, while the ardealite gypsum association appears to relate to deposits of mineralised bat guano. Isotope studies confirm that the two gypsum suites have separate sources of sulfur, one from the weathering of pyrite (-1.4 to +4.9 $\delta^{34}S$) for gypsum (selenite) and the other from alteration of bat guano (+11.4 to +12.9 $\delta^{34}S$) for the ardealite and gypsum crusts.

Keywords: sulfate, phosphate, gypsum, ardealite, speleothem, bosses, Jenolan Caves.

Izvleček UDK 551.442:552.5(944)

Ross E. Pogson, R. Armstrong L. Osborne, David M. Colchester & Dioni I. Cendón: Sulfatna in fosfatna siga v jami Jenolan Caves, Novi južni Wales, Avstralija

Sulfatni in fosfatni sedimenti se v Jenolanskih jamah pojavljajo v različnih oblikah in sestavah. Sadra (selenit) je v obliki skorij, rož in vlaknastih tvorb. Pojavljajo se tudi gomoljasti izrastki ardealita (kalcijev sulfat, fosfat in hidrat), ki jih v tem članku prvič opisujemo. Selenit se pojavlja v povezavi s paleokraškimi sedimenti, v katerih je pirit, medtem ko je pojav ardealita očitno povezan z mineraliziranim netopirjevim gvanom. Različen vir žvepla v sadri potrjujejo tudi izotopske raziskave. Žveplo v selenitu izhaja iz preperevanja pirita ($-1,4 < \delta^{34}S < 4,9$), v ardealitu in sadrinih skorjah pa iz produktov pretvorb gvana ($+11,4 < \delta^{34}S < +12,9$).

Ključne besede: sulfat, fosfat, sadra, ardealit, siga, gomoljasti izrastki, Jenolanske jame.

INTRODUCTION

Jenolan Caves (Fig. 1) are Australia's best-known and most visited show caves, attracting some 300,000 visitors annually. The caves are developed in the Late Silurian Jenolan Caves Limestone (Carne & Jones 1919), having an average composition of 97.6% $CaCO_3$ (Carne & Jones 1919). The caves are renown for their impressive calcite and aragonite speleothems but although gypsum deposits were recognised in the 19th century

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(Mingaye 1899), they were rarely reported in Jenolan Caves literature.

White (1976) and Onac (2005) considered gypsum as the second most common cave mineral and Hill & Forti (1997) considered it to be the third most common, after calcite and aragonite. Few sulfate speleothems have been described from the many caves developed in massive Palaeozoic limestones of the Tasman Fold Belt System in eastern Australia.

This is largely a consequence of the different geological setting of cavernous limestones in eastern Australia compared with those of Europe and North America where most cave mineral research has occurred. While gypsum beds are unknown in the Palaeozoic of eastern Australia; they are common in the Mesozoic and Early Cainozoic of Europe and North America, frequently interbedded with cavernous limestone, and are sometimes cavernous themselves. While the occurrence of gypsum should be anticipated in these situations, gypsum speleothems in eastern Australian limestone caves require explanation.

While there are few reports of sulfates from eastern Australian caves, Mingaye (1899), described phosphatic deposits from Jenolan Caves and gives what appears to be the first published report of gypsum from an eastern Australian cave. This could also be the first report of the potatoes in Chifley Cave described below. Mingaye reported that "The deposit was found in the floor of Grotto Cave, and is protected with a hard surface, covered with small gnarled excrescence, found to be gypsum".

Specimens of gypsum (selenite) from Jenolan collected in the 1890s are housed in the collections of the Australian Museum while specimens from Jenolan (gypsum/ardealite) and Yarrangobilly Caves are recorded in the catalogue of the former Geological and Mining Museum, Sydney (1976). James *et al.* (1982) reported gypsum crystals in Basin Cave at Wombeyan Caves. Other confirmed, but unpublished gypsum occurrences in New South Wales' caves are at Bungonia, Colong, Moparabah, Walli and Wellington.

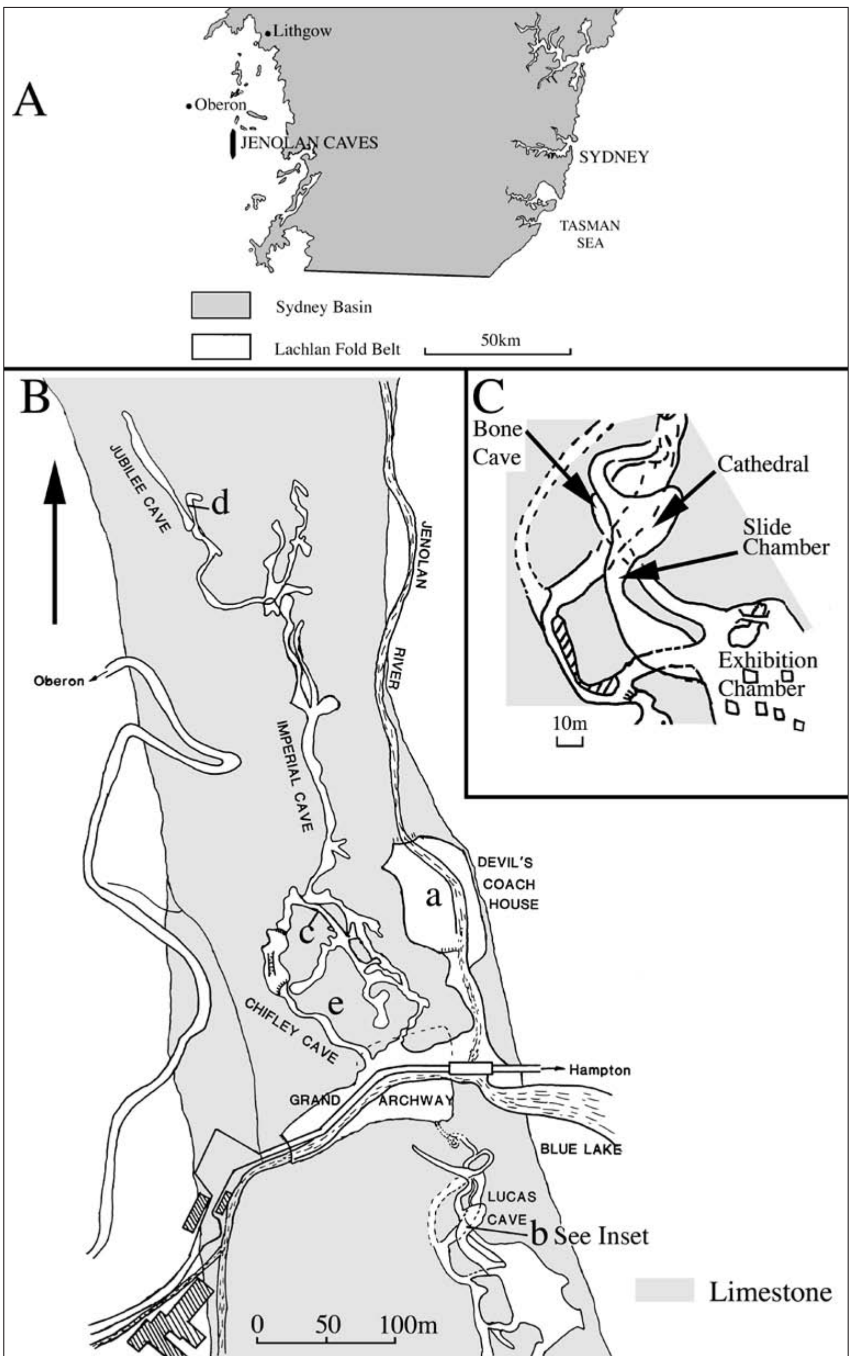

Fig. 1: A = Location. B = The Jenolan Show Cave System: a) The Devils Coach House, b) The Slide and Bone Cave sections, Lucas Cave, c) The Potatoes, Grotto Cave section, Chifley Cave, d) Transistors, Jubilee Cave, e) Flitch of Bacon section, Chifley Cave. C = detail of Cathedral-Bone Cave section of Lucas Cave.

Sulfate speleothems are abundant in caves of the Ordovician Gordon Limestone in Tasmania, with deposits in Exit Cave at Ida Bay and in the Mole Creek Caves being the best known.

Sulfate speleothems are abundant in some caves developed in the Tertiary limestones of the Nullarbor Plain. Subsequently, James (1991) considered that the major source of sulfate in these caves was aerosols derived from seawater.

Ardealite, $Ca_2(SO_4)(HPO_4).4H_2O$ (Back *et al.* 2008) is an uncommon phosphate mineral. It has been previously reported from Moorba Cave, Jurien Bay in Western Australia by Bridge *et al.* (1975) and from the now-flooded Texas Caves in Queensland (Grimes 1978). In both these localities, the ardealite was associated with guano. Recent unpublished work by Osborne & Pogson has identified ardealite in association with gypsum at Moparabah Caves, near Kempsey, NSW.

Interest in sulfate minerals arose in the early 1990s when a sample from the Potato Patch, Lucas Cave proved to be composed of sulfate rather than carbonate minerals. A detailed mineral survey of the caves resulted in examination of possible sulfate minerals from seven localities. Numbers with a prefix "D" refer to specimens housed in the Mineral collection while numbers with a prefix "DR" refer to specimens housed in the Petrology collection of the Australian Museum, Sydney.

SAMPLE DESCRIPTIONS AND LOCATIONS

DEVILS COACH HOUSE

Gypsum (selenite) is rare today in Jenolan Caves, but samples in the Australian Museum Mineral Collection suggest that significant deposits had existed in the Devils Coach House ("a" in Fig. 1-B) until the early twentieth century).

Specimen D1994 (Fig. 2-A), is a collection of bent crystals and fibrous gypsum masses from the Devils Coach House, registered at the Australian Museum on August 12, 1908. These specimens (fragments of 'flowers') are up to 80 mm long and are associated with masses of adjoining columnar crystals 30 mm long. There is no indication of their substrate or if they come from single or multiple deposits.

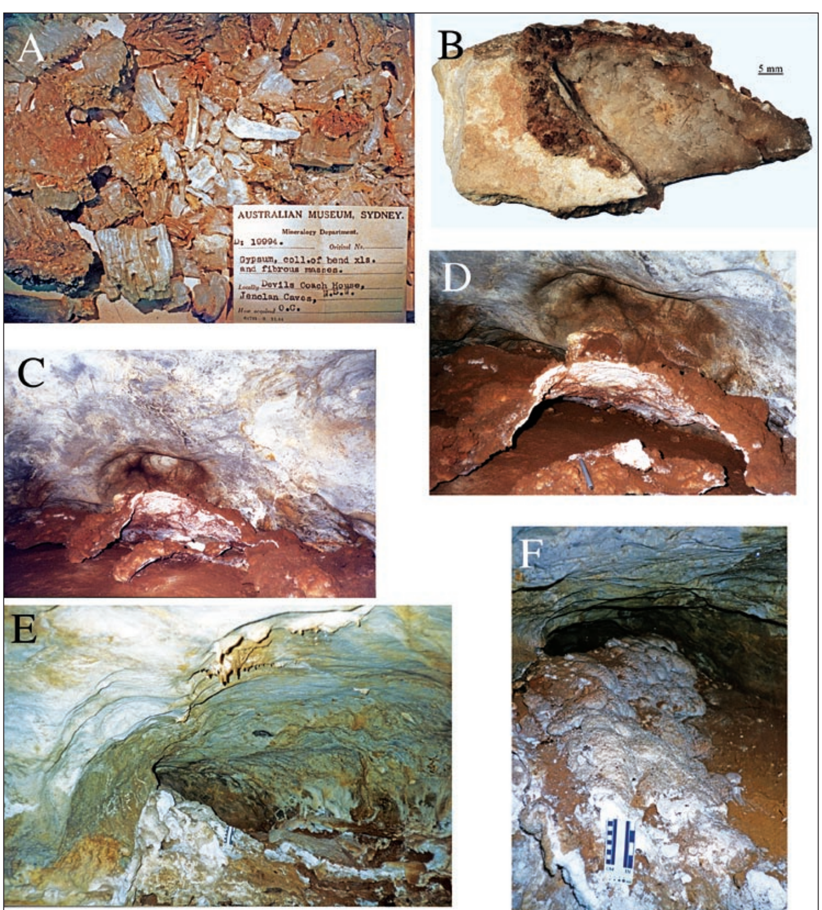

Fig. 2: A = D19994. Gypsum (selenite), showing bent crystals and fibrous masses. Specimen label 80 mm by 60 mm. B = Gypsum (selenite) growing from pyrite-bearing palaeokarst substrate, D12021. C = Distant view of crust at "B" (Fig. 3). D = Close-up view of crust at "B" (Fig. 3) showing convex shape of crust, relatively smooth inner surface and nodular outer surface. Pen = 130 mm. E = Broken edge of crust in Upper Bone Cave, grey wall on left hand side has crystalline gypsum coating. Black squares on left of scale bar = 10mm. F = Looking further SW in Upper Bone Cave from "d" (Fig. 4-C). Note cumulus surface of crust, particularly in far midfield. Black squares on left of scale bar = 10 mm.

Specimen D12021 (Fig. 2-B), also from the Devils Coach House and registered on February 2, 1898 and was presented by J. C. Wiburd, Caretaker of Jenolan Caves from 1903 to 1932. It consists of gypsum sheets and crystals growing from a yellow laminated carbonate substrate, similar to caymanite palaeokarst deposits described by Osborne (1991, 1993, 1994). In thin section, the substrate consists of finely laminated microspar, with some limonite pseudomorphs after pyrite cubes as well as framboids in the coarser laminae.

LUCAS CAVE

Thin white crusts, possible sulfate minerals occur at three localities in Lucas Cave. These occur in the Slide Chamber, the upper entrance passage of Lucas Cave, Centenary Cave and Bone Cave in the lower entrance passage of Lucas Cave (Figs. 1-C, 3 & 4).

The Slide

Sulfate minerals were identified in the wall of Slide Chamber ("A" in Fig. 3) associated with phosphatic deposits. Sample D56949 was collected from a vugh in the chamber wall.

Centenary Cave

Centenary Cave is a small segment of cave passage located below the floor of the tourist platform in the Slide Chamber of Lucas Cave (Fig. 3).

A sulphate crust (Figs. 2-C & 2-D) occurs on the southwestern side of a small chamber at the southern end of Centenary Cave ("B" in Fig. 3). It takes the form of a broad hollow cone, located under a bell hole in the sloping cave ceiling. The outer surface of the cone is nodular and coated with red-brown dust. Its northeastern side has collapsed to reveal a hollow centre with a white inner surface.

Sample D56950, from the collapsed section of the cone at "B" in Fig. 3, is a sheet about 5 mm thick. Its rough upper surface has small crystalline nodules 2-5 mm in diameter with fawn-coloured surface discolouration and when broken displays an underlying pearly white matrix.

A similar hollow crust with a fallen section occurs at "C" in Fig. 3. This deposit was not investigated, as accessing the crust would have caused unacceptable damage.

It is uncertain whether these cone-shaped crusts ever grew over subsequently removed sediment cones or if the hollow conical shape is due to crystal growth. Hill (1987) described how uneven growth of gypsum in Carlsbad Cavern, New Mexico, resulted in buckled or blistered crusts.

Brown crusts occur in places on the floor of Centenary Cave. Sample D56951 from these crusts was analysed.

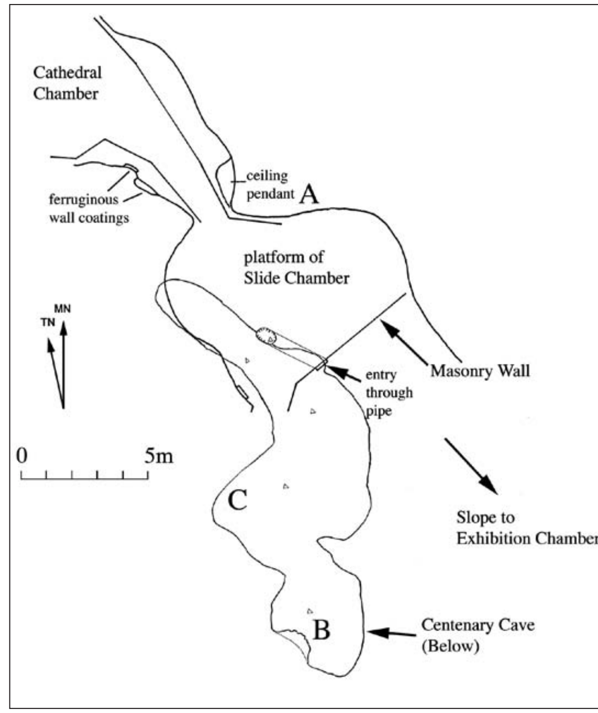

Fig. 3: Map of the Slide Chamber and Centenary Cave sections of Lucas Cave. A= Deposit on wall of Slide Chamber. B = Accessible sulfate crust. C = Inaccessible sulfate crust.

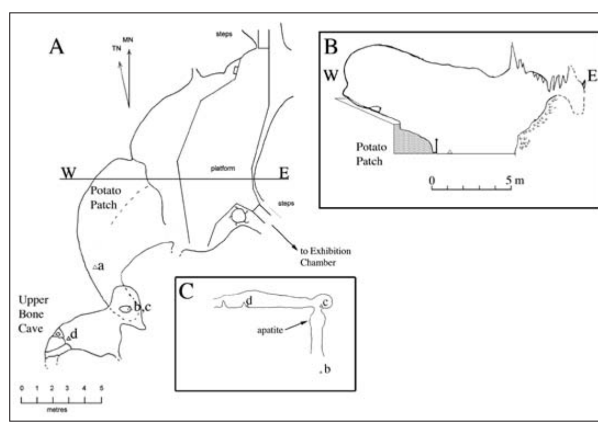

Fig. 4: A = Map of Bone Cave, Lucas Cave showing locations of the Potato Patch and Upper Bone Cave. B = Section W-E through Bone Cave. C = Section b-c-d through Upper Bone Cave.

Upper Bone Cave

Upper Bone Cave is a small, low earth-floored chamber located above and to the west of the Potato Patch in Bone Cave (Figs. 4-A & 4-C), to which it is connected by a 3.6 metre vertical shaft at the top of the slope above the Potato Patch. Soft pale yellow-brown pasty material (D56952) lines the shaft.

There is a passage extending from the west of the Upper Bone Cave, partly filled and blocked by crusts

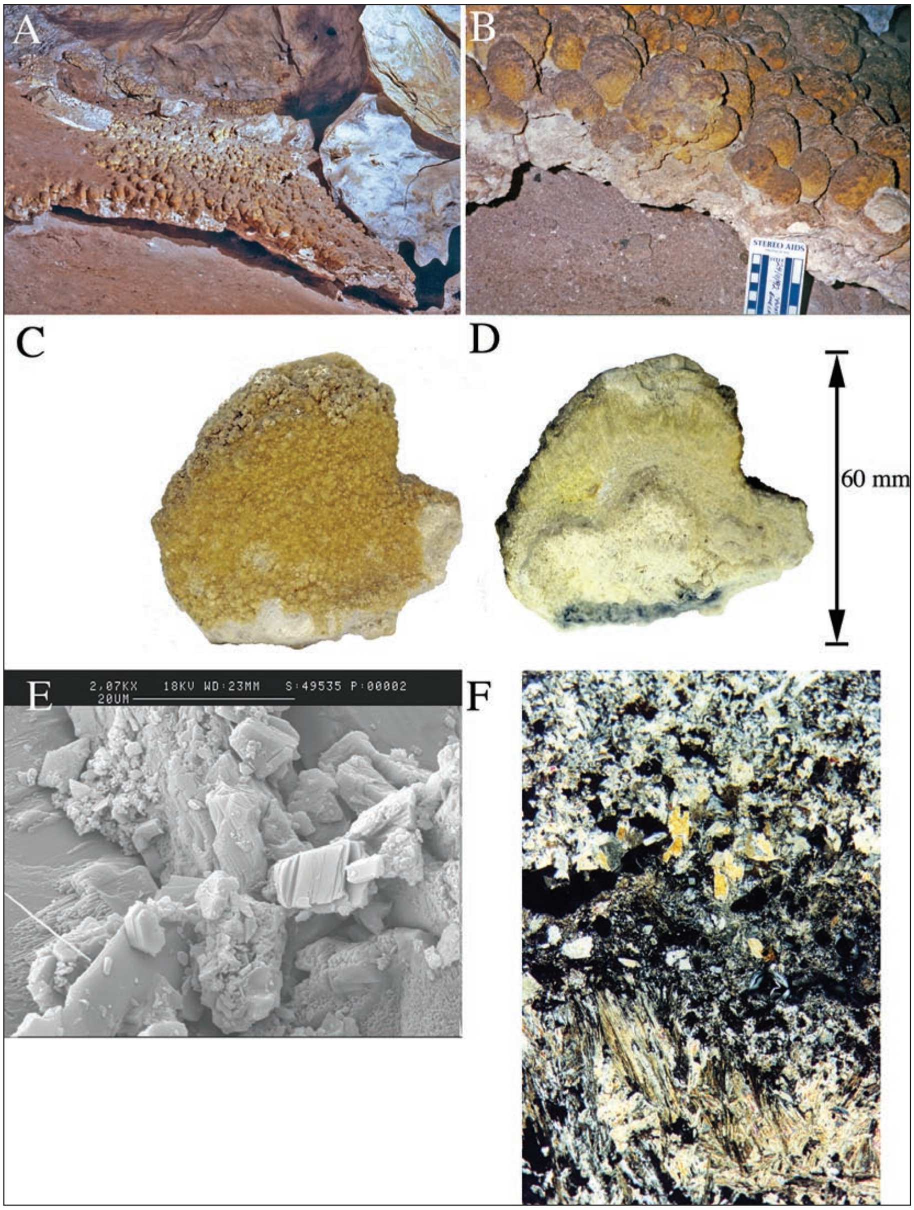

Fig. 5: A = The Potato Patch looking west, note potatoes rise vertically from crust on sloping substrate. B = Broken edge of the Potato Patch, note potatoes and basal laminated crust. Black squares on scale bar = 10 mm. C = Individual potato, side view, note pale-yellow, nodular outer surface. D = Vertical cross-section of Potato, note porous interior, poor lamination and lack of a drip-cup. E = SEM image of potato surface (D49535). Note small, well-formed gypsum plates, gypsum fragments and fretting in lower right and lower left. F = Thin section of potato (D49535), crossed nicols, showing cross-sections of radiating crystals in upper half and longitudinal sections of radiating crystals at edge of potato in lower half. Large equant crystals are approximately 0.75 mm across.

that form structures somewhat similar to rimstone pools (Figs. 2-E & 2-F). These crusts have a lemon yellow to red-brown nodular surface, white and sugary where broken (D56954). Fine crystals have grown in the bottom of these 'pools' (D56955), where they sit on a clayey substrate (D56957). Fragments of thin rust-coloured plates, (D56953), are spread over the cave floor adjacent to the crusts. Flat, star-shaped groups of crystals coat the cave wall adjacent to these crusts; which appear dark (D56956) or white (56958) (Fig. 2-E).

The Potato Patch, Bone Cave

Speleothems known as the 'Potato Patch' in the Bone Cave section of Lucas Cave (Fig. 1-C) have attracted attention for many years. Lucas Cave was discovered in 1860 (Foster 1890), but it is not known when the Potato Patch was first recognised. Foster (1890) provided the earliest description of the Potato Patch: "On the floor is a formation, composed of brown-coated lumps of carbonate of lime, which look exactly like potatoes scattered over the floor" (Foster 1890, p. 42). Trickett (1905) commented that: "Near at hand is the IRISH CORNER containing curious formations like potatoes" (Trickett 1905, p. 43) and more recently, Dunlop (1979) spoke of the Bone Cave: "Its Potato Patch is a curiously dissected piece of floor formation, unique in these caves" (Dunlop 1979, p. 56).

The Potato Patch covers an area of approximately 13 square metres (Fig. 4-A) and consists of numerous white boss-like masses 90 mm high, protruding from an 80 mm thick basal crust (Figs. 5-A & 5-B). The deposit projects above a sloping mud substrate and growth axes of the bosses are vertical. The substrate beneath the potatoes is white and powdery and approximately 100 mm thick, (D56959), underlain by 20–30 mm of dark brown clay (D56960), 40–60 mm of buff or cream layer (D56961),

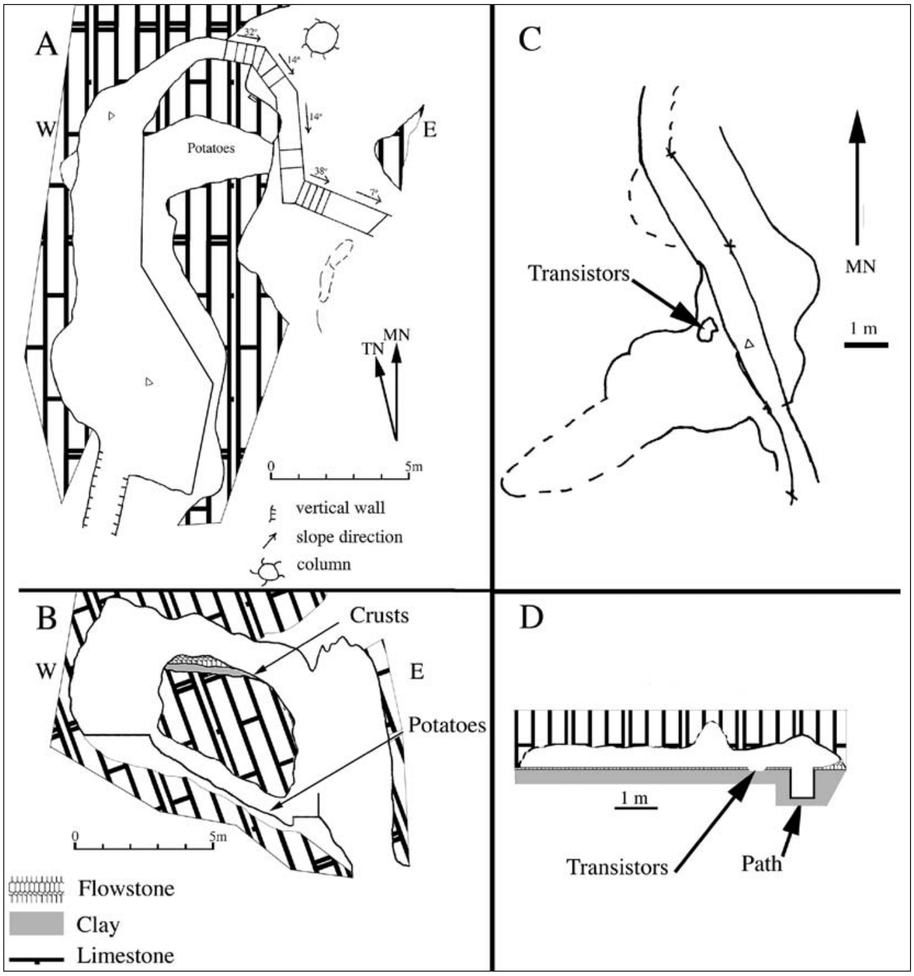

Fig. 6: A = Map showing section of Chifley Cave containing The Potatoes. B = E-W section showing location of the potatoes and crusts. C = Map showing transistor location in Jubilee Cave. D = Section NE-SW through transistor location in Jubilee Cave.

a red-brown speckled clay (D56962) and then by a dark brown clay layer of unknown depth (D56963).

An individual Potato

N. Scanlan collected approximately half of a potato with an intact outer surface (D49535) during maintenance and cleaning works. Its pale yellow outer shell, a few millimetres thick, is hard, enclosing a soft interior (Figs. 5-C & 5-D). Its surface has a sparse scattering of loosely attached, soft, white scaly crystalline aggregates and acicular crystals between 0.05 and 0.3 mm. Fig. 5-E shows a SEM image of the surface features. The specimen fluoresces weak yellow under short-wave ultraviolet, phosphorescing for 5 to 6 seconds.

The longitudinal section reveals sheaths of divergent lath-like crystal aggregates 5–10 mm radiating from centres of nucleation, having their longest axis parallel to the long axis of the potato. The base of the potato is an aggregate of equant crystals. Growth layering is developed perpendicular to the long axis of the potato.

A thin section of specimen D12021 (Fig. 5-F) reveals a mass of cloudy grey-white groups of divergent crystal laths and needles with a felted texture, radiating from centres of nucleation. These groups are 5 to 10 mm long, within which are scattered occasional euhedral, equant crystals of gypsum 0.1 to 0.2 mm. About 5% of the sample is scattered iron oxides and mud. A narrow band of finely granular gypsum forms encloses the outer rim of the bosses.

CHIFLEY CAVE

The Potatoes

The Grotto Cave potatoes in Chifley Cave ("c" in Fig. 1-B & Fig. 6-A) have a similar appearance to those in Lucas Cave (Figs. 7-A & 7-B). Like the Potato Patch, they occur on a sloping substrate as a number of bosses protruding perpendicularly from a basal crust. The potatoes sit on a white crumbly layer 5–10 mm thick (D56970) overlying 30 mm of white speckled red clay (D56967) that rests on flowstone.

Unlike the Potato Patch in Lucas Cave, the Potatoes in Chifley Cave lie under a rock shelf at a bend in the tourist path (Fig. 6-B). It seems likely that initial construction of the cave path in the early 20th century destroyed the upper and lower sections of the deposit.

Small coralloid speleothems project from the rock ceiling above the Potatoes (Fig. 7-A). A sample of these (D56968), consists of a crumbly botryoidal exterior crust (D56968a) surrounding a dense stalactitic core 10 mm in diameter having a small central tube and concentric growth bands (D56968b.)

Powdery and botryoidal crusts coat the western wall of Chifley Cave uphill from the Potatoes, near "W" in Figs. 6-A & 6-B. These crusts (D56964 & D56965) have been deposited by water running down the cave wall from above.

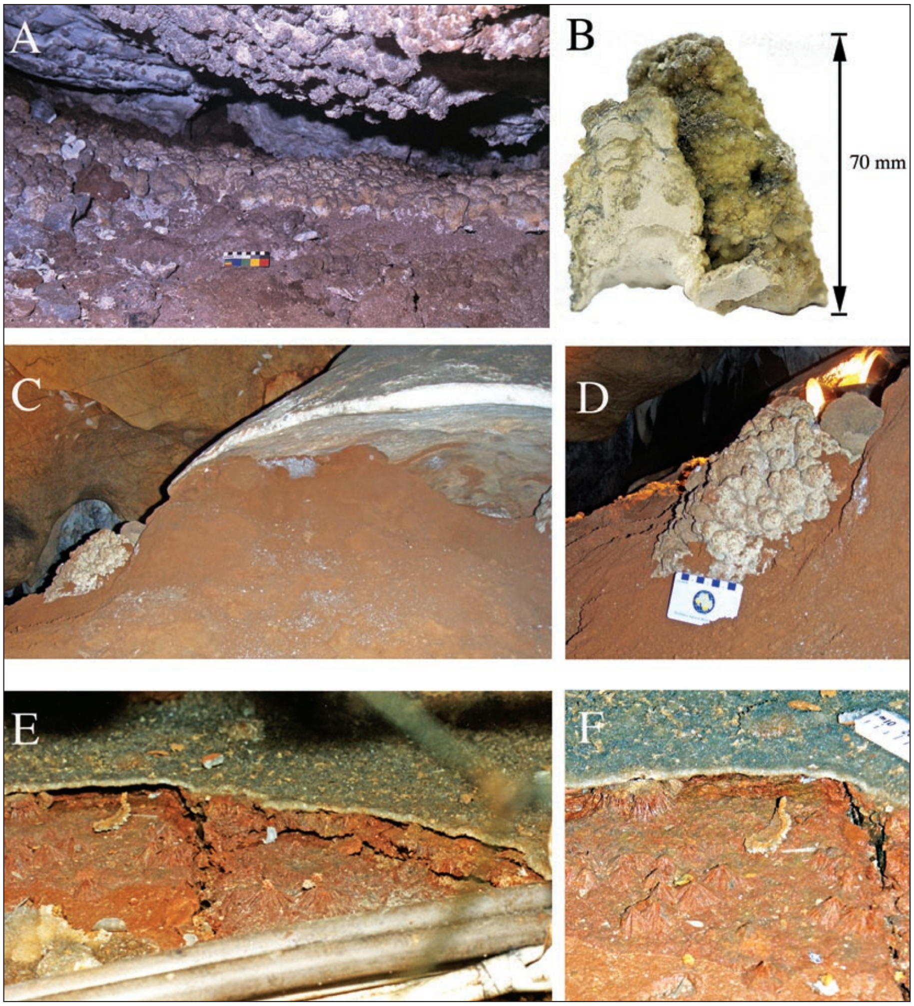

Fig. 7: A = The Potatoes in Chifley Cave looking uphill (west) from the pathway. Bosses here are shorter, more closely spaced and less regular than in Lucas Cave. Note coralloid speleothem on ceiling above Potatoes. Black squares on scale bar = 10 mm. B = Individual potato from Chifley Cave (D57257). Note poor lamination in cross-section and nodular pale-yellow outer surface. C = Crusts above The Potatoes, note clay substrate under crusts and overlying flowstone. D = Detail of crust, note nodular texture, blue squares on scale = 10 mm. E = The Transistors, Jubilee Cave. F = Detail of transistors, scale interval on rule = 5 mm.

Irregularly rounded crusts (D56969) rest on red clay (D56970) on top of the limestone mass above the Potatoes (Fig. 6-B). Unlike the Potatoes, they are oriented normal to their depositional surface (Figs. 7-C & 7-D).

JUBILEE CAVE

The Transistors

Small deposits, similar to those described as 'transistor gypsum' by Hill & Forti (1986) in Jubilee Cave ("d" in Fig. 1-B, Fig. 6-C) occur in a pool deposit revealed through a broken calcite crust (Fig. 7-E). Each transistor group is a conical aggregate of elongate crystals, approximately 15 mm high and 20 mm in diameter, and some are capped by fragments of the overlying crust, suggesting that as they grew they broke through the crust (Fig. 7-F). The transistors grow on top of very wet mud (Fig. 6-D). This mud has an in situ salmon-pink colour (D56972), but in daylight appears rusty yellow. Air-drying showed that in situ the mud is 38% water by weight. Aragonite helictites grow from sparry veins nearby.

METHODS

FIELDWORK

Reconnaissance surveys and information from cave guides helped identify potential sulfate deposits. Naturally broken material was collected where possible, otherwise small specimens were collected from unobtrusive places. Specimens were lodged in the Mineralogy Collection of the Australian Museum, and all sites were extensively photographed. The sites were surveyed and cross sections measured at a scale of 1:100 using a plane table with laser alidade and section-measuring techniques as described by Osborne (2004). In Centenary Cave and Upper Bone Cave where space was limited, detailed surveys were made by tape and compass.

X-RAY DIFFRACTION

X-ray diffraction (XRD) analysis was undertaken at the Australian Museum using Philips PW1730/PW1050 and Panalytical X'Pert Pro equipment. A graphite monochromator and proportional counter were used, with 40–45 kV and 30–40 mA of Cu–kα radiation. Scans were run from 2^0 to 70^0 2θ at 1.2 to 0.6^0/minute with 1^0 divergence slit, 0.1 mm receiver slit and 0.02^0 step size.

SIROQUANT ANALYSIS

Weight percent mineral phase contents were estimated with SIROQUANT for Windows, V.3 software (Taylor 1991; Taylor & Clapp 1992), using calculated hkl mineral library files. Refinement stages were optimised for the smallest possible χ^2 goodness-of-fit parameter for the associated Rietveld peak pattern match (Taylor 1991; Taylor & Clapp 1992).

X-RAY FLUORESCENCE

X-ray fluorescence (XRF) analysis was carried out at the Microstructural Analysis Unit, University of Technology, Sydney, using the Siemens proprietary software UniQuant. Samples of potatoes were analysed for elements from atomic number 11 (Na) to 92 (U). The XRF had a rhodium target operating at 60 Kv and 40 mA. The x-ray spectrum was analysed using the following crystals where appropriate: LiF 420, LiF 220, Ge 111 and TlAP 200.

SEM/EDS

Energy-dispersive X-ray spectrometry (EDS) analysis was undertaken at the Australian Museum using a Cambridge Stereoscan 120 Scanning Electron Microscope (SEM) with an Oxford Instruments Link Isis 200 EDS attachment. An internal cobalt calibration standard was used. Spectra were accumulated in backscatter electron mode for 100 seconds at 20 kV, 15–23µm working distance, 18–25 x magnification and instrument setup #4 (20 microsecond process time). Element mapping was carried out on a 8 mm x 12 mm polished mount.

ISOTOPIC STUDIES

Stable isotopes of sulfur were determined at Environmental Isotopes, Sydney, and at the University of Barcelona (Faculty of Geology). At Sydney, sulfate samples (<0.1 mg) were combusted in a tin cup using a modified Roboprep elemental analyser attached to a Finnigan 252 mass spectrometer. V_2O_5 was added to samples to enhance combustion. Samples were analysed relative to an internal gas standard and laboratory standards (Ag_2S-3 +0.4 ‰ $_{VCDT}$ and CSIRO-S-SO4 +20.4 ‰ $_{VCDT}$). The laboratory standards have been calibrated using international standards IAEA-S1 ($\delta^{34}S$ = -0.3 ‰ $_{VCDT}$) and NBS-127 ($\delta^{34}S$ = +20.3 ‰$_{VCDT}$). Replicate analyses of standards are within ± 0.2 ‰.

Sub-samples from the same localities were also analysed for oxygen in sulphate. In order to ensure homogeneity of the sub-samples $\delta^{34}S$ were repeated. Results obtained from both laboratories are reported in Tab. 3. All samples processed at Barcelona were converted to $BaSO_4$ and analysed for their oxygen and sulfur isotope compositions. The respective CO_2 and SO_2 gases produced from the sulfates were analysed on a continuous-flow Finnigan DELTA plus XP mass spectrometer, with TC/EA pyrolyser for oxygen and Finnigan MAT CHN 1108 analyser for sulfur. The values are given relative to the V-SMOW (Vienna Standard Mean Ocean Water) reference for $\delta^{18}O$ of sulfates, and to the V-CDT (Vienna Cañon Diablo Troilite) reference for $\delta^{34}S$ of sulfates; the measurement precisions are ±0.4‰.

RESULTS

X-RAY DIFFRACTION MINERAL IDENTIFICATION

The gypsum (selenite) from the Devils Coach House is pure gypsum (Tab. 1). The supposed gypsum from the Slide Chamber in Lucas Cave (D56949) was apatite-(CaOH) (Burke 2008). The crust in Centenary Cave (D56950), as anticipated, was gypsum and the floor crusts (D56951) contained quartz, clay minerals and apatite-(CaOH), but no gypsum.

The white crystals in the rimpools, and wall coatings in Upper Bone Cave were found to be gypsum. The rusty chips in that chamber are mixtures of goethite and quartz and the mud in the base of the pools is kaolinite and quartz. Apatite-(CaOH) was the pale yellow paste lining the shaft between Bone Cave and Upper Bone Cave.

The potato sample from the Potato Patch in Bone Cave had variable amounts of both ardealite (ICDD 00-041-0585) and gypsum (ICDD 00-036-0432), (gyp-

Tab. 1: Summary of XRD Identifications and Sample Data.

Australian Museum No.	***Location***	***Form***	***Mineral Species***
D12021	Devils Coach House	selenite, massive	gypsum
D19994	Devils Coach House	selenite, curved fibrous	gypsum
D56949	vugh lining, wall of Slide chamber, Lucas Cave	crusts, botryoidal	apatite-(CaOH)
D56950	back of chamber, Centenary Cave, Lucas Cave	crust, granular	gypsum
D56951	Centenary Cave, Lucas Cave, crusts off floor	brown clay	kaolinite, quartz, illite, minor apatite-(CaOH)
D56952	shaft above Potato Patch, Bone Cave, Lucas Cave	soft, pale yellow, pasty	apatite-(CaOH)
D56953	Upper Bone Cave, Lucas Cave, from floor	thin rusty plates	goethite, minor quartz
D56954	Upper Bone Cave, Lucas Cave, from rimpool	white fluffy	gypsum
D56955	Upper Bone Cave, Lucas Cave from floor of pool	fine crystals	gypsum
D56956	Upper Bone Cave, Lucas Cave, wall coating	clear coating with "stellar" crystals	gypsum
D56957	Upper Bone Cave, Lucas Cave, base of pools	clay	quartz, minor apatite-(CaOH), goethite
D56958	Upper Bone Cave, Lucas Cave	hard white crystals off wall	gypsum
D49535a	Bone Cave, Lucas Cave	potato, outer crust	gypsum, minor ardealite, very minor silica and calcite
D49535b	Bone Cave, Lucas Cave	potato, inner zone	ardealite, minor gypsum, very minor silica and calcite
D56959	Bone Cave, Lucas Cave, under potatoes	white powder	gypsum, ardealite
D56960	Bone Cave, Lucas Cave, under potatoes	brown clay	quartz, moderate apatite-(CaOH), minor goethite
D56961	Bone Cave, Lucas Cave, under potatoes	buff-cream powder	quartz, moderate apatite-(CaOH), minor illite, possible very minor montmorillonite
D56962	Bone Cave, Lucas Cave, under potatoes	red-brown speckled clay	quartz, moderate gypsum, minor illite & kaolinite
D56963	Bone Cave, Lucas Cave, under potatoes, bottom layer	dark brown	quartz, apatite-(CaOH) , minor goethite, very minor montmorillonite
D57257a	Grotto Cave, Chifley Cave	outer crust of potato	gypsum, minor ardealite, very minor quartz and calcite
D57257b	Grotto Cave, Chifley Cave	inner zone of potato	ardealite, minor gypsum, very minor quartz and calcite
D56964	wall, back of potatoes, Chifley Cave	powdery crusts	apatite-(CaOH)
D56965	wall, behind potatoes, Chifley Cave	crusts, botryoidal	apatite-(CaOH)
D56966	under & within potatoes, Chifley Cave	white granular material	apatite-(CaOH), minor quartz
D65967	under potatoes, Chifley Cave	fawn/white crumbly	apatite-(CaOH), moderate quartz
D56968a	speleothem from "ceiling" directly above potatoes, Chifley Cave	botryoidal exterior of speleothem	calcite + minor quartz
D56968b	speleothem from "ceiling" directly above potatoes, Chifley Cave	dense stalactitic interior	calcite
D56969	Chifley Cave, above potatoes	potato-like crust	crandallite, moderate apatite-(CaOH), minor quartz, illite
D56970	Chifley Cave, above potatoes, crust substrate	red-brown clay	clay, quartz, minor illite, minor kaolinite, minor goethite
D56971	Jubilee Cave, Transistors	crystal fragment	calcite
D56972	Jubilee Cave, under transistors	pink clay	illite, kaolinite, quartz, goethite
REFERENCE SAMPLES			
D56973	Basin Cave, Wombeyan	guano	gypsum
D41396	Whyalla, South Australia	salt lake gypsum	gypsum
D56974	Józef-hegyi Cave, Budapest, Hungary	thermal cave gypsum	gypsum
D56975	Exhibition Chamber, Lucas Cave	altered guano	apatite-(CaOH)
DR12132	Lucinda Cavern, Chifley Cave	altered guano	apatite-(CaOH), minor illite, calcite, quartz
D56976	Mt. Etna Caves, Qld	Ghost Bat guano	apatite-(CaOH), very minor gypsum
D56977	Deep Hole Cave, Walli, NSW	? thermal cave gypsum	gypsum

sum-rich outer rim or ardealite-rich inner core). Minor amounts of quartz and calcite. Two estimates of the weigh percent mineral phases using SIROQUANT for an outer mixed zone of specimen D49535 gave 18% and 24% ardealite and 76% and 82% gypsum.

Substrate from below the Potato Patch consists of quartz, apatite-(CaOH) and clay minerals, with gypsum present directly below the potatoes (D56959) and also from lower in the substrate (D56962).

Potato specimens from Chifley Cave have a similar in mineralogy to those in Lucas Cave: variable gypsum and ardealite, with small amounts of quartz and calcite. Crusts on the wall uphill and west of the Potatoes (D56964 & D56965) were identified as apatite-(CaOH). The substrate under the Potatoes (D56966 & D56967) is apatite-(CaOH) and quartz. Notably, the coralloid speleothem directly above the Potatoes (D56968) contains neither sulfate nor phosphate minerals, having a calcite core and a crusty exterior of calcite and a little quartz.

Despite its morphological similarity to potatoes, the rounded crusts above the Potatoes in Chifley Cave contain no sulfate minerals, but are composed of crandallite $\{Ca\ Al_3\ (PO_4)_2\ (OH)_5.H_2O\}$, (Back *et al.* 2008), with minor apatite-(CaOH), quartz and illite.

The 'transistors' in Jubilee Cave are composed of calcite. Their morphological similarity to 'transistor gypsum' (Hill & Forti 1997), however, suggests that they are calcite pseudomorphs after gypsum. The mud substrate under these transistors contains clay, quartz and goethite (D56972).

CHEMICAL AND ISOTOPIC STUDIES

XRF (Tab. 2) and EDS analyses of inner and outer layers of Lucas and Chifley Cave potatoes show a variation of ardealite and gypsum phases, with the outer layers being sulfate-rich and inner layers phosphate-dominant. There is also minor scattered calcite and silica EDS mapping showed they have an outer shell only a few millimetres thick of mainly gypsum with minor ardealite and calcite, while the interior is mainly ardealite with minor gypsum and calcite. Figs. 8-A & 8-C show gypsum predominating in outer layers (high sulfur), while Figs. 8-B & 8-D show ardealite dominant in the interiors (high phosphorus). The mean of fifty random EDS analyses of ardealite from the interior of a Lucas Cave potato gave CaO 58.90%, P_2O_5 20.24% and SO_3 20.86% (anhydrous basis), compared to the theoretical values for pure ardealite (anhydrous basis) give 55.98%, 21.63% and 22.39% (Tab. 2).

	1.	*2.*	*3.*	*4*	*5.*	*6.*
SiO_2	0.13	1.65	1.40	2.78		
TiO_2		0.01				
Al_2O_3	0.03	0.28		0.10		
Fe_2O_3	0.01	0.13	0.02			
MgO			0.02	0.09		
CaO	33.20	30.0	50.80	31.52	32.58	32.57
K_2O		0.15	0.02	trace		
SrO	0.02					
SO_3	45.60	30.80	43.00	28.67	23.26	46.50
P_2O_5	0.02	11.40	4.70	14.50	20.61	
Cl			0.04	trace		
CO_2				0.12		
Others	0.06					
H_2O (diff.)	-	25.21	20.93	22.59	23.55	20.93
Totals	100.00	99.93	100.00	100.37	100.00	100.00
(normalised)						

Tab. 2: Major Element Analyses.

1 = D19994, gypsum, Devils Coach House (XRF analysis), anhydrous basis.

2 = D54935b ardealite with minor gypsum, interior of a potato, Potato Patch, Lucas Cave (XRF analysis).

3 = D57257, gypsum with calcite and minor ardealite, outer crust of potato, Chifley Cave (XRF analysis)

4 = C1, "gypsum", Grotto Cave, Chifley Cave (Mingaye 1899) (wet chemical analysis).

5 = Theoretical ardealite $Ca_2(SO_4)(HPO_4)\cdot 4H_2O$.

6 = Theoretical gypsum $CaSO_4\cdot 2H_2O$.

Sulfur and oxygen isotopic compositions

Sulfur and oxygen isotope compositions were determined in 10 and 9 samples respectively from selected Jenolan Caves' materials, supplemented with 5 additional sulfur and 3 additional oxygen analyses from other caves and environments (Tab. 3). The $d^{34}S_{\ V\text{-}CDT}$ values for Jenolan caves materials ranged from -1.4 to +12.9‰ while the $d^{18}O_{\ V\text{-}SMOW}$ values varied

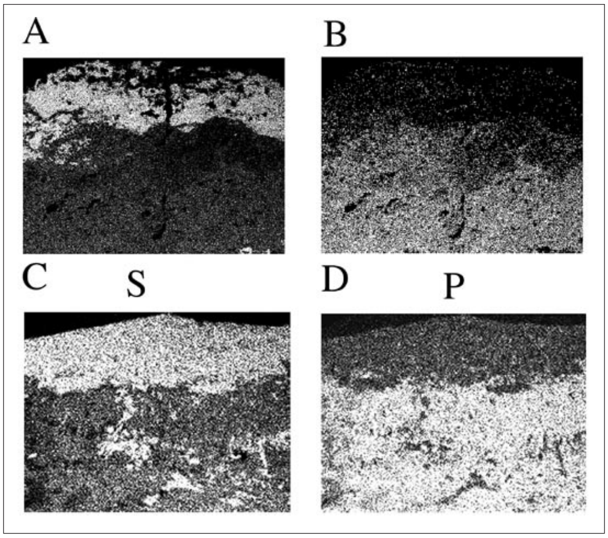

Fig. 8: Phosphorous and sulfur k-a$_1$ X-ray element maps. Top of frame is outside of potato. A = Sulfur map for Lucas Cave potato, field of view approximately 7 x 5 mm. Note concentration of S in upper third. B = Phosphorous map for Lucas Cave potato, field of view approximately 7 x 5 mm. Note concentration of P in lower two thirds. C = Sulfur map for Chifley Cave potato, field of view approximately 8x 6 mm. Note concentration of S in upper third and in irregular pores in lower two thirds. D = Phosphorous map for Chifley Cave potato, field of view approximately 8 x 6 mm. Note concentration of P in lower two thirds.

from +2.6 to +10.3 ‰. These results group around two distinctive end-members.

Gypsum (selenite) from the Devils Coach House gave average d^{34}S values of +1.8‰, while gypsum and ardealite bearing gypsum from Lucas and Chifley Caves consistently gave more enriched values averaging +11.9‰. Gypsum-bearing altered bat guano from the Exhibition Chamber section of Lucas Cave gave a d^{34}S value of +13.9‰, similar to Ghost Bat guano from Mt.

Sample	***Mineral***	***Location***	$\delta^{34}S_{CDT}$ (‰) *	$\delta^{34}S_{CDT}$ (‰) **	$\delta^{18}O_{V-SMOW}$ (‰) **
Jenolan Samples					
D12021	gypsum	Devils Coach House	+4.9	+4.85	+9.33
D19994	gypsum	Devils Coach House	+1.4	-1.42	+10.27
D49535a	gypsum, minor ardealite	Outer crust of Potato, Bone Cave	+11.4	+11.31	+4.04
D49535b	ardealite, minor gypsum	Inner section of Potato, Bone Cave	+11.6	+11.12	+4.22
D57257a	ardealite, minor gypsum	Outer crust of Potato, Chifley Cave	+12.9	+12.78	+4.31
D57257b	gypsum, minor ardealite	Inner part of Potato, Chifley Cave	+11.8	+11.31	+4.66
D56955	gypsum	floor of pool, Centenary Cave	+12.3	+12.29	+4.61
D56958	gypsum	Upper Bone Cave, Lucas Cave	+12.2		
D56950	gypsum	Crusts, end of chamber, Centenary Cave	+11.8	+12.5	+2.6
D56975	Bat guano	Exhibition Chamber, Lucas Cave	+13.9	+14.26	+3.86
Additional samples from other localities					
D56973	gypsum	Basin Cave, Wombeyan, NSW (from a guano pile)	+13.8		
D56974	gypsum	József-hegyi Cave, Budapest, Hungary (from a thermal cave)	-24.3	-22.6	-1.28
D56977	gypsum	Deep Hole Cave, Walli, NSW (from a suspected thermal cave)	-14	-14.03	+7.66
D41396	gypsum	Whyalla, South Australia (from a salt lake)	+16.7	+15.71	+13.21
D56976	Ghost Bat guano	Mt. Etna Caves, Queensland	+12.7		

Tab. 3: Isotopic Results.

* Determined at Environmental Isotopes, Sydney.

** Determined at University of Barcelona, Faculty of Geology.

Etna (Qld), analysed as +12.7‰. Gypsum samples derived from hydrothermal processes in other caves gave significantly more negative d^{34}S than either group from Jenolan while the inland South Australian salt lake gypsum showed similar d^{34}S to those samples derived from guano. The d^{18}O also grouped in two separate fields with their isotopic values derived from either guano sulfate dissolution or atmospheric sources such as rain or drip water d^{18}O and dissolve O_2 isotopic signatures.

DISCUSSION

SULFATE STABLE ISOTOPES

The sulfur and oxygen isotopic signatures of recovered sulfates can further refine the original sources of sulfate in the cave deposits. The Silurian marine dissolved sulfate d^{34}S has been inferred from lattice-bound sulfate in brachiopods to lie between +23.2‰ and +30‰ with a trend towards depleted values during the Late Silurian (Kampschulte & Strauss 2004). This is further confirmed with values found in evaporitic cements from shallow Silurian carbonates of the Carnavon Basin (WA) (El-Tabakh *et al.* 2004). In the case of oxygen, data is scarce. However, ranges proposed by Claypool *et al.* (1980) would have modern values included within the Silurian range. If we assume that diagenetic mineral transformations have not drastically altered the isotopic signature of sulfate within Silurian carbonates, none of the results obtained in the cave sulfate minerals could be derived from a Silurian marine sulfate source.

Another possible source of sulfur is the oxidation of dispersed pyrite within the limestone (Yonge & Krouse 1987). Pyrite could have a diagenetic origin from bacterially mediated reduction of original marine sulfate. Bottrell (1991) found gypsum, interpreted as formed from oxidation of diageneteic pyrite, with δ^{34}S ranging between -26.3 and -33.3% in the Ogof y Daren Cilau cave systems. Pyrite sulphur isotope signatures formed in that way would have marked δ^{34}S depletion up to 46‰ (Canfield 2001). The oxidation of this type of sulphide would result in the formation of a sulphate with a depleted isotope signature. The gypsum (selenite) from Devils Coach House falls into a group with depleted d^{34}S (-1.5 to 4.9‰). Moreover, the close proximity of pyrite pseudomorph textures reinforces the suggestion that some sulfate inherits its isotopic composition from the oxidation of sulfides and constitutes one of the sulfur end-members observed (Fig. 9).

The oxygen incorporated into the sulfate radical during the oxidation of pyrite would mostly be derived from water, with the remainder from air-dissolved oxygen (d^{18}O = +23‰), (Mizutani & Rafter 1968). Recent analyses of water stable oxygen isotopes (d^{18}O) in drips from Chifley Cave give average values of -6.3‰ (C. Waring, pers. Comm. 2009). This value is considerably depleted with respect to those found in the sulphate -d^{18}O of +9.8‰, and suggests the potential importance of atmospheric O_2 and most importantly the evaporation processes leading to precipitation of the sulfate minerals.

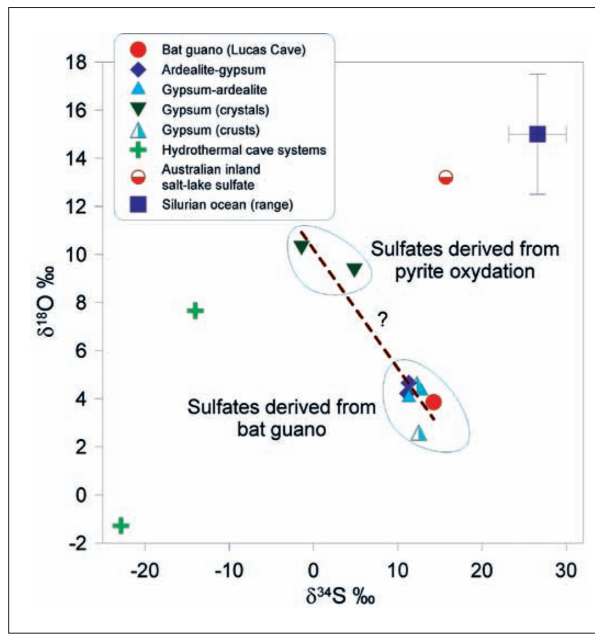

Fig. 9: Isotope Graph, Note two distinct populations, one of Lucas and Chifley Cave and the other for the Devils Coach House specimens. Also, note distance from the main populations of the hydrothermal cave gypsums (D56974 & D56977) and the salt-lake gypsum (D41396).

A further distinctive sulfur isotopic end-member corresponds to gypsum and ardealite with enriched sulfur isotopes ranging from +11.3 to +12.9‰. These match similar values for mineralised bat guano deposits in the Exhibition Chamber of Lucas Cave, and a Ghost Bat (Macroderma gigas) guano sample from Mt. Etna Caves, Queensland (Tab. 3). These results contrast with more depleted isotopic signatures of bat guano from Cambodia with average d^{34}S of +6.8‰ (Hosono *et al.* 2006). This difference with the Cambodian guano is most likely related to dietary inter-species differences. The bat species currently roosting in caves at Jenolan is the Large Bent-wing Bat; Miniopterus schreibersii, while no data is available for the Cambodian guano deposits.

The influence of hydrothermal fluids or sulfidic groundwater in gypsum precipitating karst systems has also been described (Bottrell *et al.,* 2001; Galdenzi and Maruoka, 2003, Onac *et al.,* 2009). However, the potential range of sulphate-d^{34}S values can be very wide (Tab. 3) and will be controlled by local influences such as the original d^{34}S of fluids, water-rock interactions and potential mixing processes. Bottrell *et al.,* (2001) found d^{34}S ranges of +9.8 to +13.3‰ in gypsum floor crusts from Cupp-Coutun/Promeszutochnaya cave system. While these values are similar to those identified in this work, the geological setting is totally different with no upwelling of basinal brines identified at Jenolan. The above scenarios rule out a hydrothermal source of sulphur in gypsum.

THE SOURCE OF THE SULFATE

The Jenolan Caves Limestone is mostly a massive lime mudstone containing 98% $CaCO_3$ (Carne & Jones 1919), apparently deposited in oxygenated ocean water. Pyrite is found in some of its lower thinly-bedded units, but these beds are not within the likely catchment of vadose water reaching the areas where any of the speleothems described in this paper have been deposited. J. M. James, (Pers. Comm. 1993), reported that significant sulfate ions occur in the water from the River Styx in the southern Jenolan Tourist Caves. Recent major ion analysis of drip water at the Flitch of Bacon section ("e" in Fig. 1-B) had consistent sulfate concentrations averaging 3 mg/L while surface lysimeters showed higher concentrations (C. Waring, pers. Comm. 2009).

One gypsum (selenite) specimen from the Devils Coach House, deposited on a palaeokarst substrate, has limonite pseudomorphs after pyrite. Also there are a number of similar palaeokarst deposits exposed in the walls of the Devils Coach House. The pseudomorphs after transistor gypsum in Jubilee Cave occur in close proximity to a pyrite-bearing sparry vein seem to have formed from water evaporating from their clay substrate, rather than from the cave wall. Hill & Forti (1986) regarded oxidation of pyrite as the most common source of sulfate minerals in caves, while Onac (2005) lists oxidation of sulphides, guano and fumaroles as common sulphur sources. The close relationship between pyrite-bearing deposits and the sulfates suggested that some sulfates at Jenolan were derived from the weathering of pyrite. Osborne (1994) proposed that basinal fluids, derived from the Sydney Basin, were responsible for emplacing pyrite in the palaeokarst deposits. However, work in progress suggests that this view is incorrect and that the sulfides are either authigenic, or were emplaced during a hydrothermal phase of cave development that post-dated deposition of the palaeokarst deposits.

The gypsum and ardealite-gypsum deposits in both Lucas and Chifley Caves are closely associated with other phosphate minerals. In Lucas Cave, apatite-(CaOH) occurs in the wall of Slide Chamber above Centenary Cave, in the floor of Centenary Cave underlying the gypsum crusts, in the shaft above the Potato Patch and in the substrate below the Potato Patch.

Phosphate deposits also surround the Potatoes in Chifley Cave. There is apatite-(CaOH) on the cave wall above and to the west of the Potatoes, crandallite and apatite-(CaOH) in a crust above the Potatoes and apatite-(CaOH) in the substrate below them. Just as the association between the gypsum (selenite) in the Devils Coach House and caymanite palaeokarst suggests a pyritic origin, the close relationship between the sulfates in Lucas and Chifley Cave with phosphatic deposits suggests a guano origin.

ARDEALITE-GYPSUM POTATOES AND THE SOURCE OF THE PHOSPHATE

Guano deposits can be seen in the Exhibition Chamber of Lucas Cave, but guano is not seen in the immediate vicinity of the potato deposits in the Bone Cave section of Lucas Cave or in the Grotto Cave section of Chifley Cave, although Voss Wiburd collected guano from Lucinda Cavern in Chifley Cave in 1898.

The former existence of guano deposits adjacent to potatoes can be inferred from the presence of small amounts of apatite-(CaOH) in the vertical tube joining Bone Cave to Upper Bone Cave (D56952), on a wall of the Slide Chamber adjacent to the Cathedral in Lucas Cave (vertically above the Potato Patch) and on a chemically-altered and discoloured wall behind the Potatoes in Grotto Cave section of Chifley Cave.

XRD analysis of altered guano (DR12132) collected in 1898 from the Lucinda Cavern of Chifley Cave, but not now accessible, revealed apatite-(CaOH) but no gypsum, while analysis of guano from the Exhibition Chamber of Lucas Cave revealed both apatite-(CaOH) and gypsum. A small amount of gypsum has also been found in altered bat guano from Mt. Etna Caves, Queensland.

Bats have been roosting in Jenolan Caves for a very long time and have built up guano deposits in several of the caves. Some of these deposits, such as those in the Katie's Bower and Lucinda Cavern sections of Chifley Cave, were noted in the early literature by Mingaye (1899) and Trickett (1905).

Hutchinson (1950) listed several chemical analyses of fresh and altered bat guano from caves worldwide, including Australia. Appreciable amounts of both sulfur and phosphorus are recorded, for example, in two samples of fresh bat guano from Puerto Rico, yielding 6.95% and 7.42% P_2O_5 and 3.00% and 3.8% SO_3 (Hutchinson 1950, table p. 381). Sulfur and phosphorus would be further concentrated in leachates.

Onac & Verez (2003) and Marincea *et al.* (2004) proposed that the phosphatic cave deposits in Romanian caves result from chemical reactions between calcium carbonate and acidic solutions derived from guano. These reactions first produced apatite-(CaOH) and brushite, with further alteration to ardealite, the order of formation being: apatite-(CaOH) => brushite => ardealite, with phosphate-rich then sulfate-rich solutions, accompanied by pH changes reflecting degree of carbonate dissolution.

A similar mechanism could be proposed for Jenolan, although there is gypsum but no brushite, and adjacent apatite-(CaOH) deposits are unrecognised or scarce. Crandallite, an aluminium phosphate mineral has also been found near the Potatoes in Chifley Cave, the aluminium supplied by cave clays. Marincea *et al.* (2004) commented that only apatite-(CaOH) forms at higher pH, and both apatite-(CaOH) and brushite are unstable for pH values up to 5.5. Ardealite can form where pH < 5.5 if sulfur is also available.

At Jenolan, pH changes and availability of both sulfur and phosphorus favoured formation of earlier ardealite in the core of a potato, then gypsum in its outer shell as phosphorus was depleted, although there has been some degree of intergrowth. Early-formed apatite-(CaOH) was probably the precursor of all the phosphate minerals. Hill & Forti (2004) state that almost all cave phosphate minerals are derived from guano, which can also be a source of sulfur for sulfate cave minerals, including gypsum. They also suggest that sulfates could be linked to sulfuric acid produced by sulphur oxidising bacteria harboured by the guano.

DEPOSITIONAL PROCESSES

Sulfate minerals in caves are generally considered to be evaporates, however most of the deposits described here occur in the outer sections of the caves where calcite speleothems have dry chalky surfaces indicative of evaporitic deposition. The potatoes in both the Lucas and Chifley Cave are oriented vertically, and not perpendicular to the depositional surface, suggesting they were not deposited in a pool, but rather formed under subaerial conditions. There is no evidence to suggest that the potatoes in Lucas Cave were deposited by dripping water. While there are speleothems above the Potatoes in Chifley Cave, these contain neither sulfate nor phosphate minerals, so could not have been feeders for the potatoes below. All potatoes lack the drip-cup layering characteristic of stalagmites. The gypsum (selenite) masses, crusts and transistors are also definitely not stalagmitic forms.

If the deposits were not formed in pools or by drips it is most likely that they formed by evaporation of water from their substrata. This is the accepted mechanism for the formation of gypsum crusts (Hill & Forti 1997, p. 63) and transistors, which have also been shown to grow up from their base (Hill & Forti 1997, p. 69). Potatoes are an extreme example of this process with pore water from the underlying substrate being drawn upwards depositing less soluble minerals in the porous interior and more soluble minerals on the outer surface by evaporation.

Both XRD and EDS analyses showed that gypsum was concentrated on the outside of the potatoes and ardealite was concentrated on the inside. While apatite-(CaOH) was common in the substrata of both the potatoes and gypsum crusts, gypsum was only found in two substrata samples from the Potato Patch. No gypsum, pyrite, or phosphate minerals were found in the substrate of the transistors.

CONCLUSIONS

The sulfur in sulfate and phosphate deposits such as potatoes and crusts in Jenolan Caves is derived from bat guano, while the sulfur in gypsum (selenite) deposits is derived from the weathering of pyrite. None of the gypsum deposits examined have an isotopic composition indicative of hydrothermal deposition. Sulfate and phosphate deposits form by the evaporation of seepage water, pore water or fracture water from their substrate. In the case of potatoes, evaporation draws water through the porous centre of the potatoes, resulting in the deposition of gypsum (most soluble) as a crust on the exterior of the potato and ardealite in the centre.

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REFERENCES

Back, M.E. & J.A. Mandarino, 2008: Fleischer's glossary of mineral species 2008.- The Mineralogical Record Inc., pp. 346, Tucson.

Bottrell, S.H., 1991: Sulphur isotope evidence for the origin of cave evaporates in Ogof y Daren Cilau, south Wales.- Mineralogical Magazine, 55, 2, 209–210.

Bottrell, S.H. & C. Crowley, 2001: Invasion of a karst aquifer by hydrothermal fluids: evidence from stable isotope compositions of cave mineralization.- Geofluids, 1, 103–121.

Bridge, P.J., Hodge, L.C., Marsh, N.L. & A.G. Thomas, 1975: Chiropterite deposits in Marooba Cave, Jurien Bay, Western Australia.- Helictite, 13, 19–34.

Burke, E.A.J., 2008: Tidying up mineral names: an IMA-CNMNC scheme for suffixes, hyphens, and diacritical marks.- Mineralogical Record, 39, 131–135.

Carne, J.E. & , L.J. Jones, 1919: The Limestone Deposits of New South Wales.- Mineral Resources of New South Wales, 25, 1–383.

Canfield, D.E., 2001: Biogeochemistry of sulfur isotopes.- Reviews in Mineralogy and Geochemistry, 43, 606–636.

Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H. & I. Zak, 1980: The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation.- Chemical Geology, 28, 199–260.

Department of Mines, NSW, 1976: Geological & Mining Museum Catalogue of Economic Minerals and Miscellaneous Specimens, June 1976.

Dunlop, B.T., 1979: Jenolan Caves.- Department of Tourism, New South Wales, Sydney, 11th edition, 88p.

El-Tabakh, M., Mory, A., Schreiber, B.C. & R. Yasin, 2004: Anhydrite cements after dolomitization of shallow marine Silurian carbonates of the Gascoyne Platform, Southern Carnarvon Basin, Western Australia.- Sedimentary Geology, 164, 75–87.

Foster, J.J., 1890: The Jenolan Caves.- Government Printer, Sydney.

Galdenzi, S. & T. Maruoka, 2003: Gypsum deposits in the Frasassi Caves, Central Italy.- Journal of Cave and Karst Studies, 65, 2, 111–125.

Grimes, K.G., 1978: The geology and geomorphology of the Texas Caves, Southeastern Queensland.- Memoirs of the Queensland Museum, 19, 1, 17–59.

Hill, C.A., 1987: Geology of Carlsbad Cavern and other caves in the Guadalupe Mountains, New Mexico and Texas.- New Mexico Bureau of Mines and Mineral Resources Bulletin, 117, 1–150.

Hill, C.A. & P. Forti, 1986: Cave Minerals of the World.- National Speleological Society, pp. 238, Huntsville, Alabama.

Hill, C.A. & P. Forti, 1997: Cave Minerals of the World, Second Edition.- National Speleological Society, pp. 463, Huntsville, Alabama.

Hill, C.A. & P. Forti, 2004: Minerals in Caves. – In: Gunn, J. (ed.) Encyclopedia of Caves and Karst Science. Fitzroy Dearborn, pp. 511–514 London.

Hosono, T., Uchida, E., Suda, C., Ueno, A. & T. Nakagawa, 2006: Salt weathering of sandstone at the Angkor monuments, Cambodia: identification of the origins of salts using sulfur and strontium isotopes.- Journal of Archaeological Science, 33, 1541–1551.

Hutchinson, G.E., 1950: Cave Guano.- The Biochemistry of Vertebrate Excretion.- Bulletin of the American Museum of Natural History, 96.

James, J. M., 1991: The sulfate speleothems of Thampanna Cave, Nullarbor Plain, Australia.- Helictite, 29, 1, 19–23.

James, J. M., Jennings, J. N. & H. J.Dyson, 1982: Mineral decoration and weathering of the caves.- Sydney Speleological Society Occasional Paper, 8, 121–136.

Kampschulte, A. & H. Strauss, 2004: The sulfur isotopic evolution of Phanerozoic seawater based on the analysis of structurally substituted sulphate in carbonates.- Chemical Geology, 20, 255–286.

Marincea, S., Dumitras, D-G., Diaconu, G. & B. Essaid, 2004: Hydroxylapatite, brushite and ardealite in the bat guano deposit from Pestera Mare de la Meresti, Persani Mountains, Romania.- Neues jahrbuch fur mineralogie-monatshefte, 10, 464–488.

Mingaye, J.H., 1899: On the occurrence of phosphate deposits in Jenolan Caves, New South Wales.- Records of the Geological Survey of New South Wales, 6, 2, 11–116.

Mizutani, Y. & T.A. Rafter, 1968: Bacterial fractionation of oxygen isotopes in the reduction of sulphate and in the oxidation of sulphur.- New Zealand Journal of Science, 12, 60–68.

Onac, B, P. & D.S. Verez, 2003: Sequence of secondary phosphates deposition in a karst environment: evidence from Magurici Cave (Romania).- European Journal of Mineralogy, 15, 741–745.

Onac, B.P., 2005: Minerals. - In: Culver, D. & W.B. White (eds.) Encyclopedia of Caves. Academic press, pp. 371–378 New York.

Onac, B.P, Sumrall, J., Tamăs, T., Povară, I., Kearns, J., Dărmiceanu, Veres, D. & C. Lascu, 2009: The relationship between cave minerals and H2S-rich thermal waters along the Cerna Valley (SW Romania).- Acta Carsologica, 38,1, 27–39.

Osborne, R.A.L., 1991: Palaeokarst deposits at Jenolan Caves, New South Wales.- Journal and Proceedings of the Royal Society of New South Wales, 123, 59–73.

Osborne, R.A.L., 1993: Cave formation by exhumation of Palaeozoic palaeokarst deposits at Jenolan Caves, New South Wales.- Australian Journal of Earth Sciences, 40, 591–593.

Osborne, R.A.L., 1994: Caves, dolomite, pyrite, aragonite & gypsum: The karst legacy of the Sydney and Tasmania Basins.- Twenty-Eighth Newcastle Symposium on "Advances in the Study of the Sydney Basin", University of Newcastle Department of Geology Publication, 606, 322–324.

Osborne, R.A.L., 2004: The troubles with cupolas.- Acta Carsologica, 33, 2, 9–36.

Taylor, J.C., 1991: Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile.- Powder Diffraction, 6, 2–9.

Taylor, J.C. & R.A. Clapp, 1992: New features and advanced applications of SIROQUANT: a personal computer XRD full profile quantitative analysis software package.- Advances in X-ray Analysis, 35, 49–55.

Trickett, O., 1905: Guide to the Jenolan Caves, New South Wales.- NSW Government Printer, Sydney.

White, W.B., 1976: Cave minerals and speleothems.- In: Ford T.D. & C.H.D. Cullingford (eds.) The Science of Speleology. Academic Press, pp. 267–327. London.

Yonge, C.J. & H.R. Krouse, 1987: The origin of sulphates in Castleguard Cave, Columbia Icefields, Canada.- Chemical Geology: Isotope Geoscience section, 65, 3–4, 427–433.