

Available online at scholarcommons.usf.edu/ijs

1-9

International Journal of Speleology Official Journal of Union Internationale de Spéléologie



# Sulfur $({}^{34}S/{}^{32}S)$ isotope composition of gypsum and implications for deep cave formation on the Nullarbor Plain, Australia

Matej Lipar<sup>1\*</sup>, Mateja Ferk<sup>1</sup>, Sonja Lojen<sup>2,3</sup>, and Milo Barham<sup>4</sup>

<sup>1</sup>Anton Melik Geographical Institute, Research Centre of the Slovenian Academy of Sciences and Arts, Gosposka ulica 13, SI – 1000 Ljubljana, Slovenia <sup>2</sup>Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, SI – 1000 Ljubljana, Slovenia

<sup>3</sup>Faculty of Environmental Sciences, University of Nova Gorica, Glavni trg 8, SI – 5271 Vipava, Slovenia

<sup>4</sup>Centre for Exploration and Targeting, School of Earth and Planetary Sciences, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

- Abstract: Large deep caves with little relation to surface topography are distinctive karst features on the Nullarbor Plain of Australia. The presence of gypsum deposits and chemoautotrophic bacteria within the caves have been suggested as evidence for cave formation and (or) enlargement via sulfuric acid speleogenesis. To test this hypothesis, the stable sulfur isotope compositions ( $\delta^{34}$ S) of both cave gypsum and surface gypsum were measured. Analyses yielded relatively high, positive  $\delta^{34}$ S values from both cave gypsum and surface gypsum, arguing against gypsum genesis via microbial chemoautotrophy, and more broadly, sulfuric acid speleogenesis. Instead, the gypsum is interpreted as forming via evaporation of seawater during the Quaternary.
- Keywords: gypsum, sulfuric acid speleogenesis, karst, cave, Australia Received 28 March 2018; Revised 17 July 2018; Accepted 17 July 2018

**Citation:** Lipar M., Ferk M., Lojen S. and Barham M., 2019. Sulfur (<sup>34</sup>S/<sup>32</sup>S) isotope composition of gypsum and implications for deep cave formation on the Nullarbor Plain, Australia. International Journal of Speleology, 48 (1), 1-9. Tampa, FL (USA) ISSN 0392-6672 https://doi.org/10.5038/1827-806X.48.1.2196

# INTRODUCTION

In contrast to the typical genesis of carbonatehosted caves that form by epigene karst system processes with carbonic acid dissolution, a less well studied sub-population of caves can form through the activity of sulfuric acid by a process commonly termed "sulfuric acid speleogenesis" (SAS). SAS is thought to originate most commonly from oxidation of sulfide associated with deeper basin fluids (Palmer & Hill, 2012) or from activities of chemoautotrophic sulfur-oxidizing bacteria (Engel et al., 2004). The basic principle of SAS is that sulfide reacts with oxygenated meteoric waters to form sulfate in an acidic solution, creating large cavities at and around the water table (Ford & Williams, 2007). Acidic groundwater enriched in sulfide is capable of dissolving host carbonate units and taking calcium ions into solution. Sulfide becomes oxidized in oxygenated groundwater to sulfate and a hydrogen ion, with the free sulfate and calcium ions reacting and ultimately replacing carbonate minerals with gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) (Thode, 1970, 1991; Zerkle et al., 2016 and references therein).

Speleogenesis linked to sulfuric acid has been invoked for caves in a variety of settings such as the

\*matej.lipar@gmail.com

caves in the Guadalupe Mountains of New Mexico, USA (Jagnow et al., 2000), the Frasassi caves of Ancona, Italy (Galdenzi & Maruoka, 2003), the caves in Bahia Province, Brazil (Auler & Smart, 2003), the caves of the Cerna Valley, Romania (Onac et al., 2011), and Baume Galiniére Cave, France (Audra et al., 2015). The presence and source of sulfur is a key diagnostic feature for confirming/refuting SAS, with analyzable sulfur most frequently hosted in cave gypsum.

Gypsum is a common mineral in caves (White, 1976; Hill & Forti, 1997; Onac, 2012) and has been reported from Australian caves such as Jenolan and Wombeyan Caves in eastern Australia and Exit Cave and Mole Creek Caves in Tasmania (Mingaye, 1899; Pogson et al., 2011). Gypsum from the caves on the Nullarbor Plain has been previously described by Caldwell et al. (1982), Goede et al. (1990) and James (1991), and new caves with abundant gypsum are still being discovered (Jackson, 2018). Gypsum may precipitate from supersaturated drip water or during water evaporation, with sulfur variously derived from meteogenic sources (from sea spray or precipitation), decomposition of organic matter in soil or in caves (e.g., guano), biotic or abiotic oxidative recycling of sulfide from the aquifer, or pyrite in nearby strata (Swezey et al., 2002, 2017; Onac, 2012; Onac et al., 2011; Pogson et al., 2011, White, 2015).

The presence of cave gypsum may be an indicator of SAS processes (Jagnow et al., 2000), or may be an indicator of sulfur derived from sulfide minerals in nearby strata without necessarily invoking SAS processes (e.g., Onac et al., 2011). Stable isotope compositions ( $\delta^{34}$ S) may be used to constrain the origin of sulfate in caves, because large isotope fractionation occurs in the sulfur biogeochemical cycle. In particular, microbially mediated reactions, such as bacterial sulfate reduction and sulfide oxidation result in significantly lighter  $\delta^{34}$ S values of the reaction products (Thode, 1970, 1991; Zerkle et al., 2016).

Limited knowledge of deep cave formation on the Nullarbor Plain (Webb & James, 2006), presence of chemoautotrophic aquatic microbial communities (James & Rogers, 1994; Holmes et al., 2001), little or no relation to surface karst geomorphology, and the occurrence of gypsum could link deep caves on the Nullarbor Plain to SAS. Except for a brief notice by Jennings (1983) of similarities between caves of the Nullarbor Plain and caves in the Guadalupe Mountains of New Mexico, SAS on the Nullarbor Plain has not yet been considered or tested. James (1991), however, postulated that the major source of sulfate in Nullarbor caves was aerosols derived from seawater and transported by rain.

The aim of this paper is to provide additional constraints on the origin of gypsum in the Nullarbor caves. In addition, this paper discusses the hypothesis of SAS using the sulfur isotope composition of gypsum.

# **STUDY AREA – THE NULLARBOR PLAIN**

The Nullarbor Plain in central-southern Australia (Fig. 1) represents the largest contiguous karst area globally (~200,000 km<sup>2</sup>) and the surface expression of the Cenozoic Eucla Basin. The carbonate-dominated Eucla Basin overlies Mesozoic siliciclastic strata that form the Madura Shelf, which extends offshore as part of the rift-related Bight Basin. In turn, the Bight Basin partially overlies the southerly extension of the Neoproterozoic to early Paleozoic Officer Basin in the north and east, as well as enigmatic isolated Neoproterozoic to Paleozoic strata in the west (Barham et al., 2018). Pre-Cenozoic strata underlying the Eucla Basin are sandstone and mudstone that are interpreted as recording a gradual transition from high-energy fluvio-lacustrine to open marine shelf conditions through the Cretaceous (Fig. 2; Lowry, 1970). The Madura Shelf Mesozoic strata consist of a basal unit of spatially discontinuous beds of unconsolidated, poorly sorted sand and gravel with rarer beds of clay that are mapped collectively as the Loongana Formation. This basal unit is overlain by beds of finer, commonly charcoal-bearing sandstone and siltstone that are mapped collectively as the Madura Formation. The Madura Formation is overlain by an disconformity, above which lie grey siltstone that is mapped as the Toondi Formation. In turn, the Toondi Formation is capped by a disconformity, above which lie beds of glauconitic and fossiliferous siltstone that are mapped collectively as the Nurina Formation (Fig. 2; Cockbain & Hocking, 1989). Minor pyrite is present throughout parts of the Madura, Toondi and Nurina Formations. The combined strata of the Bight and Eucla basins beneath the central Nullarbor Plain has been estimated to reach a maximum thickness of ~800 m, but is more typically ~400 m thick (Scheib et al., 2016; Barham et al., 2018). Basement underlying the entire sedimentary succession comprises Meso- to Palaeo-proterozoic crust (Kirkland et al., 2017).

The Cenozoic strata are predominantly carbonates with basal and marginal clastics. The basal Cenozoic unit is a poorly consolidated, fossiliferous quartz sand that is interpreted to be of marine origin and is mapped as the Eocene Hampton Sandstone. This sandstone is overlain by carbonate strata that are mapped as the Eucla Group, and are subdivided into the following three units (from base to top):

(i) A 150 to 300 m thick white to grey bryozoan-rich limestone (wackestone to packstone) that is mapped as the Middle to Upper Eocene Wilson Bluff Limestone. This unit is interpreted as having accumulated on a temperate marine shelf (Playford et al., 1975; James & Bone, 1991; Benbow et al., 1995).

(ii) A 5 to 100 m thick unit of yellow skeletal- and bryozoan-rich limestone (packstone to grainstone) that is mapped as the Upper Oligocene to Lower Miocene Abrakurrie Limestone. This unit is interpreted as having accumulated in cool to temperate marine conditions (Playford et al., 1975; James & Bone, 1991; Benbow et al., 1995; Miller et al., 2012).

(iii) A 20 to 35 m thick unit of bioclastic and micritic limestone (packstone to rudstone) that is mapped as the Middle Miocene Nullarbor Limestone. This unit is interpreted as having accumulated in subtropical to warm temperate marine environments (Lowry, 1970; Playford et al., 1975; James & Bone, 1991; Benbow et al., 1995; Webb & James, 2006; Miller et al., 2012; O'Connell et al., 2012). The basalt part of the Nullarbor Limestone in the center of the basin is mapped as the Mullamullang Member, and in the northern part the Nullarbor Limestone grades laterally into the quartz and carbonate sandstone with minor claystone and conglomerate mapped as the Colville Sandstone (Lowry, 1968a).

A unit of sandy clay with a few thin beds of dolomite and oolitic and shelly limestone is mapped as the Princess Royal Spongolite on the western margin of the Nullarbor Plain and is correlated with the terrigenous (a supply of non-carbonate material in the form of a delta at the edge of the Eucla Basin) upper part of the Wilson Bluff Limestone in the Kitchener area (Jones, 1990). A number of other marginal carbonate units have been described around and west of the Kitchener area (Fig 1), but these details are outside the scope of this paper.

Unconsolidated sand, clay and calcrete represent the youngest surface sediment. Limited to the southern low-lying Roe and Isrealite Plains (Fig. 1), the late Pliocene poorly cemented molluscan calcarenite is mapped as the Roe Calcarenite (James



Fig. 1. Locality map of Nullarbor Plain in Australia. DEM downloaded from Shuttle Radar Topography Mission website (NASA, 2002), geology based on Surface Geology of Australia, 1:1 000 000 scale, 2012 edition (Geoscience Australia, 2012). AL = Oligocene-Miocene Abrakurrie Limestone; C = colluvium and residual deposits; CS = Miocene Colville Sandstone; D = dunes; NL = Miocene Nullarbor Limestone; NLm = Mullamullang Member of the Nullarbor Limestone; SP = sand plain; RC = Pliocene-Pleistocene Roe Calcarenite; RSC = residual sediments and calcrete; SSM = Holocene Semaphore Sand Member of the Saint Kilda Formation.

et al., 2006), while Holocene aeolian and beach quartzcarbonate sand is mapped as the Sempahore Sand member of the Saint Kilda Formation (Stewart et al., 2008).

The Nullarbor Plain became emergent as a result of falling sea-levels and regional uplift during the Middle Miocene, approximately 15 Ma ago (Lowry, 1970; Sandiford, 2007). Since this time, the carbonate strata have been exposed to chemical weathering, denudation, and meteoric diagenesis (Miller et al., 2012).

The surface relief of the Nullarbor Plain is generally subdued with isolated local disruptions from smallscale fault scarps with a maximum of a few tens of meters vertical offset (Clark et al., 2012), vestiges of ancient river drainage (Hou et al., 2008), and areas of ridge and corridor topography (Jennings, 1983). Karst features on the Nullarbor Plain include closed depressions of various sizes such as dayas (Goudie, 2010), dongas (Gillieson & Spate, 1992), blowholes (Lowry, 1968b), and collapse dolines (Grozdicki, 1985; Gillieson & Spate, 1992) that can lead to underground cave passages and chambers.

The Nullarbor caves are typically categorized as "shallow" or "deep" (Jennings, 1963; Lowry & Jennings, 1974), extending <30 m and 50-150 m below the surface, respectively (Webb & James, 2006). Shallow cave passages range in length from 0.25 to 20 m (Miller et al., 2012) and are characterized by low passages above collapsed chambers with abundant deposits of dark brown calcite, as well as halite and gypsum (Webb & James, 2006). These shallow caves are associated with pocket valleys in the Hampton and Wylie Scarps (Fig. 1; Lipar & Ferk, 2015), and their genesis is associated with mixing corrosion during the Pliocene sea-level highstand (Burnett et al., 2013).



3

Fig. 2. A generalized stratigraphic column of the western and central Nullarbor Plain (after Jones, 1990; Benbow et al., 1995; Hou et al., 2008).

Deep caves, formed primarily in Wilson Bluff Limestone, extend upwards through collapses and are several kilometers long (the longest - Old Homestead Cave - has >30 km of explored passages) with passages tens of meters wide and high (Webb & James, 2006). Abrakurrie Cave, as an example, has the largest chamber in Australia at approximately 150,000 m<sup>3</sup> (Webb & James, 2006). Besides the significant size of their passages and chambers, the deep caves are characterized by extensive collapses, the absence of calcite deposits, and continuation below the water table. The exact genesis of the deep caves is complex, and the following several processes, which may have occurred simultaneously, have been implicated: (1) crystal weathering (e.g., salt, gypsum; Lowry, 1968a; Gillieson & Spate, 1992); (2) mixing corrosion (James, 1992); (3) biospeleogenesis (James et al., 2012); and (4) dissolution during wetter climate intervals, such as the warm-wet of the Oligocene (Webb & James, 2006) or late Miocene (Miller et al., 2012).

#### **METHODS**

Cave gypsum (Fig. 3) was collected in Mullamullang Cave, the deepest (135 m) and second longest cave (>13 km) on the Nullarbor Plain (Fig. 1; James et al., 2012). Naturally broken fragments of gypsum were found and collected ~2.5 km inside from the cave entrance (north-east direction) near the underground White Lake. Dry lake beds and other topographic depressions were located using satellite and TanDEM-X data, and later investigated in the field to search for gypsum. The nearest surface gypsum was found and collected in the dry lake bed of Boonderoo near Kitchener (Fig. 1).

Back-scattered electron imaging was performed on a Hitachi TM3030 scanning electron microscope (SEM) to investigate compositional heterogeneity in the samples. Energy dispersive x-ray spectrometry (EDS) using an Oxford Swift ED3000 connected to a Hitachi TM3030 at Curtin University (Perth, Australia) was employed to obtain semiquantitative data on the elemental compositions of sampled crusts. Imaging and analyses were carried out on uncoated rough samples attached to a carbon adhesive tab on a 25 mm aluminum stub, with an accelerating voltage of 15 kV, a working distance of 10 mm, and at low vacuum. EDS spectra were obtained on areas varying between 10x10  $\mu m$  and 200x200  $\mu m$  with 60 s acquisition time. Beam alignment and calibration of the EDS detectors were undertaken prior to the analytical session following standard procedures.

Sulfur isotope analyses were performed at the Jožef Stefan Institute (Ljubljana, Slovenia). Gypsum crystals and gypsum in carbonate crusts were manually crushed and pulverized in an agate mortar. The carbonate crusts containing gypsum were dissolved in 3 M HCl and filtered through a 0.2  $\mu$ m membrane filter (Sartorius). Sulfate was precipitated



Fig. 3. Photographs of analyzed samples and their localities.

as BaSO<sub>4</sub> after addition of 10% BaCl<sub>2</sub>. The precipitate was repeatedly washed with MiliQ water, filtered, and oven dried. For the isotope analysis, samples of 0.3 mg of gypsum and 0.4 mg BaSO<sub>4</sub> were mixed with tungsten oxide and packed into tin capsules. An IsoPrime 100 isotope ratio mass spectrometer with elemental analyzer (PyroCube) was used for the analysis. Results are reported as relative delta ( $\delta$ ) values (i.e., the difference of the isotope  ${}^{34}S/{}^{32}S$  ratio of the sample and the standard expressed in per mil). Measured values are given relative to the Vienna-Canyon Diablo Troilite (VCDT). The IAEA SO-5, IAEA SO-6, and NBS 127 reference materials with  $\delta^{34}S_{VCDT}$ values of 0.5‰, -34.1‰, and 20.3‰, respectively, were used for calibration. All samples and reference materials were analyzed in triplicate, with standard deviation equal to or less than 0.25‰.

## RESULTS

The  $\delta^{34}$ S values of gypsum samples are high (from +17.1‰ to +21.6‰, Table 1) with a 4.5‰ variation

Table 1. Sulfur isotope values of analyzed samples.

recorded in cave gypsum. The two crystals of surface gypsum returned less variable results (Table 1).

Compositional contrast imaging using backscattered electrons (BSE) indicates relatively simple mineralogies of the crystalline material sampled, with gypsum identified as the major calcium sulfate phase on the basis of elevated proportions of oxygen to calcium and sulfur (~6:1:1;  $CaSO_4 \cdot 2H_2O$ ) (Fig. 4). Sample NB\_1 comprises the most pure gypsum identified among the samples, featuring well-defined crystals with a platy cleavage and a Ca:S:O atomic ratio of 1:1:5.7. Sample NB\_2 was dominated by low-Mg calcium carbonate with at least two distinct phases of growth and only a minor gypsum component internally. Rounded detrital carbonate and siliciclastic grains (quartz and plagioclase being the most significant on the basis of Si and Al peaks in spectra) are clearly visible in sample NB\_4. Minor spectral peaks for Si and Al (in particular) in sample NB\_3 are also interpreted to represent EDS activation volumes including minor detrital phases contributing <1% to the overall sample composition.

Sample Number	Description	δ <sup>34</sup> S <sub>VCDT</sub> (‰)
NB_01	Gypsum flower – Mullamullang Cave	+17.1
NB_02	Gypsum containing crust – Mullamullang Cave	+21.6
NB_03	Gypsum sponge-work – dry lake (surface)	+18.4
NB_04	Gypsum crystals – dry lake (surface)	+18.0

#### DISCUSSION

All four samples of gypsum are characterized by  $\delta^{34}$ S values that range from +17.1‰ to +21.6‰ (Table 1; Fig. 5). This range of sulfur isotope values resembles the ranges of marine sulfate (Thode, 1970, 1991; Claypool et al., 1980).

Sulfur isotope data alone cannot distinguish between a seawater source and (or) a bedrock source of sulfur in the analyzed gypsum. However, several possible sources of sulfur may eliminated from consideration. be Gypsum derived from microbiological or hydrothermal processes in sulfuric acid caves yield significantly lighter  $\delta^{34}$ S values than either group of gypsum samples from the Nullarbor Plain. Hydrocarbon-related sulfide may have a large range of positive  $\delta^{34}S$  values (Hoşgörmez et al., 2014; Zhu et al., 2017), but is nevertheless usually several ‰ lighter than the evaporites (Krouse et al., 1988); considering the geology of the area, such an origin is unlikely.

A comparison with sulfur isotope data from gypsum in other caves throughout the world is useful. For example, sulfur isotope values range from -16% to -23% in Kraushöhle Cave, Austria (Puchelt & Blum, 1989); from -8% to -24% in the Frasassi cave system, Italy (Galdenzi & Maruoka, 2003); from -8% to -10‰ in Corkscrew Cave, Arizona, USA (Onac et al., 2007); from -8‰ to +1‰ in Cave Provalata, Macedonia (Temovski et al., 2013, 2018); from -15‰ to -24‰ in Kinderlinsk Cave, Russia (Chervyatsova et al., 2016); and from -18‰ to -1‰ in several caves in Virginia and West Virginia, USA (Swezey et al., 2002,



Fig. 4. Back-scattered electron images and associated energy dispersive x-ray spectra (EDS) of samples analyzed herein. Red boxes indicate area analyzed via EDS, with black dashed lines and boxes corresponding to relevant enlarged insets. a) sample NB\_1 gypsum crystal fragment; b) surface of carbonate sample NB\_2; c) gypsum sample NB\_3 with inset platy morphology highlighted; d) gypsum sample NB\_4 with inset detrital grain.

White, 2015). However, a relatively wider range of  $\delta^{34}$ S values (from -28‰ to +19‰) were reported by Onac et al. (2011) from the caves in the Cerna Valley of southwestern Romania.

For example, the sulfur isotope compositions of gypsum from the Nullarbor Plain are similar to reported values from surface gypsum in southern Western Australia and South Australia, where the highest  $\delta^{34}$ S values (~+21‰) occur near coastlines and decrease to  $\delta^{34}$ S values of ~+14‰ further inland (Chivas et al., 1991). This systematic variation of isotope values suggests a seawater source for the sulfur, with aerosols being a viable ionic supply mechanism in the hydrochemistry of modern continental aridzone systems up to a thousand kilometers from the coast (Warren, 2016). The results are therefore in agreement with James (1991), who postulated that the major source of sulfate in Nullarbor caves was aerosols derived from seawater.



Fig. 5. Variable  $\delta^{34}$ S values from different sources. Modified from Seal (2006) with added SAS gypsum values from Puchelt & Blum (1989), Galdenzi & Maruoka (2003), Onac et al. (2011), Temovski et al. (2013), and Chervyatsova et al. (2016).

A bedrock source of sulfur is also possible for the gypsum samples analyzed for this study. Average  $\delta^{34}$ S values of marine evaporitic and structurally substituted sulfate in carbonates from 30 to 55 Ma ago (Eocene through Early Oligocene) range from +18.7% to +22.0%, and the  $\delta^{34}$ S values from 10 to 20 Ma ago (Miocene) range from +20.4% to +22.2% (Kampschulte & Strauss, 2004; similar values are also reported by Claypool et al., 1980). These time intervals are approximately equivalent to the time of accumulation of the Wilson Bluff Limestone (Eocene) and the Nullarbor Limestone (Miocene), respectively. However, there is no evidence for evaporitic units or aquatic restriction in any of the underlying successions encountered in drillcore beneath the Nullarbor Plain.

Hill & Forti (1997) regarded oxidation of pyrite as a common source of sulfate minerals in caves. No pyrite inclusions in the Eucla Group carbonates are known to the authors, although pyrite was reported in the Princess Royal Spongolite (Jones, 1990). Furthermore, pyrite is present in the siltstone of the Madura, Toondi and Nurina Formations (Lowry, 1970). The  $\delta^{34}$ S values from this pyrite have not been published, and therefore this pyrite cannot be excluded as the source of sulfur in the cave gypsum. It is noteworthy, however, that  $\delta^{34}$ S values of pyrite in siliciclastic rocks are most

commonly much lighter than the values obtained from the Nullarbor Plain (Ohmoto & Goldhaber, 1997; Hofman et al., 2009). Furthermore, finer claystone units within the Madura, Toondi and Nurina Formations are unlikely to facilitate large-scale fluid migration, with onshore drilling encountering difficult swelling clays, and offshore lithological equivalents being recognized as seals that inhibit fluid migration (Totterdell et al., 2000). A lack of cementation in the Hampton Sandstone between the Cretaceous Madura Shelf strata and Cenozoic Eucla Group carbonates further argues against significant fluid mobilization at depth.

The only published age from gypsum of the Nullarbor Plain is a ~185 ka U/Th date obtained by Goede et al. (1990) from Thampanna Cave (Fig. 1). This relatively recent age (Late Quaternary) from the gypsum contrasts with much older (Pliocene) ages of calcite deposition (Woodhead et al., 2006; Blyth et al., 2010), and is consistent with the occurrence of substantial speleothems of gypsum superimposed on carbonate speleothems (Goede et al., 1990). Consequently, these ages suggest that the gypsum, found in the caves of the Nullarbor Plain today, may post-date the cave formation and consequently may not be a recorder of speleogenesis. Gypsum also is notably fragile and soluble, which means that an absence of deposits proven contemporaneous with cave genesis cannot exclude the possibility of SAS.

Although further research is needed to confirm/ refute the unlikely correlation of cave sulfate minerals with pyrite in underlying Madura Formation, the similar  $\delta^{34}$ S values for cave and surface gypsum, and young age of gypsum in Thampanna Cave, strongly suggest that sulfate minerals in the Nullarbor caves are evaporites derived ultimately from seawater. The gypsum analyzed during this study most probably formed by evaporation of seawater, with evaporation during increased aridity driving the increased salinity and mineral saturation of saline groundwater already influenced by marine aerosols. Strongly positive  $\delta^{34}$ S values do not indicate sulfuric acid speleogenesis of deep caves on the Nullarbor Plain, nor activity of chemoautotrophic sulfur-oxidizing bacteria.

#### CONCLUSIONS

Possible sulfuric acid speleogenesis of the deep caves on the Nullarbor Plain of Australia is suggested by several features such as little or no relation to surface karst topography, a presence of chemoautotrophic bacteria, and gypsum deposits. Stable sulfur isotope compositions of cave and surface gypsum on the Nullarbor Plain were analyzed in an attempt to test cave origin via sulfuric acid speleogenesis. The analysis of both cave gypsum and surface gypsum yielded sulfur isotope values ranging from +17.1‰ to +21.6‰. Such heavy  $\delta^{34}$ S values for the gypsum, and the similarity of values from both cave gypsum and surface gypsum, suggest that sulfuric acid speleogenesis was not a process involved in the cave formation. Instead, gypsum in caves of the Nullarbor Plain is considered to be an evaporite deposit of Quaternary age derived from saline groundwaters influenced by seawater.

## ACKNOWLEDGEMENT

The field work was financially supported by Anton Melik Geographical Institute, Research Centre of the Slovenian Academy of Sciences and Arts, Ministry of Education, Science and Sport, Slovenian Research Agency, research programme P6-0101 and OP20.01261, and Australian Speleological Federation Karst Conservation Fund. TanDEM-X data was approved and received through a science proposal DEM\_GEOL2288. Many thanks to Ann-Marie Meredith for help and support in the field.

The isotope analyses (J. Stefan Institute) were financially supported by the Slovenian Research Agency, research programme P1-0143, and the Horizon 2020 research and innovation programme under grant agreement No. 692241 (MASSTWIN – Spreading excellence and widening participation in support of mass spectrometry and related techniques in health, the environment and food analysis). Authors thank reviewer Christopher Swezey and an anonymous reviewer for thoughtful comments and suggestions, which substantially improved the manuscript.

## REFERENCES

Audra P., Gázquez F., Rull F., Bigot J.-Y. & Camus H., 2015 – Hypogene Sulfuric Acid Speleogenesis and rare sulfate minerals in Baume Galinière Cave (Alpes-de-Haute-Provence, France). Record of uplift, correlative cover retreat and valley dissection. Geomorphology, 247: 25-34.

https://doi.org/10.1016/j.geomorph.2015.03.031

- Auler A.S., Smart P.L., 2003 The influence of bedrockderived acidity in the development of surface and underground karst: evidence from the Precambrian carbonates of semi-arid northeastern Brazil. Earth Surface Processes and Landforms, **28 (2)**: 157-168. <u>https://doi.org/10.1002/esp.443</u>
- Barham M., Reynolds S., Kirkland C.L., O'Leary M.J., Evans N.J., Allen H., Haines P.W., Hocking R.M. & McDonald B.J., 2018 – Sediment routing and basin evolution in Proterozoic to Mesozoic east Gondwana: a case study from southern Australia. Gondwana Research, 58: 122-140.

https://doi.org/10.1016/j.gr.2018.03.006

- Benbow M.C., Lindsay J.M. & Alley N.F., 1995 Eucla Basin and palaeodrainage. In: Drexel J.F. & Preiss W.V. (Eds.), The geology of South Australia. Vol. 2, The Phanerozoic. South Australia Geological Survey. Bulletin, 54, p. 178-186.
- Blyth A.J., Watson J.S., Woodhead J. & Hellstrom J., 2010 – Organic compounds preserved in a 2.9 million year old stalagmite from the Nullarbor Plain, Australia. Chemical Geology, **279**: 101-105.

https://doi.org/10.1016/j.chemgeo.2010.10.006

Burnett S., Webb J.A. & White S., 2013 – Shallow caves and blowholes on the Nullarbor Plain, Australia – Flank margin caves on a low gradient limestone platform. Geomorphology, **201**: 246-253.

https://doi.org/10.1016/j.geomorph.2013.06.024

Caldwell J.R., Davey A.G., Jennings J.N. & Spate A.P., 1982 – Colour in some Nullarbor Plain speleothems. Helictite, **20**: 3-10.

- Chervyatsova O.Y., Potapov S.S. & Sadykov S.A., 2016 – Sulfur isotopic composition of sulfur deposits in Ural karst caves. Izvestiya Ural'skogo Gosudarstvennogo Gornogo Universiteta (News of the Ural State Mining University), **2**: 37-41.
- Chivas A.R., Andrews A.S., Lyons W.B., Bird M.I. & Donnelly T.H., 1991 *Isotopic constraints on the origin of salts in Australian playas. 1. Sulphur.* Palaeogeography, Palaeoclimatology, Palaeoecology, **84 (1-4)**: 309-332. https://doi.org/10.1016/0031-0182(91)90051-R
- Claypool G.E., Holser W.T., Kaplan I.R., Sakai H. & Zak I., 1980 – The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. Chemical Geology, **28**: 199-260. https://doi.org/10.1016/0009-2541(80)90047-9
- Clark D., McPherson A. & Van Dissen R., 2012 Longterm behaviour of Australian stable continental region (SCR) faults. Tectonophysics, **566-567**: 1-30. https://doi.org/10.1016/j.tecto.2012.07.004
- Cockbain A.E. & Hocking R.M., 1989 *Revised stratigraphic* nomenclature in Western Australian Phanerozoic basins. Record 1989/15, Geological Survey of Western Australia, Perth, Western Australia, 11 p.
- Engel A.S., Stern L.A. & Bennett P.C., 2004 Microbial contributions to cave formation: New insights into sulfuric acid speleogenesis. Geology, **32**: 369-372. https://doi.org/10.1130/G20288.1
- Ford D. & Williams P., 2007 Karst hydrogeology and geomorphology. John Wiley and Sons, Chichester, 562 p. https://doi.org/10.1002/9781118684986
- Galdenzi S. & Maruoka T., 2003 *Gypsum deposits in the Frasassi Caves, central Italy.* Journal of Cave and Karst Studies, **65**: 111-125.
- Geoscience Australia, 2012 Surface geology of Australia. 1:1 000 000 scale, 2012 edition. Bioregional Assessment Source Dataset.
- Gillieson D.S. & Spate A., 1992 The Nullarbor karst. In: Gillieson D.S. (Ed.), Geology, climate, hydrology and karst formation: Field symposium in Australia. Guidebook Special Publication 4, Australian Defense Force Academy, Canberra, p. 65-99.
- Goede A., Harmon R.S., Atkinson T.C. & Rowe P.J., 1990 – *Pleistocene climatic change in southern Australia and its effect on speleothem deposition in some Nullarbor caves.* Journal of Quaternary Science, **5**: 29-38. <u>https://doi.org/10.1002/jqs.3390050104</u>
- Goudie A.S., 2010 Dayas: distribution and morphology of dryland solutional depressions developed in limestones. Zeitschrift für Geomorphologie, **54 (2)**: 145-159.

https://doi.org/10.1127/0372-8854/2010/0054-0010

- Grodzicki J., 1985 *Genesis of the Nullarbor Plain caves in southern Australia.* Zeitschrift für Geomorphologie, **29**: 37-49.
- Hill C.A. & Forti P., 1997 *Cave minerals of the world* (2<sup>nd</sup> Ed.). National Speleological Society, Huntsville, 463 p.
- Hofman A., Bekker A., Rouxel O., Rumble D. & Master S., 2009 – Multiple sulphur and iron isotope composition of detrital pyrite in Archaean sedimentary rocks: A new tool for provenance analysis. Earth and Planetary Science Letters, **286**: 436-445.

https://doi.org/10.1016/j.epsl.2009.07.008

Holmes A.J., Tujula N.A., Holley M., Contos A., James J.M., Rogers P. & Gillings M.R., 2001 – *Phylogenetic* structure of unusual aquatic microbial formations in *Nullarbor caves*, Australia. Environmental Microbiology, **3**: 256-264.

https://doi.org/10.1046/j.1462-2920.2001.00187.x

Hoşgörmez H., Yalçın M.N., Soylu C. & Bahtiyar İ., 2014 – Origin of the hydrocarbon gases carbon dioxide and

hydrogen sulfide in Dodan Field (SE-Turkey). Marine and Petroleum Geology **57**: 433-444. https://doi.org/10.1016/j.marpetgeo.2014.05.012

Hou B., Frakes L.A., Sandiford M., Worrall L., Keeling J. & Alley N.F., 2008 – Cenozoic Eucla Basin and associated palaeovalleys, southern Australia – climatic and tectonic influences on landscape evolution, sedimentation and heavy mineral accumulation. Sedimentary Geology, 203 (1-2): 112-130.

https://doi.org/10.1016/j.sedgeo.2007.11.005

- Jackson A., 2018 Bunda Cliffs, Nullarbor Plain 2017. Caves Australia, **204**: 11-14.
- Jagnow D.H., Hill C.A., Davis D.G., DuChene H.R., Cunningham K.I., Northup D.E. & Queen J.M., 2000 – *History of sulfuric acid theory of speleogenesis in the Guadalupe Mountains, New Mexico.* Journal of Cave and Karst Studies, **62**: 54-59.
- James J.M., 1991 The sulfate speleothems of Thampanna Cave, Nullarbor Plain, Australia. Helictite, **29**: 19-23.
- James J.M., 1992 Corrosion par mélange des eaux dans les grottes de la plaine de Nullarbor, Australie. In: Salomon J.-N. & Maire R. (Eds.), Karst et évolutions climatiques. Presses Universitaires, Bordeaux, p. 333-348.
- James J.M. & Rogers P., 1994 The "mysterious" calcite precipitating organism of the Nullarbor caves, Australia. In: Sasowsky I.D. & Palmer M.V. (Eds.), Breakthroughs in Karst Geomicrobiology and Redoy Geochemistry. Conference Abstracts and Field Guide. Karst Waters Institute, p. 34-35.
- James J.M., Contos A.K. & Barnes C.M., 2012 Nullarbor caves, Australia. In: Culver D.C. & White W.B. (Eds.), Encyclopedia of caves (2<sup>nd</sup> Ed.). Academic Press, New York, p. 568-576.

https://doi.org/10.1016/B978-0-12-383832-2.00084-0

James N.P. & Bone Y., 1991 – Origin of a cool-water Oligo-Miocene deep-self limestone, Eucla Platform, southern Australia. Sedimentology, **60**: 323-341. https://doi.org/10.1111/j.1365-3091.1991.tb01263.x

- James N.P., Bone Y., Carter R.M. & Murray-Wallace C.V., 2006 – Origin of the Late Neogene Roe Plains and their calcarenite veneer: implications for sedimentology and tectonics in the Great Australian Bight. Australian Journal of Earth Sciences, **53**: 407-419. https://doi.org/10.1080/08120090500499289
- Jennings J.N., 1963 Some geomorphological problems of the Nullarbor Plain. Transactions of the Royal Society of South Australia, **87**: 41-62.
- Jennings J.N., 1983 The disregarded karst of the arid and semiarid domain. Karstologia, 1: 61-73. https://doi.org/10.3406/karst.1983.2041
- Jones B.G., 1990 Cretaceous and Tertiary sedimentation on the western margin of the Eucla Basin. Australian Journal of Earth Sciences, **37**: 317-329. https://doi.org/10.1080/08120099008727930
- Kampschulte A. & Strauss H., 2004 The sulfur isotopic evolution of Phanerozoic seawater based on the analysis of structurally substituted sulfate in carbonates. Chemical Geology, **20**: 255-286.
- https://doi.org/10.1016/j.chemgeo.2003.11.013
- Kirkland C.L., Smithies R.H., Spaggiari C.V., Wingate M.T.D., Quentin de Gromard R., Clark C., Gardiner N.J. & Belousova E.A., 2017 – Proterozoic crustal evolution of the Eucla basement, Australia: Implications for destruction of oceanic crust during emergence of Nuna. Lithos, **278-281**: 427-444.

https://doi.org/10.1016/j.lithos.2017.01.029

Krouse H.R., Viau C.A., Eliuk L.S., Ueda A. & Halas S., 1988 – Chemical and isotopic evidence of thermochemical sulfate reduction by light hydrocarbon gases in deep *carbonate reservoirs*. Nature, **333**: 415-419. <u>https://doi.org/10.1038/333415a0</u>

- Lipar M. & Ferk M., 2015 Karst pocket valleys and their implications on Pliocene–Quaternary hydrology and climate: Examples from the Nullarbor Plain, southern Australia. Earth-Science Reviews, **150**: 1-13. https://doi.org/10.1016/j.earscirev.2015.07.002
- Lowry D.C., 1968a Tertiary stratigraphic units in the Eucla Basin in Western Australia. Department of Mines. Annual Report 1967, p. 36-40.
- Lowry D.C., 1968b The origin of blow-holes and the development of domes by exsudation in caves of the Nullarbor Plain. Geological Survey of Western Australia Annual Report: 1967. Geological Survey of Western Australia, Perth, p. 40-44.
- Lowry D.C., 1970 *Geology of the western Australian* part of the Eucla Basin. Perth, Geological Survey of Western Australia, 199 p.
- Lowry D.C. & Jennings J.N., 1974 *The Nullarbor karst, Australia.* Zeitschrift für Geomorphologie, **18**: 35-81.
- Miller C.R., James N.P. & Bone Y., 2012 Prolonged carbonate diagenesis under an evolving late Cenozoic climate; Nullarbor Plain, southern Australia. Sedimentary Geology, **261-262**: 33-49. https://doi.org/10.1016/j.sedgeo.2012.03.002
- 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**: 111-116.
- NASA Shuttle Radar Topography Mission. http://www. jpl.nasa.gov/srtm/. U.S. National Aeronautics and Space Administration [accessed: 2013].
- O'Connell L.G., James N.P. & Bone Y., 2012 The Miocene Nullarbor Limestone, southern Australia; deposition on a vast subtropical epeiric platform. Sedimentary Geology, **253-254**: 1-16.

https://doi.org/10.1016/j.sedgeo.2011.12.002

- Ohmoto H. & Goldhaber M.B., 1997 Sulfur and carbon isotopes. In: Barnes H.L. (Ed.), Geochemistry of hydrothermal ore deposits (3<sup>rd</sup> Ed.). Wiley, New York, p. 517-611.
- Onac B.P., 2012 *Minerals*. In: Culver D.C. & White W.B. (Eds.), *Encyclopedia of caves* (2<sup>nd</sup> Ed.). Academic Press, New York, p. 499-508.

https://doi.org/10.1016/B978-0-12-383832-2.00072-4

Onac B.P., Hess J.W. & White W.B., 2007 – The relationship between the mineral composition of speleothems and mineralization of breccia pipes: evidence from Corkscrew Cave, Arizona, USA. The Canadian Mineralogist, **45 (5)**: 1177-1188.

https://doi.org/10.2113/gscanmin.45.5.1177

- Onac B.P., Wynn J.G. & Sumrall J.B., 2011 *Tracing* the sources of cave sulfates: a unique case from Cerna Valley, Romania. Chemical Geology, **288**: 105-114. <u>https://doi.org/10.1016/j.chemgeo.2011.07.006</u>
- Palmer A.N. & Hill C.A., 2012 Sulfuric acid caves. In: Culver D.C. & White W.B. (Eds.), Encyclopedia of caves (2<sup>nd</sup> Ed.). Elsevier Academic Press, New York, p. 810-819. https://doi.org/10.1016/B978-0-12-383832-2.00117-1
- Playford P.E., Cope R.N., Cockbain A.E., Low G.H. & Lowry D.C., 1975 – *Phanerozoic*. In: Geology of Western Australia. Western Australia Geological Survey, Perth, p. 223-433.
- Pogson R.E., Osborne R.A.L., Colchester D.M. & Cendón D.I., 2011 – Sulfate and phosphate speleothems at Jenolan Caves, New South Wales, Australia. Acta Carsologica, **40**: 239-254.

https://doi.org/10.3986/ac.v40i2.9

Puchelt H. & Blum N., 1989 – Geochemische Aspekte der Bildung des Gipsvorkommens der Kraushöhle/ *Steiermark*. Oberrheinische geologische Abhandlungen, **35**: 87-99.

- Sandiford M., 2007 *The tilting continent: A new constraint on the dynamic topographic field from Australia.* Earth and Planetary Science Letters, **261:** 152-163. <u>https://doi.org/10.1016/j.epsl.2007.06.023</u>
- Scheib A., Morris P., Murdie R. & Delle Piane C., 2016 A passive seismic approach to estimating the thickness of sedimentary cover on the Nullarbor Plain, Western Australia. Australian Journal of Earth Sciences, 63: 583-598.

https://doi.org/10.1080/08120099.2016.1233455

- Seal R.R., 2006 Sulfur Isotope Geochemistry of Sulfide Minerals. Reviews in Mineralogy & Geochemistry, 61: 633-677. <u>https://doi.org/10.2138/rmg.2006.61.12</u>
- Stewart A.J., Sweet I.P., Needham R.S., Raymond O.L., Whitaker A.J., Liu S.F., Phillips D., Retter A.J., Connolly D.P. & Stewart G., 2008 – Surface geology of Australia 1:1,000,000 scale, Western Australia (Digital Dataset). Canberra, The Commonwealth of Australia, Geoscience Australia.
- Swezey C.S., Piatak N.M., Seal R.R. & Wandless G.A., 2002
  Sulfur and oxygen isotopic composition of gypsum in caves of Virginia and West Virginia. Geological Society of America, Abstracts with Programs, 34: 231.
- Swezey C.S., Haynes J.T., Lucas P.C. & Lambert R.A., 2017 – Geologic controls on cave development in Burnsville Cove, Bath and Highland Counties, Virginia. In: Bailey C.M. & Jaye S. (Eds.), From the Blue Ridge to the Beach: Geological field excursions across Virginia. Geological Society of America Field Guide, **47**: 89-123. https://doi.org/10.1130/2017.0047(04)
- Temovski M., Audra P., Mihevc A., Spangenberg J.E., Polyak V., McIntosh W. & Bigot J.Y., 2013 – Hypogenic origin of Provalata Cave, Republic of Macedonia: a distinct case of successive thermal carbonic and sulfuric acid speleogenesis. International Journal of Speleology, 42: 235-246. <u>https://doi.org/10.5038/1827-806X.42.3.7</u>
- Temovski M., Futó I., Túri M. & Palcsu L., 2018 Sulfur and oxygen isotopes in the gypsum deposits of the Provalata sulfuric acid cave (Macedonia). Geomorphology, **315**: 80-90. https://doi.org/10.1016/j.geomorph.2018.05.010
- Thode H.G., 1970 Sulfur isotope geochemistry and fractionation between coexisting sulfide minerals. Mineralogical Society of America Special Paper, **3**: 133-144.

- Thode H.G., 1991 Sulphur isotopes in nature and the environment: an overview. In: Krouse H.R. & Grinenko V.A. (Eds.), Stable isotopes in the assessment of natural and anthropogenic sulphur in the environment. John Wiley & Sons, Chichester, p. 1-26.
- Totterdell J.M., Blevin J.E., Struckmeyer H.I.M., Bradshaw B.E., Colwell J.B. & Kennard J.M., 2000 A new sequence framework for the Great Australian Bight: starting with a clean slate. The Australian Petroleum Production & Exploration Association Journal, **40**: 95-117. https://doi.org/10.1071/AJ99007
- Warren J.K., 2016 *Depositional chemistry and hydrology*. In: Warren K.K. (Ed.), *Evaporites, a geological compendium* (2<sup>nd</sup> Ed.). Springer, p. 85-205. https://doi.org/10.1007/978-3-319-13512-0\_2
- Webb J.A. & James, J.M., 2006 Karst evolution of the Nullarbor Plain, Australia. In: Harmon R.S. & Wicks C. (Eds.), Perspectives on karst geomorphology, hydrology, and geochemistry – A tribute volume to Derek C. Ford and William B. White. Geological Society of America Special Paper 404, p. 65-78.

https://doi.org/10.1130/2006.2404(07)

- White W.B., 1976 *Cave minerals and speleothems*. In: Ford T.D. & Cullingford C.H.D. (Eds.), *The science of speleology*. Academic Press, London, p. 267-327.
- White W.B., 2015 *Minerals and speleothems in Burnsville Cove caves.* In: White W.B. (Ed.), *The caves of Burnsville Cove, Virginia.* Springer International Publishing, Cham, p. 421-441.

https://doi.org/10.1007/978-3-319-14391-0\_23

- Woodhead J., Hellstrom J., Maas R., Drysdale R., Zanchetta G., Devine P. & Taylor E., 2006 – U– *Pb geochronology of speleothems by MC-ICPMS*. Quaternary Geochronology, **1**: 208-221. https://doi.org/10.1016/j.quageo.2006.08.002
- Zerkle A.L., Jones D.S., Farquhar J. & Macalady J.L., 2016 – Sulfur isotope values in the sulfidic Frasassi cave system, central Italy: A case study of a chemolithotrophic S-based ecosystem. Geochimica et Cosmochimica Acta, **173**: 373-386.

https://doi.org/10.1016/j.gca.2015.10.028

Zhu G., Liu X., Yang H., Su J., Zhu Y., Wang Y. & Sun C., 2017 – Genesis and distribution of hydrogen sulfide in deep heavy oil of the Halahatang area in the Tarim Basin, China. Journal of Natural Gas Geoscience, 2: 57-71. https://doi.org/10.1016/j.jnggs.2017.03.004