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SULFURIC ACID CAVES OF THE WORLD: A REVIEW

Jo De Waele[1], Ilenia M. D'Angeli[1,2*], Philippe Audra[3], Lukas Plan[4], Arthur N. Palmer[5]

(1) Department of Biological, Geological and Environmental Sciences, University of Bologna, Via Zamboni 67, 40127 Bologna, Italy jo.dewaele@unibo.it; dangeli.ilenia89@gmail.com
(2) Department of Geosciences, University of Padua, Via G. Gradenigo 6, 35131 Padova, Italy
(3) Université Côte d'Azur, Polytech'Lab - UPR 7498, 930 route des Colles, 06903 Sophia-Antipolis, France, Philippe.audra@univ-cotedazur.fr
(4) Karst and Cave Group, Natural History Museum, Burgring 7, 1010 Wien, Vienna, Austria, lukas.plan@nhm-wien.ac.at
(5) Department of Earth and Atmospheric Sciences, State University of New York, Oneonta, NY 13820, USA, arthur.palmer@oneonta.edu

Abstract

In soluble rocks such as limestone and dolostone there are two main types of cave genesis (speleogenesis); (i) epigenic speleogenesis, in which the aggressiveness that forms caves is derived from the surface, and (ii) hypogenic speleogenesis where upwelling gases and fluids acquire their aggressiveness at depth dissolving carbonate rocks to form caves. Whereas epigenic (surface) waters can be undersaturated respect to carbonates obtaining their aggressiveness mainly from soil CO_2, hypogenic (deep rising) fluids can obtain their carbonate-dissolving capacity at depth from various processes and mechanisms. Hypogenic speleogenesis that involves dissolution of carbonate rocks by sulfuric acid, mainly derived by oxidation of upwelling hydrogen sulfide, is called sulfuric acid speleogenesis (SAS). Although this type of process has been described during the early 19th century, the first elaborated theories are rather recent, and a detailed model was proposed only in the mid-1970s. Only a few cave areas were known to host sulfuric acid caves, but studies were boosted with the discovery and understanding of the inactive Lechuguilla Cave in New Mexico (USA), and the still active Movile Cave in Romania, both discovered in 1986.

Today 84 areas globally are known to contain sulfuric acid caves, offering a wide variety of environments. This review gives a historical overview of studies concerning these caves, explains the chemistry behind the formation of the dissolving fluids and their interaction with the carbonate host rock, and describes the chemical, mineralogical, geomorphological, and microbiological signatures typical of sulfuric acid dissolution. The significance of SAS caves in landscape evolution

and their possible role in deep karstification, and thus hydrocarbon reservoirs and deep hydrogeology, is also briefly analyzed.

Keywords: hypogene speleogenesis, rising fluids, hydrogen sulfide, deep karst

1. Introduction

Caves are often defined from an anthropocentric point of view, being “natural voids beneath the land surface that are large enough to admit humans” (White, 1988; Ford & Williams, 2007; Palmer, 2007; De Waele & Gutiérrez, 2022). This definition has no genetic meaning, and caves can be voids inside a pile of boulders, an open fracture in any kind of solid rock, a lava tube, or an underground stream in soluble rock. Most caves are solutional voids, and are also referred to as “karst caves” or “dissolution caves”. They are formed by the dissolving and erosive action of underground water as it flows through open spaces in soluble bedrock. Dissolution of the host rock is a fundamental process, especially in the early phases of cave development, and it is at the basis of the formation of karst caves. Once the openings in the rock are wide enough, generally $\geqq$ 5 mm, the underground flowpaths start to be enlarged drastically by both chemical and physical erosion (Dreybrodt, 1990; Kaufmann et al., 2019).

The most common soluble rocks on Earth are limestone ($CaCO_3$) and gypsum ($CaSO_4{\cdot}2H_2O$), but also dolostone ($CaMg(CO_3)_2$), halite ($NaCl$), quartzite (SiO_2), and carbonate-cemented rocks (i.e., conglomerates) can be dissolved, and can host important cave systems. Halite and gypsum dissolve readily in water, by ionic dissociation and without requiring the presence of acids, whereas quartz dissolves by hydrolysis producing silicic acid, but extremely slowly with respect to the first two. Caves in limestones and dolostones are the most common on Earth; carbonates dissolve by dissociation, which in pure water is very slow and comparable to the dissolution of quartz. In the presence of acidity, however, the dissolution of carbonates increases very rapidly.

The most common acid on Earth is carbonic acid, and most acidity of infiltrating waters derives from slow percolation through the soil. However, other acids, such as sulfuric acid, can be involved in carbonate dissolution and speleogenesis.

The aim of this review is to give a detailed description of the chemical and microbiological processes involved in sulfuric acid speleogenesis, its chemical, mineralogical, morphological and microbiological signatures, its worldwide distribution, and its role in paleogeographical reconstructions and deep karstification.

2. Sulfuric acid speleogenesis (SAS)

2.1. Definition of sulfuric acid speleogenetic caves

The possible role of sulfuric acid in the formation of caves has been known for over two centuries. These rare "exotic" examples of caves were first found in Europe: in France (Aix-les-Bains) (Socquet, 1801 and Martel, 1935), in Austria (Kraushöhle) (Hauer, 1885), and in an artificial tunnel near Triponzo in the Central Apennines (Italy) (Principi, 1931).

Morehouse (1968) was the first to describe in detail the processes occurring when sulfuric acid, produced by the oxidation of sulfide ores, reacts with carbonate rocks. He described Level Crevice Cave (Iowa, USA), carved in sulfide ore-bearing dolostones. The same author regarded this type of speleogenesis, in which sulfuric acid is involved, as "*somewhat a special case*", and believed that the sulfuric acid mechanism described, "*in addition to being the proven mechanism of secondary enlargement, was also probably the primary enlargement or development mechanism*" of the cave.

Sulfide ores (FeS_2, PbS, ZnS, etc.) are commonly present in carbonate sequences concentrated in "inception horizons" (Lowe, 1992; 2000), where they develop a secondary porosity if exposed to oxygenated (descending) fluids. Lowe also realized that carbonate sequences often contain horizons of sulfates (mainly gypsum) that if brought at depth can be reduced to H_2S. The fluids enriched in H_2S can then migrate upwards and oxidize into sulfuric acid creating early secondary porosity, or mix with other H_2S-bearing fluids, leading to mixing corrosion phenomena in deep anoxic settings (Warwick, 1968; Hill, 1995a).

Another way of producing sulfuric acid occurs in marine environments, where H_2S is produced by microbial sulfate reduction (MSR) in the presence of organic matter in anoxic conditions on the bottom of the sea. This H_2S, when released, rises to the surface and oxidizes into sulfuric acid, which has normally a limited effect due to dilution. In coastal carbonate settings, however, H_2S migrates from the sea floor and gets trapped in the halocline (which is a density interface), where it can concentrate. Upon oxidation (often microbially mediated), this sulfuric acid increases the acidifying effect of the salt-fresh water mixing process (Stoessel et al., 1993; Marcella et al., 1994; Stinnesbeck et al., 2018; López-Martínez et al., 2020).

It is rather straightforward that sulfuric acid, when produced in a carbonate environment, is involved in the creation of solutional voids, but since sulfuric acid is often present in low concentrations it is rapidly consumed; it rarely is the dominant chemical driver in speleogenetic process. However, when sulfides are continuously introduced in an oxygenated carbonate environment, the production of sulfuric acid can be prolonged over time, and void creation can be primarily driven by this strong acid.

Before defining exactly "sulfuric acid speleogenesis" and "sulfuric acid speleogenetic caves", it is worth spending some words on the definitions of epigene and hypogene karst. Epigenic (or hypergenic) karst typically occurs in an unconfined hydrological setting, where water is recharged from the overlying land surface, in contrast to hypogenic karst, which is predominantly confined and water enters the soluble formations from below (Klimchouk et al., 2000; Ford & Williams, 2007).

In detail, epigene speleogenesis creates caves whose origin is dominated by downward groundwater flow from an overlying or adjacent recharge area (Klimchouk, 2007) enriched with acids formed at or near the present-day surface (Palmer, 2007).

Instead, hypogene speleogenesis is defined as "*the formation of caves by water that recharges the soluble formation from below, driven by hydrostatic pressure or other sources of energy, independent of recharge from the overlying or immediately adjacent surface*" (Klimchouk, 2007), and "*involves water in which the aggressiveness has been produced at depth beneath the surface, independent of surface or soil* CO_2 *or other near-surface acid sources*" (Palmer, 2000a).

The definitions of sulfuric acid speleogenesis and caves can be formulated as follows: "*Sulfuric acid speleogenesis is the formation of voids below the Earth's surface through dissolution of soluble rocks (mainly carbonates) by waters enriched in sulfuric acid, produced by the oxidation of sulfides*" and "*sulfuric acid speleogenetic caves form through the oxidation of sulfides beneath the land surface, primarily resulting from the interaction between sulfuric acid-rich water and the host rock (mainly carbonates), leading to void creation*".

Considering sulfuric acid speleogenetic caves, and according to the two definitions of hypogene caves (speleogenesis) reported above, acidity (due to sulfuric acid) is always produced at depth and independent of surface or soil CO_2, so that caves (and speleogenesis) are always hypogenic in Palmer's view. According to Klimchouk's definition, on the contrary: i) caves formed by oxidation of metal sulfides by descending oxygenated waters are epigenic; ii) whereas most sulfuric acid speleogenetic caves are related to the upwelling of H_2S-rich waters and can be defined as truly hypogenic.

In this review paper we indicate Klimchouk's first type of caves (and speleogenesis) as "supergene sulfuric acid", following Webb (2021), whereas caves created by H_2S produced at depth and rising into the oxygenated surface environment, are indicated as hypogenic sulfuric acid (sensu Klimchouk, 2007).

Both cases can be defined sulfuric acid speleogenetic caves as long as the cave's volume is mainly due to the sulfuric acid digestion of the rock. In what follows we will mostly deal with hypogene sulfuric acid speleogenetic (SAS) caves (related to rising H_2S-rich fluids). However, for completeness, we will also include some examples of supergene (epigene) sulfuric acid caves (related to metal sulfide oxidation).

2.2. Historical overview of studies on SAS caves

Although the concept of hypogenic caves has extensively received attention especially over the past 25 years (Klimchouk et al., 2000; Ford & Williams, 2007; Klimchouk, 2007, 2009; Palmer, 2007), the role of sulfuric acid in the genesis of some (hypogenic) caves has been known for quite a long time in Europe. In fact, rising warm waters with the typical smell of rotten eggs (enriched in H_2S) were recognized as related to the presence of actively developing karst voids in the thermal spring area of Aix-les-Bains (at the foot of the Bauges massif, Savoie, SE France) at the very beginning of the 19th century (Socquet, 1801). Also Philippe Martel (1935), who visited the springs of Aix-les-Bains, mentioned the importance of sulfuric acid in speleogenesis. In Central Italy, at Triponzo (Southern Umbria) an underground tunnel for the spa intercepted a small cave still containing sulfuric waters aggressive towards limestone (Principi, 1931). Also in this case, the direct relationship between H_2S-rich waters and the active dissolution of the limestone was described accurately. In both cases the direct link between acid waters and speleogenesis was straightforward since the processes were active and clearly visible. However, in Kraushöhle (Austria) the process is not active anymore, but the abundant presence of gypsum in the cave lead Franz V. Hauer (1885) to hypothesize a link between sulfuric waters, present in a luke-warm spring located 79 m below the cave, and the genesis of the cave. Also Franz Kraus, who discovered the cave, believed that limestone was replaced by gypsum, a process he argued was probably active until relatively recently (Kraus, 1891, 1894). These early ideas were however abandoned in favor of the more simplistic model of modification of an already existing cave, or to the dissolution of gypsum bodies contained in the carbonate successions (Trimmel, 1964).

The first author describing the role of sulfuric acid in cave formation with convincing detail was David F. Morehouse (1968), using as an example Level Crevice Cave, in the Tri-State lead-zinc mining district at Dubuque, Iowa, USA. Here, sulfuric acid is produced by the oxidation of pyrite (FeS_2), marcasite (FeS_2), and to a lesser extent, galena (PbS), in the Middle Ordovician Galena Dolomite. The chemistry of the waters clearly shows sulfate to be produced, inorganically or with the help of iron-oxidizing bacteria (*Crenothrix* and *Gallionella*) that are abundantly present in the cave stream. Despite the fact that the author recognized some cave morphologies typical of SAS caves (e.g., passages pinching out), he did not report replacement gypsum and stated that there are no fundamental morphological differences between caves formed by fluids carrying sulfuric acid vs. carbonic acid.

A more complete understanding of the sulfuric acid speleogenesis came 5 years later, with the PhD work of Stephen Jay Egemeier (1973), on Lower and Upper Kane caves in Wyoming, USA. His findings are based on observations and measurements in these rather small SAS caves, in the lowest of which an H_2S-rich stream with abundant white microbial filaments can be followed for slightly over 300 m (Egemeier, 1981, 1987). In this case, the H_2S rising into the cave appears to be produced by the reduction at depth of sulfate beds in petroleum-rich strata.

Some years earlier Egemeier (1971) also was the first to suggest the sulfuric acid origin of the large rooms of Carlsbad Cavern, in the Guadalupe Mountains (New Mexico). Also David H. Jagnow (1977, 1978, 1979, 1986) independently proposed the sulfuric acid origin of the Guadalupe caves, with the acid coming from the oxidation of pyrite in the Yates Formation (similar to Morehouse's ideas in Iowa). This contrasted with the earlier explanation of speleogenesis, and in particular with the abundant gypsum deposits, in this cave, observed by J Harlen Bretz, who believed the caves around Carlsbad formed in phreatic conditions, followed by vadose periods in which gypsum was deposited in large pools (Bretz, 1949). The gypsum, according to Bretz, would have come from the nearby Permian Castile Formation. It is interesting to note that endellite, also known as hydrated halloysite ($Al_2Si_2O_5(OH)_4{\cdot}2H_2O$), a mineral typically produced in hydrothermal, highly acid conditions, had already been discovered in Carlsbad Cavern many years before (Davies & Moore, 1957) but did not lead to an understanding of SAS in the cave. The discovery of native sulfur in nearby Cottonwood Cave, on the contrary, encouraged Donald Davis (1973) to relate the presence of this mineral to the H_2S present in the groundwater and derived from nearby petroleum deposits. Michael Queen (1973) and Michael Queen et al. (1977) promoted a different idea that gypsum had replaced calcite and dolomite in the Guadalupe caves by a model, in which fresh meteoric waters mixed with phreatic waters that ascended from the gypsum and evaporite-rich rocks of the Castile Formation in the Delaware Basin. These hypotheses were questioned by Donald Davis some years later, and he was the first to develop the still valid sulfuric acid model for the formation of the Guadalupe Mountains cave systems (Davis, 1979, 1980). His theory, in which he suggests the possible hydrocarbon source for H_2S and, in consequence, sulfuric acid and gypsum, was validated by stable-isotope measurements on replacement gypsum, which gave negative values compatible with an origin from hydrocarbon deposits, and not related to the evaporites in the Castile Formation (Hill, 1981). In the 1980s, Carlsbad Cavern, the surrounding caves and, later, Lechuguilla Cave became the focus of study regarding the SAS model (Jagnow et al., 2000; DuChene, 2000). The investigations of Douglas W. Kirkland (1982) and especially Carol Ann Hill (1981, 1987, 1990, 2000) laid down the basis for many other works on SAS caves carried out elsewhere in the world.

In the mid-80s other North-American caves were recognized as forming by sulfuric acid interaction with carbonate rocks: some small travertine caves in the Cave-and-Basin springs (Banff National Park, Canada), in which Elworthy (1918) had reported the presence of coatings of gypsum on the walls as early as 1918 (Van Everdingen et al., 1985), and Cesspool Cave in Virginia (Hubbard et al., 1986, 1990).

In the early 1980s Bernard Collignon described the first African SAS cave, Rhar Es Skhoun, in the Azrou Massif in Algeria. However, despite the fact that he reported abundant gypsum deposits, the origin of the caves was attributed to rising thermal and CO_2-rich fluids (Collignon, 1983, 1990). In Europe, SAS caves started to be recognized in the early 1990s, despite the fact that some were described in the early 1800's (e.g., Aix-les-Bains, Socquet, 1801) and towards the end of the 19th century (Kraushöhle, Hauer, 1885). The discovery of Movile Cave in southern Romania in 1986 shed new light on very special geoecosystems, in which sulfuric acid is still actively enlarging the cave (Sarbu et al., 1994, 1996; Sarbu & Kane, 1995; Sarbu & Lascu, 1997; Bizic et al., 2020). Visits of Serban Sarbu to Frasassi Cave in Italy in the late 1980s encouraged Sandro Galdenzi and Marco Menichetti to apply a similar genetic model to this cave (Galdenzi & Menichetti, 1990), and later to many other caves along the Apennine chain in Central Italy (Galdenzi & Menichetti, 1995). At present, Italy is the richest country in the world regarding both active and inactive SAS caves (De Waele et al., 2014, 2016; D'Angeli et al., 2019c). During the last decade an increasingly large number of SAS caves have been recognized around the world (Fig. 1). An overview of these is given in Table 1.

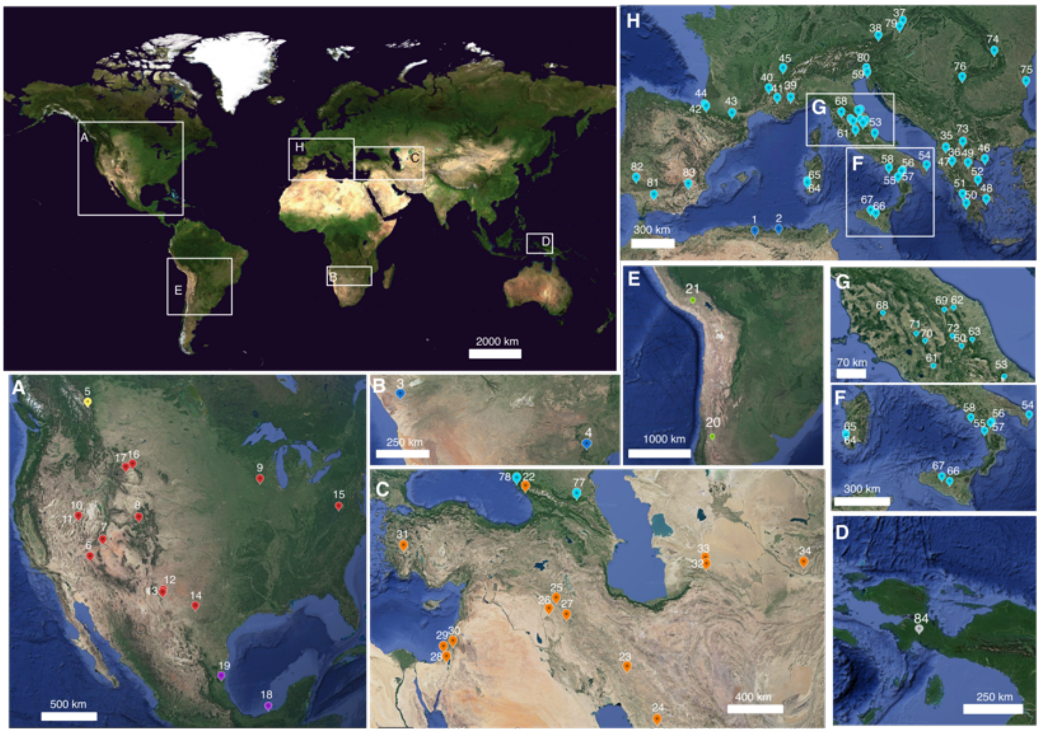

Figure 1. Map showing the location of SAS cave systems in the world. Dots and numbers refer to Table 1. A. North and Central America; B. Africa; C. Asia and part of Europe; D. Oceania; E. South America; F. South of Italy; G. Central Italy; H. Europe.

Table 1. List of sulfuric acid caves of the world. The colors on the first column are indicative of the points on the map in Figure 1. Geographical location contains information from general to more detailed and includes the physiographic region (i.e., Valley, Basin, Mountain, etc...), and municipality. In the column size S means small (length < 100 m), M medium (length 100÷1000 m), B big (length > 1000 m). Active means that the sulfuric acid corrosion is still ongoing.

2.3. Origin and evolution of hydrogen sulfide

In the surface environment, H_2S is produced by the decay of organic matter in an oxygen-depleted environment (e.g., swamps, poorly oxygenated streams or lakes), but this source of H_2S generally has a negligible role in speleogenesis (e.g., in cenotes) (Stoessel et al., 1993; Marcella et al., 1994). Hydrogen sulfide involved in SAS is mainly derived from microbial or thermochemical sulfate reduction (in short, MSR and TSR, respectively). Another possible H_2S source, independent of reduction of sulfates, is mantle degassing (magmatic). This type of hypogene H_2S is typical in areas of volcanic activity or in presence of deep active magma bodies.

MSR is typical of low-temperature diagenetic environments (0-80°C, and <2.5 km of depth in areas with a normal geothermal gradient), whereas TSR mainly occurs at greater depth with temperatures > 25°C (Worden & Smalley, 1996) increasing substantially between 100 and 200°C (2.5 to 6 km depth) (Machel, 2001). In both processes, H_2S derives from the reduction of dissolved sulfates present in original connate sea water, deeply looping marine waters, and evaporite-derived brines (gypsum and anhydrite) (Fig. 2). Reduction of these sulfates takes place in presence of organic compounds (e.g., hydrocarbons), hosted in the sedimentary sequences. The rate of either MSR or TSR depends mainly on the supply of the main reactants, represented by organic compounds and dissolved sulfate. In comparable geochemical situations, MSR occurs generally more rapidly than TSR. Distinguishing between MSR and TSR relies on a combination of different geochemical (especially stable isotopes of C, O, and S; Wynn et al., 2010; Laurent et al., 2023) and petrologic criteria.

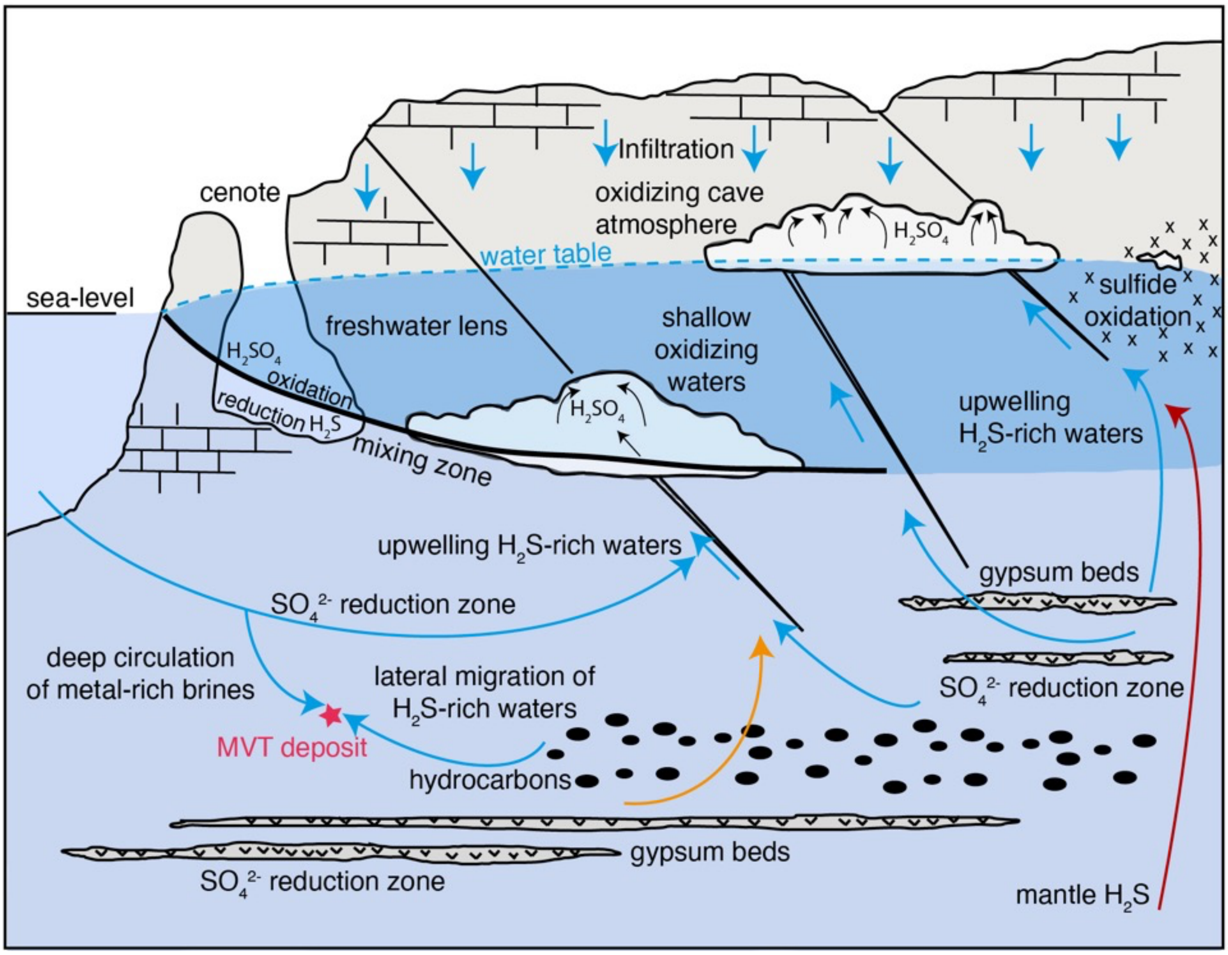

Figure 2. Schematic representation of the various origins of sulfides involved in SAS, the migration paths of fluids and gases, and zones where oxidation and reduction take place. The orange arrow indicates slightly thermal fluids, the red one hot fluids. MVT stands for “Mississippi Valley Type” ore deposit.

Both processes, through a series of similar redox-reactions, lead to the formation of the same products. Following Machel (2001) the reaction can be shown as:

$$HC + SO_4^{2-} \longleftrightarrow \text{altered HC} + \text{solid bitumen} + H_2S\ (HS^-) + HCO_3^-\ (CO_2) + H_2O + \text{heat ?} \qquad [1]$$

in which HC stands for hydrocarbons. Omitting some details, all hydrocarbons go through a maturation stage that can include aerobic biodegradation, anaerobic fermentation, and thermal maturation. These events, through different reactions, alter the organic molecules to organic acids, alcohols and other compounds (e.g., CH_4), which can then be used by sulfate-reducing bacteria during MSR. Thermal maturation of crude oil itself generates small amounts of reagents (up to 3%) in the following reaction (Machel, 2001):

$$\text{crude oil} \longrightarrow \text{light crude oil} + H_2S + \text{Polysulfides} + HC \qquad [2]$$

The simpler organic products, which are here symbolized as HC (CH_4 being one of the most important end products of the transformation of hydrocarbons by MSR and/or TSR) will then react with dissolved gypsum (or anhydrite, $CaSO_4$) producing H_2S according to the reaction (Palmer, 2007)

$$CaSO_4 \cdot 2H_2O + HC + H_2O \longrightarrow H_2S + Ca^{2+} + HCO_3^- \qquad [3]$$

In general, the H_2S which is produced by this reaction migrates elsewhere as a dissolved gas, whereas the calcium carbonate precipitates (as secondary calcite). The original gypsum or anhydrite rocks can be replaced by what has been called bio-epigenetic calcite (Hill, 1995b), with the reaction often written as

$$Ca^{2+} + 2SO_4^{2-} + 2CH_4 + 2H^+ \longleftrightarrow 2H_2S + CaCO_3 + CO_2 + 3H_2O \qquad [4]$$

In all cases one of the final products of these redox reactions is hydrogen sulfide, a gas that in normal geological situations in the shallow crust (< 6 km depth), depending on pH (Hill, 1995b), remains in solution in its molecular or dissociated form (H_2S or HS^-). Note that this redox reaction also produces CO_2, which stays in solution at these pressures and migrates with the fluids.

The organic carbon needed for bacterial sulfate reduction can also have an autochthonous source in shallower (oxygenated) zones of the aquifer, by biomass accumulation of sulfur-oxidizing bacteria, which can then descend into the anaerobic zone of the aquifer and be used by sulfate-reducing bacteria to produce H_2S (Barton, 2013). It has been shown (Engel et al., 2010) that sulfate-reducing bacteria can reduce sulfate back to H_2S in caves following the reaction:

$$SO_4^{2-} + 10H^+ + 8e^- \longleftrightarrow H_2S + 4H_2O \qquad [5]$$

This reaction removes sulfate from the shallow cave environment, allowing the dissolution of gypsum to proceed, and also adds extra (autochthonous) H_2S to the system. This microbial sulfate reduction also decreases $\delta^{34}S$ values, increasing the isotopic fractionation typical of SAS even more.

When dissolved H_2S comes into contact with, often descending, oxygenated meteoric waters, elemental sulfur forms following the reaction (Hill, 1995b)

$H_2S + \frac{1}{2} O_2 \longrightarrow S^0 + H_2O$ (in acid conditions, <pH 7) [6]

or

$2HS^- + O_2 + 2H^+ \longrightarrow 2S^0 + 2H_2O$ (in slightly basic conditions, pH 7-9) [7]

This reaction is often mediated by sulfur-oxidizing bacteria, and elemental sulfur generally forms granular deposits entombing the bacterial cells. This is why biomats and streamers in sulfidic waters often have this milky color.

However, if meteoric waters are very poor in dissolved oxygen, reactions [6] and [7] only remove minor parts of the H_2S formed during the earlier stages. Most of the H_2S (and CO_2) migrates laterally and upward and enters the adjoining more-or-less permeable carbonate rocks, often occupying structural and stratigraphic traps. Before reaching the water table, this dissolved gas can react with metal-rich chloride waters present in the reducing zone forming typical Mississippi Valley Type deposits (MVT in Figure 2) according to the following complex redox reaction [8]

$H_2S+CO_2+MeCl^++Mg^{2+}+2CaCO_3+H_2O \longrightarrow MeS+Ca^{2+}+CaMg(CO_3)_2+HCO_3^-+Cl^-+3H^+$ [8]

where Me represents metals such as Pb, Zn, and Fe (Hill, 1995b).

If, on the other hand, dissolved hydrogen sulfide comes into the aerated environment, at or close to the water table, oxidation creates the sulfuric acid involved in SAS, as explained in the following section.

2.4. Chemistry of sulfuric acid speleogenesis

The major source of solutional aggressiveness in SAS derives from the oxidation of H_2S, producing sulfuric acid. Ascending fluids rich in H_2S that oxidizes at or near the water table are responsible for the vast majority of SAS caves in the world. Although this oxidation can occur in a purely abiotic way, it is more efficiently mediated by sulfur-oxidizing bacteria.

The oxidation of H_2S into sulfuric acid for the formation of SAS caves fully described by Egemeier (1981) for Kane caves in the Bighorn Basin in Wyoming, typically occurs in two cave environments (Fig. 2): 1) where ascending H_2S-rich fluids mix with shallow oxygen-rich waters of meteoric or marine origin, or 2) above the water table in the cave atmosphere (Audra, 2008). The oxidation of H_2S can occur in different ways:

$$H_2S + 2O_2 \longleftrightarrow H_2SO_4\ (2H^+ + SO_4^{2-} \text{ in aqueous solution}) \qquad [9]$$

$$H_2S + \tfrac{1}{2}\,O_2 \longleftrightarrow S^o + H_2O \qquad [10]$$

$$2S^o + 3O_2 + 2H_2O \longleftrightarrow 2SO_4^{2-} + 4H^+\ (\text{in aqueous solution}) \qquad [11]$$

$$S_2O_3^{2-} + H_2O + 2O_2 \longleftrightarrow 2H^+ + SO_4^{2-} \qquad [12]$$

The reaction speed is increased if mediation by sulfur-oxidizing bacteria occurs, and reaction [9] takes place bypassing the intermediate phases ([10], [11] and [12]) (Engel et al., 2004a; Palmer, 2013).

These four reactions take place in the presence of oxygen, which can be delivered by the air or percolating (surface) waters, close to or above the water table (Fig. 3). Another way of producing sulfuric acid in the absence (or low concentration) of O_2 is in the presence of an alternative electron acceptor such as NO_3^- (Gevertz et al., 2000):

$$8NO_3^- + 5H_2S \leftrightarrow 4N_2 + 4H_2O + 5SO_4^{2-} + 2H^+ \qquad [13]$$

$$3NO_3^- + 4S^0 + 7H_2O \leftrightarrow 3NH_4^+ + 4SO_4^{2-} + 2H^+ \qquad [14]$$

and these reactions can be active in the presence of sulfur-oxidizing bacteria at depth, as long as temperatures are low enough to allow bacteria to survive.

Since most SAS caves are developed in carbonate environments (Palmer, 2013), these reactions generally occur in a buffering environment at pH close to 7. When sulfuric acid comes into contact with the carbonate host rock, it reacts immediately according to the following reaction:

$$CaCO_3 + SO_4^{2-} + 2H^+ + 2H_2O \longleftrightarrow CaSO_4 \cdot 2H_2O + CO_2 + H_2O \qquad [15]$$

The dissolution of limestone ($CaCO_3$) in contact with sulfuric acid (H_2SO_4) thus produces secondary gypsum ($CaSO_4 \cdot 2H_2O$) and releases CO_2 in the surrounding environment. Early in his study, Egemeier (1981) referred to a replacement-solution, in which calcite is replaced by gypsum, whereas dolomite would convert into gypsum and epsomite. This replacement is often volumetric, and original bedrock textures and fossils are sometimes perfectly preserved (Hauer, 1885; Queen, 1973; Puchelt & Blum, 1989; Buck et al., 1994; Plan et al., 2012). Gypsum, being more soluble than calcite, can then be removed in solution by running water, allowing the voids to enlarge rapidly. Also the CO_2 released during the reaction can contribute to the acidity of the water, further promoting the dissolution of limestone and other carbonate rocks according to the classic reaction

$$CaCO_3 + CO_2 + H_2O \longleftrightarrow Ca(HCO_3)_2 \qquad [16]$$

Sulfuric acid can also be produced by oxidation of other sulfides, mainly pyrite, but also sphalerite, galena and other common sulfides in Mississippi Valley Type ore deposits. One of the possible reactions is

$$4FeS_2 + 15O_2 + 14H_2O \longleftrightarrow 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-} \qquad [17]$$

This process is often very localized, creating a scattered porosity, but there are examples in which sulfuric acid produced by oxidation of abundant pyrite has created large cave systems. This type of speleogenesis in which sulfuric acid is involved has been defined as supergene (epigene) SAS (Webb, 2021). The abundant presence of pyrite in the Galena Dolomite Formation has made cave formation by sulfide oxidation viable in Iowa's Level Crevice Cave (Morehouse, 1968). The large maze cave systems in Campo Formoso (NE Brazil) are also thought to have formed by waters partly acidified by oxidation of sulfides in the Precambrian host rock (Auler & Smart, 2003; Klimchouk et al., 2016). Also the Shuanghe Cave System in Guizhou, China, the largest dolomite cave in the world, is formed by local oxidation of sulfides in the host rock along certain stratigraphic intervals, in which the dolostone is enriched in hydrocarbons. This cave is known for its widespread occurrence of both gypsum and celestite. In Transvaal (South Africa) the Mbobo Mkulu Cave has formed between a thick layer of Archean dolostone and chert breccia overlain by a sulfide-rich black shale. The oxidation of these sulfides is responsible for most of the dissolution in the dolostone (Martini et al., 1997). Localized supergene oxidation of pyrite has occurred in the Pisatela-Rana cave system in northern Italy, where gypsum formation caused haloclastic phenomena (splitting by crystal growth, Tisato et al., 2012). Gypsum derived from pyrite oxidation occurs in Mammoth Cave, the longest-known epigenic cave system in the world. Breakdown caused by gypsum crystal wedging in the rock fissures is slightly aided by sulfuric acid dissolution (Metzger et al., 2015). Gypsum found in Castleguard Cave, Canada, is also derived from the oxidation of pyrite in the surrounding limestones (Yonge & Krouse, 1987). Sulfur isotopes in gypsum deposits in Dachstein-Mammuthöhle (Austria), indicated two sources: some is derived from Upper Permian evaporites but the majority comes from the oxidation of pyrite (Seemann, 1979). Another good example in which localized acid corrosion caused by weathering of pyrite ore bodies has given rise to significant formation of voids is the fluted shaft system of Queen of the Guadalupes (Jagnow, 1979). Also in Baume Galinière, in the Vaucluse area (France), intense pyrite oxidation has created an almost 200 m-long maze cave with an exceptional occurrence of SAS-derived cave minerals (Audra et al., 2015).

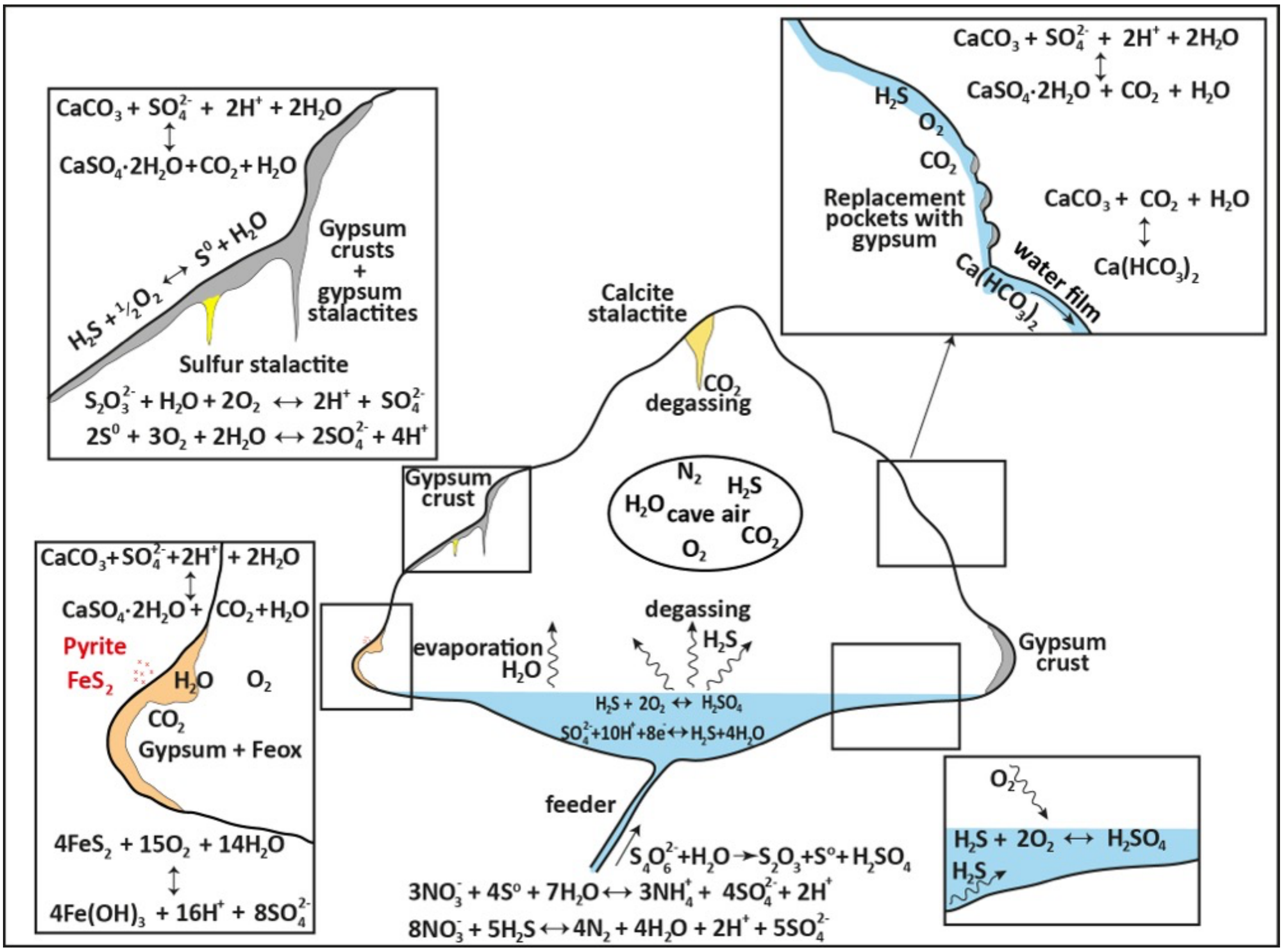

Figure 3. Schematic representation of the possible geochemical reactions involved in SAS close to and above the water table.

3. Signatures of active and past sulfuric acid speleogenesis

Caves are often the final product of a multitude of processes, and undergo a series of steps starting from the early inception phases, in which tiny discontinuities are enlarged very slowly at first, followed by a much faster enlargement phase, to the final senile stages and exhumation. During these evolutionary steps, the signs of the earlier cave-enlargement processes can be erased or hidden, making it difficult to recognize the processes that were once active. For example an initially hypogene cave, formed at great depth and nearly isolated from processes occurring at the Earth's surface, may migrate closer to the land surface by removal of overlying strata, and may begin to receive infiltration water, finally becoming completely exhumed and transforming into an unroofed cave. Earlier signs of hypogene fluids, such as those containing sulfuric acid, can become completely overprinted and therefore unrecognizable. Caves can also be enlarged by different processes at the same time: the Frasassi Cave in Italy, for example, is a SAS cave in which parts of the lower passages have been invaded by surface waters (an epigenic river). Some parts of this cave are dominantly formed by surface waters enriched in CO_2, and the imprint of the sulfidic fluids has become less pronounced. However, Frasassi Cave can be classified as dominantly formed by SAS. The following paragraphs review the various signatures that can be used as diagnostic signs of SAS in both active and inactive cave systems. Note that generally a combination of these signatures is needed to assign a sulfuric acid origin (or stage) for a cave, although some are truly restricted to this kind of speleogenesis (e.g., replacement pockets).

3.1. Stable isotope signatures of SAS

The fluids involved in SAS are, at least in part, derived from deep (hypogenic) sources. As explained earlier, these fluids are enriched in H_2S, and often also CO_2, which interact with oxygenated water in the parts of the karst systems closer to the surface, leading to the formation of sulfuric acid, which in turn reacts with the carbonate host rock. If the origin of these rising waters/gases is deep enough, or if there is an increased local geothermal gradient (e.g., in regions of active volcanism, or in presence of granitoid intrusions), these fluids will also be thermal, as documented in many active SAS caves such as: Acquasanta Terme, Italy (Galdenzi et al., 2010; Fusari et al., 2017); Montecchio Cave, Italy (Piccini et al., 2015); Chevalley and Serpents Cave, France, where water rises rapidly from depth (Audra et al., 2007); Cerna Valley caves, Romania (Wynn et al., 2010, Onac et al., 2009, 2011). However, this is not necessarily the case (e.g., Frasassi cave system, Italy, Galdenzi et al., 2008; Galdenzi, 2012), as a matter of fact, in many cases the thermal fingerprint is rather weak, such as in Movile Cave (Romania), where waters are only 8°C warmer than the mean-annual temperature (Sarbu & Kane, 1995), only 7°C warmer in Santa Cesarea Terme (D'Angeli et al., 2021) and 5°C at Cueva de Villa Luz (Hose et al., 2000). Chemical signatures indicating the former presence of sulfuric acid in now inactive caves are mainly related to stable isotopes of sulfur in replacement gypsum or SAS byproducts, whereas those of oxygen can give further constraints on the origin (meteoric or not) of the sulfuric waters. The thermal footprint of the rising (not necessarily sulfide-rich) waters can be ascertained by fluid inclusion studies, especially in the presence of well-formed barite, fluorite, and calcite samples (Cortecci et al., 1989; Bottrell et al., 2001; Temovski et al., 2022; Laurent et al., 2023).

In general, though, the most robust evidence of active or past SAS processes is based on the $\delta^{34}S$ values of gypsum and sulfur found as byproducts of the acid corrosion in the caves, or the combined study of multiple sulfur (including $\delta^{33}S$) and oxygen isotopes (Laurent et al., 2023). Sulfur has four stable isotopes in nature (^{32}S, ^{33}S, ^{34}S and ^{36}S), but only ^{32}S (95.02%), ^{33}S (0.75%), and ^{34}S (4.22%) are of interest (Eckardt, 2001; Canfield, 2001). Overall, the average values of $\delta^{34}S$ vary significantly, from -50 to +35 ‰. One of the most striking chemical signatures of SAS is the often very negative value of $\delta^{34}S$ (down to -30‰) in gypsum deposits attributable to the MSR. These low $\delta^{34}S$ values were the first compelling evidence of the implication of hydrocarbons in the origin of sulfides in the Guadalupe Mountains in New Mexico (Hill, 1981). Here, the hydrocarbons of the Delaware Basin provided the electrons for the bacterial sulfate reduction of the Castile Formation evaporites, demonstrated by a $\delta^{34}S$ shift from around +10‰ in these Permian gypsum deposits to around −20‰ for the H_2S (Hill, 1987, 1990; Spirakis & Cunningham, 1992). The low reaction rate, limited by the slow supply of hydrocarbons from the deep petroleum reservoirs to the Castile Formation evaporites, causes this fractionation to be so substantial (a lowering of ca. 30‰). This isotopic signal is retained in the final secondary gypsum deposits if the oxidation of H_2S into H_2SO_4 occurs in a closed, well-oxygenated system and is complete (i.e., no H_2S is able to escape from the system), as probably happened in the Guadalupe Mountains cave systems.

Studies of S isotope fractionation during S oxidation have shown that the $\delta^{34}S$ shift is generally rather small (no fractionation at high (>80°C) T (Ohmoto and Rye, 1979); small to moderate fractionation, only up to -5‰, at low (room) T (Fry et al., 1988)). However, if the oxidation proceeds through an intermediate phase, from H_2S to S^0, a fractionation from -0.3 to +8 ‰ has been shown to occur (Zerkle et al., 2016), whereas the subsequent complete oxidation of S^0 to SO_4 yields small to negligible fractionation. Moreover, it should be noted that during gypsum precipitation there is also a small fractionation in the range of +1 to +2‰, as reported by Thode & Monster (1965), Raab & Spiro (1991), and Van Driessche et al. (2016).

This means that the $\delta^{34}S$ values of SAS minerals (e.g., gypsum, Al-sulfates) are not always similar to those of the original source of reduced sulfur, as reported in Yonge & Krouse (1987), Bottrell (1991), and Bottrell et al. (2001). In natural situations the stable isotope signature of sulfur can be difficult to interpret, and inferring the pathways of sulfur and the source of H_2S requires the use of $\delta^{34}S$ in combination with other isotopes: $\delta^{33}S$ (Laurent et al., 2023), and/or $\delta^{18}O$ in the sulfate (Onac et al., 2011; Temovski et al., 2018).

In general, however, MSR often causes $\delta^{34}S$ values to shift by as much as -30‰, and sulfides resulting from this process have an average $\delta^{34}S$ value of -12‰ (Seal, 2006). The final $\delta^{34}S$ value depends on the initial isotopic signature of the sulfur, which can have four main sources in carbonate karst (Wynn et al., 2010): oxidation of sulfides, dissolution of marine evaporites, degradation of bat guano, and rising of volcanic fluids, as well as the fractionation processes along its path. For example, $\delta^{34}S$ of sulfur derived from a magmatic source is generally between 0 and 5‰, while $\delta^{34}S$ of marine evaporites ranges between ~+10 and ~+35‰ (Claypool et al., 1980; Halevy et al., 2012).

Low sulfur isotopic compositions of gypsum (between -24.7 and -22.1‰) have been noted in Cueva de Villa Luz (Mexico), and H_2S was believed to derive from microbial reduction of evaporite sediments using electrons from hydrocarbons from nearby oil fields (Hose et al., 2000; Rosales Lagarde et al., 2008), similar to what happened in the Guadalupe Mountains. Some geochemical studies on the gases in Cueva de Villa Luz, however, point also to a partial magmatic origin for the H_2S, whereas large parts of the water appear to have a more meteoric origin (Spilde et al., 2004).

In Movile Cave in Romania the rather positive values (between + 1 and 5‰) of sulfur isotopes in water suggest that H_2S is derived from a deep volcanic (magmatic) source, which would also explain the, albeit low, thermal anomaly in the cave waters (Sarbu & Kane, 1995).

The $\delta^{34}S$ values of gypsum in Kraushöhle (Austria) are very low (between -23.1 and -15.8‰) (Puchelt & Blum, 1989; Plan et al., 2012), because of the fractionation of Upper Permian and Lower Triassic evaporite rocks (gypsum layers in the Haselgebirge and Werfen Formation) by MSR, and successive oxidation in the Hierlatz Limestones. Similarly, the very negative values encountered in the Montecchio Cave (Italy) gypsum (between -28.3 and -24.2‰) derive from microbial reduction of Triassic gypsum layers of the Burano Formation or, alternatively, from sedimentary pyrite hosted in the Triassic carbonates or sulfide ore bodies hosted at the contact between the Permian basement rocks and the Triassic sediments (Piccini et al., 2015).

The wide range of $\delta^{34}S$ values (between -27.9 and +19.5‰) in the Cerna Valley caves is due to TSR of sedimentary sulfates and their reaction with methane, produced by bacterial decay of nearby coal deposits (Onac et al., 2011). These reactions are variously limited by methane and/or sulfate supply during reduction, and by oxygen supply during their oxidation, leading to this wide spectrum of $\delta^{34}S$ values.

In Provalata Cave in Macedonia mostly negative values (between -7.5 and +0.7‰) were first thought to be related to MSR of nearby coal deposits, which show more positive values (Temovski et al., 2013). More recent investigations on the dissolved sulfate ions in the thermal spring below Provalata Cave have shown H_2S to be derived from a magmatic source (Temovski et al., 2021), a hypothesis that was further strengthened by the noble gas composition of fluid inclusions in calcite deposited during the preceding CO_2 thermal speleogenesis of the cave, related to the youngest magmatic activity of the nearby Late Pliocene-Early Pleistocene volcanic system (Temovski et al., 2022). This example shows that the wide range of both S and O isotopes in gypsum taken from a rather small cave reflects the complexity of the chemical processes involved, and conclusions regarding the origin of the fluids and gases based on stable isotopes is not always straightforward (Temovski et al., 2018). For example, the less depleted values in δ^{34}S encountered in Grotte du Chat (France) (-9.4‰) and in Acqua Fitusa (Sicily) (between -1.0 and +10.6‰) are still not explained. In both cases the H_2S is probably derived from the reduction of sedimentary sulfates present in the underlying stratigraphic sequence, with a possible contribution from other sources (De Waele et al., 2016). The decisively negative values of δ^{34}S (between -20.0 and -8.0‰) in Frasassi Cave are explained by MSR of deep organic-rich Triassic anhydrites (Burano Fm.) (Galdenzi & Menichetti, 1995).

The Cavallone-Bove cave systems showed δ^{34}S values ranging between -8.9 to +9.3 ‰ which are thought to be influenced by rising fluids in contact with the deep-seated Triassic evaporites that interacted with bitumen layers (D'Angeli et al., 2019b). In Corkscrew Cave (Arizona, USA), the isotopically light sulfur isotope signal (between -10.2 and -8.1‰) is compatible with a sulfuric acid speleogenetic mechanism which is responsible for at least part of the recent cave passages that dissect older karstified and mineralized breccia bodies (Onac et al., 2007).

Sulfuric springs were also studied on the sea floor in front of Izola west of Koper in Slovenia (Adriatic Sea), and some small sulfuric acid caves have been explored in a carbonate outcrop surrounded by flysch near Izola. Sulfur stable isotopes in spring water sulfates (between 20.3 and 23.6‰) indicate a marine origin of S, with some signs of sulfur fractionation due to anaerobic bacterial activity (Šušmelj et al., 2021).

A rather different scenario is provided by the sulfur isotope signature of sulfates in Cupp-Coutunn Cave, that generally retain a distinct hydrothermal imprint (with positive δ^{34}S values of around 10‰, very close to that of the original sulfides) (Bottrell et al., 2001). This would suggest MSR of primordial sulfates to be less important than in other SAS situations reported above. The fluids that gave rise to the speleogenetic gypsum are believed to be basinal brines that mixed with meteoric infiltration waters that might also have contained evaporitic sulfates.

Table 2. List of the values of δ^{34}S (‰) of byproduct gypsum deposits from SAS caves.
Isotope ratios are reported in the conventional δ-notation with respect to V-CDT (Vienna Cañon Diablo Troilite). MSR and TSR refer to microbial or thermochemical sulfate reduction respectively.

Location	Cave-Cave system	Gypsum δ^{34}S (‰)	Source	Sulfate reduction	Reference

			MIN	MAX			
NORTH AMERICA	Arizona	Corkscrew Cave	-10.2	-8.1	Hydrocarbons	TSR	Onac et al., 2007
	New Mexico	Endless Cave	-8.6		Oil field	MSR	Hill, 1987
		Dry Cave	-12.4		Oil field	MSR	Hill, 1987
		Cottonwood Cave	-0.8	+5.0	Oil field	MSR	Hill, 1987
		Lechuguilla Cave	-25.6		Oil field	MSR	Hill, 1987; Spirakis & Cunningham, 1992
		Carlsbad Cavern	-25.6	+9.2	Oil field	MSR	Kirkland, 1982; Hill, 1987
CENTRAL AMERICA	Mexico	Cueva de Villa Luz	-22.1	-24.7	Oil field; Volcanic	MSR	Spirakis & Cunningham, 1992; Pisarowicz, 1994; Hose et al., 2000; Spilde et al. 2004
ASIA	Turkmenistan	Cupp-Coutunn	9.6	13.3	Basinal brines	MSR	Bottrell et al., 2001
EUROPE	Austria	Kraushöhle	-23.1	-15.8	Permian-Triassic Evaporites	MSR	Puchelt & Blum, 1989; De Waele et al., 2016
	France	Grotte du Chat	-9.4		Evaporites	MSR	Audra, 2007
	France	Ermite	-7.33	-3.56	Triassic evaporites	TSR	Laurent et al., 2021
	Italy	Acqua Fitusa	-1.0	10.6	Evaporites	MSR	De Waele et al., 2016
	Italy	Cavallone		8.9	Triassic evaporites; Bitumen	Chemical	D'Angeli et al., 2019b

	Italy	Frasassi	-20	-8	Triassic evaporites	MSR	Galdenzi & Maruoka, 2003
	Italy	Montecchio	-28.3	-24.2	Triassic evaporites; Pyrite	MSR	Piccini et al., 2015
	Macedonia	Provalata	-7.5	0.7	Coal deposits; Volcanic	MSR	Temovski et al., 2013, 2018, 2022
	Romania	Cerna Valley	-27.9	19.5	Evaporites, Methane	TSR	Onac et al., 2011
	Russia	Sheki-Heh	-21.6	-10.3	Marine	Chemical	Chervyatsova et al., 2016, 2020; Sadykov et al., 2020

3.2. Mineralogic signatures of SAS

More than 300 minerals are known to form in caves as secondary deposits, the most abundant of which are calcite and aragonite (Onac & Forti, 2011). The third most abundant mineral is gypsum, and the sulfur necessary for its formation in carbonate host rock can derive from a wide variety of sources, such as marine aerosols, guano, volcanic fluids, sulfides, among others. Many SAS caves are characterized by the occurrence of this sulfate, but the presence of gypsum is not necessarily correlated to the fact that the cave, somehow, was carved with the aid of sulfuric acid.

Some minerals are more or less diagnostic of SAS, others are less clear indicators but compatible with the involvement of sulfuric acid. The following minerals can be distinguished: 1) those derived by the reaction between S-bearing fluids with the carbonate bedrock; 2) those formed by the interaction of sulfuric acid with insoluble minerals present in the host rock or its insoluble residuum and 3) those related to the S-bearing fluids themselves. The first two are often clear indicators of sulfuric acid involvement in at least some of the speleogenetic phases.

3.2.1. Minerals derived from the reaction between sulfuric acid and soluble host rock

As explained above, the reaction of sulfuric acid with limestone [15] gives rise to the formation of gypsum (Galdenzi & Maruoka, 2003) (Fig. 4A-D). Because of the exothermic reaction between calcite and sulfuric acid and the low activity coefficient of water, anhydrite crystals also form along the reaction front, but are rapidly transformed into gypsum in the moist cave environment. SAS-derived gypsum often occurs as pure saccharoidal white masses, or crusts, in contrast to SAS-related gypsum formed by oxidation of pyrite (or other sulfides) that can be stained with yellow-brownish iron oxides.

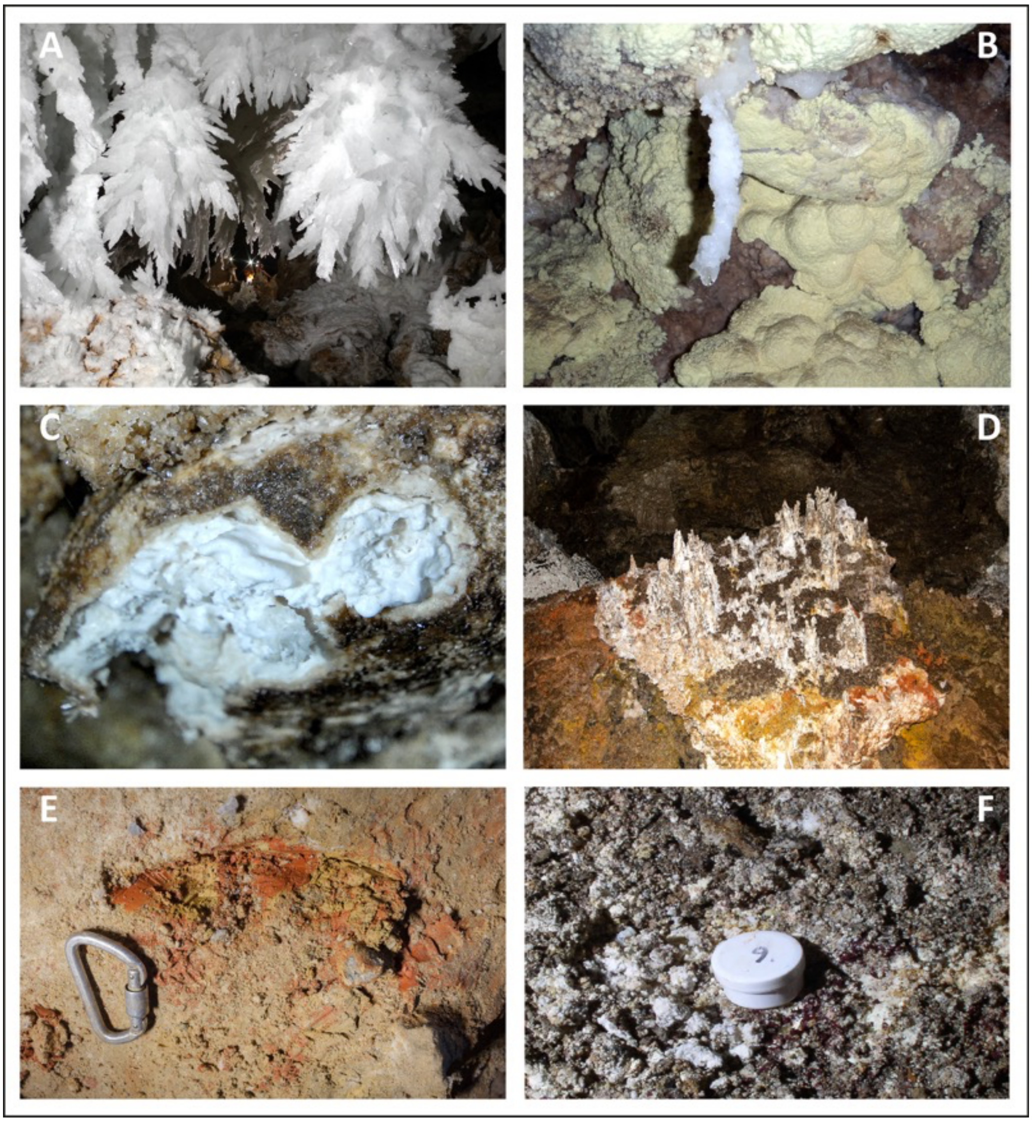

Figure 4. Typical SAS minerals: A. The meters-long gypsum chandeliers in Lechuguilla Cave, New Mexico (person in center background for scale) (Photo Lukas Plan); B. One-decimeter long gypsum stalactite growing from a native sulfur crust a centimeter thick in Gattulla Cave, Santa Cesarea Terme, Italy (Photo Mario Parise); C. One decimeter-wide toothpaste-like white gypsum moonmilk patch in Fetida Cave, Santa Cesarea Terme, Italy (Photo Marco Vattano); D. Meter-size block of secondary replacement products in Avulit Cave, Albania. The white is gypsum, the reddish orange is jarosite (Photo Ivano Fabbri); E. Reddish and orange jarosite in Sant'Angelo Cave, Cassano allo Ionio, Italy (Photo Orlando Lacarbonara); F. White greyish crumbly aggregates of alunite with gibbsite, in Kraushöhle, Austria (white box is 2 cm in diameter) (Photo Lukas Plan).

Gypsum deposits in SAS caves normally occur as wall rinds (white crystalline crusts, up to 30 cm thick). When these repeatedly break off and fall to the floor (often in gypsum-saturated water bodies), they can form meter-thick floor deposits (Polyak & Provencio, 2001). SAS-derived gypsum can form in different conditions: as a subaqueous replacement crust or disseminated as solids in gypsum-saturated waters (rather rare, requiring arid conditions that lead to evaporation and supersaturated pools), or in the subaerial environment as replacement crusts, a replacement-crust breccia or evaporitic crusts (Buck et al., 1994).

Another byproduct of the reaction of sulfuric acid with the carbonate bedrock is celestine, especially when in association with gypsum. The Sr needed for the formation of celestine normally comes from the carbonate bedrock. Precipitation of gypsum first leads to an increase in the Sr/Ca ratio of the remaining fluids, eventually leading to the precipitation of celestite (Hill & Forti, 1997). In Shuanghe Cave (Guizhou, China) entire passage walls are covered with bluish celestine, always occurring below a gypsum crust.

Secondary dolomite is another mineral that can typically be found in sulfuric acid caves. This mineral derives from the preferential removal of Ca in limestone weathering, replaced by gypsum. The enriched Mg-solution can then precipitate dolomite as soon as pH levels are high enough to allow this carbonate to be preserved. This speleogenetic dolomite has been found in Lechuguilla and Carlsbad Cavern, embedded in replacement gypsum, and derives from the partial leaching of the original limestone (as preserved Permian fossils indicate) (Polyak & Provencio, 2001). This dolomite can thus be used as an independent geochronometer alongside alunite and jarosite, using the U-Th and U-Pb methods (Polyak et al., 2016).

A suite of other sulfates, resulting from the reaction between host rock and sulfuric acid, can be found in still-active SAS caves. Tamarugite and pickeringite were found together with gypsum and orpiment In Aghia Paraskevi Cave (Greece) (Lazaridis et al., 2011). A wide variety of SAS-related minerals has been discovered in the active caves of the Cerna Valley (Romania) (Onac et al., 2009). The most remarkable is Diana Cave, a very small but the most interesting active sulfuric acid cave in this area. Here, native sulfur, gypsum, anhydrite, pickeringite, apjohnite, halotrichite, epsomite, tamarugite (Puşcaş et al., 2013), and rapidcreekite (Onac et al., 2013) were found. In the active thermal sulfuric springs of Cassano allo Ionio (Calabria, S-Italy) located in a thermal spa (Terme Sibarite) copiapite, pickeringite, tamarugite, hexahydrite, and epsomite were found together with abundant gypsum (D'Angeli et al., 2018). Gypsum was accompanied by tschermigite and copiapite in the nearby Ninfe Cave at Cerchiara di Calabria. In the Acqua Fitusa thermal sulfidic spring in Sicily eugsterite and thenardite are deposited, probably indicating that the ascending fluids derive from the underlying evaporites (brines) (D'Angeli et al., 2018).

3.2.2. Byproducts derived from the reaction between sulfuric acid and insoluble minerals

Alongside speleogenetic gypsum, a series of other SAS byproducts has been reported from the many sulfuric acid caves in the world, and especially from those in the Guadalupe Mountains in New Mexico (Polyak & Provencio, 2001) and the large number of Italian SAS caves (D'Angeli et al., 2018). The most important of these minerals are hydrated halloysite (also known as endellite), and the alunite-jarosite group minerals.

Hydrated halloysite was first reported from Carlsbad Cavern by Davies & Moore (1957), but it was not until the 1980s that its genesis was related to the acidic conditions of SAS (Hill, 1987; Polyak & Güven, 1996, 2000a,b). This mineral is formed by the weathering of montmorillonite (smectite group) and other clays in the presence of H_2SO_4. It often occurs as inclusions in weathered bedrock, together with gypsum, alunite, and the unaltered clay residues. Hydrated halloysite in Amazing Maze Cave (Texas), together with gypsum and the typical hypogene morphologies, indicate this cave to belong to the sulfuric acid type (Stafford et al., 2008). Its presence is highly indicative of very acidic conditions, typical but not exclusive to SAS caves. In fact, halloysite has also been found in caves close to sulfide ore bodies in Sardinia (De Waele et al., 2008), related to the weathering of volcanic ash by oxidation of sulfides in a subaqueous environment, or trapped in paleokarst after intense tropical weathering (Quinif, 2022).

Alunite and natroalunite also form by alteration of clay minerals containing K, Na, and Al by H_2SO_4 (Polyak & Güven, 1996). These minerals, and especially alunite (Fig. 4F), can be used to date the timing of speleogenesis using the K^{40}-Ar^{39} or Ar^{40}-Ar^{39} methods (Polyak et al., 1998; Polyak & Provencio, 2000). Alunite also forms in quartz-dominated environments, as long as kaolinite is present, sulfur is provided and pH is sufficiently low (Wray, 2011). In the quartzite cave of Corona 'e Sa Craba in Sardinia (Italy), sulfuric acid processes have also allowed alunite and natroalunite to form (Sauro et al., 2014). The jarosite group minerals form (Fig. 4E) instead of the alunite ones when sufficient Fe is present. Where abundant Fe (pyrite) and other ions are present in the host rock, using Baume Galinière (France) as an example, the whole suite of jarosite minerals can be formed (jarosite, argentojarosite, ammoniojarosite, hydroniumjarosite, natrojarosite, and plumbojarosite), together with fibroferrite (Audra et al., 2015). Like alunite, jarosite can be used to date the timing of speleogenesis (both minerals contain K suitable for K-Ar or Ar-Ar dating) (Temovski et al., 2013).

Other sulfates often found in SAS caves are hydrobasaluminite, felsőbányaite (correct name for discredited basaluminite), aluminite, and metalunogene. These form by acid alteration of kaolinite, thus giving rise to these Al-rich sulfates. In Serpents Cave (France) the rare aluminum sulfates alunogen, jurbanite, and tschermigite have been found together, due to the sulfuric reaction with the aluminum frame of a door (Audra & Hobléa, 2007). Depending upon conditions (hydration and dehydration, pH) these minerals can transform into each other (Polyak & Provencio, 1998; Plan et al., 2012). In Corona 'e Sa Craba (Sardinia) felsőbányaite occurs alongside alunite and walthierite, a Ba-Al-sulfate, formed here because of abundance of Ba in the thermal and sulfate-rich cave-forming waters (Sauro et al., 2014).

The uranyl vanadates tyuyamunite and metatyuyamunite, found in association with secondary speleogenetic quartz and opal coatings on dolomite and gypsum crusts, and together with clays in Spider Cave (New Mexico), have formed after the SAS processes came to an end, at pH above 8 (Polyak & Mosch, 1995). These U-V rich minerals precipitated as a result of the concentration of U and V along oxidation/reduction zones in the presence of excess silica derived from clay alteration by H_2SO_4 (Polyak & Provencio, 2001). Tyuyamunite is also reported from Cupp-Coutunn Cave in Turkmenistan (Maltsev, 1997), and metatyuyamunite from the Caverns of Sonora, Texas, and are diagnostic of a sulfuric acid dissolution at least at some stage during their evolution (Onac et al., 2001). Cupp-Coutunn Cave is also the only SAS cave in which ferrohexahydrite has been found (Maltsev, 1997; Onac & Forti, 2011).

In Pickle Alley, Carlsbad Cavern (USA), alongside gypsum and celestine, small crystals of the minerals copiapite, römerite, and coquimbite have been found (Mosch & Polyak, 1996). These result from the acid attack of Fe-rich minerals (e.g., pyrite).

Other frequently found secondary minerals in SAS caves are quartz and/or opal. The acid alteration of clays, in fact, produces significant amounts of silicic acid that can then precipitate as low-temperature quartz or opal as soon as the pH increases, probably during the final stages of speleogenesis or soon after (Polyak & Provencio, 2001; Polyak et al., 2016). Also in Mbobo Mkulu Cave (South Africa) opal, allophane, and hydrated halloysite are abundant byproducts of sulfuric acid alteration of the dolostone and the quartzite breccia overlying the carbonate bed (Martini et al., 1997). This cave also contains many sulfates, including the rare K-Alum, chalcoalumite and nickelalumite (Martini et al., 1997).

Acid dissolution of Al-rich sediments can ultimately cause the formation of gibbsite, found in several SAS caves including Kraushöhle (Plan et al., 2012), Cupp-Coutunn Cave (Maltsev, 1997), Cavallone-Bove cave system (Abruzzo, Italy) (D'Angeli et al., 2019b), and Mbobo Mkulu in South Africa (Martini et al., 1997).

The widespread, mainly subaerial, acid corrosion of the limestone also leaves a residue of Fe- and Mn oxides and hydroxides that are often, but not always, closely related to the corrosion pockets and the SAS-related suite of sulfates (e.g., alunite, hydrated halloysite). Typical minerals identified in these Fe-Mn oxide residues are ranciéite and todorokite (Polyak & Provencio, 2001). These often poorly mineralized residues are not reported in Table 3, which only lists the most typical SAS minerals found in these sulfuric acid environments.

3.2.3. Minerals derived from direct precipitation from S-rich fluids

Celestine, together with barite, can be found in sulfuric acid caves, especially where the rising waters are thermal. Although the mere presence of barite does not necessarily mean that the cave was formed by the corrosive action of sulfuric acid, this mineral has also been found in active SAS caves. Celestine has been described from the Guadalupe Mountain caves, Cupp-Coutunn Cave in Turkmenistan, and in several Italian SAS caves. In the caves of Monte Cucco (Central Italy) and Cupp-Coutunn Cave celestine occurs together with barite and fluorite (Forti et al., 1989; Maltsev & Malishevsky, 1990; Maltsev & Self, 1992; Maltsev & Korshunov, 1998). The presence of barite and celestine shows that solutions rich in dissolved Ba and Sr reacted with sulfate-rich fluids. Barite is often present as small inclusions, but can also be the predominant mineral coating entire cave walls: this has occurred in Temple of Doom Cave in Namibia (Martini & Marais, 1996), and in Santa Barbara Cave in Sardinia (Pagliara et al., 2010; De Waele et al., 2013, 2017). In the Namibian cave, deep circulation of fluids in contact with basement rocks has allowed them to accumulate barium. The sulfur in these fluids could remain in a reduced form also because of the high organic content of the sedimentary rocks. Once these thermal Ba- and sulfide rich fluids reached the oxygenated environment, sulfuric acid was formed, voids were created, and barite precipitated (Martini & Marais, 1996). In the caves of the Iglesiente mining district in Sardinia, barite deposition, carbonate dissolution, and strong oxidation phases are repeatedly documented in many areas of this MVT deposit, pointing to several phases of sulfuric acid speleogenesis, and intervening phases of deposition of barite. Barite speleothems have recently also been found in non-thermal pools in Lechuguilla Cave, and their origin is explained in two ways: intense evaporation, or mixing of sulfate-poor and sulfate-rich fluids (Wisshak et al., 2020). It is possible that bacteria might also be involved in their formation in cool waters, since sheaths of three types of microbes have been found encrusted on the crystals.

In many SAS caves the incomplete oxidation of H_2S also produces elemental sulfur (Fig. 4B). These yellow coatings, crusts, and crystalline materials have been reported from many sulfuric acid caves, including inactive ones such as those of the Guadalupe Mountains (New Mexico) (Davis, 1973; Hill, 1987; Cunningham et al., 1994a) and Faggeto Tondo Cave in Umbria, but especially still active systems such as Lower Kane Cave in Wyoming (Egemeier, 1981), Cueva de Villa Luz in Mexico (Pisarowicz, 1994), Cala Fetente south of Naples (Italy) (Forti, 1985), Santa Cesarea Terme caves in Apulia (S-Italy) (Hill & Forti, 1997; D'Angeli et al., 2017), Diana Cave in Cerna Valley (Romania) (Onac et al., 2009) and Sulfur Cave in NW Greece (Audy, 2022; Audy et al., 2022). Elemental sulfur is mainly stable at low pH, so it often occurs on gypsum and not on carbonates.

Table 3. The most typical secondary SAS minerals reported from all known sulfuric acid caves of the world. Minerals are ordered following the Dana classification.

SAS Minerals	Chemical formula
Native elements	
Sulfur	S^0
Hydroxides	
Gibbsite	$Al(OH)_3$
Nordstrandite	$Al(OH)_3$
Oxides	
Todorokite	$(Ca,Mn)Mn_5O_{11} \cdot 4H_2O$
Ranciéite	$(Ca,Mn)Mn_4O_9 \cdot 3H_2O$
Carbonates	
Dolomite	$CaMg(CO_3)_2$
Sulfates	
Thenardite	Na_2SO_4
Barite	$BaSO_4$
Celestine	$SrSO_4$
Anhydrite	$CaSO_4 \cdot ½ H_2O$
Eugsterite	$Na_4Ca(SO_4)_3 \cdot 2H_2O$
Metavoltine	$Na_6K_2FeFe_6(SO_4)12O_2 \cdot 18H_2O$
Tamarugite	$NaAl(SO_4)_2 \cdot 6H_2O$
K-Alum	$KAl(SO_4)_2 \cdot 12H_2O$
Tschermigite	$(NH_4)Al(SO_4)_2 \cdot 12H_2O$
Gypsum	$CaSO_4 \cdot 2H_2O$
Rozenite	$Fe^{2+}SO_4 \cdot 4H_2O$
Hexahydrite	$MgSO_4 \cdot 6H_2O$
Ferrohexahydrite	$Fe^{2+}SO_4 \cdot 6H_2O$
Epsomite	$MgSO_4 \cdot 7H_2O$
Römerite	$Fe^{2+}Fe^{3+}{}_2(SO_4)_4 \cdot 14H_2O$
Pickeringite	$MgAl_2(SO_4)_4 \cdot 22H_2O$

Halotrichite	$Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$
Apjohnite	$Mn^{2+}Al_2(SO_4)_4 \cdot 22H_2O$
Coquimbite	$Fe^{3+}{}_2(SO_4)_3 \cdot 9H_2O$
Alunogen	$Al_2(SO_4)_3 \cdot 17H_2O$
Meta-alunogen	$Al_2(SO_4)_3 \cdot 14H_2O$
Alunite	$KAl_3(SO_4)_2(OH)_6$
Natroalunite	$NaAl_3(SO_4)_2(OH)_6$
Jarosite	$KFe^{3+}(SO_4)_2(OH)_6$
Natrojarosite	$NaFe^{3+}(SO_4)_2(OH)_6$
Hydroniumjarosite	$(H_3O)Fe^{3+}(SO_4)_2(OH)_6$
Argentojarosite	$AgFe^{3+}(SO_4)_2(OH)_6$
Plumbojarosite	$PbFe^{3+}{}_6(SO_4)_4(OH)_{12}$
Chalcoalumite	$CuAl_4SO_4(OH)_{12} \cdot 3H_2O$
Nichelalumite	$(Ni,Cu)Al_4(SO_4,(NO_3)_2)(OH)_{12} \cdot 3H_2O$
Felsőbányaite (former Basaluminite)	$Al_4(SO_4)(OH)_{10} \cdot 4H_2O$
Hydrobasaluminite	$Al_4(SO_4)(OH)_{10} \cdot 15H_2O$
Aluminite	$Al_2(SO_4)(OH)_4 \cdot 7H_2O$
Jurbanite	$Al(OH)(SO_4) . 5H_2O$
Fibroferrite	$Fe^{3+}SO_4(OH) \cdot 5H_2O$
Copiapite	$Fe^{2+}Fe^{3+}{}_4(SO_4)_6(OH)_2 \cdot 20H_2O$
Rapidcreekite	$Ca_2(SO_4)(CO_3) \cdot 4H_2O$
Vanadates	
Tyuyamunite	$Ca(UO_2)_2(VO_4)_2 \cdot 5\text{-}8H_2O$
Metatyuyamunite	$Ca(UO_2)_2(VO_4)_2 \cdot 3H_2O$
Silicates	
Kaolinite	$Al_2Si_2O_5(OH)_4$
Hydrated halloysite (Halloysite-10A or endellite)	$Al_2Si_2O_5(OH)_4 \cdot 2H_2O$
Allophane	$Al_2O_3(SiO_2)_{1.3\text{-}2.0} \cdot 2.5\text{-}3.0H_2O$
Quartz	SiO_2
Opal	$SiO_2 \cdot nH_2O$

3.3. Morphological (solutional) signatures of SAS

The strength of acidic rising fluids creates a series of solutional features very typical of hypogene caves (Klimchouk, 2007, 2009; Audra et al., 2009a, 2009b), ranging from the overall 3D-pattern of the voids, to solutional features on the wall, and to microscopic changes on mineral surfaces. These features on the walls of the cave voids greatly depend on the setting in which they have formed. We can distinguish phreatic and subaerial settings, and their interface (close to the water table).

3.3.1. Overal cave passage organization of SAS caves

In contrast to epigenic cave systems, where flow rates can change by several orders of magnitude and temperature of inflowing waters depends on the season (colder in winter and spring, warmer during summer and autumn), flow in hypogenic caves is generally relatively stable, and the temperature of the water varies only slightly. Epigenic waters often maintain their aggressiveness over long distances, and passages generally enlarge downstream because of the arrival of tributaries. On the contrary, sulfuric acid caves have very typical patterns that mostly depend on the position of the fractures and joints delivering rising sulfidic waters (Palmer, 2013). From a morphological perspective, this is not necessarily different from hypogene caves related to rising CO_2 rich fluids. In both cases (CO_2- and H_2S-based hypogene caves) dissolution mostly occurs around linear features (named "feeders") where acidity is introduced into the system and is rapidly consumed (Hill, 1987).

The fact that aggressivity of the fluids is related to where these enter the cave environment, gives most SAS caves a typical elongated plan view if the feeder (fracture along which fluids rose) was an isolated one (i.e., Lower Kane Cave, Egemeier, 1981), and an anastomotic or maze pattern, in the case of a denser network of recharging fractures (Carlsbad Cavern and Lechuguilla Cave, Hill, 1987) (Fig. 5). The size of the passages is an indication of both quantity of acidic fluids that reacted with the host rock, and time during which the fluids continued rising into the cave. Cave voids are thus larger where H_2S rose into the cave (i.e., feeders), or at intersections of fractures, and tend to diminish in size moving away from these injection points, eventually pinching out and ending in blind passages. If separate feeders give rise to adjacent caves, their enlargement over sufficient periods of time can cause these to intercept and merge into large and complex cave systems.

This merging between adjacent solutional voids in both CO_2- and H_2S-related hypogenic caves causes the formation of sometimes very fragile and thin rock partings, or forms such as pillars, pendants, blades, projecting corners, arches, and half-tubes (Osborne, 2007) and eventually larger passages and chambers (Audra, 2007). Walls can be characterized by spongework, made of variously widened and intersecting rounded hollows, indicating formation in very slowly moving aggressive fluids typical also for flank margin (coastal mixing) caves.

Sulfuric acid caves are thus mainly influenced by the spatial distribution of fractures that allow the rising fluids to reach the aerated zone. Bedding planes and other primary structures generally only influence the shape of the passages at a very local scale, and often cave rooms and voids cut straight through these structures, assuming a nearly horizontal development around the injection points. If the overlying beds are less permeable, though, these act as barriers that guide the H_2S (or CO_2) flow along their lower boundaries. Where this occurs in SAS caves, the passages tend to follow these hydraulic boundaries updip, since H_2S mainly oxidizes in these stratigraphic positions. A good example is offered by the Acquasanta Terme caves (Rio Garrafo, Italy, Galdenzi, 2017).

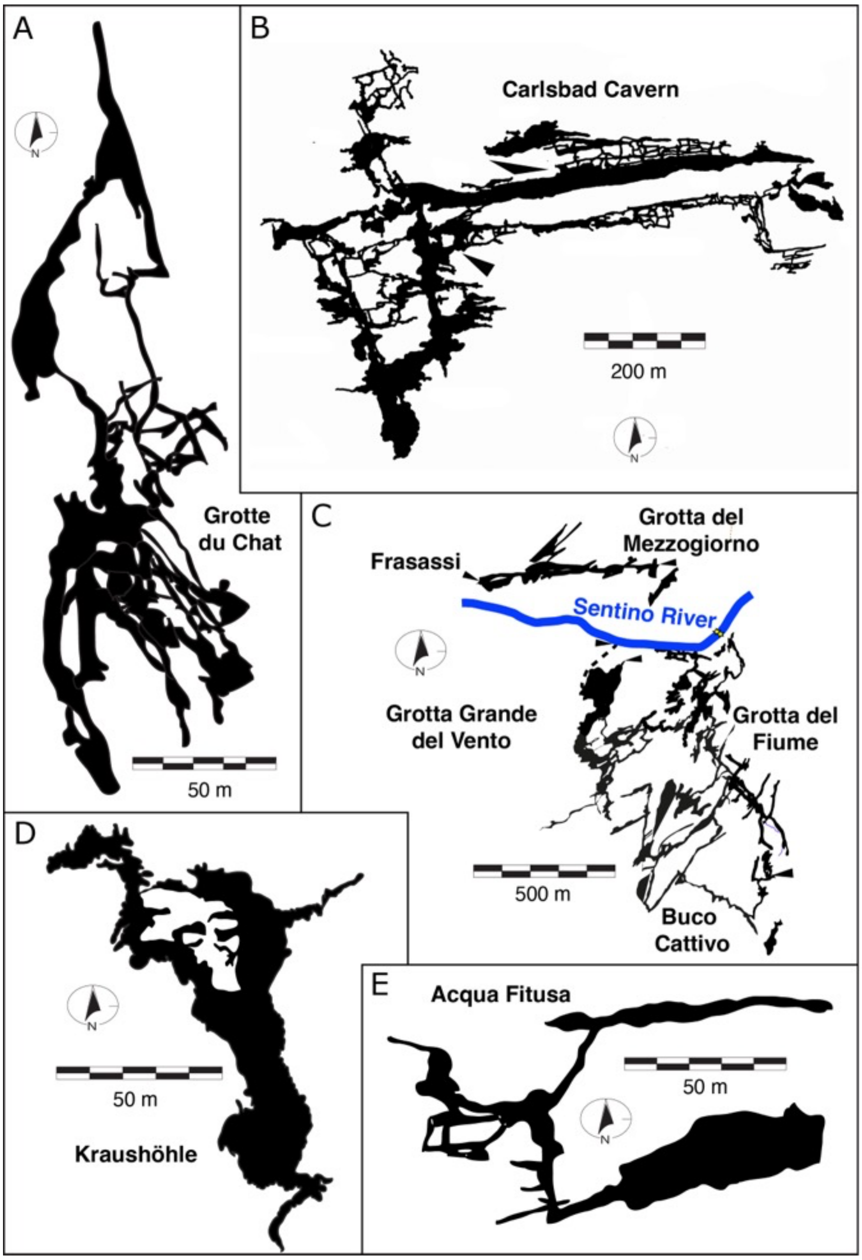

Figure 5. Plans of caves formed by SAS: A. Grotte du Chat; B. Carlsbad Cavern; C. Frasassi Cave; D. Kraushöhle, and E. Acqua Fitusa Cave. Note larger scale bars for Carlsbad Cavern and Frasassi Cave.

3.3.2. Morphology in the phreatic setting

In contrast to most epigenic caves where phreatic passage enlargement is overwhelmingly important, the phreatic setting in SAS caves is characterized by poorly developed void volumes. Flow rates in hypogene caves are generally rather low, and recharge is distributed along multiple pathways (i.e., fractures). Enlargement of these fractures mainly depends on dissolution, since physical erosion in these very slow flow regimes is almost negligible. Also the dissolving capacity of these rising fluids is very low in the deeper phreatic settings, the acidity being acquired mostly close to the water table where both CO_2 and O_2 (required to oxidize H_2S into sulfuric acid) can diffuse from the air into the water.

Where visible, these recharging fractures, known as "*feeders*", are typically elongated features with a close-to-vertical downward development and are often too small to be explored (e.g., Grotte du Chat, France, D'Antoni-Nobécourt et al., 2008; Acqua Fitusa Cave in Sicily, De Waele et al., 2016). This is an indication that corrosion by sulfuric acid is very subdued deep below the water level. Many of the active sulfuric acid caves have explorable underground streams, but the fissures from which H_2S rises are generally not accessible, and are often even masked by sediments (i.e., Cueva de Villa Luz, Hose et al., 2000; Santa Cesarea Terme caves, D'Angeli et al., 2017).

3.3.3. Morphology close to the water table (interface)

The major aggressiveness in SAS caves is created shortly below and above the water table, related to CO_2 degassing (at lower pressures) and its re-dissolution (at lower temperatures), and H_2S oxidation, respectively, both processes occurring in shallow phreatic and aerated environments. Generally, sulfuric waters can be seen in active caves as gently running springs/small rivers (e.g., Lower Kane Cave, Egemeier, 1981; Cueva de Villa Luz, Hose et al., 2000; Acquasanta Terme, Galdenzi et al., 2010, Diana Cave, Puşcaş et al., 2013) or, more frequently, as very slowly running waters or more or less still standing pools (e.g., Triponzo, Principi, 1931; Cesspool Cave, Hubbard et al., 1986; Ninfe Cave, Galdenzi, 1997; Frasassi Cave, Galdenzi, 2001; Movile Cave, Sarbu & Lascu, 1997; Galdenzi, 2001). In these, often, large water bodies the uppermost part of the water column will normally have a greater aggressiveness with respect to the deeper water, because of the greater oxygen levels required to oxidize the rising H_2S into sulfuric acid. Condensation waters descending along the walls and extremely low in dissolved species, increase the dissolving capacity of the surface layers of water pools even more. Most of the time these water bodies are able to enlarge the cave passages laterally in discrete levels, sometimes leaving "*lateral corrosion notches*" at various heights (Fig. 7B and E, e.g., Kraushöhle, Plan et al., 2012). Notches can also be vadose features, formed by small convection cells of rising and descending air above the standing water body, and these are roughly aligned along the same level (contrary to lateral corrosion notches, which develop perfectly along a horizontal plane). However, these notches can also be found in non-sulfuric thermal caves and are not unique to SAS caves. When (epigenic) infiltration waters are abundant, the water bodies can be stratified, with the less dense fresh infiltration water standing above the slightly denser hypogene fluids (e.g., Frasassi Cave in Italy). This can slow down the upward diffusion of H_2S and other gases, thus retarding subaerial speleogenesis.

In some caves (e.g., Grotte du Chat in France, Stephanshöhle in Austria, Acqua Fitusa in Sicily, Italy) the floor close to the feeder is almost perfectly horizontal (Fig. 6). These horizontal erosional forms, known as "*corrosion tables*", were described from Lower Kane Cave by Egemeier (1981), and are exclusive to SAS caves (De Waele et al., 2016). They show very gentle slopes (generally <1%) from the passage walls toward the feeder, caused by the combined effects of turbulence in the flowing water films and their oxygenation. On their exterior, away from the feeder, lateral corrosion notches are dissolved by the oxygenated surface layers of the sulfidic waters (where acidity is highest). Subsequent lower water levels cause different corrosion tables to develop. This causes the formation of a succession of stacked cave floors, as in Grotte du Chat (France) where up to twelve corrosion tables and related notches occur in only 6 m of elevation (Audra, 2008).

Upon draining, when the sulfuric water level falls (because of regional uplift or local entrenching of the river network), feeders become dry but can still act as (thermal) vents, in which vapor-laden air rich in H_2S continues to rise (as long as a thermal water source remains closeby). The edges of these feeders are often lined with calcite popcorn and gypsum crusts, caused by evaporation processes occurring in the cool subsiding air (Audra et al., 2007).

3.3.4. Morphology in subaerial settings

Most of the rock dissolution in SAS caves occurs above the water level, by condensation-corrosion processes boosted by the oxidation of H_2S in the water films attached to the walls in the oxygen-rich cave atmosphere. Condensation is especially important the higher are the temperature differences between the rising fluids and the cave atmosphere (and walls). Condensation-corrosion morphologies are especially well developed above feeders, where H_2S-rich water (or air) enters the aerated cave environment (Fig. 7A-B). In general, the width of the passages is greatest close to the floor, creating rather typical triangular cross-sections (Fig. 7A). The lateral extension of these water levels also causes many SAS caves to have a nearly horizontal profile (i.e., Carlsbad Cavern (Hill, 1987); Grotte du Chat and Kraushöhle (De Waele et al., 2016)).

Many smooth and rounded roof and wall morphologies above the feeders, often believed to be of phreatic origin, are indicative of enlargement in the aerated environment. Condensation-corrosion normally attacks the host rock uniformly, regardless of most primary and secondary structures in the rock, unless mineral grain size shows large variations. For example, microcrystalline calcite will dissolve more rapidly with respect to macrocrystalline formations, leaving mineral veins (boxwork) and fossils in relief. Furthermore, sulfuric acid-rich fluids are able to corrode different rocks (i.e., dolostone and limestone) in the same manner and at the same rate. However, the slow and relentless weathering (dissolution) of the rock leaves the less soluble parts reduced to a powdery residue (i.e., leaving a dolomite sand in a cave carved in dolomitic limestone).

Most void volumes in Kraushöhle and Grotte du Chat are characterized by the widespread occurrence of impressive ceiling *cupolas* (Fig. 6 and 7F) and large *"wall convection niches"* (Fig. 6 and 7E) (De Waele et al., 2016; Spötl et al., 2017). Rising air flow also carves large rounded hollows delimited by *"crests and megacusps"*, with dimensions typically greater than half a meter (D'Angeli et al., 2019b). The coalescence of several cupolas gives rise to rounded "*dome-like chambers"*, such as those in Grotte du Chat (Fig. 6) (D'Antoni-Nobécourt et al., 2008). These upward developing ceiling cupolas and spheres represent convection cells in which condensation is likely to occur prevalently at the cooler ceiling, greatly increasing their upward development. Eventually they can breach the surface, or be cut by lateral wall retreat in valleys, thus creating occasional entrances to otherwise inaccessible caves (i.e., Kraushöhle in Austria, Cavallone Cave in Italy, Cueva de Villa Luz in Mexico). Stacked hemispherical cupolas are well known also from thermal caves such as those described in Hungary (Szunyogh, 1990) where they have, erroneously, been interpreted as a result of phreatic convection (Rudnicki, 1989).

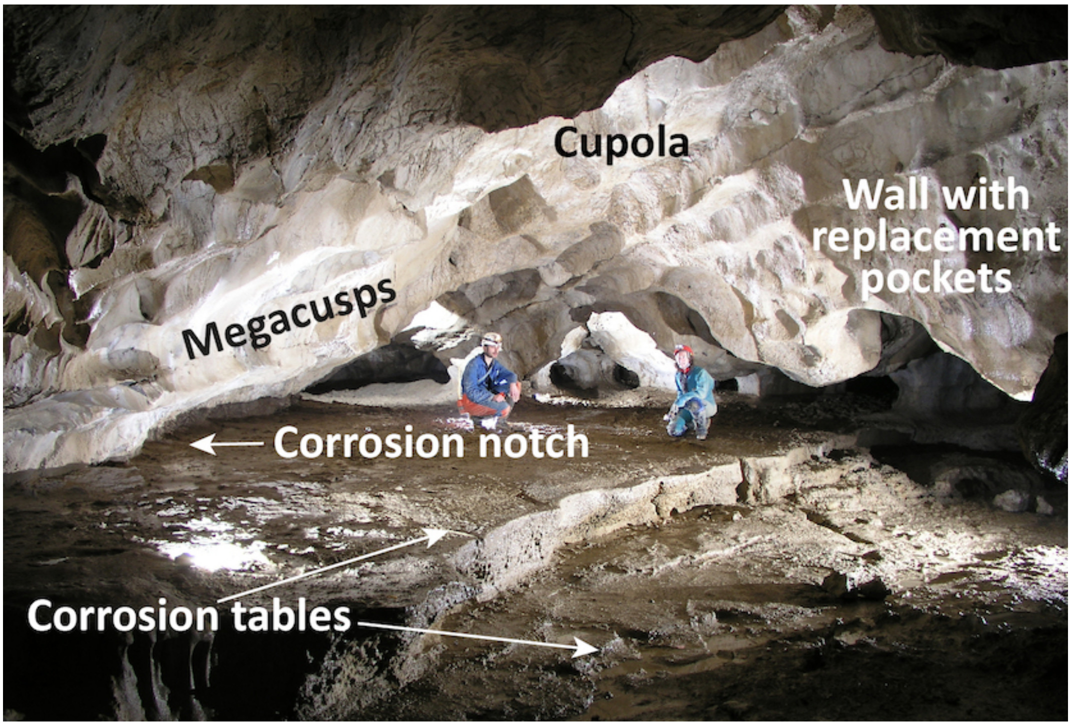

Figure 6. Cave passage with the cave floor, -wall and -ceiling morphologies typical of sulfuric acid caves (Grotte du Chat, France, Photo Jean-Yves Bigot). The central room has developed above the feeding fissure (not visible, a few meters out of sight to the right) and the ceiling is highest above the linear feeder, tapering laterally away from it. Note the two levels of corrosion tables.

The warmer rising air will follow the overhanging walls forming a condensation path that will eventually develop into a *"condensation-corrosion channel"*. These winding smooth channels differ from most paragenetic ceiling half-tubes because of their development on overhanging surfaces, their smooth and wavy roof profile, and the lack of sediments in the channels themselves (Renault, 1968; Pasini, 2009). They might resemble channels developed between soft sediments and vertical or overhanging cave walls in subaqueous conditions, although these are generally less winding. Condensation-corrosion channels also differ from bubble trails that are generally an order of magnitude smaller (around a centimeter in width) (Chiesi & Forti, 1987; De Waele & Forti, 2006; Audra et al., 2009b; Ginès et al., 2014). Condensation-corrosion channels, common also in thermal (CO_2) hypogene caves, are often characterized by the presence of a succession of *"megacusps and -crests"* that give them their wavy long profile.

The most diagnostic morphological features of SAS caves are *"replacement pockets"*, hemispherical corrosion forms some centimeters wide and deeply embedded into the wall (Fig. 7C). These cup-like depressions are denser on vertical or the upper parts of inclined rock surfaces, and become sparser on overhanging walls or roofs. Their origin is related to focused acid corrosion and simultaneous replacement of calcite by microcrystalline gypsum (Galdenzi & Maruoka, 2003), which is often still visible inside the pockets. The presence of this hygroscopic sulfate causes the acid fluids to persist and corrosion to proceed (as if by an acid-soaked sponge), leading to a deepening of the forms. This can ultimately lead to the formation of swiss-cheese-like morphology of the corroded bedrock, forming a *"spongework"* (Fig. 7D). Replacement pockets do not develop on roofs where condensation-corrosion is too intense, and the water films are able to wash sulfates away, typically leaving only boxwork. Replacement pockets are also less expressed on these roofs because the gypsum tends to fall down, limiting the time in which the "acid-soaked sponge" effect can take place. On the lower walls, on the contrary, stronger evaporation causes gypsum crusts to be more continuous, limiting the formation of replacement pockets. As a consequence, replacement pockets are best formed and preserved at mid height along the walls. As in all condensation-corrosion morphologies, their inner rock surface is generally very smooth and regular.

Acidity of condensation drip waters can be very high, pH going below zero in some cases (Cueva de Villa Luz, Hose et al., 2000; Hose & Macalady, 2006) especially in places where the direct contact of the sulfuric acid fluid with the carbonate host rock is prevented (e.g., drips hanging from gypsum or from acidic biofilms). These extremely acid droplets account for the origin of *“sulfuric karren”* and associated solution pans (Cueva de Villa Luz, Grotte du Chat, Acqua Fitusa) (De Waele et al., 2016), and of the unique decimetric bowl-shaped floor basins on the floor of Kraushöhle (*“ceiling pendant drip holes”* in Plan et al., 2012).

Figure 7. SAS morphologies: A. Vertical feeder and typical trapezoidal cross-section in Sette Nani Cave, Cassano allo Ionio (Italy) (Photo Orlando Lacarbonara); B. Giant feeder, corrosion table, notches and replacement pockets in Sant’Angelo Cave, Cassano allo Ionio (Italy). Note white replacement gypsum powders on the floor (Photo Orlando Lacarbonara); C. Replacement pockets in Shpella Kaceverrit, Albania (Photo Jo De Waele); D. The Boneyard, a sponge-like pattern in Carlsbad Cavern, USA (Photo Arthur Palmer); E. Lateral coalescent niches (pseudonotches); F.

Cupola and megacusps and -crests in Kraushöhle, Austria (Photos Lukas Plan); G. Giant rounded conduit with white replacement gypsum on the left, Cavallone Cave, Italy (Photo Giuseppe Antonini).

4. Microbiology and its role in SAS

4.1. History of microbiological studies in SAS caves

Sulfuric acid caves are extremely oligotrophic environments, in which the nutrients are not related to the classical organic (photosynthetic) chains and heterotrophs. In deep-phreatic settings, these hypogene karst environments are also relatively poor in oxygen, in contrast to subaerial environments or the subaqueous ones close to the water table.

The discovery in 1986 of Movile Cave in Romania, an active slightly thermal sulfuric acid cave found by drilling a shaft down to 18 m, gave direct access to an active acidic habitat. The upper passages in this cave are essentially dry, lack speleothems, and appear to be disconnected from the relatively arid surface above (i.e., small quantities of infiltration waters and limited supply of organic carbon from the surface) (Sarbu, 1991; Sarbu et al., 1991; Sarbu & Popa, 1992). In general, the atmosphere in the cave has high CO_2 and low O_2 contents, further evidence of the poor connection with the surface. In the submerged parts, some air pockets are even more isolated, and characterized by even higher CO_2 and lower O_2 levels. Despite these severe limitations for life, Movile Cave revealed a surprisingly rich biodiversity, with around 50 known species of stygo- and troglobionts (ca. 20 and 30 respectively) (Sarbu & Kane, 1995; Sarbu et al., 1996, 2000). It immediately became clear that this rich biodiversity was sustained by the abundant microbial material produced by an extremely diverse and rich chemolithotrophic community (bacteria and archaea) thriving on energy available from sulfur oxidation, methanotrophy, methanogenesis, ammonia oxidation, and iron oxidation (Engel et al., 2004b, 2010; Hutchens et al., 2004; Dattagupta et al., 2009; Porter et al., 2009; Jones et al., 2012; Desai et al., 2013; Paterson & Engel, 2015; Wischer et al., 2015; De Bruin et al., 2022). These chemolithotrophic sulfide ecosystems are comparable to those found on the deep ocean bottom (hydrothermal vents and cold seeps), and are taken as examples for possible extraterrestrial chemiosynthetic ecosystems (Boston et al., 2006).

A similar very rich subterranean fauna has also been found in Frasassi Cave in Italy, some specialized species feeding on the food chain produced by the sulfur-oxidizing microbes (Sarbu et al., 2000, 2022). This is true for many other active SAS systems around the world (Engel, 2007). In Cueva de Villa Luz in Mexico, this chemolithotrophic ecosystem also sustains a wide variety of arthropods (as in Movile Cave), and even some species of vertebrates (fish) (Hose et al., 2000).

Given their interest from both an ecological and biodiversity point of view, many still active SAS cave systems have been studied for their microbial communities. Movile Cave was the first to be investigated with traditional microbiological methods (Sarbu et al., 1994; Vlasceanu et al., 1997, 2000; Bizic et al., 2020), and later with more sophisticated and modern techniques (Brad et al., 2021). The springs in Cesspool Cave in Virginia (USA) were studied for their microbial diversity by Engel et al. (2001, 2003), Lower Kane Cave by Engel et al. (2003, 2004a, 2010), Meisinger et al. (2007), and Rossmassler et al. (2012), Glenwood springs by Barton et al. (2004, 2007) and Rossmassler et al. (2016), Frasassi Cave (Italy) by Macalady et al. (2006, 2007) and Jones et al. (2008), Acquasanta Terme Cave (Italy) by Jones et al. (2010), the active sulfidic thermal spring in the travertine Kaklik Cave by Gulecal-Pektas et al. (2016), and the Sheki-Heh Cave in the Caucasus by Kuzmina et al. (2022). Sulfidic springs in contact with sea water were studied at Capo Palinuro (Italy) (Mattison et al., 1998), and Fetida Cave (Santa Cesarea Terme, Southern Italy) (D'Angeli et al., 2019a; Jurado et al., 2021).

Nowadays inactive SAS cave systems have also been studied from a microbiological point of view, such as Lechuguilla Cave in New Mexico (Cunningham et al., 1995; Northup et al., 1995), and Grand Canyon Caves (USA), studied by Keeler & Lusk (2021).

4.2. (Micro)biological communities typically found in active SAS caves

The microbial diversity of active SAS caves appears to show many similarities worldwide (Porter & Engel, 2008). Many active SAS caves are characterized by the widespread presence of acidic biofilms, which were named *"snottites"* for their slimy appearance (Hose & Pisarowicz, 1999; Jones & Macalady, 2016). Snottites are dominated by autotrophic bacteria of the genus *Acidithiobacillus*, which are able to obtain energy by oxidizing sulfide in extremely acidic conditions (e.g., in biofilms with pH as low as 0) (Macalady et al., 2007; Jones et al., 2014, 2016, 2023).

Other sulfur-oxidizing genera often encountered in the aerobic layers of sulfidic cave streams are *Thiothrix* and *Beggiatoa*, typically making up the white filaments (*"streamers"*) (Engel et al., 2003, 2004b, 2007, 2010). The abundant genus *Sulfurovumales* found in Acquasanta Terme (Italy) by Jones et al. (2010) still has a poorly known metabolism (sulfur-oxidizing, -reducing, or even mixotrophy), whereas *Thiobacillus* is a typical sulfur-oxidizing genus. White filaments in the seawater-influenced Fetida Cave in southern Italy are instead dominated by the genus *Arcobacter*, but also contain *Thiothrix*, *Beggiatoa*, and other sulfur-oxidizing genera including *Sulfurimonas*, *Sulfurovum*, *Thioflexothrix*, and *Thiomicrospira* (Jurado et al., 2021). The same streamers also contain sulfur-reducing bacteria, such as *Desulfocapsa*, also found in both Frasassi Cave and Lower

Kane Cave (Engel, 2007), showing both reduction and oxidation to be used for energy production in these shallow sulfidic streams.

Many sulfuric acid caves are also characterized by the abundant presence of vermiculations, which were studied in Cueva de Villa Luz (Mexico) (Hose & Northup, 2004) and in Frasassi Cave in Italy (Fig. 8D) (Jones et al., 2008). Although vermiculations are common features also in epigene limestone and gypsum caves (Addesso et al., 2019, 2021; Jurado et al., 2020), they are particularly abundant in active sulfuric acid caves, and were called *"biovermiculations"* by Jones et al. (2008). Microbiological studies have shown these muddy and clayey worm-like deposits in SAS caves to be inhabited by sulfur- and nitrite-oxidizing bacteria, and both chemoautotrophic and heterotrophic communities, whose activity leads to the production of sulfuric acid and thus carbonate dissolution.

Figure 8. A. The milky color of the sulfidic water with white filaments in Ninfe Cave, Calabria (Italy) (Photo Orlando Lacarbonara); B. acidic snottite hanging from the wall in Porretta Terme Spa, Italy, an artificial sulfuric acid environment (Photo Jo De Waele); C. Ferromanganese deposits in Spider Cave (New Mexico) stain the walls in reddish and orange colors (Photo Lukas Plan); D. Brownish vermiculations in Fetida Cave, Italy (Photo Mario Parise).

4.3. Speleogenetic role of microbes

Microbes, with their multiple activities, must be involved in speleogenesis (Barton, 2013), participating in the production of sulfuric acid in aerobic conditions, and reconverting sulfate into H_2S in the anaerobic zone in presence of organic carbon. The first speleogenetic models for SAS cave formation were exclusively based on abiotic sulfide oxidation (Egemeier, 1981; Palmer, 2007; Klimchouk, 2007). However, the abiotic oxidation of free H_2S is a very slow process. Microbial involvement in cave formation was first suggested for Lower and Upper Kane caves (Engel et al., 2004a), and then for Glenwood springs (Colorado) (Barton & Luiszer, 2005), the microbial activity speeding up the oxidation of sulfide and the formation of sulfuric acid, and thus making the process of void formation faster. Microbially driven carbonate dissolution aided by the action of sulfidic bacteria was then also used to explain the high karstic permeability of the Edwards Aquifer (Engel & Randall, 2008).

The complex biogeochemistry related to these microbes has been studied by several authors, at Cueva de Villa Luz (Hose et al., 2000) and Frasassi Cave (Italy) (Macalady et al., 2008; Jones et al., 2014; Jones & Macalady, 2016). Microbial involvement leaves traces in the isotopic composition of sulfur (Jones et al., 2015; Zerkle et al., 2016), calcium (Harouaka et al., 2016), and even nitrogen (nitrogen fixation of volatilized ammonia degassing from the stream in Lower Kane Cave (Stern et al., 2003)). Microbes catalyze sulfide oxidation especially below the water table (Engel et al., 2004b), where oxygen is less concentrated. In Lower Kane Cave this microbially-driven oxidation of H_2S rapidly oxidizes most of the sulfide into sulfuric acid and elemental sulfur, and only small amounts of H_2S manage to escape from the waters into the cave atmosphere (Engel et al., 2004a). This appears to be due to the combination of rapid water flow and low initial H_2S concentrations. In Frasassi Cave (Italy) microbial oxidation of H_2S, although occurring, is much less effective, and most of this gas can escape into the cave atmosphere, boosting speleogenesis especially at or above the water table. Here H_2S concentrations in the cave air are higher in areas where H_2S-rich waters are turbulently flowing (Jones et al., 2015). In other locations in Frasassi Cave where water is standing still, very little H_2S escapes into the air, most of it being oxidized in the water.

The flowing waters in SAS caves have often a milky color (Fig. 8A), related to the presence of white floating filaments or microbial mats composed of sulfide-oxidizing microorganisms (Engel et al., 2003, 2004b; Macalady et al., 2006; Jones & Macalady, 2016; D'Angeli et al., 2019a; Jurado et al., 2021) and the presence of elemental sulfur particles derived from the incomplete oxidation of the sulfides in these oxygen-depleted environments. This elemental sulfur can then be oxidized by bacterial respiratory activity leading to the formation of acid also in oxygen-poor environments. In oxygen-deprived areas nitrate can also serve as an electron acceptor, oxidizing the sulfide under anaerobic conditions. This microbially-mediated reaction creates, alongside sulfuric acid, also nitrogen or ammonia, and dissolved sulfate in excess (Gevertz et al., 2000), and is a possible mechanism that forms voids also deep below the water table (i.e., deep-seated carbonate reservoirs). At the water table, in turbulent cave streams, and in microbial mats and snottites hanging on the cave walls and from the roofs (Fig. 8B), oxidation is greatly aided by the metabolic activity of chemolithoautotrophic sulfide-oxidizing bacteria and organotrophic acidophiles (Hose et al., 2000; Jones and Macalady, 2016; D'Auria et al., 2018; Mansor et al., 2018; D'Angeli et al., 2019a). When these biofilms hang on gypsum substrates, or are large enough to be separated from the carbonate bedrock, acidity can reach very low pH values (even below 1), favoring the presence of extremophiles such as the sulfide-oxidizing bacteria of the genus *Acidithiobacillus* (Macalady et al., 2007; Jones et al., 2016; Mansor et al., 2018; D'Angeli et al., 2019a).

The presence of sulfur-reducing genera (e.g., *Desulfocapsa*) in the anoxic areas of the water biofilms (streamers) of several SAS caves shows that part of the oxidized sulfate can also be reduced using SO_4^{2-} as an electron acceptor and different organic molecules (e.g., acetate, formate) as electron donors, converting sulfate back into H_2S (Barton, 2013). This process has a double function: i) it takes away sulfate from the solutions (causing them to become undersaturated again) and, ii) it creates H_2S that can be released into the cave environment, leading to renewed aggressity. Another possible product of sulfate-reducing bacteria in anaerobic environments is the transformation of tetrathionate, with its mixed valence of sulfur atoms (-2 and +6), into both reduced and oxidized products (thiosulfate, elemental sulfur, and sulfuric acid) (Barton, 2013). Both processes can lead to enlargement of cave passages in anaerobic situations, well below the oxygenated parts of the hydraulic systems (i.e., deep below the water table).

4.4. Microbial involvement in cave mineral and speleothem formation

Ever since the early investigations in Lechuguilla Cave (New Mexico) researchers noticed the presence of an unexpectedly rich microbial ecosystem in this oligotrophic environment, more than 400 m from the arid surface above (Cunningham et al., 1995). These authors suspected the microbes to be chemolithoautotrophs using iron, manganese and sulfur from the bedrock as energy sources, forming the base of a food chain which also contained heterotrophic bacteria and fungi. Samples taken in Lechuguilla and Spider caves (Guadalupe Mountains, New Mexico) have shown reddish to brownish and blackish secondary mineral deposits to be composed of low-density ferromanganese deposits up to three orders of magnitude richer in Fe and Mn than the original host rock (Fig. 8C). Although these deposits were initially thought to be the corrosional residue of the bedrock, weathered away abiotically through condensation-corrosion processes (Queen, 1994a; Cunningham et al., 1994b), microbial studies have revealed them to be inhabited by a unique metabolically active microbial community (Northup et al., 2000, 2003; Spilde et al., 2005). These Mn- and Fe-oxidizing bacteria use the energy from the oxidation of the reduced metals to fix CO_2 for autotrophic growth. The term *"speleosol"* was used for this kind of deposit (Spilde et al., 2009). Cave microorganisms are not only involved in the formation of corrosion residues, but can also be associated with some very special kinds of speleothems. Some of these are found in Lechuguilla, and have entombed bacterial cells and structures, representing fossil evidence of these communities. *Rusticles* are subaqueous eccentric stalactites and columns with cores of iron oxides (mainly goethite) encased in calcite. The inner iron-oxide core is thought to be produced by iron-oxidizing bacteria, forming "streamers" where trickling water is continuously introducing Fe^{2+} into standing water pools. Calcitization has made them hard, fossilizing these fragile structures (Davis, 2000). Other speleothems of bacterial origin are the *"poolfingers"* and *"U-loops"* in Lechuguilla Cave, which are also found in other caves of the Guadalupe Mountains and in several SAS caves in the world, although they can also be found in epigene caves. *Poolfingers* and *U-loops* are entirely composed of calcite, with only trace amounts of iron or other metals, and their core is made of bacterial filaments or have preserved their imprint (Davis, 2000; Northup et al., 2000; Melim et al., 2001, 2009, 2016). All these speleothems, in which the microbial involvement appears to be crucial, have been termed *"biothems"* (Queen & Melim, 2006).

5. SAS caves and landscape evolution

As described above, the major enlargement phases of SAS caves are intimately related to more or less stable water tables. Changes in the altitude of the water table cause the formation of different levels of speleogenesis (cave levels), as long as the water table position is stable over a period long enough to dissolve large passages. In other words, the water table links SAS to landscape evolution. The timing of speleogenesis can be determined using the mineralogical byproducts of sulfuric acid weathering (alunite, jarosite, and dolomite), which are the only dating methods that precisely pinpoint the timing of speleogenesis in these conditions (Polyak et al., 1998; 2016).

5.1. SAS caves as fast recorders of landscape evolution

Several studies have shown that the formation of cave levels in SAS cave systems is fast compared to that occurring in normal, CO_2-related, epigenic speleogenesis. Cave levels in limestone form in periods as short as 10 kyr because of the aggressive sulfuric waters. This corrosion rate is similar to the one encountered in epigenic caves carved in gypsum in the same geographical area (i.e., the Italian Apennines, Columbu et al., 2015, 2017).

At Acquasanta Terme, the homonymous cave and those developed along Rio Garrafo river are part of the same SAS cave system, with an active level 50 m below the surface stream (Rio Garrafo), and some fossil horizontal levels some meters above it. The evolution of these two cave levels is controlled by two different factors: i) geological structure of the limestones in the vadose zone, where the action of infiltrating waters and the condensation-corrosion processes prevail; ii) the zone where mixing occurs between epigenic infiltration waters and the thermal sulfidic groundwater body. The position of the two cave levels shows a rather abrupt change in water table level, caused by the incision of the Tronto River, and its tributary Rio Garrafo. This apparently must have happened in rather recent times, similar to the short time spans found in other active SAS caves, but the timing of this event has not yet been constrained (Galdenzi, 2017).

Montecchio Cave (Tuscany) also shows two main levels (an active one and a fossil level around 25 m higher) with the entire cave formed during the last 70 kyr (Piccini et al., 2015). In this case the intermediate cave level appears to have formed in a time span of 10 kyr or less.

Kane caves in Wyoming, composed of single more or less rectilinear passages, are developed on two cave levels separated by 30 m, the lower one having five active sulfidic springs. Speleothems in Lower Kane Cave have very young ages (16-20 ka), and using incision rates of the Bighorn River, the Upper Kane Cave would have an age of around 170 ± 60 ka (Polyak et al., 2022).

Often the cave levels are separated by some tens of meters, and the timing of their formation has not been determined. This is the case for the Calabrian caves (Galdenzi, 1997), and Acqua Fitusa Cave in Sicily (Vattano et al., 2013, 2017).

In alpine settings, where river entrenchment can also be very rapid because of the interplay between fluvial and glacial erosion, also now fossil SAS caves appear to have formed over rather short (kyr) periods of time. Alunite dating in Kraushöhle, only 79 m above the Gams thalweg, has yielded an age of <160 ka and thus an incision rate >0.5 m ka^{-1} (Plan et al., 2012). This cave is composed of a single horizontal level, demonstrating river entrenchment to have occurred rapidly enough to prevent the formation of intermediate levels (unless they remained undiscovered).

The evolution of the SAS caves in many cases is rather straightforward, having only a single (active or fossil) cave level. Examples are the caves in Tabasco (Mexico) (Hose et al., 2000), the Romanian caves (Movile Cave, Diaconu & Morar, 1993; Diana Cave, Puşcaş et al., 2013), Cala Fetente (Forti, 1985) and Santa Cesarea Terme (D'Angeli et al., 2017) in Italy.

5.2. SAS caves as long-time recorders of landscape evolution

The formation of some SAS cave systems can span over long periods of time, reflecting changes in both landscape and climate over hundreds of thousands or even millions of years. When this occurs, especially in tectonically active areas (e.g., Apennines), some fossil SAS cave systems are rather complex, and show a superposition of both hypogenic and epigenic phases (e.g., La Grotta in Monte Cucco, Umbria, Galdenzi, 2004a, 2004b; Galdenzi & Menichetti, 1995, 2017). The evolutionary phases of an active SAS cave with some epigenic overprinting, for example, are clearly visible in the Frasassi area (Italy), where a total of seven cave levels can be seen, with only the lowest one still active (Galdenzi & Jones, 2017). The highest cave levels (almost 300 meters above the present base level corresponding to the Sentino River) are probably Early-Middle Pleistocene in age. Cosmogenic burial ages of quartz pebbles found in the lower entrance of the Frasassi-Mezzogiorno Cave at 360 m asl (160 m above base level) gave a date of 0.75 ± 0.26 million years (Ma) (Cyr & Granger, 2008). The oldest dated speleothems come from the fifth level of Frasassi Cave, around 65 m above the local base level (i.e., Sentino River), and are 200 thousand years (kyr) old (Tuccimei et al., 2005). Third-level speleothems (50 m above base level) are 130 kyr years old, and these data indicate cave levels formed during glacial periods, when the river enlarged its thalweg and aggraded, thus remaining stable for a period of 5-10 kyr (Bocchini & Coltorti, 1990; Tuccimei et al., 2005). In this case cave levels have developed in response to river entrenchment and following aggradation, and this evolution is closely linked to the uplift of the Apennine Chain, with rates ranging between 0.2-0.4 m ka^{-1} during the Early-Middle Pleistocene (Cyr & Granger, 2008).

In the Majella massif, the Cavallone and Bove caves are perched high up in the mountain (ca. 1 km above the current local base level, given by the Aventino River). These caves are multi-level relict SAS caves that were abandoned by the sulfidic waters rapidly due to mountain uplift. Alunite dating in Cavallone Cave gave an age of 1.52 ± 0.28 Ma, giving a high uplift rate (0.7 m ka^{-1}) for this external part of the Apennines (D'Angeli et al., 2019b). Alunite from La Grotta in Monte Cucco, around 500 meters above present base level (Scirca Spring) has been dated to 2.3 ± 0.07 Ma, showing a rather slow uplift rate of this part of the inner Apennine Chain (ca. 0.2 m ka^{-1}).

In the case of Provalata in Macedonia (Temovski et al., 2013, 2018, 2022) the earlier cave formation appears to be linked to a simple hypogenic thermal CO_2-rich environment, followed by infilling due to the formation (and aggradation) of the nearby Mariovo Basin, and finally by river entrenchment, emptying of the voids and the onset of a phase in which H_2S-rich fluids rose into the cave. This last phase has been dated using alunite and jarosite to the Lower Pleistocene (between 1.6 and 1.46 Ma) (Temovski et al., 2013).

Similarly, in the Azrou massif located at the southern margin of the Tellian Atlas, Algeria, initial speleogenesis occurred about 2-3 Myr ago in deep phreatic conditions. The consecutive stages of baselevel lowering (mountain uplift) are recorded in the cave levels, and morphological and geochemical evidence show the speleogenesis to have shifted from a carbonic acid-dominated phase to a more sulfuric acid-dominated one. U/Th dating of speleothems in cave levels and travertine deposits yielded incision rates of about 0.1 m ka^{-1} (Audra et al., 2022).

In the Plavecký Karst (Slovakia) fossil SAS cave levels are preserved in two caves: three levels in the higher Péc Cave, and another five levels in the Plavecká jaskyňa. Whereas the difference between the cave levels in each cave is only a little over 10 m (12 m in Péc and 11 m in Plavecká jaskyňa), in total the caves have registered a base level lowering of around 80 m. No cave levels formed over an altitudinal interval of 60 meters (between 285 and 225 m asl). This would indicate a rapid subsidence of the nearby Vienna Basin between ca. 1 and 0.6 Ma, preceded and followed by more stable tectonic periods probably also accompanied by a favorable climate for cave formation (Bella et al. 2019, 2022)

The evolution of the Guadalupe caves in New Mexico spans a very long period between 13 and 4 Ma, as shown by argon-argon dating of speleogenetic alunite (Polyak et al., 1998), and is related to the tectonic evolution of the Rio Grande Rift. Various cave levels, from the highest caves to the west, around 1100 meters above today's water table (Carlsbad springs at 945 m asl) show the apparent decline of the water table during this 9 Myr time window. Successive episodes of tectonic activity during the gradual formation of the Rio Grande rift disconnected portions of the recharge areas of the Guadalupe Mountains caves from at least 12 Ma onwards, until the present orographic configuration was attained around 4 Ma ago, with no recharge occurring from the west, and a water table below the lowest levels in Lechuguilla Cave (DuChene & Cunningham, 2006).

From all the examples provided above it is clear that SAS caves, due to their rapid formation at the water table, can be very useful markers for both rather rapid and slower landscape evolution studies.

6. Possible deep karstification by SAS

Hypogene sulfuric acid speleogenesis is typically related to the rising of H_2S fluids into a carbonate host rock, and the creation of aggressive H_2SO_4-rich waters at or slightly above the water table by mixing with O_2-rich fluids (air or water). The formation of sulfuric acid is faster and more efficient when mediated by sulfur oxidizing bacteria, largely overruling abiotic processes. Sulfur-oxidizing bacteria are most active both at and just below the water table and in water films above the water table where sulfuric acid is abundant in the moisture on the walls in caves where high H_2S concentrations persist in the air. These high levels, in turn, depend on the degassing, which is strictly related to the H_2S concentration and the turbulence of the flowing waters (Jones et al., 2015). Sulfur-oxidizing bacteria normally use O_2 as an electron acceptor, but in low oxygen or even anoxic environments nitrates can take on this role. This extends the range of environments in which it is possible to transform sulfides to sulfuric acid much deeper into the aquifer, thus making void creation theoretically possible also at depth. Carbonate sequences also often contain sulfates (mainly gypsum) that can be reduced to H_2S at depth. These H_2S fluids migrate and can oxidize into sulfuric acid creating early secondary porosity, that later can act as inception horizons for further karst development (Lowe, 1992, 2000). Also the mixing of two H_2S-saturated fluids can produce an undersaturated solution, in many ways similar to the well-known mixing corrosion effect for CO_2-containing waters (Laptev, 1939; Bögli, 1964; Warwick, 1968; Palmer, 1991; Hill, 1995a).

A large number of important hydrocarbon deposits in the world are hosted in karstified carbonate reservoirs, and karst porosity is generally explained by mixing corrosion processes (often fresh-salt water mixing). The karstic porosity of hydrocarbon reservoirs is often characterized by interconnected, often structurally controlled vugs and pores of various sizes (from less than a millimeter to several meters), and more or less chaotic breccias and spongework solution cavities. The concentration of voids encountered by drilling, such as in the Yates oil field in western Texas, is comparable to that of maze-like hypogenic SAS caves (Craig, 1988; Hill, 1995b; Klimchouk, 2007). Some of these reservoirs extend over very long distances, and most are located along structural and stratigraphic traps in which hydrocarbons are conveyed and stored. Several of these karst reservoirs might well be developed by sulfuric acid dissolution, as suggested already by Hill (1995b).

7. Conclusions

Although the first sulfuric acid caves were described near the end of the 19th century (Kraushöhle, Austria; Hauer, 1885; Kraus, 1891), their number was very low and they were treated as natural oddities. The discovery of two famous SAS caves in 1986 (Lechuguilla Cave in New Mexico, USA, and Movile Cave in Romania) boosted scientific research largely due to the seemingly alien inorganic materials and biology associated with these caves, attracting geologists and biologists. In only four decades of time, enormous advancements have been made in the understanding of the processes occurring in SAS caves. The signs of past SAS activity are not easy to recognize in sulfuric acid caves that have been partly overprinted by more recent epigenic morphologies and deposits. Recognizing active and inactive SAS relies on a combination of geomorphological, geochemical and mineralogical signatures.

Active sulfuric acid caves are extremely interesting for the astrobiological and microbiological communities, and their study can shed light on interesting metabolic pathways and strategies, resistance to extreme conditions, and adaptation of life forms to oligotrophic and acidic conditions. SAS cave systems can also be used for the reconstruction of landscape evolution, where mountain uplift, river entrenchment and cave level formation can be determined by dating the mineralogical byproducts of sulfuric acid weathering (alunite, jarosite, and dolomite), which are the only precise dating methods that pinpoint the exact timing of speleogenesis. The abiotic and biotic processes involved in the generation of sulfuric acid are well known in shallow karst settings, and can generate large voids in short time spans (in the order of kyrs). Generation of sulfur-derived acidity can also take place in deeper karst settings, a poorly explored research topic that can be of great industrial interest for the understanding of interconnected karst porosity at great depths (i.e., hydrocarbon reservoirs). This last topic, and in general the processes occurring in deep karst settings, are probably the most promising future research frontiers in applied karstology.

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