

GYPSUM DEPOSITS IN THE FRASASSI CAVES, CENTRAL ITALY

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The Frasassi Caves are hypogenic caves in central Italy, where H₂S-rich groundwater flows in the lowest cave level. Near the water table, the H₂S is converted to sulfuric acid by biotic and abiotic processes, which have enhanced cave development. The sulfate generally deposits above the water table as a replacement gypsum crust coating limestone walls or as large gypsum crystals. Although the oxidation of sulfide also occurs below the water table, sulfate saturation is not achieved, therefore, sulfate does not precipitate below the water table.

In the upper dry levels of the cave, three main types of ancient gypsum deposits occurs: (1) replacement crusts, similar to the presently forming deposits of the active zone, (2) microcrystalline large and thick floor deposits, and (3) euhedral crystals inside mud. The study of the depositional setting and the analysis of sulfur isotopes in the gypsum and groundwater clearly demonstrate that all the sampled gypsum in the cave formed by H₂S oxidation above the water table. Some fraction of small sulfur isotopic differences between H₂S in the water and gypsum can be explained by isotopic fractionation during abiotic and/or biotic oxidation of H₂S.

Caves formed by sulfuric acid from the oxidation of H₂S are found in many different parts of the world and contain conspicuous gypsum deposits. A review of the concepts can be found in *The Caves of the Guadalupe Mountains Research Symposium* (DuChene *et al.* 2000). Oxidation generally involves bacterial activity, and these bacteria may represent the main source of organic matter inside the cave.

Many caves in carbonate bedrock contain small gypsum deposits formed by evaporation of sulfate-rich water on cave fills or walls. Water seeping into the cave picks up gypsum from oxidation of pyrite in the bedrock, which precipitates upon reaching the cave, or anhydrite (gypsum) is dissolved along the flow path and carried to the cave wall, where evaporation causes precipitation of gypsum. Large-size (up to m-scale) gypsum deposits are less common in carbonate caves, and are generally considered the result of H₂S-rich water circulation inside the cave. Such gypsum deposits are known in North America (Guadalupe Mountains: Hill 1987), in South America (Las Brujas Cave: Forti *et al.* 1993), and in Europe (Galdenzi & Menichetti 1995; Galdenzi 1990, 1997). Unfortunately, gypsum is not actively forming in most of these caves.

Some caves do include actively forming gypsum deposits (Egemeier 1981; Galdenzi 1990; Sarbu & Kane 1995; Hose *et al.* 2000), but these caves are generally short, and gypsum is forming only on the cave walls above the water table. No large bedded gypsum deposits have been found similar to the ones found in the Guadalupe Mountains caves (New Mexico) or in the Frasassi Caves (Italy).

The Frasassi Caves are unique in that they include both

active and relict meter scale gypsum deposits. Therefore, we can compare both types of gypsum deposits directly from a single cave system, which is a great advantage in understanding how the gypsum forms. In this study, we will discuss the depositional setting and the sulfur isotopic compositions of the gypsum in the Frasassi Caves in order to understand how and where the gypsum forms.

GEOLOGIC SETTING

The Frasassi Caves make up one of the most famous Italian karst systems. They are the most visited show caves in Italy, and about 350,000 tourists visit the caves every year. The caves are in central Italy, on the eastern side of the Apennine Mountains, 40 km from the Adriatic Sea. This area is characterized by a mountainous landscape, with altitudes ranging between 200 m at the bottom of the valleys to ~1000 m in the surrounding mountains. The climate is Apenninic subcontinental, with an annual average temperature of about 13°C and an average annual rainfall of about 1000 mm/year. Precipitation generally reaches a maximum in autumn and spring, whereas evaporation exceeds precipitation in summer. About 100 caves are known in the Frasassi area: all these caves are developed in the small area around the step cliffs of the Sentino River Gorge, a 2 km long and 500 m deep canyon cut in the core of a small anticlinal ridge (Fig. 1). The major cave (i.e., Grotta del Fiume–Grotta Grande del Vento Cave System) consists of >20 km of cave passages located at altitudes between 200 and 360 m. Two important caves (Buco Cattivo, 5000 m long, and the Grotta del Mezzogiorno–Grotta di Frasassi System, 3500 m

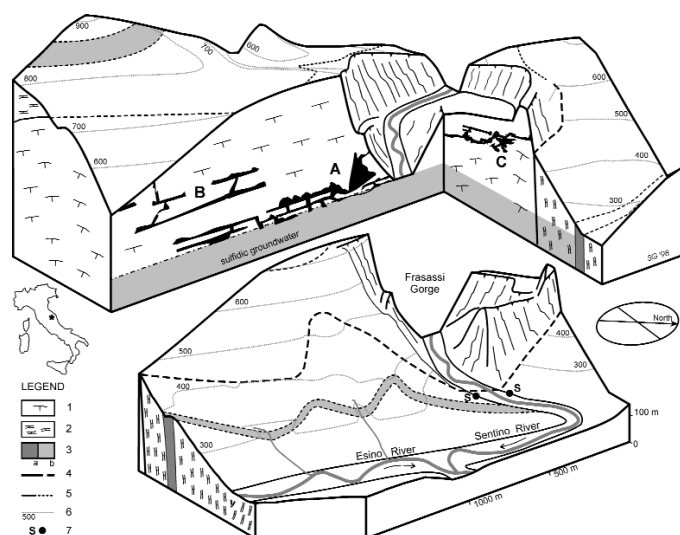


Figure 1. Block diagram of the Frasassi karst system. (1) Calcare Massiccio Formation; (2) cherty limestone; (3) Cretaceous marl: a – section; b – outcrops; (4) faults; (5) stratigraphic boundary; (6) contour intervals; (7) sulfidic spring. Caves: (A) Grotta del Fiume-Grotta Grande del Vento Cave System; (B) Buco Cattivo; (C) Grotta del Mezzogiorno-Grotta di Frasassi Cave System.

long) occur at a higher altitude, ranging from 360 to 500 m.

The Frasassi Gorge offers a spectacular cross-section of the core of the anticline, where the geology is well exposed. The caves are formed mainly in the Calcare Massiccio Formation, a thick Jurassic (Lower Lias) limestone unit exposed in the gorge. The Calcare Massiccio formed in an epicontinental platform setting, and it is a very pure limestone (over 99% calcium carbonate), consisting mainly of wackestone and pack-stone facies, without any significant clay or silica minerals. It is a very permeable limestone, due to high syngenetic porosity and to a well developed network of fractures.

The Calcare Massiccio makes up the lower part of the sedimentary sequence outcropping throughout the region (Fig. 2). The thickness of this formation can reach ~1000 m, and it overlies a buried 2000 m thick Upper Triassic evaporitic sequence, consisting mainly of anhydrite and dolomite (Burano Formation: Martinis & Pieri 1964). A 50 m thick Triassic limestone unit, rich in organics, is interbedded between the Calcare Massiccio and the Burano formations. Near the Frasassi Gorge, the Calcare Massiccio is overlain by a 60 m thick unit (Bugarone Formation) formed in the Jurassic after drowning of the carbonate platform in the shallower depositional areas. This condensed Jurassic unit is mainly micritic, nodular limestone with small amounts of pyrite, and makes up a 10 m thick interbedded marly layer. This formation represents a low permeable bed that is thin and discontinuous and can influence underground drainage. A Lower Cretaceous cherty limestone (Maiolica Formation), ~300 m thick, forms another permeable and karstified section. The Calcare Massiccio and the Maiolica formations host the main aquifer

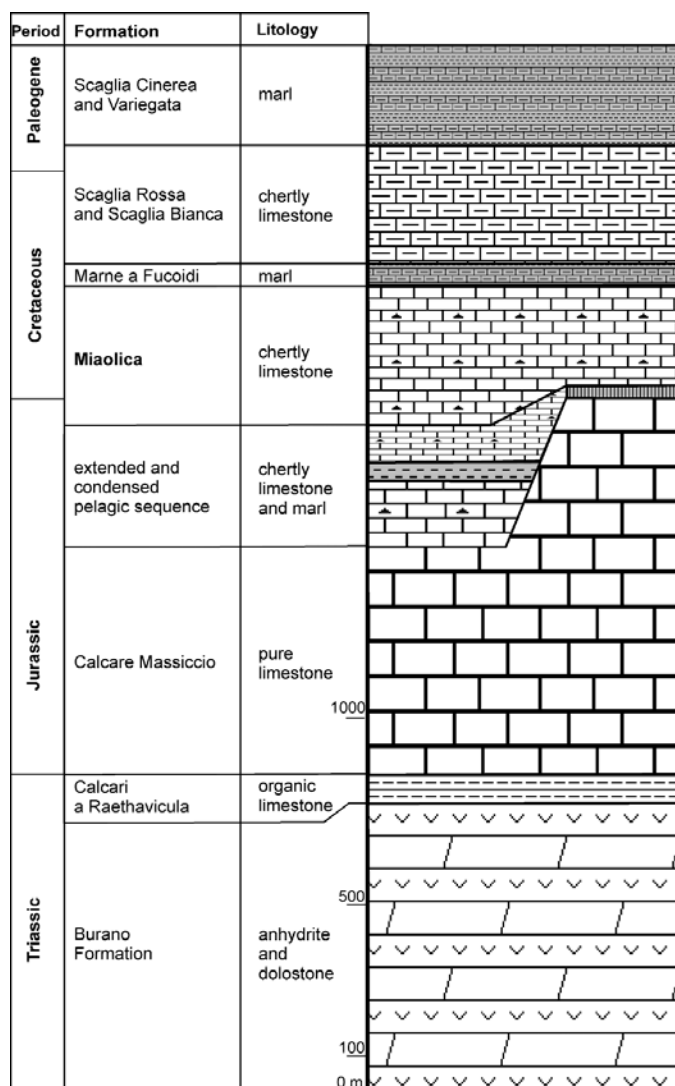


Figure 2. Simplified stratigraphic succession of the Frasassi area.

in the central Apennine chain. A 50 m thick Cretaceous marly formation (Marne a Fucoidi) forms a continuous aquiclude and isolates the lower section of the stratigraphic sequence from overlying permeable limestone formations of Late Cretaceous and Tertiary age.

The Frasassi Anticline was formed in the late Miocene during a tectonic compressive phase that also caused the Apennine uplift and emersion. The fold is asymmetric, with a main northeast vergence, and the caves are developed mainly in the eastern limb of the anticline, where a fault has concentrated the groundwater flow. The surface drainage formed at the end of the early Pleistocene, when entrenchment of the valleys cut into a preexisting "planation surface". At that time, the gorges cut into the anticlinal structures, and a landscape similar to the present one was formed (Ambrosetti *et al.* 1982; Ciccacci *et al.* 1985). During the Pleistocene, climate changes also heavily influenced geomorphic evolution. In the mountain areas, during glaciations, the valleys were filled with alluvial gravel

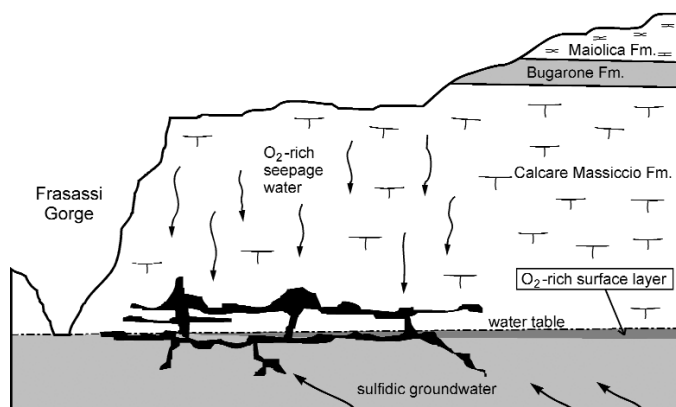


Figure 3. Hydrologic setting in the Frasassi Gorge. The significant recharge of O₂-rich freshwater increases water aggressiveness when it reaches H₂S at the water table. The very low water flow induces the stratification of groundwater in the inner parts of the cave.

deposits, while, during interglacials, the alluvial deposits and the bedrock were eroded by the river (Bisci & Dramis 1991).

GROUNDWATER

Groundwater in the Frasassi area consists of two types: Carbonate and sulfidic, which can be characterized by their chemical compositions and origin. The carbonate water is derived from diffuse infiltration of surface meteoric water through the limestone. It characterizes all the vadose zone and some small aquifers perched on interbedded marls (Fig. 3). This water has a low salinity (~200-400 mg/L; Cocchioni 2002) with a very low sulfate content and high dissolved oxygen (~0.32 mM/L). The sulfidic water characterizes the main aquifer, developed in the Calcare Massiccio and Maiolica formations at the core of the anticline (Fig. 1). This sulfidic groundwater is cold (~13°C), but shows a higher salinity, up to 2 g/L, than the carbonate water. It is enriched in sodium and chloride, and contains a high amount of sulfate (up to 2.5mM/L), but it is undersaturated with respect to gypsum. The most significant feature of this water is the presence of hydrogen sulfide. The H₂S concentrations reach up to 0.5 mM/L. These dissolved components are probably acquired as groundwater flows upward through the underlying anhydrite formation. Isotopic data on δ¹⁸O, δD, and tritium suggested a meteoric origin for the sulfidic groundwater (Tazioli *et al.* 1990). These authors estimated a recharge area located at altitudes of 600-1000 m, with a relatively brief residence time in the aquifer.

The sulfidic aquifer occurs at the core of the anticline in the Calcare Massiccio and Maiolica formations, where the mineralized groundwater can rise through the deep faults at the eastern limb of the anticline. Here groundwater flow is concentrated, and the main springs are located (Fig. 1). The water table can be reached in the lower section of the cave, at the same level as the river. The groundwater flow is generally very slow,

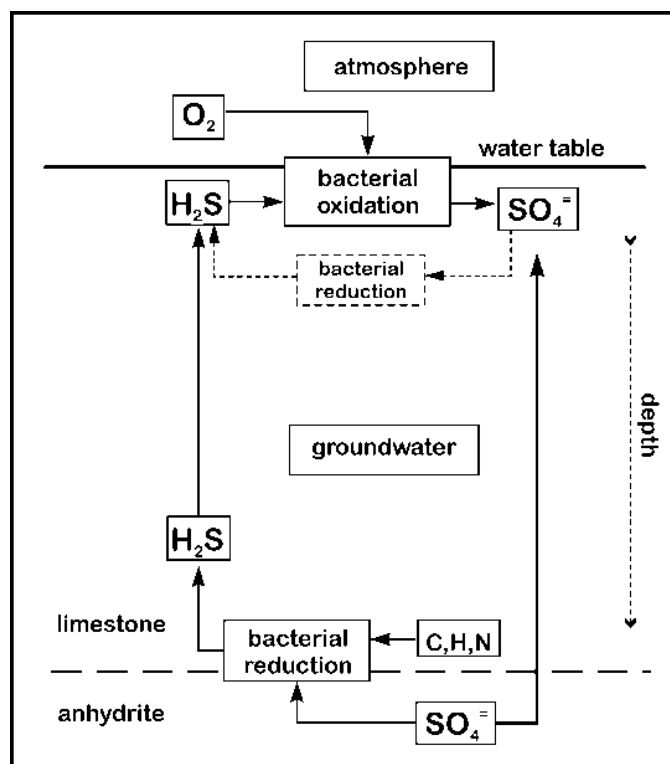


Figure 4. Sketch showing the redox processes involving sulfur in the Frasassi aquifer. Reduction of sulfate from underlying evaporites prevails in the deep phreatic zone, while sulfide oxidation occurs near the water table, causing cave development and limestone replacement with gypsum.

and flowing water is only found in the eastern part of the cave. The water levels are controlled by rainfall events, although river water enters the cave directly in narrow restricted zones near the spring. The conductivity and temperature of the sulfidic stream are also correlated with precipitation (Sarbu *et al.* 2000). These observations indicate that fresh water recharge, derived from surface precipitation, dilutes the sulfidic groundwater (Sighinolfi 1990; Tazioli *et al.* 1990).

The very low water flow in a large part of the cave leads to groundwater stratification. Fresh water seepage stays near the surface of the water table due to its lower salinity (Fig. 3). This surface layer can be rich in dissolved O₂, without any measurable H₂S. The thickness of this freshwater layer ranges from 20 cm up to 5 m (Galdenzi 2001). On the contrary, in some narrow zones the groundwater can have a higher salinity, because there is less dilution by the descending fresh water (Cocchioni 2002).

Hence the underground flow path is complex. The recharge area in the surrounding limestone is about 5 km². There infiltration quickly reaches the water table, dilutes the mineralized groundwater and flows toward the spring. Some meteoric water could reach the underlying evaporitic sequence, where it could pick up sodium chloride, sulfate, and sulfide (Fig. 4).

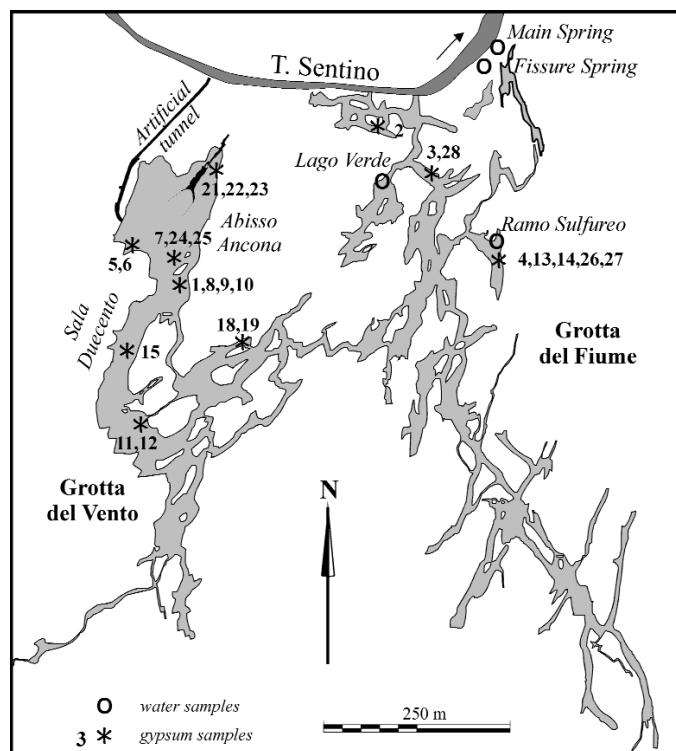


Figure 5. Map of Grotta del Fiume-Grotta Grande del Vento Cave System, with sample locations.



Figure 6. View of Abisso Ancona, the main room in Fiume-Vento Cave System. All photos by S. Galdenzi.

Sulfate reduction could occur in the underlying Triassic limestone rich in organic matter. Near the water table, oxygen in the fresh water causes oxidation of the sulfide in the sulfidic water. A small amount of sulfate could be reduced to sulfide in the shallow phreatic zone, mainly in the organic-rich mud covering the floor of the submerged passages.



Figure 7. Sala del Limone, a wide room in Grotta del Vento, with a shape similar to half a lemon. The rounded ceiling was formed by condensation corrosion. The flat rock floor is cut by shafts and fissures that formed below the sulfidic groundwater level.

CAVE FEATURES AND ORIGIN

The Frasassi Caves (Fig. 5) consist of a network of ramifying horizontal passages, where wide rooms alternate with smaller tubes and also with spongework zones. The major room, Abisso Ancona, has a volume of $\sim 10^6$ m³ (Fig. 6). The system is clearly developed in several superimposed levels that are interconnected by short shafts or inclined passages. The genesis of the cave levels can be related to tectonic uplift and climatic changes that occurred during the Pleistocene. At least 4 main horizontal, often overlapping levels occur in the caves, whereas some further levels occur even lower (Fig. 1). The water table is in the lowest sections of the cave, where active sulfidic water is mainly in flooded passages.

The 2 lowest main levels, corresponding to the III and V level in Bocchini & Coltorti (1990), are between 200 and 300 m msl and occur mainly in the Fiume-Vento System (Fig. 1). These passages developed in settings similar to the present, during the deposition of the surface alluvial gravel terraces in the Sentino River Valley, in the middle to late Pleistocene (Bocchini & Coltorti 1990). Ages were obtained by uranium series dating of speleothems (Taddeucci *et al.* 1992). In level V, those authors obtained stalagmite ages of up to 200 ka; in level III some stalagmites are 80 ka old, while a collapsed stalagmite has a range of ages between 170 ka and 120 ka. In the less-developed levels near the water table (e.g., I and II levels in Bocchini & Coltorti 1990), only Holocene dates were documented.

Each cave level has typical phreatic features with mainly horizontal tubes (1-10 m in diameter) that can form complex mazes or can alternate with large rooms characterized by flat, erosional rock surfaces at the floor and by rounded ceilings (Fig. 7). Shafts and fissures in the floor of the cave represent the original sources of H₂S-rich waters that formed the cave. Cupolas of different sizes are developed in the walls and ceil-

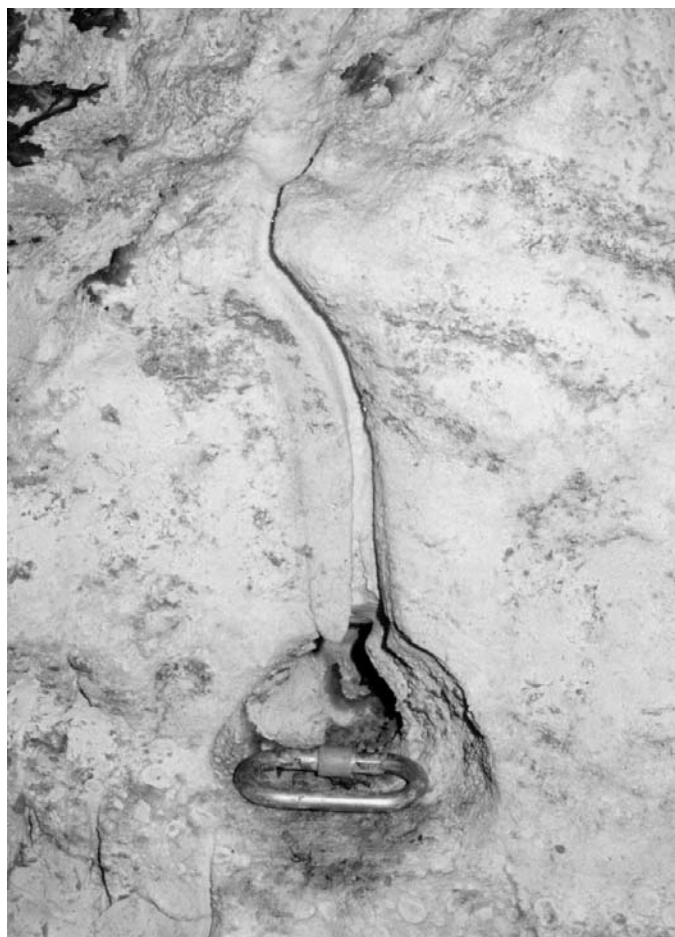


Figure 8. A bubble trail in Grotta del Vento. It consists of a rill that originates below the water table inside a pocket, a fissure or in a small side passage on the cave wall and rises upward. It can be some meters long and few decimeters deep, and can have also a meandering pattern.

ings of the cave. They could have formed either in the phreatic or vadose zones as a result of condensation corrosion. Bubble trails (Fig. 8) are common in many phreatic environments, indicating rising corrosive gas in the shallow phreatic zone. Some areas are covered by gypsum replacement crusts, while some thick floor deposits are common in the main rooms.

The two upper main levels are developed mainly in the Buco Cattivo and Mezzogiorno-Frasassi Caves at altitudes of 350 to 500 m (Fig. 1). The features of these caves are slightly different from those in the Fiume-Vento System. A few gypsum deposits indicate that sulfidic water circulation also occurred in this caves, but some important branches clearly developed in a deep phreatic zone. It may be supposed that during the formation of these upper caves, the hydrogeologic setting was different from the present one.

The oxidation of H_2S is considered the main cave-forming process (Galdenzi 1990). The oxidation of hydrogen sulfide to sulfate [1] can occur in the presence of oxygen from drip water, and can occur both in the shallow phreatic zone and dur-

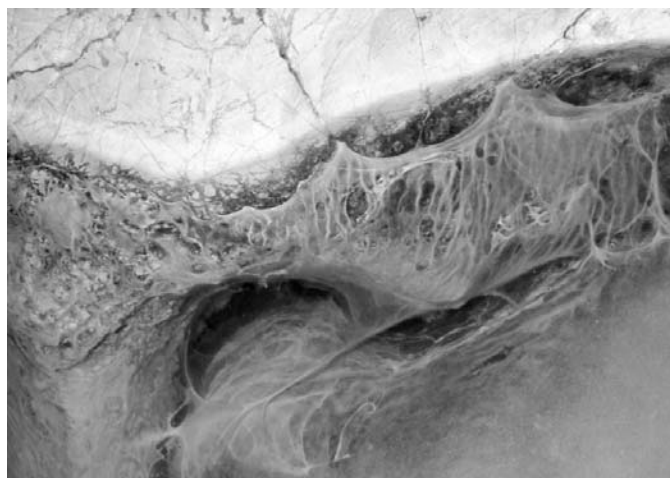
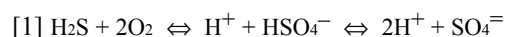


Figure 9. Microbial mats covering limestone walls in the sulfidic groundwater of Frasassi Caves.

ing vadose conditions, causing the dissolution of limestone [2] and cave development.



Cave development by O_2 -rich infiltrating meteoric water plays only a secondary role, and it is limited to a network of narrow passages formed in the vadose zone in the Frasassi karst area and in the surrounding mountains (Galdenzi 1996). Here, infiltrating meteoric water descends quickly to the water table. Similar networks can also facilitate sulfuric acid speleogenesis, by quickly delivering O_2 -rich meteoric water to the groundwater, where H_2S oxidation can proceed (Fig. 3).

Recent investigations pointed out the role of microbial activity in speleogenesis. Chemoautotrophic microorganisms live near the redox interface between the sulfidic groundwater and the oxygen present in the atmosphere and in the seepage water, using the chemical energy resulting from the oxidation of H_2S . C and N stable isotopic results showed that the organic matter produced *in situ* by these microbial communities represents the trophic support for the rich community of invertebrates that inhabit the sulfidic sections of the caves (Sarbu *et al.* 2000). Biologic activity can significantly accelerate the oxidation of H_2S , causing the production of H_2SO_4 as a by-product of their metabolism. This has an important role in the cave development, increasing the water aggressiveness on the cave walls and accelerating the dissolution of the limestone. Therefore, cave development can be considered, at least partly, a consequence of bacterial activity (Galdenzi *et al.* 1999).

PRESENT GYPSUM DEPOSITION

The morphologic effects of the oxidation of H_2S can be directly observed in the lower parts of the Frasassi Caves, where the corrosive processes on the limestone are still active in the sulfidic water. Here, bacterial colonies cover the bottom

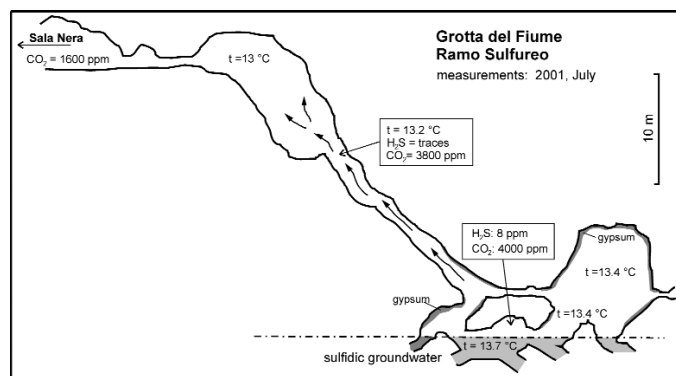


Figure 10. Schematic profile through the Frasassi sulfidic section. Small thermal differences cause water vapor to rise and condense at higher levels. CO₂ diffuses into the upper levels, while H₂S is present only near the water table. Gypsum replacement crusts are growing on the limestone walls directly exposed to H₂S (after Galdenzi 2001).



Figure 11. White, finely crystalline gypsum, growing on limestone pockets, Ramo Sulfureo, Grotta del Fiume. (Image width = 30 cm).

of the flooded galleries (Fig. 9) and cause the oxidation of H₂S, but gypsum deposition cannot occur in the water because saturation of sulfate is not achieved. In some pools and streams, H₂S and CO₂ are released to the cave atmosphere from the water and can diffuse to the nearby rooms. The concentration of H₂S and CO₂ reached peaks at 8 ppm and 5800 ppm, respectively, in the cave air near the sulfidic streams (Galdenzi 2001). The gas can rise toward the upper cave levels due to the small differences in the temperature (~1°C), but the H₂S concentration decreases quickly away from the water table (Fig. 10).

The gas concentration that can build up where air exchange is low was simulated by creating an air bell floating on the water table. Here the concentration of H₂S exceeded 120 ppm, while O₂ decreased to 7% (Galdenzi 2001). On the other hand, rapid air flow in the open cave disperses the H₂S and keeps the concentration low.



Figure 12. Organic "stalactites" growing on gypsum crystals coating the cave walls in Grotta del Fiume. They consist of mucous glycocalyx, secreted by sulfur-oxidizing bacteria to protect themselves from the very acidic environment. The droplets are rich in H₂SO₄ and their pH is always < 1.

The limestone walls exposed to H₂S vapors are highly corroded and partially or completely covered by gypsum crusts (Fig. 11), sometimes associated with small amounts of elemental sulfur. The gypsum crust generally consists of white, finely crystalline gypsum, whereas some large crystals grow on the gypsum crusts or directly on the limestone. The limestone surface under the gypsum crust is severely corroded, with hemispheric corrosion pockets some cm deep. The intensity of limestone corrosion was measured using limestone tablets (80 x 40 x 10 mm), exposed to acidic vapors in the cave atmosphere for 5 years (Galdenzi *et al.* 1997). At the end of the experiment, these tablets were completely covered with replacement gypsum, and the limestone surface under the gypsum crust was irregularly corroded, with incipient erosional pockets. The average weight loss, measured after gypsum removal, was about 15 mg/cm²/a, with significant variation due to small variations in the location of each tablet. This weight loss can correspond to an average loss of about 0.05 mm/a at the limestone surface. In the same experiment, quite similar values were obtained for limestone tablets placed in the sulfidic groundwater, where gypsum deposition did not occur.

Galdenzi *et al.* (1997) also discovered a biofilm at the limestone-gypsum interface. This means that bacterial communities played an important role in the H₂S oxidation. The microbial biofilm can grow and cover the walls with a layer of organic mucous matter, that forms organic "stalactites", secreting acidic drops, rich in H₂SO₄, with a pH < 1 (Galdenzi *et al.* 1999) (Fig. 12). Microbiologic studies of these biofilms found sulfur-oxidizing bacteria that play an important role both in limestone corrosion and in the cave food web (Vlasceanu *et al.* 2000). These organic formations are quite similar to those described in the Cueva de Villa Luz, Mexico, by Hose and Pizarowicz. (1999).

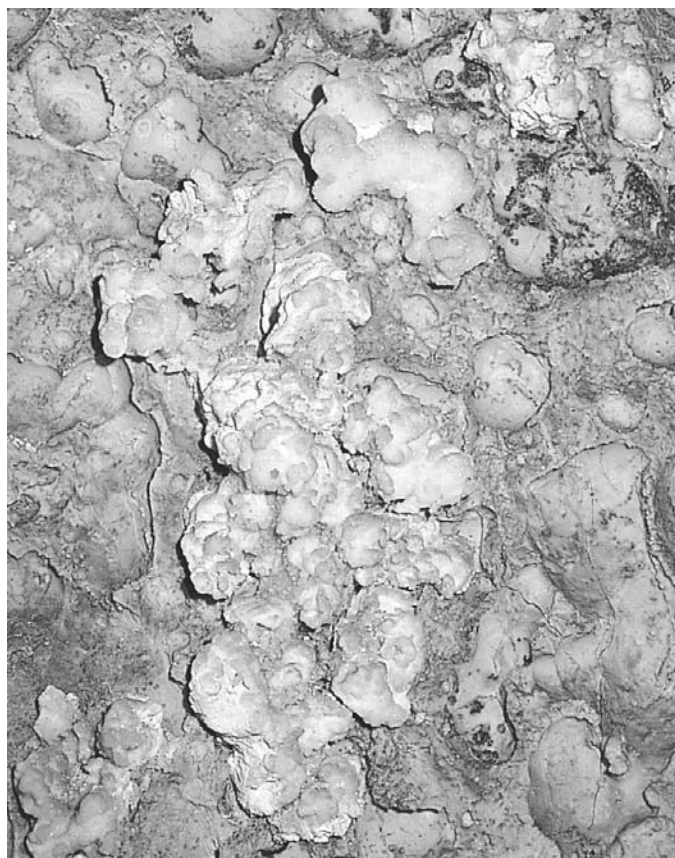


Figure 13. Limestone pockets on the cave walls after gypsum removal by dripping water and gravity, Abisso Ancona, Grotta del Vento. (Image length = 60 cm)

ANCIENT GYPSUM DEPOSITS

Gypsum deposition in limestone caves is fairly common in central Italy (Galdenzi & Menichetti 1995). Some large and interesting gypsum deposits are found particularly in the Faggeto Tondo Cave (Forti *et al.* 1989) and in the Monte Cucco Cave (~20 km to the west). Large gypsum deposits also occur in the dry, upper levels of Frasassi Cave. Three main types of deposits can be observed: (1) replacement crusts, (2) large floor deposits, and (3) gypsum crystals inside mud.

REPLACEMENT CRUSTS

This is the only type of ancient gypsum deposit that can be compared with gypsum presently forming in the cave. The old gypsum replacement crusts are quite common in many horizontal passages and rooms. Later seepage water often dissolved these old crusts, exposing small, rounded corrosion pockets on the limestone walls (Fig. 13). Commonly these corrosion pockets represent the only evidence of a preexisting gypsum crust. The replacement gypsum is generally recrystallized on the surface, but its characteristics are similar to the gypsum crusts that are forming in the sulfidic section of the cave, and they are believed to be a product of subaerial replacement of limestone (Bertolani *et al.* 1977; Ciarapica & Passeri 1978; Cigna & Forti 1986; Galdenzi 1990). In some



Figure 14. Evidence of the old water table in a dry passage of Fiume-Vento Cave System. Note the rough limestone surface above the water level and the rounded features in the flooded zone. A bubble trail is near the speleologist's head.

passages, Galdenzi (1990) also reported that their lower parts show typical phreatic features such as rounded cupolas and bubble trails, while in the upper parts corrosion pockets or residual gypsum crusts cover the limestone walls (Fig. 14).

The distribution and thickness of gypsum forming today in the Frasassi Caves is much more limited than it was in the past. This may be due to the present hydrologic setting, because a free interface between groundwater and cave air generally exists only at the bottom of shafts or descending passages, where gypsum is forming in restricted areas (Fig. 3). Moreover, in most of these places, a layer of infiltration water overlies the sulfidic groundwater, preventing the release of H_2S and the subaerial growth of gypsum replacement crusts. In the past, the cave was an almost ideal water table cave, with many partly flooded rooms and passages formed as a result of degassing (Galdenzi 1990). At that time, condensation-corrosion could have been more important in enlarging the cave, as the wide distribution of old replacement crusts testifies.

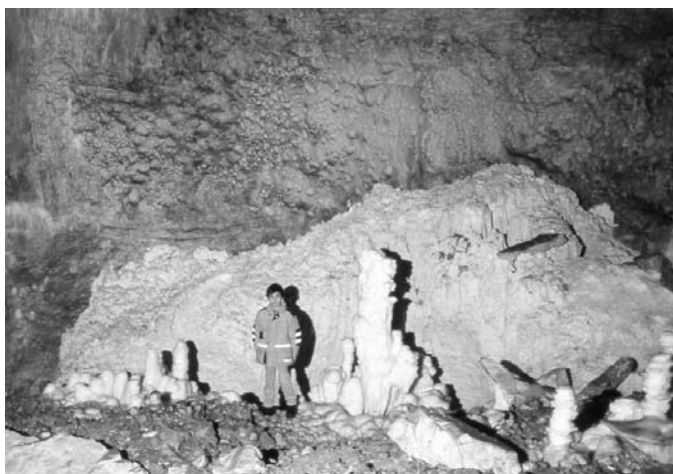


Figure 15. Gypsum floor deposit below a wall covered by corrosional limestone pockets near Lago Cristallizzato, Grotta del Vento.



Figure 16. Piles of gypsum on the cave floor overlying mud with gypsum crystals, Sala Duecento, Grotta del Vento.

LARGE FLOOR DEPOSITS

Some large deposits of massive gypsum occur on the floor of the main rooms, where they are generally associated with replacement crusts that cover the limestone walls (Fig. 15). These floor deposits consist of white, finely crystalline gypsum, very similar to the replacement crusts. The floor deposits form mounds several meters thick, often below wide cupolas (Fig. 16), or form small gypsum “glaciers”, similar to the ones described in Lechuguilla Cave (Davis 2000). Maximum thickness reaches 5 m, and volume exceeds 1000 m³ (Fig. 17).

The large gypsum deposits in the Frasassi Caves were formerly thought to be the by-product of sulfate-saturated phreatic water (Bertolani *et al.* 1977; Ciarapica & Passeri 1978). Ciarapica & Passeri (1978) proposed that the massive gypsum deposition could be produced by the rapid cooling of warm water. Bertolani *et al.* (1977), based on cave mineral associations, excluded the possibility of thermal water flow in the cave, but believed the gypsum deposition was a result of super-

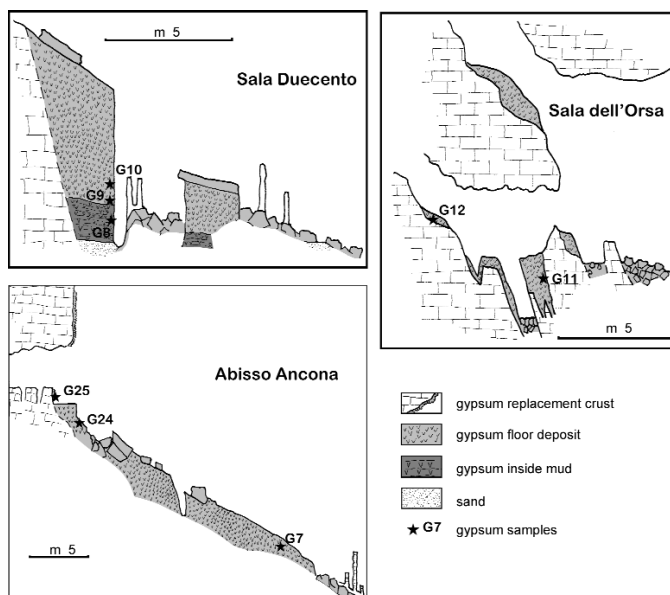


Figure 17. Profiles through some of the most significant gypsum deposits in Grotta del Vento.



Figure 18. Gypsum crystals growing inside mud in Frasassi Caves.

saturated groundwater. However, based on depositional settings and characteristics, Galdenzi (1990) concluded that these large gypsum deposits were produced above the water table.

Table 1. Mineralogical composition of sediment samples inside cave.

	dominant	abundant	present	scarce or trace
1- sand	calcite	quartz	feldspar, mica	illite
2- mud	quartz	calcite, gypsum	illite, mica	chlorite, feldspar, montmorillonite
4- mud	quartz	calcite	feldspar	kaolinite, amesite
6- mud	quartz	illite	mica, feldspar	chlorite, cristobalite
7- mud	quartz		illite, mica	chlorite

Galdenzi showed that these deposits lack any sedimentary structure or texture that can be attributed to a subaqueous environment. In particular, the gypsum is never interbedded with mud layers, while in the entire cave, mud deposits that originate below the water table are very common. Clear evidence of an origin above the water table also includes: (1) rare breccias of fallen gypsum crusts and (2) the corrosion runnels on bedrock below the floor deposit formed by flowing corrosive water. However, the main evidence for deposition above the water table is the depositional setting of these gypsum deposits in the western parts of the cave where recent gypsum is not forming. Here gypsum deposits in the lower part of the main rooms, below the old water table, are missing. Therefore, these large floor deposits were interpreted to have formed by the detachment and flow of slushy gypsum produced on the limestone walls as replacement crusts in zones exposed to intense H₂S vapors.

GYPSUM CRYSTALS INSIDE MUD

The last type of gypsum deposit typically occurs inside mud layers that, in places, underlie the large floor deposits. The quartz-rich mud (Table 1), contains authigenic, euhedral gypsum crystals that grew inside the sediments (Fig. 18). Ciarapica & Passeri (1978) proposed a phreatic origin for this type of gypsum via seepage and trapping of sulfate in solution inside mud sediments.

ISOTOPIC ANALYSIS: PURPOSE AND METHODS

Sulfur isotope ratios (³⁴S/³²S) can vary as a result of biologic and inorganic reactions involving the chemical transformation of sulfur species. Sulfur isotope studies have been useful in understanding the processes of sulfur cycling in many sulfur-related systems (see Canfield 2001, for a recent review). Here we use sulfur isotopes of gypsum to see whether gypsum formed by oxidation of H₂S or by precipitation of sulfate from saturated water.

Isotopic compositions of sulfur were measured in sulfides and sulfates using a helium-gas continuous-flow isotope-ratio mass spectrometer (CF-IR-MS: Micromass Optima; Maruoka *et al.* 2002, 2003). The samples were weighed into 12 x 5 mm tin capsules, together with a mixture of V₂O₅ and SiO₂ to promote full combustion (Yanagisawa & Sakai 1983). The sulfur isotopic compositions are expressed in terms of δ³⁴S (‰) rela-

tive to the Canyon Diablo standard. Results of three IAEA silver sulfide standards (IAEA-S-1, -0.30‰; IAEA-S-2, 22.67‰; IAEA-S-3, -32.55‰; Ding *et al.* 2001) were compared to constrain the δ³⁴S values. The isotopic compositions of sulfur were determined at a precision of ± 0.2‰ (1σ).

SAMPLING SITES

SULFIDIC WATER

The isotopic composition of sulfide and sulfate in the water can be used to discuss the origin of gypsum deposits inside the cave. Tazioli *et al.* (1990) also analyzed δ³⁴S in the water and in a gypsum sample, without discussing its characteristics and location, and confirmed its derivation from the H₂S dissolved in the water. Some water samples at different sites were collected November 11, 2000, at the end of a dry period when freshwater recharge to the groundwater and discharge were low. We sampled sulfate and sulfide in two different springs and in two cave pools with different water salinities (Fig. 5). The concentration of the oxidized and reduced sulfur in these water samples was determined by Cocchioni (2002).

The sulfide in the Main Spring water was collected from the main surface spring along the river, in the gorge. Here, many small springs have the same temperature and conductivity, about 13.5°C and 1600 μS, respectively. They can be considered to represent the “normal” sulfidic groundwater in the shallow phreatic zone, formed by the mixing of the rising mineralized water and the descending meteoric freshwater in the cave.

The Fissure Spring is a small emergence, very near the Main Spring. The sulfidic water in the Fissure Spring is significantly different compared to the “normal” sulfidic spring water. Throughout the year the temperature is ~0.5°C higher and the conductivity is ~30% higher. This spring is probably supplied by water rising from a deeper phreatic zone, with a lower dilution of descending freshwater (Cocchioni 2002).

The sulfide and sulfate of a sulfidic stream were sampled in the most studied cave room (Ramo Sulfureo: Galdenzi *et al.* 1997, 1999; Sarbu *et al.* 2000). Here, a direct influence from meteoric fresh water is well documented (Sarbu *et al.* 2000) and the chemical characteristics of the groundwater are similar to the Main Spring water (Cocchioni 2002). A large surface area of flowing sulfide water allows the release of H₂S into the cave air. The sulfide and sulfate of a stagnant sulfidic pool, Lago Verde, was also sampled. Here, groundwater has a chemical composition similar to the Fissure Spring (Cocchioni 2002).

The concentrations of sulfide in total sulfur range between 5.5 and 17.9% (Table 2). The Fissure Spring and the Lago Verde sulfidic pool, supplied by deeper water, appear to be more enriched in H₂S and have a higher ratio of sulfide/sulfate. The Main Spring and the Ramo Sulfureo water, on the contrary, has an higher value of oxidized sulfur owing to recharge by oxygen-rich freshwater. Sulfide δ³⁴S values in the water range between -13.30‰ and -15.03‰, while sulfate δ³⁴S val-

Table 2. Isotopic composition of sulfide and sulfate in the groundwater.

	sulfide-total sulfur ratio	$\delta^{34}\text{S}$ sulfide	$\delta^{34}\text{S}$ sulfate
Main Spring	12.1%	-14.47	+20.34
Fissure Spring	17.9%	-13.30	+22.06
Ramo Sulfureo	5.5%	-15.03	+20.11
Lago Verde	17.2%	-14.49	+22.17
Triponzo Spring		-9.09	+17.45

ues range between +20.11 and +22.17‰ (Table 2). The sulfate $\delta^{34}\text{S}$ is lower in the Main Spring water than in the Fissure Spring water. As the Main Spring water mixed with the descending oxygen-rich freshwater, part of the H_2S , depleted in ^{34}S , in the Main Spring water would be oxidized to sulfate before degassing from the surface. This could cause the low sulfate $\delta^{34}\text{S}$ values in the Main Spring water.

GYPSUM DEPOSITS

Gypsum deposits were sampled in various areas of the cave system (Fig. 5) in order to analyze their isotopic compositions. Here they will be briefly described (Table 3).

Recent gypsum

Some gypsum, both microcrystalline and large crystals, up to several cm long, were collected at two different sites where gypsum is actively forming. A sample was also obtained from the surface of the limestone tablets described in previous experiments (Galdenzi *et al.* 1997).

Grotta del Vento, level III

This cave level is well developed in the Grotta del Vento: here a layer of freshwater over the sulfidic groundwater prevents the escape of H_2S , therefore all gypsum deposits can be considered inactive. Some of the largest gypsum deposits are located in this part of the cave.

Lago Cristallizzato. A small floor deposit in the Abisso Ancona, the main cave room, is under a limestone wall completely covered by corrosional limestone pockets with some residual replacement crusts (Fig. 15). Seepage water removed a large amount of the original deposit, while the replacement crust on the cave wall is almost entirely missing. Both the replacement crusts and the floor deposit were sampled.

Abisso Ancona. This is the largest gypsum deposit in the cave. It developed like a gypsum “glacier” under a high wall, completely covered by corrosional limestone pockets with some residual replacement crusts (Fig. 17). Both the replacement crusts and the floor deposit were collected for this study.

Table 3. Isotopic composition of sulfur in gypsum deposits in the caves.

Cave	sample	locality	karst level	depositional setting	fine-grained gypsum $\delta^{34}\text{S}$	gypsum crystals $\delta^{34}\text{S}$
Grotta del Fiume	G4	Ramo Sulfureo	active	limestone tablet	-19.17	
	G19-18	Laghi di Lucia	active	active wall crust	-19.62	-17.64
	G27-26	Ramo Sulfureo	active	active wall crust	-18.80	-10.79
	G14-13	Ramo Sulfureo	partly active	wall crust	-15.52	-13.90
	G2	old branches	II	wall crust	-14.07	
	G3	Pozzo Cristalli	unclear	wall crust	-7.82	
	G28	Pozzo Cristalli	unclear	wall crust	-10.33	
Grotta del Vento	G5	Lago Cristallizzato		III	floor deposit	-14.75
	G6	Lago Cristallizzato		III	wall crust	-16.06
	G7	Abisso Ancona	III	floor deposit	-12.14	
	G24	Abisso Ancona	III	floor deposit	-11.69	
	G25	Abisso Ancona	III	wall crust	-16.04	
	G8	Sala Duecento	III	floor mud		-14.05
	G9	Sala Duecento	III	floor deposit	-14.14	
	G10	Sala Duecento	III	floor deposit	-13.37	
	G1	Sala Duecento	III	floor deposit	-12.19	
	G12	Sala Orsa	III	floor	-11.69	
	G11	Sala Orsa	III	crevasse	-12.59	
	G15	Piano Superiore	V	floor deposit		-10.58
	G21	Abisso Ancona	V	floor deposit	-9.54	
	G22-23	Abisso Ancona	V	floor deposit	-7.93	-7.53
	T3-4	Triponzo		wall crust	-24.24	-22.52
Triponzo Spring	T5	Triponzo		wall crystals		-19.09

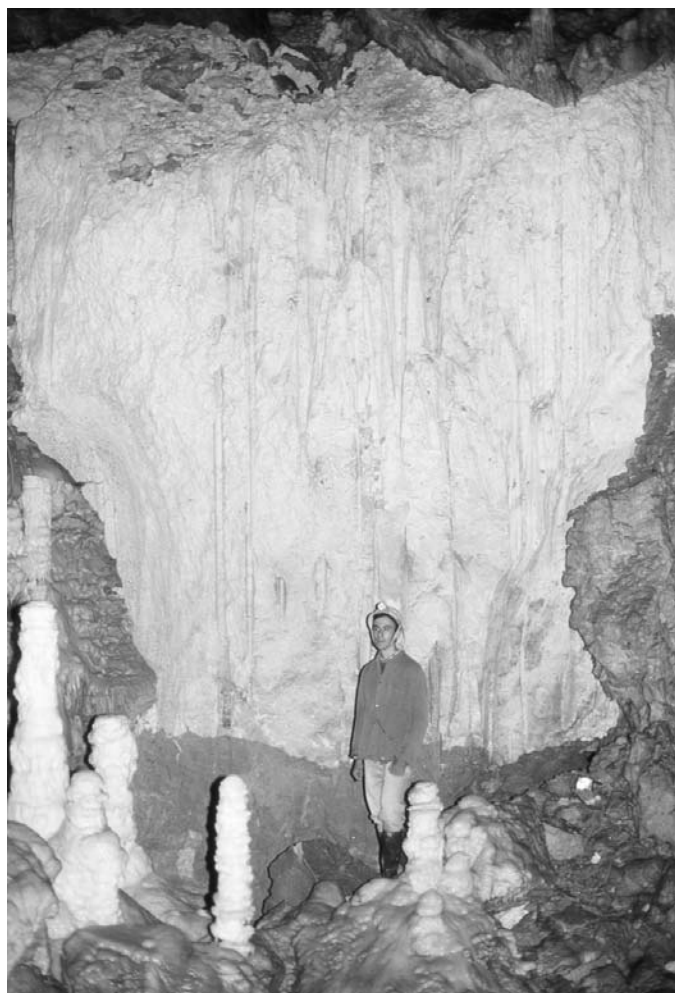


Figure 19. A natural section through one of the largest gypsum floor deposits of Sala Duecento, Grotta del Vento. Compare with the section in Figure 17.

Sala Duecento. This part of the cave consists of many interconnected rooms developed around a main large passage. This part of the cave includes two very interesting deposits, from which we collected samples. The first one represents the most spectacular natural section in the cave (Fig. 19). Here a small gypsum “glacier” is deeply dissected by dripping water. A succession of fine sand and mud with gypsum crystals (Table 1, samples G1 and G2), is overlain by thick, white, microcrystalline gypsum. The other deposit in Sala Duecento is on the floor of a wide room, cut by many shafts (Fig. 16). The gypsum overlies gray mud including small gypsum crystals (Table 1, samples G4 and G6), whereas the overhanging walls and roof are corroded by wide cupolas and by small pockets with a few residual gypsum replacement crusts. Gypsum is not present inside the shafts, which acted as vents for the sulfidic water when the cave level was forming.

Sala dell’Orsa. This room constitutes an intermediate part of a large shaft that opens in the flat rock floor of a big room at level V and reaches the actual water table. The lower part of



Figure 20. Pile of gypsum cut by dripping fresh water in the level V, Grotta del Vento.

this shaft, below level III, is deeply corroded by rounded phreatic features, while in its upper part scattered gypsum deposits occur inside the deeply corroded limestone wall or cover the floor. Three other cave minerals related to the sulfidic water (halloysite, barite, and jarosite) have been detected in this zone (Bertolani *et al.* 1977). Here we sampled a wall deposit and a nearby fissure filled with gypsum (Fig. 17).

Grotta del Vento, level V

Some samples were collected in this upper dry level in a short, lateral branch of the Abisso Ancona Room. The gypsum lies on the floor, under wide cupolas in the roof. It is the typical, white, finely crystalline gypsum, recrystallized on the surface. It lies where a rising phreatic passage reaches the main room. A further sample of large gypsum crystals was collected from the top of piles in the large passage above Sala Duecento that are deeply dissected by dripping water (Fig. 20).

Grotta del Fiume deposits

In this part of the cave system, sulfidic water flows in the lower cave passages, therefore condensation-corrosion occurs near the sulfidic pools and in adjacent upper level passages. Moreover, in this zone two minor cave levels are well developed between level III and the water table. Therefore, H_2S can easily rise from the water table toward the upper dry level, and gypsum deposition can occur in the same cave level at different times.

Old Branch. This part of the cave represents a network of passages developed near the surface, ~10 m above the water table. Widespread replacement crusts can be observed on the cave walls. A few small floor deposits and gypsum crystals inside mud are also present (Table 1, sample G7).

Pozzo dei Cristalli. This shaft opens up below level III and is directly connected with the lower passages and with the water table. The walls are completely covered by a thick crust

of replacement gypsum, and the corrosional processes are still weakly active. The sulfidic water is the same as Lago Verde and the Fissure Spring.

Ramo Sulfureo. In this part of the cave, corrosion by the cave air is the most intense. Some deposits are still growing, and here the main research on the sulfidic zones was concentrated.

TRIPONZO SPRING: A COMPARISON

Triponzo Spring is a sulfidic thermal spring located ~60 km south of Frasassi. The deep valley of the Nera River cuts the Calcare Massiccio Formation in the northern periclinal termination of an anticline, where the spring reaches the surface, in a geologic setting similar to the Frasassi Gorge. Sulfide and sulfate in the Triponzo water were sampled in August 2000. The temperature of the water was 29–30°C, the conductivity was 2.14 mS/cm; the sulfate $\delta^{34}\text{S}$ value was +17.45‰, and the sulfide $\delta^{34}\text{S}$ was -9.09‰.

In this area, the deep karst is not well known. Only a few small caves were explored in the steep mountain sides, but an interesting room was encountered in a hydroelectric tunnel. This small cave is no longer accessible, but it was described during the drilling by an Italian geologist interested in cave origin (Principi 1931). He understood the importance of the cave and suggested that “the cave did not form by normal karst dissolution, but developed as a consequence of the sulfidic water action, that replaced limestone with gypsum, which could be easily removed by flowing water”. The active corrosion of sulfidic water on the limestone walls could be observed until recently in a partly flooded artificial tunnel, where the sulfidic water flowed to the old thermal baths. The new thermal baths, built recently, reach the sulfidic water through boreholes, therefore the old flooded tunnel was destroyed. A remaining dry tunnel allowed a glimpse inside the karstified limestone near the spring. Here a network of open fissures and fractures is entirely covered by gypsum. In places, the limestone is replaced by a thin layer of finely crystalline gypsum, with small crystals on the surface. By turns, small gypsum crystals can grow directly on the limestone. These gypsum deposits were sampled to determine their sulfur isotopic composition (Table 3).

ORIGIN OF GYPSUM DEPOSITS

The Frasassi Caves make it possible to compare the isotopic content of sulfur in the water and in the gypsum deposits. It can help in the study of gypsum deposition and is very useful in deciphering the origin of the gypsum deposits in the upper dry levels. The $\delta^{34}\text{S}$ values of the gypsum collected in the cave range from -7.82 to -19.60‰. These are much lower than those of sulfate in the sulfidic groundwater (from +20.11 to +22.17‰). As it is impossible to produce such large isotopic fractionations during precipitation from water, the gypsum cannot have been produced by precipitation from saturated

groundwater. These low $\delta^{34}\text{S}$ values are related to H_2S ($\delta^{34}\text{S} = -13.30\text{‰}$ and -15.03‰). Moreover, the sulfide oxidation occurred in the air. If the oxidation had occurred in the water, the sulfate from H_2S would mix with the abundant sulfate in the water, and the lower $\delta^{34}\text{S}$ values would not be preserved in the gypsum. This conclusion is consistent with the sub-aerial depositional settings of the gypsum (Galdenzi 1990).

REPLACEMENT CRUSTS

The gypsum replacement crusts in the upper dry levels have $\delta^{34}\text{S}$ values similar to those of sulfide now dissolved in the water. Therefore, the sulfur in the replacement crust came from H_2S released from groundwater. This conclusion is consistent with many observations, such as the gravity-controlled shape of the corrosion pockets on cave walls, the analogies with the present depositional setting, and the localization above the original old water table level in many passages.

FLOOR DEPOSITS

The massive floor deposits are not forming today in the cave, and they occur mainly in cave levels III and V, which formed in the middle and late Pleistocene (Bocchini & Coltorti 1990; Taddeucci *et al.* 1992). These gypsum deposits were considered the result of sulfate saturation in the groundwater (Bertolani *et al.* 1977; Ciarapica & Passeri 1978) or the result of collapse and flow of gypsum replacement crusts (Galdenzi 1990). In the Guadalupe Mountains caves, U.S.A., where past gypsum deposition is well documented, both phreatic and vadose gypsum deposition are described, although the largest deposits are generally considered the result of sulfate supersaturation in the groundwater (Hill 1987; Buck *et al.* 1994; Palmer & Palmer 2000). The sedimentary structures that suggest a phreatic deposition for gypsum in Guadalupe Mountains caves (Hill 1997) are not clearly developed in the Frasassi deposits, therefore the depositional setting is not necessarily the same.

In the Frasassi Caves, since we can compare the isotopic composition of sulfidic water and gypsum, we can easily see that the gypsum $\delta^{34}\text{S}$ values clearly exclude the possibility that these massive floor deposits formed by precipitation below the water table in sulfate-supersaturated groundwater. Furthermore, the $\delta^{34}\text{S}$ of the floor deposits is similar to the adjacent replacement crusts (i.e., Lago Cristallizzato, Abisso Ancona, Table 3), suggesting that the growth of the replacement crusts and the deposition of nearby floor deposits were related. Judging from their thickness, we can exclude direct limestone replacement of the cave floor by H_2S oxidation in the cave air. Therefore, these gravity piles or “gypsum glaciers”, lying below walls or roofs covered with limestone pockets or replacement crust, can be considered the result of the detachment and flow of moonmilk-like replacement gypsum produced on the cave walls over a long time, as Galdenzi (1990) proposed.

GYPSUM IN MUD DEPOSITS

The low- $\delta^{34}\text{S}$ values of the euhedral gypsum crystals incorporated in mud also can be explained by the result of H_2S oxidation. Therefore, we can conclude that they could not form below the water table as a consequence of sulfate saturation inside the mud. Moreover, their values are quite similar to the overlying massive floor deposits. So these gypsum crystals grew by the seepage of sulfate-rich water from the overlying massive gypsum deposits. The chemical composition of this mud (Table 1) differs from the other mud deposits of the cave (Bertolani *et al.* 1977) and also implies etching by strong acid. The seepage of acidic water below the large gypsum deposits is also evidenced by meandering corrosional rills on the floor, formed where gypsum floor deposits directly overlie limestone, without interposed mud layers.

SULFUR ISOTOPIC FRACTIONATION

Although the low $\delta^{34}\text{S}$ values in the gypsum are related to H_2S , the values do not correspond exactly to those of H_2S . The $\delta^{34}\text{S}$ in the cave gypsum differs between deposits, and values can be lower or higher than values of present-day H_2S rising in the groundwater. The $\delta^{34}\text{S}$ in gypsum deposits ranges between -7.82‰ and -19.62‰ , whereas in water the $\delta^{34}\text{S}$ values of H_2S range from -13.30‰ to -15.03‰ , with an average value of about -14.2‰ . These differences in the $\delta^{34}\text{S}$ of gypsum and H_2S could represent the depositional setting in that the gypsum deposits formed in different places, over a period of ~ 200 ka.

ACTIVELY FORMING GYPSUM

The $\delta^{34}\text{S}$ values of actively forming microcrystalline gypsum are relatively constant. The $\delta^{34}\text{S}$ values of this gypsum on the active cave walls are $\sim 5\text{‰}$ lower than those of sulfide in the water. This depletion of ^{34}S may be related to kinetic isotopic fractionation during oxidation of sulfide (Fry *et al.* 1988). In the Triponzo aquifer, where gypsum growth is presently occurring, $\delta^{34}\text{S}$ in water sulfide is -9.09‰ , while microcrystalline gypsum in the limestone fissure network is -24.24‰ , with a depletion of about -14‰ of ^{34}S . Similar values were also obtained in other active H_2S caves: Hose *et al.* (2000) reported from Cueva de Villa Luz, Tabasco, Mexico, $\delta^{34}\text{S}$ values of -1.7‰ for H_2S and -23.4‰ for gypsum.

Isotopic fractionation of sulfur during abiotic oxidation is generally believed smaller than that measured from these caves (up to 5‰ : Fry *et al.* 1988; Canfield 2001). Furthermore, sulfur oxidizing organisms are believed capable only of a small isotopic fractionation, even though this subject is not well explored (Canfield 2001). Therefore, a large fractionation should not be due only to isotopic fractionation during oxidation. Part of the isotopic fractionation might be explained by the additional production of H_2S in the shallow phreatic zone, which might be more depleted in ^{34}S than that rising in the aquifer. Although sulfate-reducing bacteria are not reported in those caves, they may be responsible for producing more depleted ^{34}S .

Sulfur isotope compositions of associated large and microcrystalline gypsums are shown in Table 3. The $\delta^{34}\text{S}$ values of the euhedral crystals are higher and closer to those of H_2S than those of the respective microcrystals. The $\delta^{34}\text{S}$ value of sample G26 is even higher than that of H_2S in the water. As biotic H_2S -oxidation is presently believed to cause a smaller isotopic fractionation than abiotic oxidation (Canfield 2001), the $\delta^{34}\text{S}$ values similar to those of H_2S may imply that the sulfate in those gypsums is mainly produced by sulfide-oxidizing bacteria rather than by abiotic oxidation. Actually, actively forming gypsum crystals are often covered with biofilms that contain sulfide oxidizing bacteria.

As mentioned above, the $\delta^{34}\text{S}$ value of sample G26 is even higher than those of H_2S in the water. This cannot be explained by only H_2S oxidation. Therefore, a more complex biologic activity affecting the gypsum should be considered. Sulfate-reducing bacteria are known to cause high isotopic fractionation, producing sulfide depleted in ^{34}S (Kaplan & Rittenberg 1964; Canfield 2001). Therefore, small amounts of sulfate in the gypsum might have been re-reduced to volatile H_2S . This process could have produced the ^{34}S -enriched sulfate because ^{34}S -depleted H_2S would have been released after the reduction. Similar considerations could explain the high $\delta^{34}\text{S}$ value of gypsum in the Pozzo dei Cristalli where finely crystalline gypsum is about $+9\text{‰}$ enriched in ^{34}S compared with gypsum forming in the other cave areas, and it is also $+5\text{‰}$ enriched in ^{34}S compared with water sulfide.

UPPER LEVEL DEPOSITS

In the upper dry III level of Grotta del Vento, where gypsum deposits probably formed before the Holocene, we observe some variation in the $\delta^{34}\text{S}$ values. The sulfur in the big floor deposits is enriched in ^{34}S compared to the associated replacement crusts. In the Lago Cristallizzato, the difference between the floor deposit and the nearby replacement crust is $+1.3\text{‰}$, while in the Abisso Ancona it is about $+4\text{‰}$. These differences between replacement crust and related floor deposit suggest that changes in the isotopic composition of gypsum might have occurred after gypsum formed on the walls.

Furthermore, the $\delta^{34}\text{S}$ values in the upper levels gypsum is generally higher than those in actively forming gypsum areas, and also in groundwater H_2S . In level V, all the 4 samples have a $\delta^{34}\text{S}$ value higher than -11‰ ; in level III the average value is -13.5‰ (11 samples), ranging between -11.69‰ and -16.06‰ . These variations of isotopic composition might have been induced by the isotopic compositions of the H_2S released from the water. That could be caused by the activity of sulfate-reducing bacteria in the aquifer. As the bacterial activity should be influenced by environmental factors, such as the groundwater temperature, the amount of fresh water recharge, and the extension of the free interface between groundwater and cave atmosphere, the $\delta^{34}\text{S}$ values in the ancient gypsum may represent such factors at the time when the gypsum was produced.

CONCLUSIONS

The development of the Frasassi Caves can be clearly related to the oxidation of H_2S rising in the groundwater. H_2S oxidation can involve bacterial activity and occurs mainly in the shallow phreatic zone, utilizing oxygen dissolved in dripwater or diffusing from the cave atmosphere. At present, gypsum deposits form above the water table, where crusts of slushy gypsum including some large crystals replace the limestone walls. Below the water table limestone corrosion occurs without gypsum deposition, because sulfate saturation is not reached in the groundwater.

Three main types of gypsum can be observed in the dry upper levels of the cave: Replacement crusts similar to the actively forming deposits, large and thick microcrystalline floor deposits, and euhedral crystals in mud. The sulfur isotopic composition of these gypsum deposits shows that the sulfate was supplied by the oxidation of H_2S in the cave atmosphere. In the Frasassi caves, phreatic sulfate precipitation are (and were) prohibited due to the dilution of the groundwater by sulfate-poor meteoric water. These data agree with the sedimentary characteristics and the sub-aerial depositional setting of the gypsum.

The size of the old massive deposits and their distribution in the upper cave levels imply that there were some periods with a gypsum formation more intense than recent one. It probably can be related to the development of widespread interfaces between sulfidic groundwater and the cave atmosphere, which could exist while the cave was an almost ideal water table cave. Similar conditions repeatedly occurred during the cave history, depending on the surface geomorphic evolution. Small hydrologic changes inside the cave seem capable of influencing the solutional and depositional effects of the sulfidic water circulation inside the same cave system.

The sulfur isotopic data also confirm that large gypsum floor deposits could form by the flow of slushy gypsum from the walls and ceilings to the floor. This conclusion might be helpful in studying similar gypsum deposits, known in other dry caves of central Italy.

A comparison of the active and dry gypsum deposits made it possible to show the changes in the sulfur isotopic composition of the gypsum during limestone replacement. Because the sulfur isotope composition was related to the depositional setting of the gypsum deposit, H_2S caves could represent a good natural environment in order to study isotopic fractionation of sulfur for oxidation-reduction processes involving biologic activity.

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