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Fate of sulfide in the Frasassi cave system and implications for sulfuric acid speleogenesis

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ABSTRACT

The oxidation of hydrogen sulfide (H_2S) has led to the formation of some of the world's largest caves through a process known as sulfuric acid speleogenesis (SAS). Here we present a multi-year study of the large, sulfidic, and actively-forming Frasassi cave system, Italy. We show that despite the presence of abundant sulfide-oxidizing biofilms in Frasassi streams, $H_2S(g)$ degassing to the cave atmosphere was the major sink for dissolved sulfide. Degassing rates ranged from 0.9 to 80 μmol m^{-2} s^{-1}, whereas microbial oxidation rates were between 0.15 and 2.0 μmol m^{-2} s^{-1}. Furthermore, microsensor measurements showed that sulfuric acid is not a major end product of microbial sulfide oxidation in the streams. Our results suggest that subaerial SAS will be important for karstification, and more important than subaqueous SAS, wherever ground waters with high sulfide concentrations emerge as flowing streams in contact with cave air.

1. Introduction

Sulfuric acid speleogenesis (SAS) produces porosity in carbonate aquifers where anoxic, hydrogen-sulfide (H_2S)-bearing fluids interact with air-filled voids or oxygenated ground water to produce sulfuric acid (H_2SO_4). Ancient karst features formed as a result of SAS include some of the world's largest and most spectacular caves, such as the massive Lechuguilla Cave and Carlsbad Caverns in New Mexico (Palmer, 2007) and the exquisitely decorated Kap-Kutan Cave in Turkmenistan (Bottrell et al., 2001). As many as 5% of explored caves may have had a sulfidic origin (Palmer, 2007), with indications from subsurface drilling that many more are present but inaccessible (Palmer, 1991). In addition to caves, SAS is associated with widespread porosity development in stratified carbonate aquifers and petroleum reservoirs (Hill, 1987; Hill, 1995; Engel and Randall, 2011), with important implications for fluid flow and migration. CO_2 release from sulfuric acid dissolution of carbonates may also have long-term climate impacts and represent an understudied component of the geological carbon cycle (Torres et al., 2014).

The H_2S in anoxic carbonate aquifers is most commonly derived from organic-rich sediments or volcanic sources (Egemeier, 1981; Hose et al., 2000; Sarbu, 2000a). Where those ground waters are exposed to oxygen, often at the cave water table, the complete oxidation of H_2S to sulfuric acid,

$$H_2S + 2O_2 \rightarrow H_2SO_4, \tag{1}$$

can result in extremely rapid carbonate dissolution and aggressive speleogenesis. Depending on where the H_2S is oxidized, carbonate dissolution could occur in air-filled areas above the water table (subaerial dissolution) or in the zone below the water table (subaqueous dissolution).

In pioneering studies, sulfidic caves were proposed to form primarily above the water table where $H_2S(g)$ degasses into the cave atmosphere and oxidizes to sulfuric acid on moist cave walls and ceilings (Principi, 1931; Egemeier, 1981). Where subaerial limestone surfaces are exposed to sulfuric acid, limestone is replaced by a gypsum corrosion residue,

$$SO_4^{2-} + 2H^+ + CaCO_3 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2. \tag{2}$$

Cave enlargement proceeds as gypsum crusts thicken and eventually detach, falling to the cave floor where they can be removed by gypsum-undersaturated ground waters (Egemeier, 1981; Hose et al., 2000) or

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remain as gypsum floor deposits and 'glaciers' (Davis, 2000; Galdenzi and Maruoka, 2003).

However, recent work on SAS has cast doubt on the importance of sulfuric acid corrosion above the water table. H_2S oxidation represents a rich source of chemical energy, and sulfidic aquifers with inputs of electron acceptors such as oxygen and nitrate are extensively colonized by chemolithoautotrophic sulfide-oxidizing microorganisms (Hose et al., 2000; Engel et al., 2004; Macalady et al., 2008). Because microorganisms can oxidize sulfide much faster than abiotic rates alone, they may play an important role in acid production and limestone dissolution in microaerophilic streams where sulfide oxidation is otherwise abiotically limited (Galdenzi et al., 1999; Hose et al., 2000; Engel et al., 2004). Engel et al. (2004) demonstrated that more than 90% of sulfide disappearance from the stream in Lower Kane Cave, WY, USA, is due to microbial oxidation. Engel et al. (2004) also found evidence that sulfide-oxidizing bacteria enhance limestone dissolution by localizing sulfuric acid production at mineral surfaces, and a later study by Steinhauer et al. (2010) showed that aqueous bioreactors inoculated with sulfidic cave biofilms dissolve limestone up to seven times faster than abiotic control reactors.

Observations made in ancient sulfidic caves provide evidence for both subaerial and subaqueous limestone corrosion by SAS. Some studies have argued that, based on morphological evidence, sulfuric acid production below the water table is the main dissolution process for SAS (Davis, 1980; Hill, 1987; Forti et al., 2002). Indeed, the role of subaerial versus subaqueous processes in Carlsbad Cavern currently remains controversial (e.g., Jagnow et al., 2000; Forti et al., 2002; Palmer et al., 2009; Calaforra and De Waele, 2011). However, morphological evidence for subaerial corrosion including cupolas, megascallops, domes, vents, niches, notches, and other features can be found in many sulfidic caves, suggesting that subaerial SAS may be more widespread than generally considered (Audra et al., 2007; Audra et al., 2009; Plan et al., 2012; Temovski et al., 2013). In early work in Frasassi, Galdenzi (1990) proposed a model for cavern development in the Frasassi cave system in which both subaerial and subaqueous processes were important.

Thus, the relative importance of subaerial, subaqueous, and microbial processes in SAS remains controversial, perhaps because a quantitative accounting of the mechanisms and rates of these processes under differing environmental conditions is lacking. In light of this, we made *in situ* measurements of $H_2S(g)$ degassing and microbial sulfide oxidation over multiple sites and seasons in the large, actively-forming, and hydrologically dynamic Frasassi cave system (Italy). In Frasassi, morphological and mineralogical observations provide qualitative evidence that significant limestone corrosion has occurred both above and below the water table in the recent past (Galdenzi, 1990). Furthermore, comparable rates of subaerial and subaqueous limestone dissolution are occurring within several meters of the air–water interface (Galdenzi et al., 1997; Mariani et al., 2007). Based on prior observations of pervasive colonization of Frasassi streams and pools by sulfur oxidizing microorganisms (Macalady et al., 2006; Macalady et al., 2008), we hypothesized that biological oxidation below the water table would account for the majority of dissolved H_2S disappearance from cave streams. In contrast, here we found that most sulfide lost from streams is released to the cave atmosphere, and that sulfuric acid is not an important end product of microbial sulfide oxidation within submerged biofilms covering rock and sediment surfaces.

2. The Frasassi cave system

The Grotta Grande del Vento–Grotta del Fiume (Frasassi) cave system (43.4012 N, 12.9656 E) is located in the Mt. Frasassi–Mt. Valmontagnana anticline in the northeastern Apennines, Italy (Fig. 1). The system includes over 25 km of irregular and ramiform passages in pure platform limestones of the Hettangian Calcare Massiccio Formation (Galdenzi and Maruoka, 2003; Mariani et al., 2007). General characteristics of the hydrology and geochemistry of the cave system have been previously described (Galdenzi et al., 2008; Galdenzi, 2012). Dissolved sulfide in the Frasassi aquifer is likely derived from bacterial sulfate reduction in organic-rich lenses within underlying evaporites of the Triassic Burano Formation. In the Northeast sector of the active cave level, multiple H_2S-rich springs emerge at the cave water table and flow into streams and pools accessible by technical caving routes. Total dissolved sulfide (H_2S_T) concentrations in streams and pools vary from below detection (<2 μM) to 600 μM (Galdenzi et al., 2008; Macalady et al., 2008), whereas dissolved oxygen concentrations in the same waters range from below detection (<2 μM) to 30 μM (Macalady et al., 2008). Nitrate concentrations are perennially undetectable (<0.1 μM) (Macalady et al., 2008). Sulfidic cave waters are slightly saline (conductivity 1.5–3.5 mS/cm), and consistently between 13 and 14 °C year round. Within 1 m of the water table, $H_2S(g)$ concentrations in the cave air range from <0.2 to 25 parts-per-million by volume (ppmv), and are typically less than 10 ppmv (Macalady et al., 2007).

3. Methods

3.1. Field sampling and chemical analyses

Concentrations of H_2S_T (total dissolved sulfide) and O_2 in cave streams were measured with a portable spectrophotometer (Hach, Loveland, CO) using methylene blue (Hach method 690) and indigo carmine (Hach method 8316) methods, respectively. Replicate H_2S_T analyses were within 3% of each other, and replicate O_2 analyses were within 25% of each other. Water temperature, pH and conductivity were measured using a 350i multimeter and handheld probes (WTW, Weilheim, Germany). Water samples for laboratory analyses were filtered immediately in the field (0.2 μm) into acid-washed containers. Samples for dissolved calcium and other cations were preserved with concentrated nitric acid and measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) at the Penn State Materials Characterization Laboratory. Dissolved inorganic carbon (DIC) was determined by headspace $CO_2(g)$ measurements using the method of Dawson et al. (2013).

Surface flow velocity was determined using floating indicators. Discharge was calculated by multiplying surface flow velocity with the stream cross sectional area and a factor of 0.85, which corrects for differences between surface and depth-averaged subsurface flow velocities (Gallagher and Stevenson, 1999).

3.2. H_2S degassing rate

The rate of $H_2S(g)$ degassing was measured using a portable flux chamber connected to a handheld gas detector (MX2100, ENMET Corp., USA) (Fig. A.1). Similar flux chamber approaches have been widely applied for measuring air–water gas exchange (Frankignoulle, 1988; Kremer et al., 2003; Borges et al., 2004). The flux chamber was connected to the detector by a BX2100 air pump (ENMET Corp., USA), and the degassing flux was calculated from the rate of increase of $H_2S(g)$ in the chamber, after correcting for air removed by the pump and for detector response time (Appendix A.1, Fig. A.1 and A.2). To compensate for uncertainty introduced by the flux-chamber system, between 2 and 5 measurements were performed at each sampling location. Complete details on $H_2S(g)$ degassing measurements are provided in the Supplementary methods (Appendix A.1).

3.3. In situ microsensor analyses

H_2S_T consumption due to microbial oxidation was determined by microsensors attached to a custom-designed portable microsensing apparatus (Weber et al., 2007). Vertical concentration profiles of H_2S_T, O_2 and pH were measured in biofilms covering the submersed

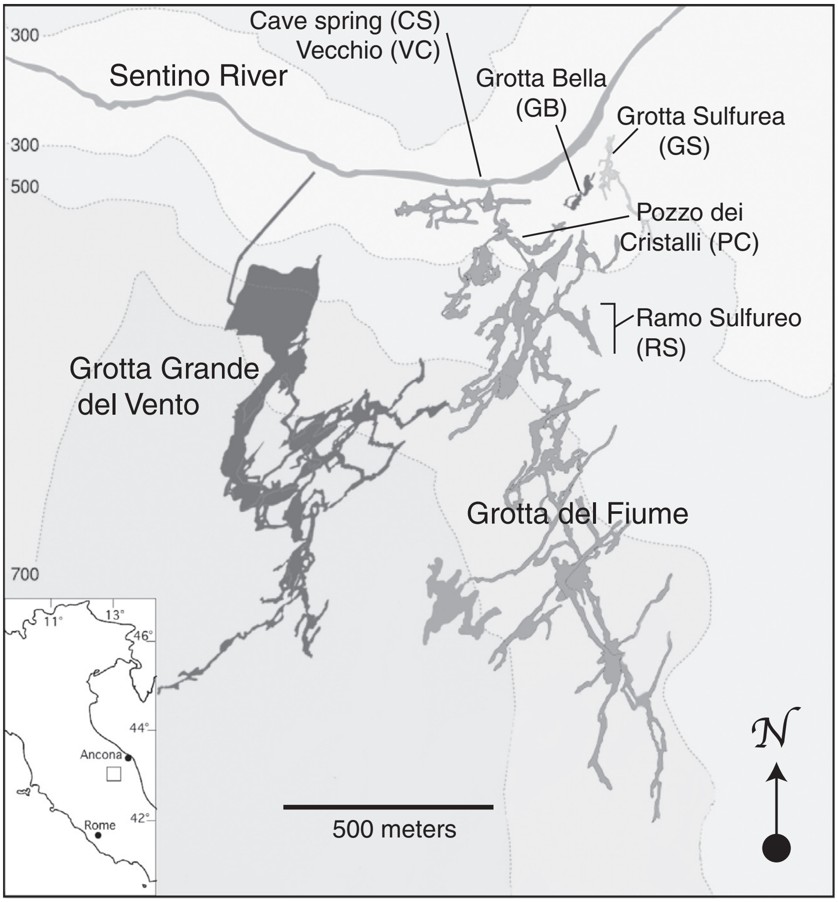

Fig. 1. Map of the Frasassi cave system, showing sampling locations. Base map after Mariani et al. (2007). No technical caving is required to access sites CS and VC.

sediments and rocks, and H_2S_T flux was determined from the H_2S_T gradient using Fick's first law of diffusion.

Microsensors (tip diameters of 20–30 μm) were prepared, calibrated and used as previously described. Clark-type O_2 electrodes (Revsbech, 1989) were calibrated by a linear two-point calibration in oxygen-saturated water and anoxic sediment. H_2S electrodes (Kühl et al., 1998) were calibrated by linear two-point calibration in sulfidic stream water and a Na_2S standard. H_2S_T values were calculated from microsensor-derived $H_2S(aq)$ concentrations and pH values using equation $H_2S_T = H_2S(aq) \times [1 + K_1 / H_3O^+]$, with the K_1 value corrected for temperature and salinity according to Millero et al. (1988). pH electrodes (de Beer et al., 2006) were calibrated using buffer solutions of pH 4.01 and pH 7.00 (Mettler-Toledo, Giessen, Germany).

We first attempted microsensor measurements in cave biofilms in 2009, but despite many successful measurements in sulfidic springs outside the cave, we had no success with H_2S sensors and limited success with oxygen sensors inside the cave. The following year we returned with the Caver Operated Microsensor System (COMS; Fig. A.3C), which is a smaller and more robust version of the motorized Diver Operated Microsensor System (DOMS) described by Weber et al. (2007). By packing the sensor contacts with hygroscopic beads and sealing all contacts as completely as possible prior to entering the cave, the COMS electronics were protected from moisture and $H_2S(g)$ vapors in the cave air, which resulted in a substantially improved stability of the signal.

Fluxes of microbial sulfide oxidation (J_{micH_2S}) in the biofilms were derived from the measured H_2S_T gradients according to the Fick's first law of diffusion, assuming steady state,

$$J_{micH_2S} = D\frac{dC_{H_2S_T}}{dz}, \qquad (3)$$

where D is the diffusion coefficient of $H_2S(aq)$ corrected for *in situ* temperature according to Jørgensen and Revsbech (1983). Fluxes measured at each site were averaged from three separate microsensor profiles collected within 1 cm^2 of investigated biofilm.

3.4. Stream model

A 1-dimensional reaction-transport model was used to relate the loss of H_2S_T to chemical changes in the bulk stream water. The processes affecting the H_2S_T loss included (1) $H_2S(g)$ degassing from the stream surface to the cave atmosphere, (2) microbial sulfide oxidation in stream biofilms, and (3) abiotic sulfide oxidation, all of which were constrained by the field measurements. Assuming steady state approximation, changes in H_2S_T concentration (denoted C_s, mol m^{-3}) along the stream (x, m) are given by

$$\frac{dC_s}{dx}v = -J_{gas}\frac{1}{h} - J_{mic}\frac{1}{h} - R_{abio}, \qquad (4)$$

where v is stream flow velocity (m s^{-1}) and h is depth (m). The $H_2S(g)$ degassing flux, J_{gas} (mol m^{-2} s^{-1}) was dependent on stream flow velocity and followed an empirical relationship derived from field measurements (Fig. 2). The H_2S_T removal flux due to microbial oxidation, J_{mic} (mol m^{-2} s^{-1}), was assumed to span the range determined by microsensors across all measured sites. The rate of abiotic chemical oxidation, R_{abio} (mol m^{-3} s^{-1}), was calculated based on concentrations of dissolved H_2S_T and O_2 using kinetic equations from Millero et al. (1987). Rates for air–water exchange of CO_2 were calculated using theoretical volatilization equations (Schwarzenbach et al., 1993) using measured $CO_2(aq)$ values and the assumption that mass transfer coefficients for $CO_2(aq)$ and $H_2S(aq)$ were proportional. Downstream

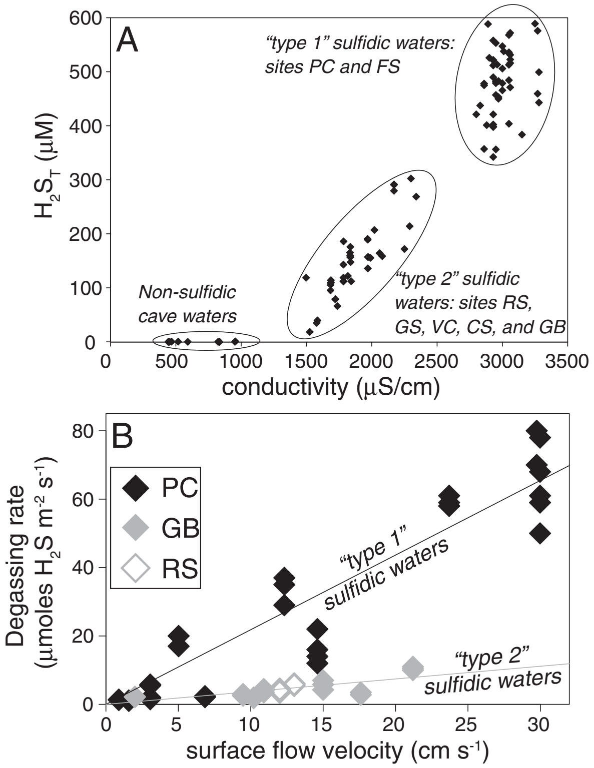

Fig. 2. (A) Conductivity versus H_2S_T for Frasassi springs and streams measured from 2007 to 2010. (B) Measured $H_2S(g)$ degassing rates versus surface flow velocities. At the times of measurement, H_2S_T concentrations at site PC were between 450 and 560 µM and between 100 and 190 µM at sites GB and RS.

changes in pH were calculated based on $H_2S(g)$ and $CO_2(g)$ degassing, using the reaction block in PHREEQC (Parkhurst et al., 1999) to incrementally remove $H_2S(aq)$ and $CO_2(aq)$ from the stream water. Complete model derivation and input parameters are provided in the Supplementary materials (Appendix A.2).

4. Results

Gas flux chamber measurements of areal rates of $H_2S(g)$ degassing in Frasassi streams varied by two orders of magnitude, from 0.9 to 80 µmol m^{-2} s^{-1} (Table 1). The large range in rates was mainly due to variation in stream flow velocity and bulk H_2S_T concentration (Fig. 2). In "type 1 sulfidic" cave waters (Fig. 2A), the degassing rates increased approximately linearly with the surface flow velocity with a slope of 218 µmol m^{-3} ($r^2 = 0.89$, $p < 0.001$). A similar linear correlation was found for "type 2 sulfidic" waters, but with a lower slope (23.7 µmol m^{-3}, $r^2 = 0.59$, $p < 0.001$).

Table 1
Areal rates of H_2S_T loss from cave streams.

Water type	Site	Range of values (µmol m^{-2} s^{-1})	n
$H_2S(g)$ degassing			
1	PC	0.9–80	31
2	RS	1.4–7.4	6
2	GB	3.0–4.0	19
Microbial sulfide oxidation			
2	GS	0.45–0.73	2[a]
2	CS	0.15–2.01	5[a]
2	VC	0.08–0.34	8[a]
Abiotic sulfide oxidation[b]			
1 and 2		$4.3 \cdot 10^{-3}$–$3.9 \cdot 10^{-5}$	

[a] Each measurement consists of three separate microsensor profiles from 1 cm^2 of biofilm.

[b] Calculated by multiplying volumetric rates of abiotic oxidation by stream depth in the model. Range of values for all streams and stream locations is given.

Conspicuous white biofilms at the sediment–water interface or attached to submerged limestone surfaces were observed for all sampling events. In these biofilms, O_2 and H_2S_T concentrations exhibited steep gradients, confirming the role of microbial sulfide oxidation as a sink for sulfide (Fig. 3 and Fig. A.4). Microbial sulfide oxidation rates calculated from microsensor profiles ranged from 0.08 to 2.0 µmol m^{-2} s^{-1} (Table 1). pH did not change significantly across biofilm–water interfaces or within the biofilms. However, pH did decrease in organic-rich, anoxic sediments below the biofilms (Fig. 3).

At a site where a spring-fed sulfidic stream flowed without additional ground water inputs or outputs (site PC; Fig. 1, Fig. A.3), bulk water concentrations of H_2S_T decreased while O_2 and pH increased downstream from the emergence (Fig. 4, symbols, and Fig. A.5). There was no measurable change in dissolved Ca^{2+} (Tables A.1 and A.2). The measured H_2S_T and pH gradients were in good agreement with those predicted by the reaction-transport model (Fig. 4, solid lines). This confirmed that degassing was the major driver of H_2S_T loss (contributing on average 88% to 98%) and pH increase in the bulk stream water. Benthic microbial sulfide oxidation was only minor (on average 2% to 12%), and abiotic oxidation in the bulk water was negligible (<0.03%; Table A.3). Due to the fragility of the microsensor apparatus, we were not able to obtain microsensor profiles from all sites (Table 1). However, we were able to use rates measured in the cave to constrain the model.

After successful validation of the model at site PC, we applied it to other sites (GB, RS, GS) where stream flow is more complex. At these type 2 sulfidic water sites (Fig. 2A), $H_2S(g)$ degassing fluxes were generally lower than at site PC (Fig. 2B), although still larger than microbial oxidation rates (Table 1). Model predictions suggested that, similar to site PC, degassing was the major driver of H_2S_T loss (contributing on average 75% to 86% of total H_2S_T depletion), whereas microbial sulfide oxidation was less important (on average 14% to 25%; Table A.4). Because these sites were influenced by non-quantified ground water inputs, model predictions could not be reliably compared with field data.

5. Discussion

5.1. Fate of H_2S in Frasassi streams

As expected based on previous studies comparing biological and abiotic sulfide oxidation rates (e.g., Jørgensen et al., 1979; Jannasch

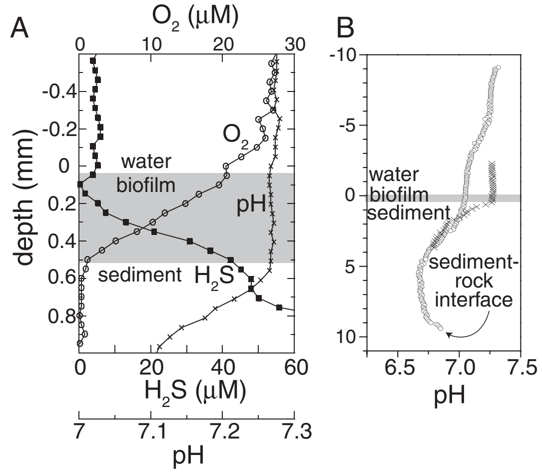

Fig. 3. Microsensor profiles from Frasassi stream biofilms for a site where O_2, H_2S_T, and pH data were all available (A). Panel (B) shows a pH profile (open circles) measured to the sediment–rock interface at the same location, which resulted in the microsensor breaking. A second pH profile from the same site is also shown (× symbols).

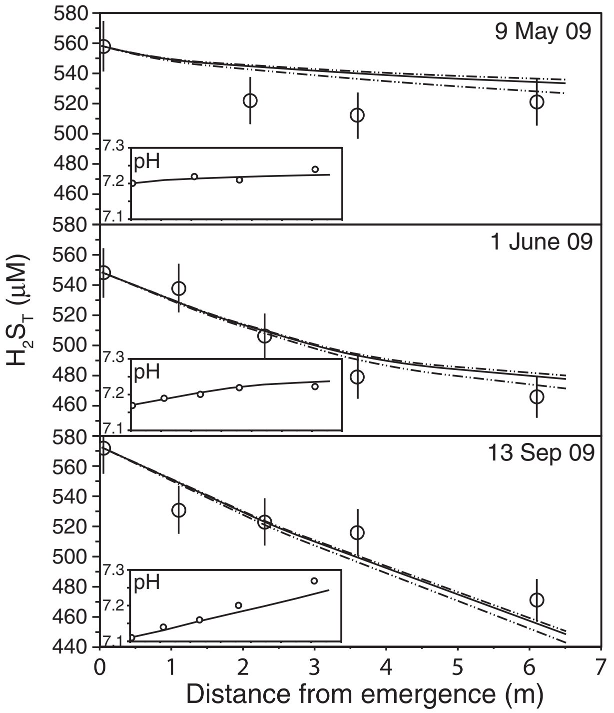

Fig. 4. Comparison of modeled versus measured changes in H_2S_T for the PC stream at three different times of the year. Circles are measured H_2S_T values and lines are model output. The solid curve was modeled using the average microbial oxidation rate (0.49 μmol m^{-2} s^{-1}), and dashed lines are with the minimum and maximum measured rates (Table 1). Insets show modeled versus measured changes in pH due to $H_2S(g)$ and $CO_2(g)$ degassing.

et al., 1991; Jensen et al., 2009; Luther et al., 2011), sulfide removal by microbial oxidation is much faster in Frasassi streams than abiotic oxidation (Table 1). Our measured microbial oxidation rates are consistent with microsensor-based measurements of microbial sulfide oxidation in aphotic biofilms from a variety of other sulfidic environments, which can vary from 0.05 to 1.16 μmol m^{-2} s^{-1} (see compilation by Schwedt et al., 2011). Due to the fragility of the microsensor apparatus, we were not able to obtain microsensor profiles from all sites. However, our measured rates nonetheless provide an appropriate constraint for the model. Both *in situ* measurements and transport modeling show that $H_2S(g)$ degassing rates are at least an order of magnitude higher than microbial sulfide oxidation (Table 1). Additionally, degassing explains the downstream increase in pH observed at site PC (Fig. 4). Therefore we can be confident in the conclusion that most of the sulfide lost from Frasassi streams is released to the cave atmosphere. Our results directly challenge the notion that microbial sulfide oxidation below the water table is generally the primary driver in SAS, as some previous studies have suggested (Davis, 1980; Engel et al., 2004).

5.2. Role of biological sulfide oxidation

Although biological oxidation accounts for some of the sulfide disappearance from Frasassi streams, pH microsensor profiles show that the biofilms do not produce significant amounts of sulfuric acid (Fig. 3). Therefore, the majority of the sulfide is likely oxidized to intermediate sulfur species such as zero-valent sulfur,

$$2H_2S + O_2 \rightarrow 2S^\circ + 2H_2O. \tag{5}$$

In contrast, pH decreases are regularly observed in biofilms from other environments where sulfide is completely oxidized to sulfuric acid (e.g., Jørgensen and Revsbech, 1983; Schwedt et al., 2011). Consistent with this interpretation, abundant intracellular and/or extracellular S° particles are perennially observed in Frasassi biofilms and sediments, regardless of their taxonomic composition or the surrounding water chemistry (Macalady et al., 2006; Macalady et al., 2008), which give the stream biofilms their conspicuous white color (Fig. A.3). Incomplete sulfide oxidation thus supports a thriving chemosynthetic ecosystem in the streams, but does not contribute directly to acid production.

Decreases in pH and increases in H_2S_T concentration were, however, observed in the anoxic sediments immediately below the zone of sulfide oxidation, indicating that sulfur and/or carbon recycling produces acid (Fig. 3). Furthermore, a single pH profile obtained by a microsensor that broke when it accidentally hit hard rock indicated that the pH remained low in deeper sediments down to the sediment–rock interface (Fig. 3B). The observed pH decrease in the sediments could be due to organic acid and CO_2 production via fermentation, sulfate reduction in the absence of metal sulfide precipitation (Ben-Yaakov, 1973; Boudreau and Canfield, 1988; Meister, 2013), and/or disproportionation of S° (Finster et al., 1998). Although sulfur-oxidizing autotrophs in the biofilms supply organic matter for fermentation and sulfate reduction and S° for sulfur disproportionation (Macalady et al., 2008), it appears that sulfide oxidation and acid production are only weakly coupled.

5.3. Implications for speleogenesis in the Frasassi cave system

Most of the $H_2S(g)$ that degasses from cave streams is thought to oxidize to sulfuric acid on moist wall surfaces in the oxygen-rich cave atmosphere. Near flowing sulfidic streams, cave walls and ceilings are covered with acidic ($pH < 4$) gypsum corrosion residues often >10 cm thick, and the gypsum surface is colonized by extremophilic sulfur-oxidizers that produce highly acidic (pH 0–2) subaerial biofilms (Macalady et al., 2007). In some locations, small yellow elemental sulfur rosettes are associated with wall and biofilm surfaces (Macalady et al., 2007; Jones et al., 2012). Further from flowing streams, gypsum crusts thin and eventually give way to exposed limestone and mildly acidic (pH 6) wall communities (Jones et al., 2008). In addition to biological sulfide oxidation by these wall microbial communities, abiotic sulfide oxidation may also be important above the water table.

Widespread evidence for aggressive subaerial corrosion has been documented in multiple cave levels that lie above the currently active level, including cave passage geometries, cupolas and other corrosion features above vertical phreatic conduits, and extensive microcrystalline gypsum deposits with light S isotopic signatures (Galdenzi, 1990; Galdenzi and Maruoka, 2003; Galdenzi, 2012). These features indicate that conditions favorable for strong $H_2S(g)$ degassing have existed over long periods, at least in the last phases of the 2–3 million year history of cave development in the Frasassi system (Taddeucci et al., 1992; Galdenzi and Maruoka, 2003).

In multi-year limestone tablet dissolution experiments conducted at sample site RS (Galdenzi et al., 1997), average mass loss was similar for tablets incubated above and below the stream surface (Fig. 5; see also Galdenzi, 2012). Methods for this experiment are provided here in the Supplementary content (Appendix A.3). Since microbial sulfide consumption in Frasassi streams does not appear to result in significant sulfuric acid production, these results imply that other processes in the stream water may also be important for speleogenesis. Notably, rapid carbonate dissolution also occurs at Frasassi below stable haloclines in stratified lakes where oxygen is below detection limits (Mariani et al., 2007).

5.4. Implications for sulfuric acid speleogenesis

Our results suggest that apparently conflicting views on subaerial versus subaqueous SAS near the water table can be reconciled using a conceptual model that takes H_2S_T concentrations and water flow characteristics into account (Fig. 6). Near flowing waters in Frasassi, degassing predominates due to high H_2S_T concentration and rapid

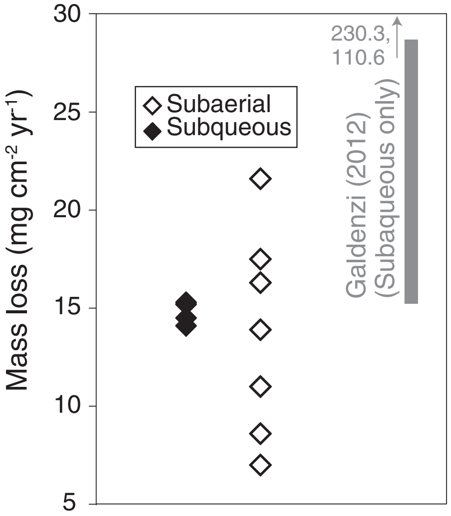

Fig. 5. Mass loss from replicate limestone tablets installed above and below the water table at site RS over a 5-year period (Galdenzi et al., 1997). For comparison, the range of values determined at the same site for submerged tablets in a later study (Galdenzi, 2012) are also shown (gray bar, n = 17), including two extreme values (arrow). Subaerial dissolution was not measured in this later study (Galdenzi, 2012).

stream flow. In contrast, streams in Lower Kane Cave, WY, USA, have rapid flow but much lower H_2S_T concentrations, and microbial oxidation is therefore faster than degassing (Engel et al., 2004). Consistent with our conceptual model, Engel et al. (2004) report $H_2S(g)$ degassing fluxes between 0.35 and 1.3 μmol m^{-2} s^{-1} for the Lower Kane Cave stream, which are slower than $H_2S(g)$ degassing fluxes at most Frasassi locations but within the range of microbial oxidation fluxes measured here (Table 1).

Near sulfidic Frasassi lakes such as Lago Verde and Lago Claudia, there is no detectable $H_2S(g)$ in the cave air and little to no subaerial gypsum deposition above the water table due to very slow water flow. Similarly, Movile Cave (Romania) has high dissolved sulfide but low cave air $H_2S(g)$, slow gypsum precipitation, and scarce subaerial corrosion features (Sarbu, 2000b; Galdenzi, 2001), consistent with its largely stagnant water table. Rapid $H_2S(g)$ degassing and subaerial corrosion are expected for most locations within Cueva de Villa Luz, Mexico, due to high H_2S_T and turbulent water flow (Hose et al., 2000), as well as near the highly sulfidic and turbulent cave streams in Grotta Nuova di Rio Garrafo near Acquasanta Terme, Italy (Galdenzi et al., 2010; Jones et al., 2010). Water temperature and thermal air flow may also impact $H_2S(g)$ dynamics in these and other caves (Galdenzi, 2001; Audra et al., 2007; Audra et al., 2009), and future research will continue to explore how H_2S_T concentration, stream flow characteristics, and other factors impact subaerial sulfuric acid speleogenesis and the evolution of sulfidic karst systems.

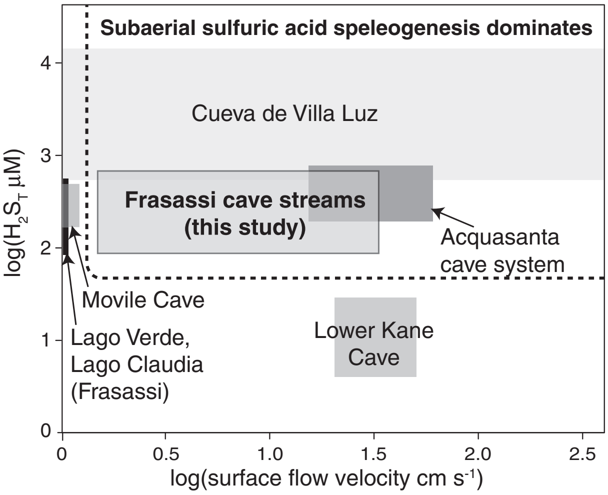

Fig. 6. Conceptual framework for predicting when and where subaerial corrosion is expected as the dominant mechanism for speleogenesis in sulfidic caves. Boxes represent the range of H_2S_T and flow velocity for sulfidic waters reported this study and for previously studied sulfidic cave systems.

We were surprised to find that the presence of a conspicuous sulfide-oxidizing microbiota is not a reliable indicator for subaqueous SAS. However, we also note that microbial recycling of chemoautotrophic biofilms produces acidity that may contribute to limestone dissolution even under conditions where sulfuric acid is not directly produced by chemosynthesis. Microbially-driven speleogenesis may therefore occur in a broader range of carbonate-hosted subsurface ecosystems, powered by chemosynthetically-derived organic carbon.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2015.06.002.

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