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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