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Biogeochemical cycling of sulphur in karst and transfer into speleothem archives at Grotta di Ernesto, Italy

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Abstract Trace amounts of sulphur in speleothems suggest that stalagmites may act as archives of sulphur deposition, thereby recording aspects of atmospheric variability in sulphur content. Accurate interpretation of this novel sulphur archive depends upon understanding how biogeochemical cycling in the soil and epikarst above the cave may modify the precursor atmospheric values of sulphur concentration and isotopic composition prior to incorporation into the speleothem record. Dual isotope analysis of δ^{34}S-SO$_4$ and δ^{18}O-SO$_4$ is used to trace biogeochemical transformations of atmospheric sulphur through the cave system at Grotta di Ernesto in the Italian Alps and builds towards a framework for interpretation of speleothem sulphur archives which depends on overlying ecosystem dynamics and karst hydrological properties. A three component model of atmospheric sulphate signal modification is proposed to be driven by (1). vegetation and soil cycling, (2). the degree of groundwater mixing in the karst aquifer; and (3). redox status. The relative influence of each process is specific to individual drip flow sites and associated stalagmites, rendering each sulphur archive a unique signal of environmental conditions. Under conditions found in the soil and epikarst above Grotta di Ernesto, the dual isotope signatures of sulphate sulphur and oxygen incorporated into speleothem carbonate, closely reflect past conditions of industrial sulphur loading to the atmosphere and the extent of signal modification through biogeochemical cycling and aquifer mixing.

Keywords Sulphur · Isotopes · Biogeochemistry · Speleothem · Karst

Introduction

Sulphur in stalagmites has recently added to the expanding repertoire of trace elements within

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speleothems which are capable of recording signatures of environmental change (see reviews by Fairchild and Treble 2009; Fairchild et al. 2006a). Due to the good degree of material preservation, stability of their chemical properties and the accurate age-dating which can be undertaken, this makes cave calcite speleothems a most valuable record of local to regional sulphur pollution dynamics in karst environments (Frisia et al. 2005; Wynn et al. 2008, 2010). However, despite success at extracting the archived sulphur signal for elemental concentration and isotopic values (Wynn et al. 2008, 2010), knowledge of precursor signal modification in the soil and epikarst is essential for a full understanding of the signals recorded in the speleothem calcite. The transformation of sulphate concentrations and isotopic values from atmospheric deposition to cave drip site depends on overlying ecosystem dynamics (Likens et al. 2002; Mayer et al. 1995; Shanley et al. 2005; Novak et al. 2007) and karst hydrological properties (e.g. Fairchild et al. 2006b; Williams 2008; Bradley et al. 2010). A three component model of signal modification is suggested to be driven by (1). vegetation and soil cycling; (2). the degree of hydrological mixing between sources containing sulphur of differing isotopic composition; and (3). redox status. In the simplest scenario, preferential flow routing through the soil and epikarst will result in speleothem capture of a sulphate signal which is largely unmodified from atmospheric source (e.g. stalagmite BFM-BOSS; Wynn et al. 2008). However, mixing of atmospheric sulphate with stored soil and ground water sulphate will introduce ‘memory effects’ and biogeochemical cycling of sulphur through vegetation and soils of variable redox status will delay, concentrate and fractionate any chemical or isotopic signal prior to incorporation into the speleothem host. Here we present a detailed isotopic study of sulphate, building towards a framework for understanding transformations between source precipitation and cave drip waters at Grotta di Ernesto, Italy. We specifically address the record of sulphur dynamics in stalagmite ER78, interpreted in Wynn et al. (2010) as recording changes to atmospheric pollution levels from the industrial era, and build towards a process understanding of carbonate-associated sulphate in speleothem archives of environmental change. In a subsequent paper, we assess the influence of carbonate crystallisation upon sulphate incorporation and the controls on this partitioning at the annual scale.

Review of sulphur cycling in forested catchments

Despite a declining flux of sulphur to the atmosphere in many countries, the effects of sulphur release from ecosystem storage continue to impact receiving water bodies and delay acidification reversal long after emissions to the atmosphere have peaked (Alewell 2001; Prechtel et al. 2001). This has been well documented in forested ecosystems through the use of watershed sulphur budgets (e.g. Mitchell et al. 2011) and tracing using naturally occurring stable isotopes ($^{34}S/^{32}S$ and $^{18}O/^{16}O$. e.g. Shanley et al. 2005; Alewell et al. 1999; Novak et al. 2007). However, biogeochemical cycling of sulphur in karst environments is relatively poorly established. Whilst sulphur sources and processes of transformation have been identified within the karst aquifer (e.g. Einsiedl and Mayer 2005; Einsiedl et al. 2009; Bottrell et al. 2000; Gunn et al. 2006; Han and Liu 2004), linkage between atmospheric sulphur loading and the speleothem record has yet to take into account the biogeochemical modifications which may occur.

Retention of sulphur within a catchment can occur by both inorganic adsorption of sulphate and biological cycling (Mitchell et al. 1998). Inorganic sorption capacity is pH-dependent and largely negligible above pH 6.5 (Mayer et al. 1995). Where the karst system is overlain by deep calcareous soils, sorption capacity should be negligible at depth. For upper humus layers and thin soil horizons, acidity may lead to a significant reservoir of sorbed sulphate (e.g. Nodvin et al. 1986) which will be of consequence in understanding the flux of sulphur to deeper within the karst aquifer, although this will not have an impact upon isotopic tracing (Van Stempvoort et al. 1990). Additional mechanisms of immobilisation/release include (1). assimilation: the uptake and incorporation of inorganic sulphate into plants and soil microorganisms; (2). mineralisation: the conversion of carbon bonded sulphur compounds released from decaying vegetation and soil organic matter into sulphate; (3). oxidation; the incorporation of oxygen into inorganic sulphides; and (4). dissimilatory reduction: the removal of oxygen from sulphur compounds to ultimately produce H_2S, occurring under reducing conditions.

Sulphur isotopes as tracers of biogeochemical cycling

Input values from bulk atmospheric sulphate deposition represent a mixture of sources, each with characteristic δ^{34}S values. Upper limits are close to +21 ‰, representative of primary sea-salt aerosols (Rees et al. 1978). The lower end-member compositions are less well defined but are typically present as biogenic emissions of gaseous organic sulphur formed through the decomposition of organic matter under reducing conditions (Nriagu et al. 1987), or as biogenic H_2S arising from dissimilatory sulphate reduction. Bulk isotopic values from incoming precipitation may then be modified through microbiological activity in the soil and epikarst and cycling through vegetation. Processes of inorganic adsorption/desorption will affect the flux of sulphur compounds through the soil and groundwater systems (e.g. Nodvin et al. 1986), but do not cause isotopic fractionation (Van Stempvoort et al. 1990). Under oxidising conditions, microbial fractionation of sulphur isotopes is small, although the influence of assimilation and mineralisation is frequently reported to demonstrate a slight preference for incorporation of ^{32}S into the reaction products (Mitchell et al. 2001; Krouse et al. 1991; Thode 1991). Net uptake (assimilation) of sulphate by plants typically leaves soil sulphate solutions slightly enriched in ^{34}S (Zhang et al. 1998; Skrzypek et al. 2010). If plants utilize a sulphur source from deep groundwater, differences in isotopic composition between plant and surface waters may appear greater than the slight preference for ^{32}S quoted above (Bartlett et al. 2005; Coulson et al. 2005). Where inorganic sulphide oxidation is present, product sulphur compounds retain values close to the source sulphide value (Toran and Harris 1989), typically depleted in ^{34}S (e.g. Bottrell et al. 2000; Gunn et al. 2006; Han and Liu 2004). Dissolved organo sulphur compounds display variable sulphur isotopic composition depending upon sulphur source, which may then be re-oxidised/mineralised into the composite sulphate pool (Bartlett et al. 2005; Einsiedl et al. 2007; Bottrell et al. 2010). As a diagnostic tool for tracing sulphur biogeochemical cycling under well aerated conditions, sulphur isotopes undergo limited fractionation and thereby only provide limited insight into ecosystem functioning. Under reducing conditions however, sulphate is used as an oxidising agent in the metabolism of organic carbon. Dissimilatory sulphate reduction is widely recognised to impart strong fractionations to sulphur isotopes, leaving residual sulphate enriched in ^{34}S, and product sulphide ^{34}S depleted, thus forming a good indicator of aquifer redox status (e.g. Bottrell et al. 2000; Strebel et al. 1990; Spence et al. 2001). Mobilisation and re-oxidation of product sulphides can impart strong isotopic control on the composite sulphur pool with depth through a soil/aquifer profile (Bartlett et al. 2005; Einsiedl et al. 2007; Bottrell et al. 2010).

Sulphate oxygen isotopes as tracers of biogeochemical cycling

During mineralisation and oxidation, sulphur is oxidised to sulphate and oxygen isotopes are reset to reflect processes of biogeochemical cycling rather than precursor end member sources. Soil sulphate formed through mineralisation or oxidation, obtains four oxygen atoms from two isotopically distinct environments (atmospheric oxygen and ambient soil water), thereby re-setting the input isotopic signature depending upon source availability and stoichiometry of incorporation (Eq. 1).

$$\delta^{18}\text{O-SO}_4 = \left[\left(\delta^{18}\text{O}_{\text{atmO}_2} - \varepsilon_{\text{SO}_4-\text{atm}}\right) \times f_{\text{O}_2\text{atm}}\right] + \left(\delta^{18}\text{O}_{\text{water}} \times \left(1 - f_{\text{O}_2\text{atm}}\right)\right) \quad (1)$$

where $\varepsilon_{\text{SO}_4-\text{atm}}$ represents the isotopic enrichment associated with incorporation of molecular oxygen into sulphate and has an experimentally obtained value of −8.7 ‰ (Lloyd 1968). f_{O2} atm denotes the fraction of oxygen obtained from the atmosphere. Intermediate oxidation species between reduced sulphur and sulphate are susceptible to isotopic exchange with water, meaning the proportion of atmospheric oxygen incorporated in the final sulphate molecule (f_{O2} atm) is dependent upon a rate competition between oxidation and water oxygen isotopic exchange. Rates of exchange are thought to be determined by intermediate speciation, which is in turn controlled by pH (e.g. Balci et al. 2007). Only the final oxygen incorporated into the sulphate molecule therefore records a true signature of oxygen source. Based on experiments of abiotic pyrite oxidation, under high pH, aerobic conditions, rates of exchange are greater than rates of oxidation, meaning at least 75 % of the oxygen is derived through isotopic exchange. Under conditions of lower pH (<7), rates of oxidation frequently exceed those of exchange allowing a degree of oxygen source preservation and >25 % O_2 oxygen in the final sulphate molecule (Kohl and Bao 2011). For this reason, the oxygen isotopic composition of sulphate contained within many soils and groundwater fed streams derived by mineralization (e.g. Mayer et al. 1995; Shanley et al. 2005; Einsiedl and Mayer 2005; Einsiedl et al. 2007) or as oxidation products of pyrite (Gunn et al. 2006; Han and Liu 2004) display a distinctively clustered signature close to 0 ‰.

Where sulphate is reduced to sulphide, the remaining reactant pool of SO_4–O invariably becomes enriched in the heavier isotope. Whereas fractionation of sulphur during reduction is thought to be kinetic, oxygen within the residual sulphate pool is recognised to approach equilibrium with the surrounding groundwater at an advanced stage of reaction, with a temperature dependency such that at 5 °C, enrichment can be +29 ‰ if equilibrium is approached (Fritz et al. 1989). Where reactant pools of sulphate are small or isolated, and dissimilatory sulphate reduction is intense, total fractionation of sulphate sulphur may be limited, whilst progression of sulphate oxygen towards equilibrium with water can invoke extensive fractionation. Interpretation of sulphate oxygen from calcite speleothems has previously invoked this equilibrium fractionation in a case where overlying boulder clay had a control on the delivery of water to the speleothem forming drip (Wynn et al. 2008).

Methodology

Grotta di Ernesto site description

Grotta di Ernesto, is a shallow Alpine cave site located in NE Italy (1167 m. a.s.l., 45°58′37″N, 11°39′28″E). The cave is developed in dolomitize Jurassic limestone, overlain up-slope by well-bedded red and marly limestones. The dolomite host rocks in which the cave is cut do not contain any pyrite. The overlying Rosso Ammonitico Veronese and Biancone formations have been reported to contain traces of pyrite at other locations within the Dolomite region (Lukeneder 2011), although this has never been observed in samples obtained from above Ernesto cave. Given that fragments of these formations are apparent in the soils above the cave, there is the possibility that small amounts of pyrite may be present in the soil zone, contributing to the sulphur budget. The soil, up to 1 m thick, is a clay-rich calcareous brown soil (Rendzic Leptosol, pH 6.5–7.7) that supports a mixed conifer-deciduous forest, composed primarily of *Fagus sylvatica*, *Picea abies* and *Abies alba* (Fairchild et al. 2009; Miorandi et al. 2010; Frisia et al. 2011). The aquifer system has a dual porosity with a rapid fracture flow component that feeds fast-dripping stalactites in the central part of the cave, and a slower seepage flow through minor fissures and the porous limestone matrix (Miorandi et al. 2010). Drip rate characteristics reflect seasonality in aquifer recharge, which occurs primarily during the spring snowmelt (April to May) and autumn (October to November). Water infiltration deficits in winter and summer are related to frozen soil conditions and high evapotranspiration rates respectively (Miorandi et al. 2010).

Precipitation and soil water collection

Bulk precipitation was collected at two sites during the study period (May 2005 to February 2007) as monthly aggregate water samples. Throughout the two year period of monitoring, bulk precipitation was collected from Lavarone meteorological station, situated 30 km West from the cave site and at a similar elevation. From December 2005, these rainfall collections were duplicated at the cave site and found to be very similar in both isotopic composition and concentration. Both collectors were of an open design to collect bulk deposition and contained a layer of paraffin to prevent evaporation.

Soil waters were collected from two lysimeters installed directly above the cave site at a depth of about 0.7 m (installation June 2002). The lysimeters were put under vacuum at the beginning of each sampling period and water samples were extracted on a monthly basis as determined by water availability by means of a syringe attached to a capillary tube.

Drip site characteristics and sampling regime

Drip waters were collected from two sites within the cave representing flow pathways of contrasting hydrological characteristics. Drip site st-ER78 is located 30 m below the surface, emerging from a soda straw stalactite and formerly feeding stalagmite ER78 (Frisia et al. 2003; Borsato et al. 2007; Miorandi et al. 2010). Drip discharges are between 0.003 and 0.2 ml min^{-1}, with increased flow rates after recharge (‘Group 2—seasonal low drip’ following the classification of Miorandi et al. 2010). A component of fracture-fed flow is suggested by the rapid transmission of surface signals into the cave environment (Borsato et al. 2007; Frisia et al. 2008). Drip site st-1 is located just 20 m below the surface, feeds an active flowstone, and is characterised by a fast response to infiltration and high sensitivity to dry periods, but never completely dries up during even the most arid conditions (drip discharges between 0.007 and 44 ml min^{-1}, 'Group1—seasonal fast drip' following the classification of Miorandi et al. 2010). An inverse relationship between drip rate and conductivity (also seen through individual trace element ratios) is suggestive of dilution effects due to some degree of connectivity to external precipitation events (Borsato 1997; Fairchild et al. 2000; Huang et al. 2001; Miorandi et al. 2010). Such characteristics are suggestive of a predominant fracture flow and subordinate seepage flow through minor fissures and the porous limestone matrix. Fracture connectivity of both drip sites is deemed responsible for the transport of organic acids and colloids into the cave environment during autumn recharge events (Hartland et al. 2012), recorded as thin UV-fluorescent layers in speleothem calcite (ER78) (Frisia et al. 2003; Borsato et al. 2007). For st-ER78, collection bottles were positioned beneath the drip and replaced on a monthly basis, representing a monthly aggregated water sample. Flow rates at drip site st-1 were rapid enough to enable collection of a 1 l water sample during cave monitoring, thus representing an hourly aggregated sample. All samples were bottled and shipped to the UK for further analysis.

Laboratory based sulphate extraction

All water samples were filtered through 0.45 µm cellulose nitrate filter papers and aliquots removed for determination of major ions by ion chromatography (precision based on repeat analysis of reference standard material of comparable concentration to the samples being analysed was calculated as <5 %). Using sulphate concentration data obtained by ion chromatography, the volume of water required to obtain 350 µg of barium sulphate (the amount required for analysis by continuous flow isotope ratio mass spectrometry) was loaded onto a 1 ml volume of ion exchange resin (AG2-X8 and 50 W-X8 for anion and cation removal respectively). Anions were removed from the AG2-X8 resin using aliquots of 1 M Aristar grade HCl to a total volume of 1.5 ml and stored in micro-centrifuge tubes.

Sulphur concentration in carbonate bedrock samples collected from above the cave site (host dolomite and Rosso Ammonitico Veronese which both form a constituent of the overlying soil) was determined by high resolution inductively coupled plasma mass spectrometric analysis (HR-ICPMS) at Kingston University, UK, using 2 mg aliquots drilled from a fresh surface of the sample dissolved in 8 ml of 2 % HNO_3 (Aristar Grade). Depending upon concentration, larger aliquots of powder were drilled in preparation for sulphur isotope determination and digested in 1 ml of 4 M HCl (Aristar grade) following Wynn et al. (2008). Digested samples were filtered through 0.2 µm nylon filter capsules (puradisc, Whatman®) and stored in micro-centrifuge tubes.

The extraction of sulphate as barium sulphate was undertaken following methods outlined in Wynn et al. (2008). Addition of 0.2 ml 1 M $BaCl_2$ solution to resin eluents and digested carbonate bedrock samples enabled precipitation of sulphate as barium sulphate. Addition of similar quantities of quartz powder (Eurovector isotopic grade) was added to each sample to serve as an inert medium onto which barium sulphate could precipitate. Inert quartz powder also served to produce an excess of oxygen during combustion, thus buffering the oxygen composition of product SO_2 gas and overcoming any potential fractionation effects following Fry et al. (2002). Sulphate for $\delta^{18}O$ analysis was precipitated onto powdered glassy carbon as the inert medium, increasing the mass of product to enable sample handling, as well as providing an immediate supply of carbon. Samples were allowed to crystallise for approximately 72 h under refrigeration prior to centrifugation and repeated washing. Product pellets of barium sulphate/quartz powder and barium sulphate/glassy carbon powder were oven dried before transfer into tin or silver capsules for $\delta^{34}S$ and $\delta^{18}O$ analysis respectively.

Mass spectrometric analysis

$^{34}S/^{32}S$ and $^{18}O/^{16}O$ ratios of product barium sulphate were determined using a EuroVector elemental analyser linked to a GV Isoprime continuous flow mass spectrometer at the University of Birmingham following Wynn et al. (2008). Combustion of samples within tin capsules in the presence of vanadium pentoxide at 1,030 °C yielded SO_2 for determination of δ^{34}S-SO$_4$ and pyrolysis within silver capsules in the presence of nickelised carbon at 1,250 °C yielded CO for determination of δ^{18}O-SO$_4$. δ^{34}S values were corrected against CDT using within run analyses of international standard NBS-127 and SO5 (assuming δ^{34}S values of +20.3 and +0.5 ‰ respectively and δ^{18}O was corrected to VSMOW using NBS-127 and SO6 (assuming δ^{18}O values of +9.3 and –11.3 ‰ respectively). Within-run standard replication (1 SD) was <0.3 ‰ for both sulphur and oxygen isotope ratios. Procedural standard solutions of calcium sulphate precipitated as barium sulphate ($n = 12$; 0.3 ‰ 1 SD) following the above methods yielded mean δ^{34}S-SO$_4$ values within 0.3 ‰ of raw calcium sulphate powder ($n = 13$; 0.3 ‰ 1 SD). Sodium sulphate precipitated as barium sulphate ($n = 8$; 0.4 ‰ 1 SD) yielded mean δ^{18}O-SO$_4$ isotopic values within 0.4 ‰ of analyses obtained following the centrifuging method of pre-concentration under analogous acidified conditions ($n = 6$; 0.7 ‰ 1 SD).

Results

Sulphur concentrations and δ^{34}S-SO$_4$ values for each of the key study sites are compiled and presented within Fig. 1 and Table 1. δ^{34}S of precipitation ranges between −1.4 and +7.3 ‰ and samples contain low sulphur concentrations ranging between 162 and 864 ppb. Drip and soil water values demonstrate lower variability in isotopic composition throughout the two years of monitoring such that the seasonal input range of precipitation δ^{34}S (up to 8.7 ‰), is reduced in amplitude to 1.6 ‰ for soil waters and 2.0 and 0.8 ‰ for drip sites st-1 and st-ER78 respectively. These characteristics of isotopic homogenisation are well recognised at many cave sites, reflecting properties of storage and mixing along the drip water flow pathway. However, concentrations of S show an increase up to 1,500 ppb. All soil/drip water samples show clear distinction in sulphur isotopic composition from bedrock CAS (bedrock average δ^{34}S +19.7 ‰), and sulphate concentrations within soil and drip waters comprise an average of just 2.1 % of sulphate sourced from the surrounding bedrock (calculated using ratios to calcium following methods in Wynn et al. 2008), confirming minimal impact of bedrock dissolution upon the sulphur concentration and isotopic composition of soils and drip waters. SO$_4$/Cl ratios show limited evidence for evapoconcentration within the soil zone or along the drip water flow path feeding site st-1, suggesting the increase in sulphur concentration with depth is due to an additional sulphur source more depleted in ^{34}S compared to that found in the soil zone (+4.7 ‰ average soil δ^{34}S-SO$_4$, +3.3 ‰ average st-1 δ^{34}S-SO$_4$). However, drip site st-ER78 demonstrates sulphate concentrations which are disproportionate to (less than) those expected from ratios to chloride, invoking a more complex set of biogeochemical processes despite similar δ^{34}S-SO$_4$ values to those at site st-1.

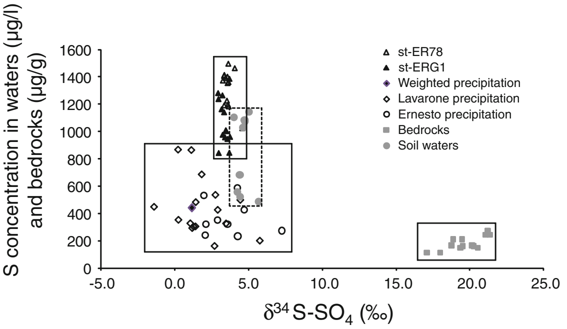

Fig. 1 Sulphur concentrations and δ^{34}S-SO$_4$ values in cave seepage waters and atmospheric precipitation at Grotta di Ernesto

Whilst δ^{18}O-SO$_4$ precipitation values range between +6.6 and +37.4 ‰, a distinct shift in isotopic composition is apparent between atmospheric precipitation and drip/soil waters (range +0.8 to +10.9 ‰) (Fig. 2; Table 1). Soil waters, and drips st-1 and st-ER78 display individual δ^{18}O-SO$_4$ compositions which reveal a complex suite of site specific biogeochemical processes supported by those invoked through changes in δ^{34}S.

Discussion

Sulphur biogeochemical cycling through forest soils is largely understood to be a product of vegetative cycling, source mixing, and microbial isotopic fractionation. However, the chemical signature of many of these processes may be overprinted before point of emergence as cave drip waters, depending upon hydrological dynamics within the epikarst. In the following discussion, we draw on knowledge from the fields of cave hydrology and sulphur biogeochemistry to build an appreciation of the speleothem sulphur

Table 1 Sulphur concentration and isotope characteristics of cave waters and bedrocks

Sample type	*n* =	[S] (μg/l)	Cl^- (ppm)	SO_4^{2-}/Cl^-	$\delta^{34}S-SO_{4\ CDT}$ (‰)	$\delta^{18}O-SO_4\ V_{SMOW}$ (‰)
Precipitation	17	447 (162–867)	0.83	2.05	+2.5 (−1.4 to +7.3)	20.4 (6.7–37.4)
Soil water	11	788 (450–1,142)	0.75	4.07	4.7 (4.0 to 5.7)	1.5 (0.8–2.1)
st-1	16	1,060 (842–1,387)	0.71	4.59	3.3 (3.0 to 4.6)	4.3 (2.9–5.7)
st-ER78	14	1,350 (1,181–1,495)	1.22	3.40	3.6 (3.3 to 4.1)	7.4 (2.8–10.9)
Ernesto bedrocks	14	187 (113–269)	–	–	19.7 (17.1 to 21.4)	–

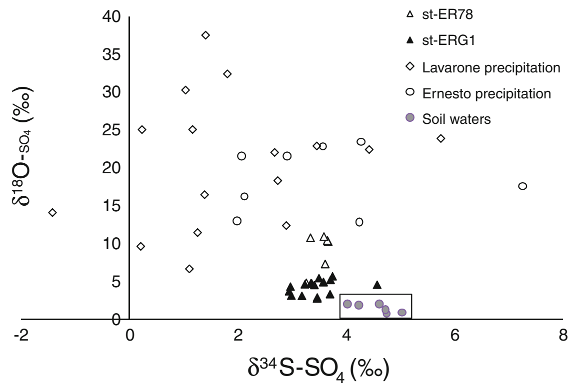

Fig. 2 $\delta^{18}O-SO_4$ and $\delta^{34}S-SO_4$ values in cave seepage waters and atmospheric precipitation at Grotta di Ernesto

archive as an end product of a complex hydrological system and biogeochemical cycle.

Interpreting the sulphur biogeochemical cycle at Ernesto cave

Precipitation input

The sulphur isotopic composition of sulphate contained within input precipitation at Ernesto cave ranges between −1.4 and +7.3 ‰ (weighted mean value = +1.2 ‰; concentration range 162–867 ppb; weighted mean concentration= 423 ppb). This falls within the range of values considered to be indicative of European pollution (−3 to +9 ‰; Mayer, 1998), and supports the work of Gabrielli et al. (2006), suggesting the Eastern Italian Alps to receive a high input of atmospheric sulphate deposition sourced from anthropogenic emissions (reported mean concentration in Italian Alpine snow= 530 ppb). The alpine region in which Grotta di Ernesto is located thereby appears to receive a significant input of sulphur from industrial activity and road traffic within the nearby Valsugana and Po valley. This is likely facilitated by strong vertical air mixing, enabling transport of anthropogenic pollution up to approximately 4,000 m altitude (Gabrielli et al. 2006).

Soil and epikarst processes

Concentrations of sulphur within cave drip and soil waters are increased compared to those in precipitation and are accompanied by $\delta^{34}S$ values which converge into a much narrower range of values (+3.0 to +4.6 ‰ for cave drip waters and +4.0 to +5.7 ‰ for soil waters). Such isotopic convergence in both soil and epikarst zones are typical of many cave hydrological studies addressing dynamics of $\delta^{18}O/^{2}H-H_2O$ and indicate variability in residence time due to mixing between pools and groundwater stores (e.g. Chapman et al. 1992; Kluge et al. 2010).

A shift in $\delta^{34}S$ between the weighted precipitation signal (+2.5 ‰) and soil water values (+4.7 ‰) (Fig. 1), would suggest biological activity as the fractionating and concentrating mechanism in the soil zone (SO_4/Cl ratios provide no evidence for evapo-concentration, and sulphate contribution from bedrock dissolution is calculated as just 2.1 %). Biological utilisation of sulphate through assimilatory reduction into plant tissues typically preferentially utilises ^{32}S, leaving behind a soil solution enriched in ^{34}S by approximately 1–2 ‰ (Krouse et al. 1991). Providing the current overall trend is one of net sulphur removal from the soil zone through assimilation, remaining soil waters may be enriched in ^{34}S (Zhang et al. 1998). Soil waters demonstrate increased concentrations compared to precipitation input due to dynamics of inorganic sulphate adsorption/desorption dependent upon pH, and the large available pool of organic matter, which adds to the soil sulphate pool through processes of mineralisation (Fig. 3, Pathway A). The presence of trace amounts of pyrite within the soil zone, sourced from the Rosso Ammonitico Veronese

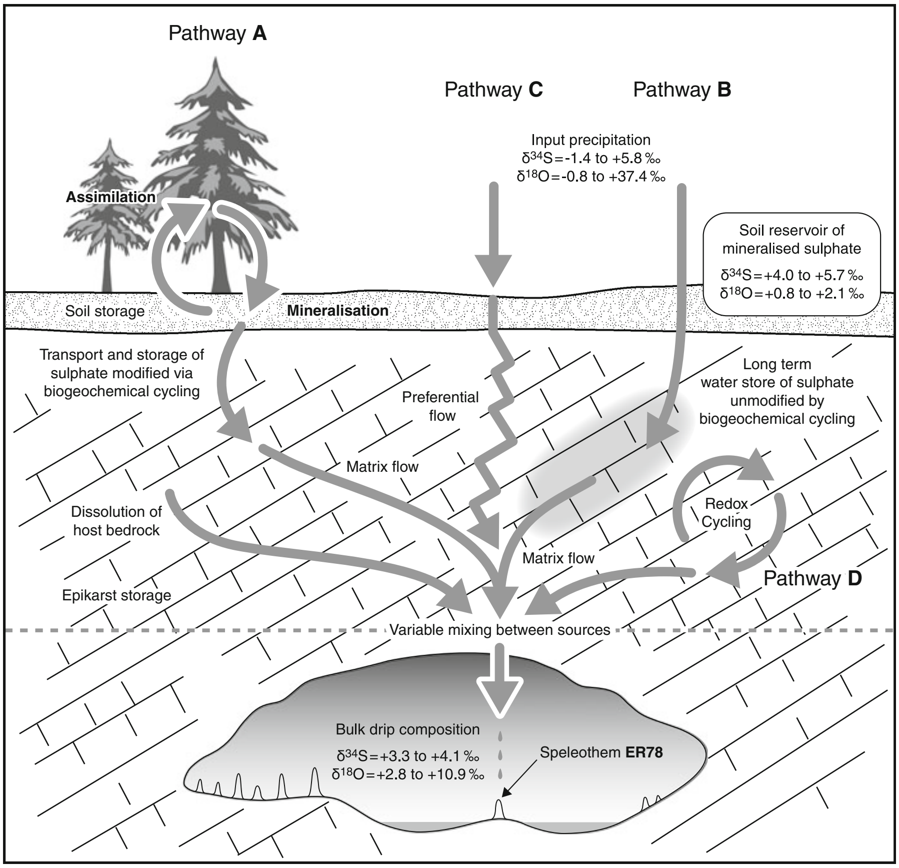

Fig. 3 Conceptual model of sulphur acquisition in the Grotta di Ernesto system. Sulphur sourced from atmospheric deposition may be biogeochemically modified prior to entering the epikarst (*Pathway A*); be transmitted rapidly with an unmodified signature into the karst via fracture flow (*Pathway B*); enter with an unmodified signature if the relative significance of biogeochemical cycling is diminished during times of high sulphate deposition (*Pathway C*); or be subjected to intense redox cycling within the epikarst (*Pathway D*). Each drip site within the cave represents a unique mix of all pathways. Drip site st-ER78 featured here draws most sulphate from a matrix based reservoir of sulphate emplaced during times of high SO_2 loading to the atmosphere, followed a component of intense redox cycling

and Biancone formations cannot be discounted (Lukeneder 2011). However, based on isotopic compositions of sulphur being more enriched in ^{34}S in the soil zone, oxidation of pyrite seems an unlikely source of sulphur to explain the concentration increase and associated isotopic shift.

Further increase in sulphur concentration between point of soil water extraction and emergence in the cave chamber as drip water is accompanied by a shift to a lower (^{34}S depleted) and more homogenised sulphur isotopic composition than apparent in the soil (Fig. 1). This suggests the soil zone is not buffered as well as the deeper epikarst. There are three possible mechanisms for driving sulphur isotopes towards lower values at depth within the epikarst beyond the soil zone: (1). further mixing with long residence time water of lower sulphur isotopic composition and greater concentration at depth within the karst aquifer; (2). acquisition of additional sulphate from sulphide oxidation; (3). internal re-oxidation of organo sulphur compounds formed by the incorporation of H_2S from bacterial sulphate reduction into dissolved organic material. Any additional component of long term ground water storage containing a greater proportion of sulphur is likely sourced from industrial activity and emplaced in the karst aquifer during times of high SO_2 emissions to the atmosphere (cf. Frisia et al. 2005). At high deposition rates in Europe (15–120 kg S ha^{-1} $year^{-1}$) (Alewell, 2001), the relative contribution of biological sulphur turnover is diminished, thereby increasing the importance of inorganic adsorption/desorption dynamics in controlling the flux of atmospheric sulphate straight into the seepage water/ground water system (Alewell, 2001; Prechtel et al. 2001). In soils on karst bedrock where pH may be high enough to minimise processes of adsorption, this will likely encourage a large flux of sulphate straight into epikarst storage. Whilst there is a lack of mineral sulphide observed within the dolomite bedrock, oxygen isotopic values of sulphate in cave drip waters further preclude consideration of sulphide oxidation or also the re-oxidation of organo-sulphur compounds into the composite sulphate pool .

The hydrology of drip site st-1 which is characteristic of a predominant fracture fed system and subordinate seepage flow through minor fissures and the porous limestone matrix (fast drip rate, responding rapidly to surface climate, but never completely drying up) (Miorandi et al. 2010), is consistent with a lesser degree of sulphur isotopic homogenisation compared to drip site st-ER78 and suggests the composite sulphur signal to be obtained in varying proportions from Pathways A–C in Fig. 3. At drip site st-ER78, chloride concentrations are increased compared to those in the soil waters suggesting evapoconcentration (assuming chloride to be a conservative tracer) between point of soil water extraction and drip water collection. Sulphate concentration data and isotopic values are less variable, and hydrological characteristics support a model where sulphur sources are obtained from Pathways A–C, but a greater proportion of seepage flow through minor fissures and the porous limestone matrix leads to greater signal homogenisation than at site st-1.

Overall, sulphur isotopes suggest a two-step acquisition of sulphur during passage through the karst: (1) concentration enhancement and ^{34}S-enrichment in the soil zone through storage, assimilation and mineralisation; and (2) further sulphur acquisition at depth within the epikarst of an ^{34}S depleted source, possibly sourced from a ground water storage component emplaced during times of high industrial SO_2 emissions.

Interpreting sulphate–oxygen isotopes within the sulphur biogeochemical cycle at Ernesto cave

Precipitation input

The oxygen isotopic composition of sulphate within incoming precipitation has values ranging between +6.7 and +37.4 ‰ and lies within the range of published values (see compilation of published values in Jamieson and Wadleigh 1999; Jenkins and Bao 2006), representing a mixture of primary aerosol sourced from industrial activity and secondary aerosol from gaseous SO_2 oxidation in the atmosphere (Table 1 ; Fig. 2). Sulphate-oxygen isotopic values enriched in ^{18}O indicate a high proportion of primary sulphate aerosol sourced directly from industrial activity (Holt et al. 1982), most likely due to the close proximity of the Valsugana and Po valley. Lower isotopic values are almost purely of secondary aerosol origin, following equilibration of sulphoxy intermediate species with meteoric δ^{18}O and further oxidation to sulphate (Holt and Kumar 1991).

Soil and epikarst processes

Whilst ultimately sourced from atmospheric precipitation, cave drip and soil waters demonstrate a large shift in δ^{18}O-SO_4 values ranging between +0.8 and +2.1 ‰ for soil waters and +2.8 to +10.9 ‰ for drip waters. Oxidation of sulphide minerals, H_2S, and the mineralisation of carbon-bonded sulphur to sulphate under oxidising conditions in the soil zone are the only known processes capable of effecting such a large scale shift in oxygen isotopic composition. During this process, reduced sulphur (either carbon bonded sulphur released from decaying vegetation, H_2S, or sourced from pyrite) is oxidised, incorporating oxygen from O_2 and water in variable proportions. This depends upon pH and reaction time, but typically utilises up to three oxygen atoms from the surrounding soil water. Deviations from this value are dependent upon rate competition between isotopic exchange and oxidation (Kohl and Bao 2011). Given the observed enrichment in ^{34}S between weighted precipitation and soil waters, not depletion as would be expected from sulphide oxidation, soil waters appear to contain sulphate which has either been transformed through at least one cycle of biological assimilative reduction and re-mineralisation (Fig. 3. Pathway A).

Cave drip waters have δ^{18}O-SO_4 isotopic values enriched in ^{18}O compared to those in soil waters. There are three ways in which δ^{18}O-SO_4 isotopic values may become enriched in ^{18}O at depth within the karst aquifer, referred to as pathways B–D in Fig. 3 and explained as follows:

- Pathway B; Drip water sulphur isotopes depleted in ^{34}S compared to those in extracted soil waters dictate that stored water within the karst aquifer may have been emplaced during earlier conditions of high sulphur loading to the atmosphere when the relative contribution of biological sulphur turnover is diminished. In soils on karst bedrock where pH may be high enough to minimise processes of adsorption, this will likely encourage a large flux of atmospheric sulphate with high δ^{18}O-SO$_4$ straight into epikarst storage.
- Pathway C: Rapid routing of surface water via fracture flow into the cave chamber may supply δ^{18}O-SO$_4$ of atmospheric composition.
- Pathway D: intense sulphur cycling between reducing and oxidising conditions can demonstrate little effect upon δ^{34}S, but cause δ^{18}O-SO$_4$ to move towards equilibrium with the surrounding water.

Variability in mixing between all three sulphate sources comprising high δ^{18}O-SO$_4$ depends upon hydrological dynamics and appears as a difference in SO$_4$-O isotopic values between the two drip sites. Drip site st-1 (range = +2.6 to +5.7 ‰) represents values typical of those reported in the literature for partial mineralisation of organic S to sulphate (e.g. Einsiedl and Mayer 2005). This reflects a large proportion of sulphate to be sourced from biogeochemical cycling (Fig. 3, Pathway A, calculated as 88 % based on SO$_4$/Cl ratios in soil waters), and minor components (22 %) to be obtained from unadulterated sulphate, either within storage within the epikarst (Fig. 3, Pathway C), or as fracture delivery of contemporary event water (Fig. 3, Pathway B). Closure of the isotope balance model indicates this isotopic end member (either pathway B or C) to be approximately +14 ‰. However, at drip site st-ER78, waters have a much greater range of sulphate oxygen isotope values (range = +2.8 to +10.9 ‰). Chloride concentrations are increased compared to those in the soil waters suggesting evapoconcentration (assuming chloride to be a conservative tracer). However, SO$_4$/Cl ratios are lower than those of soil waters, suggestive of net sulphate loss rather than acquisition from epikarst processes. Intense sulphur redox cycling causing sulphate–oxygen values to move towards values in equilibrium with surrounding matrix water are suggested to explain this isotopic increased in ^{18}O, concurrent with sulphate concentration out of proportion with expected ratios to chloride. Hydrological characteristics (matrix fed seepage flow) suggest only minor influence from fracture flow delivering precipitation direct to the drip site consistent with the limited range in sulphur isotope values (Fig. 3, Pathway C). Both δ^{34}S-SO$_4$ and δ^{18}O-SO$_4$ isotope dynamics at these two drip sites, suggest more of the water feeding drip site st-1 is sourced directly from the soil zone, whereas that from drip site st-ER78 undergoes intense redox cycling. Both drips are subject to variable degrees of mixing with long term storage water and fracture delivery events.

Implications for interpreting the archived signal in stalagmite ER78

Drip sites st-1 and st-ER78 at the Ernesto cave site undergo a two stage modification to sulphur dynamics through biogeochemical cycling and aquifer mixing (Fig. 3). Despite a common sulphur input, vegetation composition, and soil structure, variability in aquifer properties and redox status render each drip site unique in terms of sulphate signatures delivered to the cave environment. Mixing seems to occur between three sulphate sources of variable age and isotopic composition. These can be identified as (1) sulphate which has been biogeochemically modified through the processes of assimilation and mineralisation (Fig. 3, Pathway A), (2) sulphate which enters the karst by fracture flow on an event basis (Fig. 3, Pathway C), and (3) sulphate which entered the karst aquifer directly during times of high sulphur deposition (Fig. 3, Pathway B). Karst hydrology and redox status then determines the degree of mixing between sources and isotopic characteristics imparted to each drip site. The sulphur contained within recipient stalagmites (specifically stalagmite ER78), is therefore representative of not only atmospheric sulphur provenance, but the signature is complicated through biogeochemical cycling and mixing with older sources of sulphur contained within the karst aquifer. The ultimate determinant of signal delivery is hydrological flow pathway. Stalagmite ER78 (analysed at high resolution by SIMS ion microprobe for δ^{34}S in Wynn et al. 2010) grew beneath the st-ER78 drip site analysed as a part of this paper. The speleothem archive is interpreted to closely approximate SO$_2$ loading to the atmosphere, despite the acknowledged

15 year lag between peak emissions in the atmosphere and signal capture in the stalagmite (Frisia et al. 2005). The lag at this site can now be understood to predominantly be a product of biogeochemical cycling through vegetation and mixing with long term storage in the karst reservoir. Under these conditions, the sulphur isotopic composition of speleothem ER78 is deemed to closely represent atmospheric sulphur loading when aquifer and biological retention is taken into account.

Conclusion

In karst environments, sulphur reaching the cave system prior to incorporation into the speleothem record must be interpreted in light of modification to any input signal. This follows a three component model of concentration change and isotopic fractionation and can be summarised as (1) biogeochemical cycling, (2) hydrological mixing and (3) redox status of the soil and epikarst. At any one time, all three processes work together to determine the unique sulphur signals in the drip waters and associated speleothems. In the case of Ernesto cave, two drips (st-1 and st-ER78) are demonstrated to respond differently to a common sulphur input. Sulphur inputs are concentrated and isotopically modified through initial biogeochemical modification in the vegetation and soil zone, and subsequent attenuation and mixing with a stored groundwater component. δ^{34}S-SO$_4$ and δ^{18}O-SO$_4$ analysis has confirmed the interpretation of sulphur dynamics in stalagmite ER78 (Frisia et al. 2005; Wynn et al. 2010) as recording a composite atmospheric signal, delayed by approximately 15 years between point of atmospheric deposition and incorporation into speleothem calcite. Isotopic analysis of sulphate within the karst environment is a profound indicator of ecosystem and aquifer properties, of which a full understanding is essential for speleothem palaeoclimate and groundwater studies.

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References

Alewell C (2001) Predicting reversibility of acidification: the European sulfur story. Water Air Soil Pollut 130:1271–1276

Alewell C, Mitchell MJ, Likens GE, Krouse HR (1999) Sources of stream sulphate at the hubbard brook experimental forest: long term analyses using stable isotopes. Biogeochemistry 44(3):281–299

Balci N, Shanks WC III, Mayer B, Mandernack KW (2007) Oxygen and sulphur isotope systematics of sulphate produced by bacterial and abiotic oxidation of pyrite. Geochim Cosmochim Acta 71:3796–3811

Bartlett R, Bottrell S, Coulson J (2005) Behaviour of sulphur during diagenesis of a maritime ombotrophic peat from Yell, Shetland Islands, UK. Appl Geochem 20:1597–1605

Borsato A (1997) Drip water monitoring at Grotta Di Ernesto (NE Italy): a contribution to the understanding of karst hydrology and the kinetics of carbonate dissolution. In: 6th conference on limestone hydrology and fissured media, La Chaux-de-fonds, Switzerland, 1997, proceedings, vol 2, 57–60

Borsato A, Frisia S, Fairchild IJ, Somogyi A, Susini J (2007) Trace element distribution in annual stalagmite laminae mapped by micrometer resolution X-ray fluorescence: implications for incorporation of environmentally significant species. Geochim Cosmochim Acta 71:1494–1512

Bottrell SH, Moncaster SJ, Tellam JH, Lloyd JW, Fisher QJ, Newton R (2000) Controls on bacterial sulphate reduction in a dual porosity aquifer system: the Lincolnshire limestone aquifer, England. Chem Geol 169:461–470

Bottrell SH, Hatfield D, Bartlett R, Spence MJ, Bartle KD, Mortimer RJG (2010) Concentrations, sulphur isotopic compositions and origin of organosulfur compounds in pore waters of a highly polluted raised peatland. Org Geochem 41:55–62

Bradley C, Baker A, Jex CN, Leng MJ (2010) Hydrological uncertainties in the modelling of cave drip-water δ^{18}O and the implications for stalagmite palaeoclimate reconstructions. Quatern Sci Rev 29:2201–2214

Chapman JB, Ingraham NL, Hess JW (1992) Isotopic investigation of infiltration and unsaturated zone processes at Carslbad cavern, New Mexico. J Hydrol 133:343–363

Coulson JP, Bottrell SH, Lee JA (2005) Recreating atmospheric sulphur deposition histories from peat stratigraphy: diagenetic conditions required for signal preservation and reconstruction of past sulphur deposition in the Derbyshire Peak District, UK. Chem Geol 218:223–248

Einsiedl F, Mayer B (2005) Sources and processes affecting sulphate in a karstic groundwater system of the Franconian Alb, Southern Germany. Environ Sci Technol 39:7118–7125

Einsiedl F, Schäfer T, Northrup P (2007) Combined sulphur K-edge XANES spectroscopy and stable isotope analyses of fulvic acids and groundwater sulphate identify sulphur cycling in a karstic catchment area. Chem Geol 238:268–276

Einsiedl F, Maloszewski P, Stichler W (2009) Multiple isotope approach to the determination of the natural attenuation potential of a high-alpine karst system. J Hydrol 365:113–121

Fairchild IJ, Treble PC (2009) Trace elements in speleothems as recorders of environmental change. Quatern Sci Rev 28(5–6):449–468

Fairchild IJ, Borsato A, Tooth AF, Frisia S, Hawkesworth CJ, Huang Y, McDermott F, Spiro B (2000) Controls on trace element (Sr-Mg) compositions of carbonate cave waters: implications for speleothem climatic records. Chem Geol 166:255–269

Fairchild IJ, Smith CL, Baker A, Fuller L, Spötl C, Mattey D, McDermott F, EIMF (2006a) Modification and preservation of environmental signals in speleothems. Earth Sci Rev 75:105–153

Fairchild IJ, Tuckwell GW, Baker A, Tooth AF (2006b) Modelling of dripwater hydrology and hydrogeochemistry in a weakly karstified aquifer (Bath, UK): implications for climate change studies. J Hydrol 321:213–231

Fairchild IJ, Loader N, Wynn PM, Frisia S, Thomas PA, Lageard JGA, Momi A, Hartland A, Borsato A, LaPorta N, Susini J (2009) Sulphur fixation in wood mapped by synchrotron X-ray studies: implications for environmental archives. Environ Sci Technol 43(5):1310–1325

Frisia S, Borsato A, Preto N, McDermott F (2003) Late Holocene annual growth in three Alpine stalagmites records the influence of solar activity and the North Atlantic Oscillation on winter climate. Earth Planet Sci Lett 216:411–424

Frisia S, Borsato A, Fairchild IJ, Susini J (2005) Variations in atmospheric sulphate recorded in stalagmites by synchrotron micro-XRF and XANES analyses. Earth Planet Sci Lett 235:729–740

Frisia S, Borsato A, Susini J (2008) Synchrotron radiation applications to past volcanism archived in speleothems: an overview. J Vulcanol Geotherm Res 177(1):96–100

Frisia S, Fairchild IJ, Fohlmeister J, Miorandi R, Spötl C, Borsato A (2011) Carbon mass-balance modeling and carbon isotope exchange processes in dynamic caves. Geochim Cosmochim Acta 75:380–400

Fritz P, Basharmal GM, Drimmie RJ, Ibsen J, Qureshi RM (1989) Oxygen isotope exchange between sulphate and water during bacterial reduction of sulphate. Chem Geol (Isotope Geoscience) 79:99–105

Fry B, Silva SR, Kendall C, Anderson RK (2002) Oxygen isotope corrections for online δ^{34}S analysis. Rapid Commun Mass Spectrom 16:854–858

Gabrielli P, Cozzi G, Torcini S, Cescon P, Barbante C (2006) Source and origin of atmospheric trace elements entrapped in winter snow of the Italian eastern Alps. Atmospheric Chemistry and Phys.Discussions 6:8781–8815

Gunn J, Bottrell SH, Lowe DJ, Worthington SRH (2006) Deep groundwater flow and geochemical processes in limestone aquifers: evidence from thermal waters in Derbyshire, England, UK. Hydrogeol J 14:868–888

Han GL, Liu CQ (2004) Water geochemistry controlled by carbonate dissolution: a study of the river waters draining karst-dominated terrain, Guizhou Province, China. Chem Geol 204:1–21

Hartland A, Fairchild IJ, Lead JR, Borsato A, Baker A, Frisia S, Baalousha M (2012) From soil to cave: transport of trace metals by natural organic matter in dripwaters. Chem Geol 304:68–82

Holt BD, Kumar R (1991) Oxygen isotope fractionation for understanding the sulphur cycle. In: Krouse HR, Grinenko VA (eds) Stable isotopes: natural and anthropogenic sulphur in the environment, vol 43. SCOPE/Wiley, New York, pp 27–41

Holt BD, Kumar R, Cunningham PT (1982) Primary sulphates in atmospheric sulphates: estimation in oxygen isotope ratio measurements. Science 217:51–53

Huang Y, Fairchild IJ, Borsato A, Frisia S, Cassidy N, McDermott F, Hawkesworth CJ (2001) Seasonal variations in Sr, Mg and P in modern speleothems (Grotta di Ernesto, Italy). Chem Geol 175:429–448

Jamieson RE, Wadleigh MA (1999) A study of the oxygen isotopic composition of precipitation sulphate in Eastern Newfoundland. Water Air Soil Pollut 110:405–420

Jenkins KA, Bao H (2006) Multiple oxygen and sulphur isotope compositions of atmospheric sulphate in Baton Rouge, LA, USA. Atmos Environ 40:4528–4537

Kluge T, Reichelmann DFC, Wieser M, Spötl C, Sültenfuß J, Schröder-Ritzrau A, Niggemann S, Aeschbach-Hertig W (2010) Dating cave dripwater by tritium. J Hydrol 394: 396–406

Kohl L, Bao H (2011) Triple-oxygen-isotope determination of molecular oxygen incorporation in sulphate produced during abiotic pyrite oxidation (pH=2–11). Geochim Cosmochim Acta 75:1785–1798

Krouse HR, Stewart JWB, Grinenko VA (1991) Pedosphere and biosphere. In: Krouse HR, Grinenko VA (eds) Stable isotopes in the assessment of natural and anthropogenic sulphur in the environment. SCOPE/Wiley, New York, pp 267–306

Likens GE, Driscoll CT, Buso DC, Michell MJ, Lovett GM, Bailey SW, Siccama TG, Reiners WA, Alewell C (2002) The Biogeochemistry of sulphur at Hubbard Brook. Biogeochemistry 50:235–316

Lloyd RM (1968) Oxygen isotope behaviour in the sulphate-water system. J Geophys Res 73:6099–6110

Lukeneder A (2011) The Biancone and Rosso Ammonitico facies of the northern Trento Plateau (Dolomites, Southern Alps, Italy). Annals of the natural history museum. Wien. Series A 113:9–33

Mayer B. (1998) Potential and limitations of using sulphur isotope abundance ratios as an indicator for natural and anthropogenic induced environmental change. In: Isotope techniques in the study of environmental change. Proceedings of an international conference in Vienna, Austria. 14–18th April 1997 IAEA, Vienna, Austria, pp 423–435

Mayer B, Fritz P, Prietzel J, Krouse HR (1995) The use of stable sulphur and oxygen isotope ratios for interpreting the mobility of sulphate in aerobic forest soils. Appl Geochem 10:161–173

Miorandi R, Borsato A, Frisia S, Fairchild IJ, Richter DK (2010) Epikarst hydrology and implications for stalagmite capture of climate changes at Grotta di Ernesto (NE Italy): results from long-term monitoring. Hydrol Process 24(21): 3101–3114

Mitchell MJ, Krouse HR, Mayer B, Stam AC, Zhang Y (1998) Use of stable isotopes in evaluating sulphur biogeochemistry of forest ecosystems. In: Kendall C, McDonnell JJ (eds) Isotope tracers in catchment hydrology. Elsevier, Amsterdam, pp 489–518

Mitchell MJ, Mayer B, Bailey SW, Hornbeck JW, Alewell C, Driscoll CT, Likens GE (2001) Use of stable isotope ratios for evaluating sulphur sources and losses at the Hubbard Brook experimental forest. Water Air Soil Pollut 130:75–86

Mitchell MJ, Lovett G, Bailey S, Beall F, Burns D, Buso D, Clair TA, Courchesne F, Duchesne L, Eimers C, Fernandez I, Houle D, Jeffries DS, Likens GE, Moran MD, Rogers C, Schwede D, Shanley J, Weathers KC, Vet R (2011) Comparisons of watershed sulphur budgets in southeast Canada and northeast US: new approaches and implications. Biogeochemistry 103:181–207

Nodvin SC, Driscoll CT, Likens GE (1986) The effect of pH on sulfate adsorption by a forest soil. Soil Sci 142:69–75

Novak M, Mitchell MJ, Jackova I, Buzek F, Schweigstillova J, Erbanova L, Prikryl R, Fottova D (2007) Processes affecting oxygen isotope ratios of atmospheric and ecopsystem sulphate in two contrasting forest catchments in central Europe. Environ Sci Technol 41:703–709

Nriagu JO, Holdway DA, Coker RD (1987) Biogenic sulfur and the acidity of rainfall in remote areas of Canada. Science 237:1189–1192

Prechtel A, Alewell C, Armbruster M, Bittersohl J, Cullen JM, Evans CD, Helliwell R, Kopácek J, Marchetto A, Matzner E, Meesenburg H, Moldan F, Moritz K, Veselý J, Wright RF (2001) Response of sulphur dynamics in European catchments to decreasing sulphate deposition. Hydrol Earth Syst Sci 5(3):311–325

Rees CE, Jenkins WJ, Monster J (1978) The sulphur isotopic composition of ocean water sulphate. Geochim Cosmochim Acta 42(4):377–381

Shanley JB, Mayer B, Mitchell MJ, Michel RL, Bailey SW, Kendall C (2005) Tracing sources of streamwater sulphate using S and O isotope ratios of sulphate and ^{35}S activity. Biogeochemistry 76:161–185

Skrzypek G, Jezierski P, Szynkiewicz A (2010) Preservation of primary isotope signatures of peat-forming plants during early decomposition–observation along an altitudinal transect. Chem Geol 273:238–249

Spence MJ, Bottrell SH, Thornton SF, Lerner DN (2001) Isotopic modelling of the significance of sulphate reduction for phenol attenuation in a polluted aquifer. J Contam Hydrol 53:285–304

Strebel O, Böttcher J, Fritz P (1990) Use of isotope fractionation of sulfate-sulfur and sulfate-oxygen to assess bacterial desulfurication in a sandy aquifer. J Hydrol 121:155–172

Thode HG (1991) Sulphur isotopes in nature and the environment: an overview. In: Krouse HR, Grinenko VA (eds) Stable isotopes in the assessment of natural and anthropogenic sulphur in the environment. SCOPE/Wiley, New York, pp 267–306

Toran L, Harris RF (1989) Interpretation of sulphur and oxygen isotopes in biological and abiological sulfide oxidation. Geochim Cosmochim Acta 53:2341–2348

Van Stempvoort DR, Reardon EJ, Fritz P (1990) Fractionation of sulphur and oxygen isotopes in sulphate by soil sorption. Geochim Cosmochim Acta 54:2817–2826

Williams PW (2008) The role of the epikarst in karst and cave hydrogeology: a review. Int J Speleol 37(1):1–10

Wynn PM, Fairchild IJ, Baker A, Frisia S, Borsato A, Baldini J, McDermott F (2008) Isotopic archives of sulphur in speleothems. Geochim Cosmochim Acta 72:2465–2477

Wynn PM, Fairchild IJ, Frisia S, Spötl C, Baker A, Borsato A, EIMF (2010) High-resolution sulphur isotope analysis of speleothem carbonate by secondary ionisation mass spectrometry. Chem Geol 271:101–107

Zhang Y, Mitchell MJ, Christ M, Likens GE, Krouse RH (1998) Stable sulphur isotopic biogeochemistry of the Hubbard Brook Experimental Forest, New Hampshire. Biogeochemistry 41:259–275