



High-resolution sulphur isotope analysis of speleothem carbonate by secondary ionisation mass spectrometry

Peter M. Wynn^{a,*}, Ian J. Fairchild^a, Silvia Frisia^b, Christoph Spötl^c, Andy Baker^{a,2}, Andrea Borsato^d
EIMF^e

^a School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, Edgbaston, B15 2TT, UK

^b School of Environmental and Life Sciences, The University of Newcastle, Callaghan, New South Wales, Australia

^c Institut für Geologie und Paläontologie, Leopold-Franzens-Universität Innsbruck, Innrain 52, 6020 Innsbruck, Austria

^d Museo Tridentino di Scienze Naturali, via Calepina 14, 38100 Trento, Italy

^e Edinburgh ion microprobe facility, Institute of Earth Science, School of Geosciences, University of Edinburgh, EH9 3JW, UK

ARTICLE INFO

Article history:

Received 13 March 2009

Received in revised form 28 December 2009

Accepted 6 January 2010

Editor: J.D. Blum

Keywords:

Sulphur isotopes

Secondary Ionisation Mass Spectrometry

Speleothem

ABSTRACT

Sulphur emitted into the atmosphere from industrial activity is regarded as a key mechanism in forcing recent climate and has impacts upon the environment and human health at both local and regional scales. Trace amounts of sulphate present within speleothem carbonate can be used to provide an emissions inventory for regional sulphur loading to the atmosphere where sulphur isotopes can be extracted and used as a tool for provenance. However, speleothem sulphur concentrations are low and manual techniques for sulphur isotope analysis allow only low sampling resolution. SIMS (Secondary Ionisation Mass Spectrometry) is used here to develop records of sulphur isotopic change in speleothems from the Italian and Austrian Alps, where annual laminae are less than 100 μm thick. Analysis at annual resolution over the past 100 years demonstrates an excursion in sulphur isotopic composition from values close to the carbonate bedrock end-member composition in the pre-industrial era, to values isotopically depleted in ^{34}S . This trend is mirrored by increasing concentrations of sulphate and is suggested to reflect the increase in SO_2 emissions with industrial activity. Subsequent decline in speleothem sulphate concentrations in one of the stalagmites reflects the recent European decline in industrial atmospheric SO_2 content and is matched by a rebound in sulphur isotopic composition to values more enriched in ^{34}S . Superimposed on this general secular trend are smaller (annual) variations in concentration reflecting cave environmental conditions. High magnitude events of short duration, potentially reflect volcanic inputs of SO_2 or the incorporation of dust particulates into the speleothem carbonate. This is the first micro-analysis of carbonate-associated sulphate (CAS) sulphur isotopes by SIMS. SIMS analysis of $\delta^{34}\text{S}\text{-SO}_4$ in speleothem carbonate reveals a high resolution archive depicting a regional sulphur emissions inventory for SO_2 loading to the atmosphere.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Control of rising anthropogenic SO_2 emissions, released to the atmosphere through industrial activity, has long been recognised as an international problem (see Fig. 1 for European emissions trends; re-plotted from Fig. 1. Vestreng et al., 2007). Polar ice cores have traditionally been used to document the broad trends in emissions history throughout the era of industrialisation (e.g. Patris et al., 2002), although they have been unable to accurately define changing source contributions to the global atmospheric load in an era when the source and impact of

emissions is undergoing rapid change (eg. Smith et al., 2001; Vestreng et al., 2007). In order to compile an accurate picture of emission sources and total global SO_2 fluxes, this needs to be approached from a regional perspective (Smith et al., 2001). Ensuing impacts upon the environment and human health are often regional to local in character, so effects are better documented by proxy records which are site-specific in capturing the signal. To date, archives which have been used to document changing atmospheric sulphur loads at the local to regional scale include archived soils (Zhao et al., 2003), tree rings (Kawamura et al., 2006; Fairchild et al., 2009), peat sediment cores (e.g. Novák et al., 2005) and Alpine glacier snow/ice samples (Pichlmayer et al., 1998). Speleothems also provide a local archive of atmospheric deposition (eg. Fairchild et al., 2006) and frequently contain appreciable concentrations of sulphur as sulphate which may be interpreted to reflect sulphur loading in the atmosphere (Frisia et al., 2005a). In order to distinguish between different sources contributing to the total speleothem sulphur load, isotopic analysis is required as a provenance tool (e.g. Wynn et al., 2008). Where redox

* Corresponding author. Tel.: +44 1524 510235.

E-mail address: p.wynn@lancaster.ac.uk (P.M. Wynn).

¹ Present address: Lancaster Environment centre, University of Lancaster, Lancaster, LA1 4YQ, UK.

² Present address: The University of New South Wales, 110 King St, Manly Vale, NSW 2093, Australia.

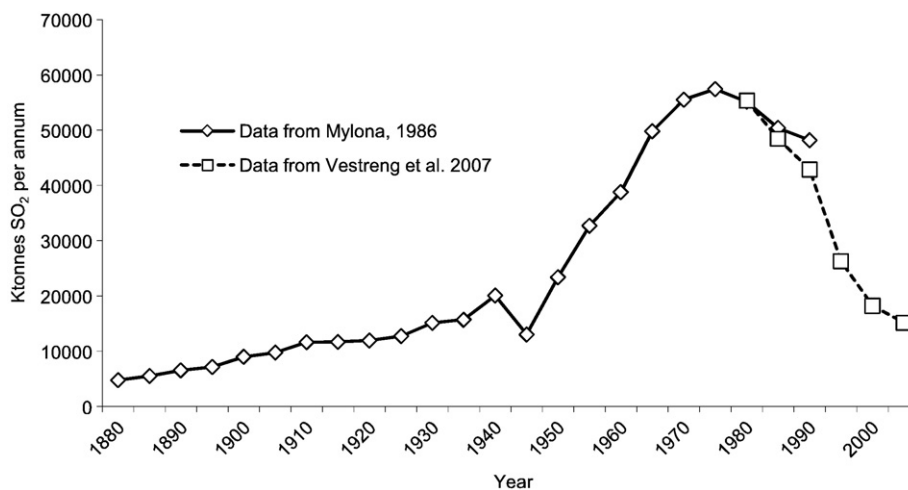


Fig. 1. Trend in atmospheric sulphur emissions in Europe 1880–2004, re-plotted and presented from data in Mylona 1986 and Vestreng et al., 2007 (cf. Fig. 1. Vestreng et al., 2007).

conditions in the bedrock and soils above the cave are oxidising, sulphur isotopes are largely refractory, undergoing very little fractionation during vegetative cycling. Sulphur isotopes can thus be used to distinguish between sulphur derived from seaspray (+21%; Rees et al., 1978), marine biogenic origin (dimethyl sulphide) (DMS = +15 ± 3%; Calhoun et al., 1991), volcanic (~0%; Nielson, 1974); continental biogenic (0 to -30%; Nielson, 1974) or industrial origin (-3 to +9%; Mayer, 1998), providing an emissions inventory for local to regional atmospheric sulphur loading. However, speleothems that grew more slowly or have lower S concentration than in the study of Wynn et al. (2008) would not yield a S isotope record at high resolution. In such materials, microanalytical techniques are required to extract sulphur depositional history. This study uses SIMS analysis to determine sulphur isotopes from speleothem carbonate at high resolution over the past 100 years. Two stalagmites from the Italian and Austrian Alps with growth rates less than 100 µm/yr and concentrations of sulphate between 10 and 90 ppm are used to pioneer this technique, demonstrating how speleothems can be used to decode sulphur depositional history at the annual scale.

2. Site and sample description

2.1. Grotta di Ernesto cave; stalagmite ER 78

Grotta di Ernesto, is a shallow Alpine cave site located in NE Italy (1167 m above sea level, 45°58'37"N, 11°39'28"E). The cave is developed in dolomitized Jurassic limestone, overlain upslope by well-bedded red and marly limestones, on top of which calcareous brown forest soil has developed (McDermott et al., 1999; Fairchild et al., 2001). A significant component of fracture-fed flow ensures rapid transmission of groundwater into the cave system, whilst slower seepage flow fed by minor fissures and water stored within the porous limestone matrix completes the dual-porosity aquifer system (Miorandi et al., 2010). The sampled stalagmite (ER78) was collected whilst still actively growing in the year 2000 from a single passage located about 30 metres below the surface (Frisia et al., 2005a). The stalagmite was fed by a soda-straw stalactite characterized by relatively low discharge (average 0.03 ml/min) and marked seasonal variability (coefficient of variation approximately 100; Smart and Friederich, 1986). Coupled with seasonal changes in cave air PCO₂, this results in a marked seasonal pattern of calcite precipitation and visible textural annual laminae (Frisia et al., 2003). Maximum calcite deposition at site ER78 occurs from November to April, with minimal deposition from August to October (Miorandi et al., in press). This cyclic pattern of calcite precipitation influences the incorporation of trace elements into speleothem calcite. In ER78 each annual lamina consists of a couplet of translucent calcite and a thin brown UV

fluorescent layer, the latter being formed in autumn, at the end of the warm season (Borsato et al., 2007). Growth rates are governed by discharge and variations in cave air PCO₂ leading to average annual laminae thicknesses of ca. 100 µm between 1860 and 2000 (Borsato et al., 2007). The age model for ER78 during the most recent 150 years was developed using laminae counting from the speleothem growth surface known to be actively growing when collected in the year 2000. Sulphate concentrations in dripwaters from the same chamber as stalagmite ER78 averaged 6.5 ± 0.8 mg/l during the monitoring period from 1995–1997 with no clear seasonal pattern of variation (average of 38 observations from 7 dripwater sites in the chamber). Average sulphate concentrations comprise just 1.2% sulphate sourced from the bedrock and 1.9 % from seasalt, based on Ca/SO₄ ratios, and standard marine ratios to chloride respectively. In the same period, the pH of dripwaters averaged 7.97 ± 0.8 and the carbonate saturation index was 0.17 ± 0.15; these parameters do vary seasonally at this site (Frisia et al., 2000; Unpublished data).

2.2. Obir cave; stalagmite Obi84

Obir is an alpine cave (46.51°N, 14.54°E), situated in south-east Austria at 1100 m above sea level. The overlying terrain is forested and speleothem growth is forced by degassing from the enhanced PCO₂ levels, on average 10^{-2.6} atm, developed in the brown forest soils (Spötl et al., 2005). A detailed cave monitoring program at Obir cave revealed strong annual fluctuations in the carbonate system related to cave ventilation resulting in seasonally low PCO₂ in cave air and increased pH in cave dripwaters (Spötl et al., 2005). Sample Obi 84 (Smith et al., 2009) was collected from the Säulenhalle chamber (see map in Spötl et al., 2005) in December 2002. Säulenhalle is at a depth of ca. 70 m below the surface and has a near-constant temperature of 5.7 °C. Obi 84 shows annual trace element variations and infiltration laminae that are in many ways comparable to Ernesto cave stalagmites (Smith et al., 2009; Fairchild et al., 2010). The age model used annual laminae, counted using thin section petrography from the speleothem growing tip, known to be active at point of collection (Smith et al., 2009). Monitoring of aggregated bimonthly water samples from a nearby drip between 1999 and 2002 showed that sulphate concentrations gradually declined from 6 to 5 mg/l over the period, with no seasonal variations (Spötl et al., 2005). Dripwater data from the drip feeding stalagmite Obi 84 (SH4) showed similar characteristics and a slightly lower sulphate concentration of 4.5 mg/l. Of this sulphate, just 1.1% is sourced from the bedrock (calculated following Wynn et al., 2008), and 1.24% derived from seasalt based on standard marine ratios to chloride. pH was in the range 8.1 to 8.4 and

the carbonate saturation index was 0.58 ± 0.07 based on 7 observations (2002–2004) (Fairchild et al., 2010).

3. Methodology

Analyses of speleothem carbonate were conducted on polished, gold coated thin sections approximately 150 μm thick using the Cameca 1270 ion probe at the University of Edinburgh, School of Geosciences. $^{34}\text{S}/^{32}\text{S}$ ratios are expressed using the delta convention in per mille notation relative to VCDT.

Samples were pre-sputtered for 60 seconds prior to analysis using Cs ions at a primary beam current of 2 nA, over an analytical spot size of 10 μm . Analyses were undertaken in mono-collector mode at a mass resolution of approximately 6500. Secondary ion beam centering was undertaken using $^{16}\text{O}_2$ on the Faraday cup, and $^{34}\text{S}/^{32}\text{S}$ ratios were detected by electron multiplier. Charge neutralization was achieved using the normal incidence electron gun. Each sulphur analysis comprised of 50 ratio measurements using 5 s for ^{34}S and 1 s for ^{32}S . Isotope ratios were calculated as $\delta^{34}\text{S}$ VCDT by comparison with internal standard M93, a nearshore reef coral, *Porites* sp, with a sulphur isotopic composition of +22.3‰ and sulphur concentration of 1694 ppm. Sulphur concentrations were calculated from total ^{32}S counts from the same analysis, standardized against the primary beam current and in-house standard M93. The composition of this standard material was determined by continuous flow isotope ratio mass spectrometry (CFIRMS) and high resolution inductively-coupled plasma mass spectrometry (HR-ICPMS) for isotopes and concentrations respectively, following the same methodologies outlined in Wynn et al. (2008) and as described below.

Analysis of an assumed homogenous material (M93 carbonate standard material) under identical instrumental conditions had a precision of $\pm 0.09\%$ and ± 20 ppm (standard error of the mean, $n = 45$). The internal error on M93 between standard blocks (average standard error of the mean; 0.24‰) is similar to that predicted by counting statistics ($\pm 0.3\%$). Because concentrations of S are much lower in the speleothems, the internal error on each analysis is larger than that of the standard material ($\pm 5\%$ at 10 ppm speleothem sulphur concentration and $\pm 1.6\%$ for speleothem sulphur concentrations of ~ 70 ppm). Replication of sampling tracks for $\delta^{34}\text{S}$ and sulphur concentration analyses enabled the integrity of SIMS measurements at low concentrations to be confirmed.

To cross-check sulphur concentrations and sulphur isotopes in speleothem calcite measured by SIMS, manual measurements were undertaken following methods outlined in Wynn et al. (2008). For sulphur concentrations, 2 mg aliquots of calcite powders were drilled from the central portion, along the vertical growth axis of the stalagmites and digested in 8 ml of 2% HNO_3 (Aristar grade) and analysed by HR-ICPMS at Kingston University, UK. Aliquots of speleothem calcite were sampled for isotopic analysis by drilling up to 500 mg of powder from the stalagmite, digested in 4 M hydrochloric acid (aristar grade) and precipitated as barium sulphate in the presence of pure quartz (SiO_2) powder as an inert medium. Samples were left to mature for ~ 72 h prior to centrifugation and repeated washing with de-ionised water to remove excess barium. Pellets of quartz powder/barium sulphate were oven dried at $\sim 70^\circ\text{C}$ and stored in tin capsules prior to $\delta^{34}\text{S}$ analysis by CFIRMS.

$^{34}\text{S}/^{32}\text{S}$ analysis of product barium sulphate was undertaken using a EuroVector elemental analyser linked to a GV Isoprime continuous flow mass spectrometer at the University of Birmingham. Pellets of quartz powder / barium sulphate were combusted in tin capsules in the presence of vanadium pentoxide at 1030°C to yield SO_2 for the determination of $\delta^{34}\text{S}-\text{SO}_4$. Values were corrected against VCDT using within-run analyses of international standards NBS-127 and SO5 (assuming $\delta^{34}\text{S}$ values of +21.1‰ and +0.5‰ respectively). Within run standard replication was $< 0.3\%$. Procedural standard solutions of calcium sulphate precipitated as barium sulphate were used to test the integrity of the method. These yielded $\delta^{34}\text{S}$ values of +2.7‰

(0.3‰ 1SD, $n = 12$) compared to values of +3.0‰ (0.3‰ 1SD, $n = 13$) for analysis of the raw calcium sulphate powder. Blank contamination associated with $\delta^{34}\text{S}$ determination was zero.

4. Results

Average concentrations of sulphur and $\delta^{34}\text{S}-\text{SO}_4$ values undertaken using conventional HR-ICPMS and CFIRMS respectively, are shown in Table 1. Before 1967, concentrations of speleothem sulphur are low (average 25.2 and 14.2 ppm for stalagmites ER78 and Obi84 respectively) compared to those detected in the post-1967 speleothem calcite and the overlying bedrock. Due to these very low concentrations of speleothem sulphur before 1967 and the limitations of current techniques, it was not possible to use CFIRMS to gain an average $\delta^{34}\text{S}$ value for this period in either stalagmite. After 1967, stalagmite sulphur concentrations increase to average values of 52.4 and 53.2 ppm for stalagmites ER78 and Obi84 respectively. Bulk $\delta^{34}\text{S}-\text{SO}_4$ analysis of speleothem carbonate post 1967 by CFIRMS gives signatures of +7.7‰ and +8.4‰ for ER78 and Obi84 respectively, representing depletion in ^{34}S compared to the bedrock. These values include an amplitude correction of +1.6‰ (based on correction factors using international IAEA standard NBS-127).

Increases in speleothem sulphur concentration broadly reflect trends in European emissions (Fig. 1) and are occasionally punctuated by short-lived events of high sulphur content (Fig. 2). Discrepancies between peak concentration measurements given by the two techniques represent bulk integration by HR-ICPMS as opposed to sub-annual resolution achievable by SIMS.

Combined trends of sulphur concentration and $\delta^{34}\text{S}$ measured by SIMS are shown in Fig. 3a and b for speleothems ER78 and Obi84 respectively. The steady increase in sulphur content towards the most recently deposited calcite is mirrored by a trend towards lighter values of $\delta^{34}\text{S}-\text{SO}_4$. Austrian stalagmite Obi84, demonstrates a rebound in $\delta^{34}\text{S}-\text{SO}_4$ signatures back towards the bedrock end-member value and an associated reduction in concentrations of sulphate in the most recently deposited speleothem calcite (post 2000). Where sulphur concentrations are less than 20 ppm, the errors associated with $\delta^{34}\text{S}$ measurement were deemed too great to allow meaningful interpretation ($> \pm 3\%$), although the data are still displayed for completeness. Duplicate sampling tracks undertaken on separate thin sections of the same speleothem (ER78), demonstrated the ability of SIMS analysis to replicate for determination of $\delta^{34}\text{S}-\text{SO}_4$ and sulphur concentrations at high resolution in speleothem calcite when concentrations are greater than 20 ppm.

5. Discussion

5.1. The impact of industrialisation upon speleothem sulphur content

The isotopic composition of sulphur incorporated into pre-1960 calcite approaches the $\delta^{34}\text{S}$ signature of the surrounding karst bedrock and soil material. The contribution from marine sources of sulphur

Table 1

Sulphur concentration and isotope data for stalagmites ER78 and Obi84. Measurements are taken using ICPMS and CFIRMS respectively.

Cave site	<i>n</i>	S (ppm)	$\delta^{34}\text{S}-\text{SO}_4$
<i>Ernesto cave</i>			
Bedrock (dolomite)	7	187 (56)	20.5 (1.3)
Stalagmite ER78			
1967–2000	2	52	7.7
Pre-1967	13	25	Not determined
<i>Obir cave</i>			
Bedrock	6	134 (44)	15.8 (0.7)
Stalagmite Obi84			
1967–2002	3	53	8.4
Pre-1967	17	14	Not determined

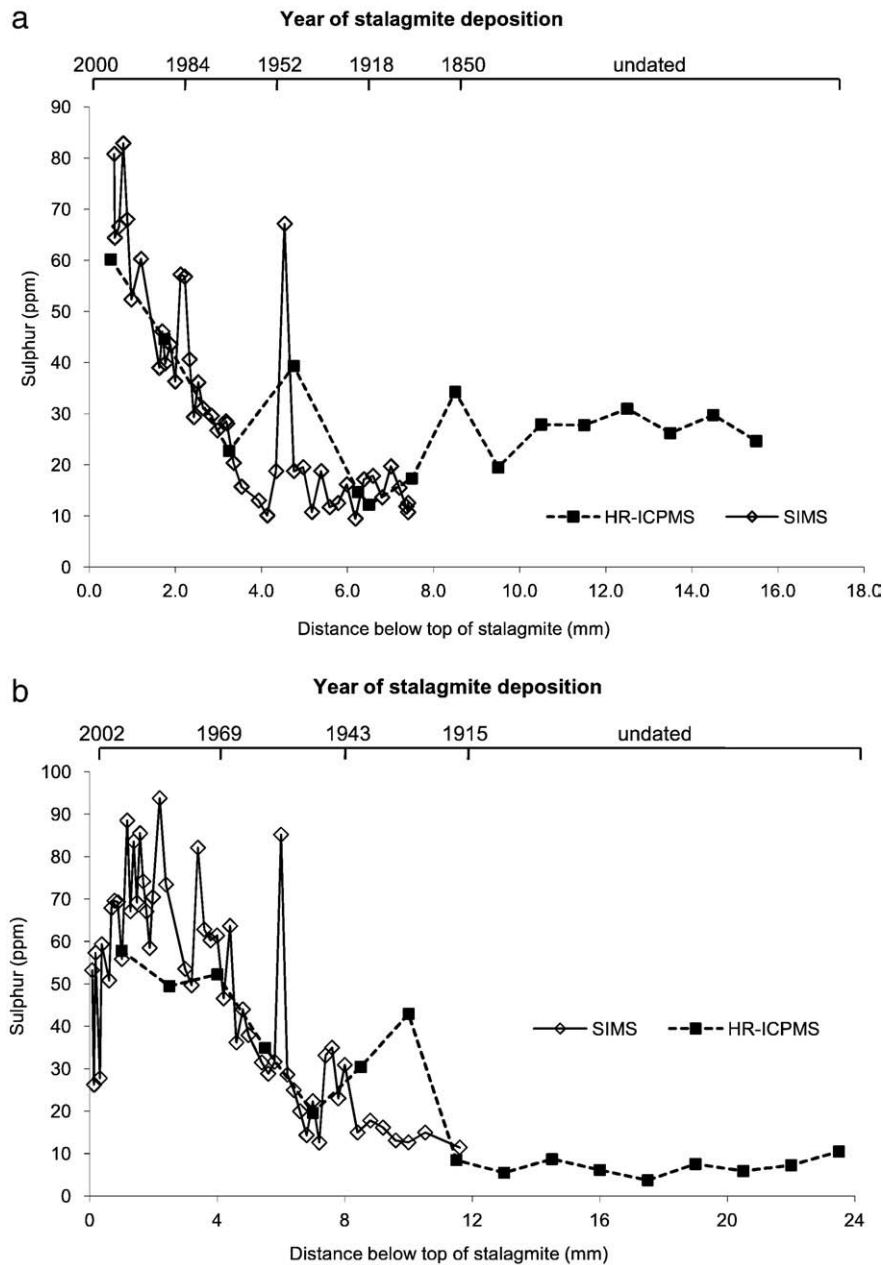


Fig. 2. The close association between sulphur concentrations measured by HR-ICPMS and those measured by ion probe for a) ER78 and b) Obi84.

(+21‰ for seasalt aerosol; Rees et al., 1978, DMS = $+15 \pm 3\%$; Calhoun et al., 1991) is limited when calculated from modern dripwater compositions using standard molar ratios to chloride (1.9% marine sulphate composition of feeding drip to stalagmite ER78, Ernesto cave; and 1.24% marine sulphate in feeding drip to stalagmite Obi84, Obir cave (Fairchild et al., 2010)). Pollution-dominated isotopic signals during this period (-3 to $+9\%$; Mayer, 1998) are also low, suggesting the main source of sulphate in the karst groundwater pre-1960 is likely to be released from dissolution of the surrounding bedrock, tempered towards slightly lighter signatures by any biogenic emissions

Analysis of sulphur concentrations and isotopes at annual resolution encompassing the past 50 years demonstrates an inverse association between $^{34}\text{S}/^{32}\text{S}$ ratios and sulphate abundance. The inverse association post 1960 produces a trend of increasing concentration and an excursion in sulphur isotopic composition to values depleted in ^{34}S . On the basis that precipitation sourced predominantly from anthropogenic emissions of SO_2 is documented to typically have a $\delta^{34}\text{S}-\text{SO}_4$

composition between -3 and $+9\%$ in the northern hemisphere (Mayer, 1998), this would be consistent with the additional source of speleothem sulphur originating from industrial pollution (Fig. 3a). This is also reflected in the manual measurements of $\delta^{34}\text{S}-\text{SO}_4$ post 1967, representing a concentration and volume weighted average of the annual sulphur signal which is isotopically lighter than the bedrock signature. $\delta^{34}\text{S}-\text{SO}_4$ composition extracted at lower resolution from other published regional archives also document a similar shift in sulphur isotopic composition, attributed to anthropogenic SO_2 pollution. This is particularly significant in the case of Pichlmayer et al. (1998), where snowpack samples collected between 1991 to 1994 demonstrate sulphur isotopic signatures (range 2.5‰ to 4.4‰) similar to those obtained in speleothem Obi84 during a similar time period.

Where speleothem Obi84 demonstrates declining sulphate concentrations post 1992, these are not synchronised with the rebound in sulphur isotopes back towards bedrock end member compositions (Fig. 3b). Speleothem $\delta^{34}\text{S}-\text{SO}_4$ reaches a composition with maximum

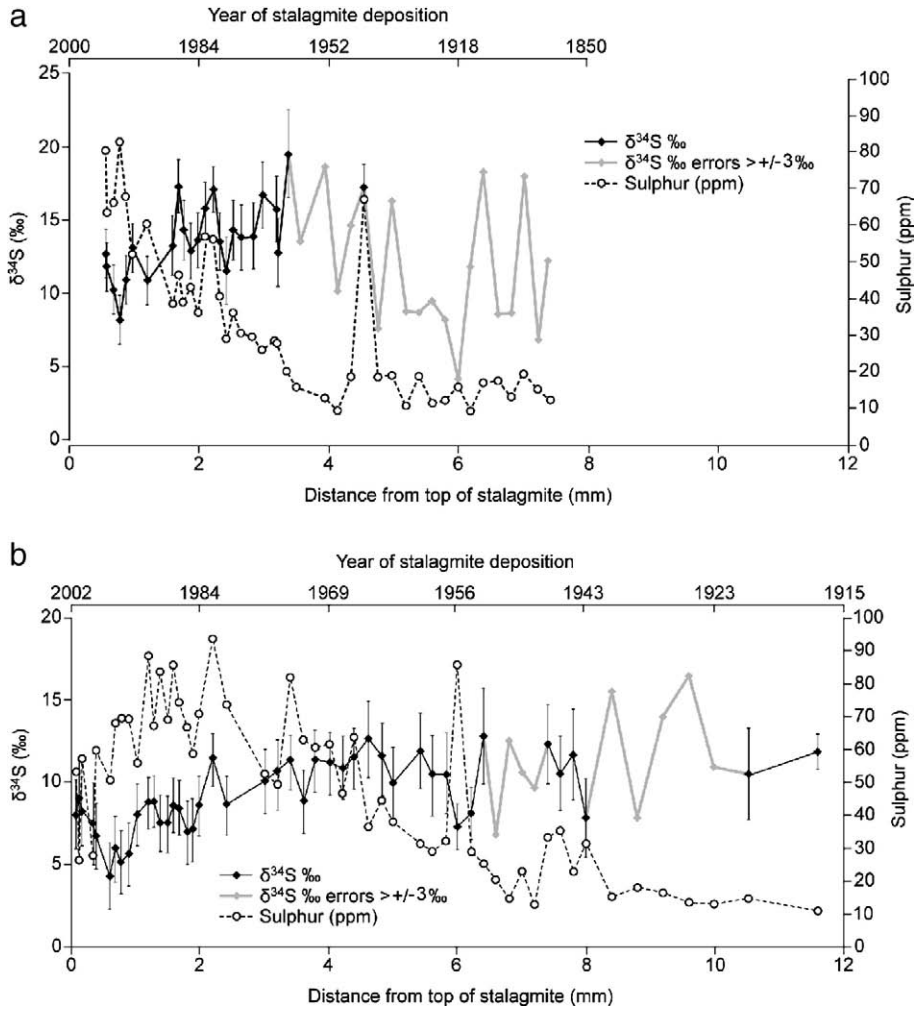


Fig. 3. Sulphur concentrations and isotopes measured by SIMS in a) ER78 and b) Obi84.

depletion in ^{34}S during 1997 ($\delta^{34}\text{S}\text{-SO}_4 = +4.3\text{‰}$) demonstrating a 5 year delay since the peak in sulphur concentration. This suggests a shift to lighter pollution end member signatures in accordance with the reduction of SO_2 emissions across Austria. Application of a two-component mixing model between the bedrock sulphur composition and pollution source is illustrated in Fig. 4. The isotopic composition of the pollution end member is labelled on the two mixing lines. Data are confined between mixtures of bedrock sulphate (constant at $+15.8\text{‰}$)

and pollution end member compositions ranging from $+11\text{‰}$ to $+3\text{‰}$, with the younger pollution source of lighter isotopic composition.

5.2. Transfer from atmosphere to speleothem and perturbation to the secular trend

Stalagmite ER78 from Ernesto cave, Italy, does not clearly document the late-industrial decline in atmospheric SO_2 emissions and the rebound

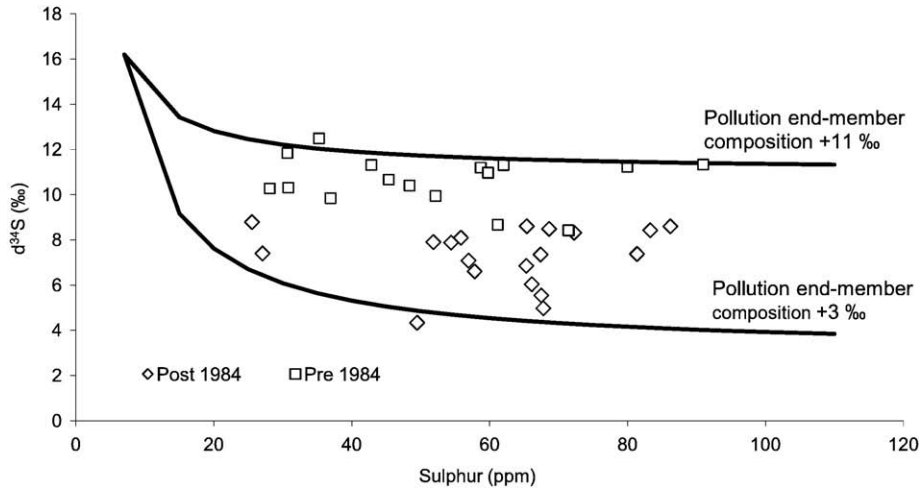


Fig. 4. End member mixing between bedrock and pollution signatures for speleothem Obi84.

in isotopic composition towards the bedrock end member value is not apparent. This is due to an extensive delay in the transfer of sulphur from atmosphere to speleothem due to vegetative cycling and storage in the regolith above the cave. Through processes of assimilation, inorganic sulphate is incorporated into vegetation and stored as organic sulphur until returned to the soil through vegetative cycling (e.g., Likens et al., 2002). Mineralisation of carbon bonded sulphur back to inorganic sulphate mobilises the sulphur pool enabling transfer into ground water storage, cave drip waters and speleothem calcite. The overall transfer time between atmosphere to speleothem is therefore a product of vegetative cycling, microbial transformation and soil properties of groundwater storage. Where sulphur is encapsulated in organic form in trees, dendrochemical records of S thus form local archives capable of complementing those in nearby speleothems (Fairchild et al., 2010). A declining trend in the sulphate content of speleothem dripwaters at Ernesto cave between 1995 to 1998 support this model of vegetative cycling, suggesting a typical sulphur storage time of 10 to 15 years after the peak in atmospheric sulphur loading (Frisia et al., 2005a). This is consistent with the release rate of stored sulphate across other European catchments (e.g. Pretchel et al. 2001) and a similar offset of approximately 10 years is also seen to occur between peak emissions of SO₂ to the atmosphere and peak sulphate concentrations in stalagmite Obi84.

Where secular trends of sulphate concentration are punctuated by short-lived events enriched in sulphate, there is ambiguity over their origin. Concentrations of sulphate delivered to the cave site in excess of that which can be assimilated into vegetation would be free to enter the ground and cave water system. Fracture-fed flow during periods of intense autumnal precipitation is suggested to account for the rapid delivery of available sulphate to the site of speleothem growth as a peak of short duration. Previous work has indicated that sulphate peaks could be either markers of volcanic eruptions or micro-particles (Frisia et al., 2005a,b; Frisia et al., 2008). In the case of the concentrated spike of sulphate in stalagmite ER78 at 4500 µm (approx 1943), the S-isotopic composition of +17.0‰ (error ± 1.6‰) is close to the bedrock end member composition and likely represents a contribution, either as micro-particulates or as dissolved sulphate incorporated within the calcite of non-volcanic, non-anthropogenic origin. Similar sulphate peaks at around 1940 characterized the ice core record of Colle Gnifetti, in the Alps of NW Italy. On the basis of the relatively high Ca concentration, these were interpreted as related to Saharan dust deposits which are a relatively common phenomenon on Alpine glaciers and are associated with warm and moist air masses of Mediterranean provenance (Schwikowski et al., 1999). Three small peaks in Si concentration, as detected by synchrotron radiation microfluorescence in stalagmite ER78 coincide with the S-peak at ca. 1943 (Frisia et al., 2005a, Fig. 2). Similar layers of dust separating precipitation events in the snow pack overlying Grotta di Ernesto suggest the S isotopic composition in the 1943 S peak may be due to a major event of Saharan dust deposition. Stalagmite Obi84 hosts a short lived event of high concentration at 6000 µm depth (approximate age 1956) with an isotopic signature of +7.4‰ (error ± 2.6‰). This is further away from the isotopic end member composition of the bedrock, perhaps representing source mixing between sulphate derived from bedrock and a lighter source of short duration from volcanic activity or pollution.

High frequency variations in speleothem sulphate concentration are superimposed on the rising secular trend and are thought to represent concentration variations within annual lamina. Anion drip water composition changes little on an annual basis, thus variations within annual laminae are thought to represent the influence of cave environmental conditions upon trace element incorporation during carbonate deposition (Frisia et al., 2005a). Cave air PCO₂ is known to modulate through annual cycles according to processes of cave ventilation (Spötl et al., 2005), inducing seasonal cycles in dripwater pH and thus HCO₃⁻/CO₃²⁻ ratios. In turn, this affects sulphate incorporation into speleothem calcite, such that low PCO₂ of cave air

during winter promotes drip water degassing, increase in alkalinity, super-saturation, rapid speleothem growth rates and thereby limited sulphate incorporation in the calcite lattice (Frisia et al., 2005a). As the analyses were regularly spaced in distance not in time, successive analytical spots occur randomly within the annual cycle and so, concentration variations between sequential analyses likely reflect this variability in the annual range of sulphate incorporation. This provides a limit to the quantitative interpretation of sulphur concentrations at the annual scale, but should not however, influence measured sulphate isotopic compositions as sulphate incorporation into calcite is known to be independent of fractionation effects (e.g., Burdett et al., 1989).

Sulphur concentrations and isotopic signatures extracted from speleothem archives on an annual basis, thus appear to record several different phenomena intrinsic to both external and internal forcing mechanisms. Based on secular trends of increasing concentration and declining sulphur isotope values, speleothem calcite appears to be responsive to changing atmospheric loads of anthropogenic pollution. The rate of response to external forcing is dependent upon delays associated with ecosystem storage above the cave, regional pollution sources and patterns of air mass movements controlling the supply of sulphur pollution to the cave site. Mechanisms of calcite precipitation, the incorporation of impurities during calcite deposition and the occurrence of short lived events such as volcanic activity injecting SO₂ into the atmosphere are thought to generate variations superimposed on this secular trend.

6. Conclusion

This study has demonstrated the use of SIMS technology to measure sulphur concentrations and isotope ratios in speleothem calcite at annual resolution. Two speleothems from the Austrian and Italian Alps show increasing concentrations of sulphur which peak in the mid 1980's (Austrian stalagmite Obi84) or show a continuously rising trend at the time of collection (Italian stalagmite ER78). The increasing concentrations in both stalagmites are mirrored by a shift towards lighter isotopic signatures thought to be indicative of industrial pollution. There is a lag between timing of peak SO₂ content in the atmosphere and maximum sulphate concentration in the speleothems, reflecting the time taken for sulphur to cycle through the overlying vegetation and transit the ground water system. Discrepancies between timing of peak sulphate concentration in stalagmite Obi84 and lightest isotopic values are taken to reflect changing isotopic composition of pollution end member sources delivering atmospheric sulphur for deposition over the cave site. Superimposed on this secular trend depicting changes in atmospheric sulphur loading are variations in both sulphur concentration and isotopic signatures associated with cave environmental conditions, incorporation of impurities into deposited calcite and short lived events such as volcanic activity. This is the first study to document and interpret the sulphur isotopic composition of speleothem calcite at such high resolution, forming a valuable inventory of regional sulphur emissions to the atmosphere. Such interpretation requires an appreciation of both the linkages between speleothem and external forcing factors, but also processes which are internal to the cave system, superimposing short term variations in sulphur on the general secular trend.

Acknowledgements

The authors would like to thank the UK Natural Environment Research Council (NERC) for funding this work (Grant NE/C511805/1). SIMS analysis was undertaken at the NERC Edinburgh Ion Microprobe Facility. Thanks are also expressed to Drs. K. Jarvis and K. Linge at the NERC ICP-MS facility, Kingston University for assistance with sulphur analysis; and to Renza Miorandi for continued support in cave monitoring at Grotta di Ernesto, Italy.

References

- Borsato, A., Frisia, S., Fairchild, I.J., 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. *Geochimica et Cosmochimica Acta* 71, 1494–1512.
- Burdett, J.W., Arthur, M.A., Richardson, M., 1989. A Neogene seawater sulphur isotope age curve from calcareous pelagic microfossils. *Earth and Planetary Science Letters* 94, 189–198.
- Calhoun, J., Bates, T., Charlson, R., 1991. Sulphur isotope measurements of submicrometer sulphate aerosol particles over the Pacific Ocean. *Geophysical Research Letters* 18, 1877–1880.
- Fairchild, I.J., Baker, A., Borsato, A., Frisia, S., Hinton, R.W., McDermott, F., Tooth, A., 2001. Annual to sub-annual resolution of multiple trace element trends in speleothems. *Journal of the Geological Society, London* 158, 831–841.
- Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spötl, C., Matthey, D., McDermott, F., E.I.M.F., 2006. Modification and preservation of environmental signals in speleothems. *Earth-Science Reviews* 75, 105–153.
- Fairchild, I.J., Loader, N., Wynn, P.M., Frisia, S., Thomas, P.A., Lageard, J.G.A., 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. *Environmental Science and Technology* 43 (5), 1310–1325.
- Fairchild, I.J., Spötl, C., Frisia, S., Borsato, A., Susini, S., Wynn, P.M., Cauzid, J., EIMF, 2010. Petrology and geochemistry of annually laminated stalagmites from an Alpine cave (Obir, Austria): seasonal cave physiology. In: Pedley, M., Rogerson, M. (Eds.), *Tufas and Speleothems*. Geological Society of London Special Publication.
- Frisia, S., Borsato, A., Fairchild, I.J., McDermott, F., 2000. Calcite fabrics, growth mechanisms, and environments of formation in speleothems from the Italian Alps and southwestern Ireland. *Journal of Sedimentary Research* 70 (5), 1183–1196.
- 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 and Planetary Science Letters* 216, 411–424.
- Frisia, S., Borsato, A., Fairchild, I.J., Susini, J., 2005a. Variations in atmospheric sulphate recorded in stalagmites by synchrotron micro-XRF and XANES analyses. *Earth and Planetary Science Letters* 235, 729–740.
- Frisia, S., Borsato, A., Susini, J., Somogyi, A., 2005b. Climate forcings and their influence on Alpine history as reconstructed through the application of synchrotron based X-ray microfluorescence on layered stalagmites: archaeometry special theme-issue 'The linking role of the Alps in past cultures: An archaeometric approach'. In: Artioli, G., Krause, R., Wolf, S. (Eds.), *Archaeometry* 47 (2), pp. 209–219.
- Frisia, S., Borsato, A., Susini, J., 2008. Synchrotron radiation applications to past volcanism archived in speleothems: An overview. *Journal of Volcanology and Geothermal Research* 177 (1), 96–100.
- Kawamura, H., Matsuoka, N., Momoshima, N., Koike, M., Takashima, Y., 2006. Isotopic evidence in tree rings for historical changes in atmospheric sulfur sources. *Environmental Science & Technology* 40 (18), 5750–5754.
- Likens, G.E., Driscoll, C.T., Busco, D.C., Mitchell, M.J., Lovett, G.M., Bailey, S.W., Siccama, T.G., Reiners, W.A., Alewell, C., 2002. The biogeochemistry of sulphur at Hubbard Brook. *Biogeochemistry* 60, 235–316.
- Mayer, B., 1998. Potential and limitations of using sulphur isotope abundance ratios as an indicator for natural and anthropogenic induced environmental change. Isotope techniques in the study of environmental change. Proceedings of an international conference in Vienna, Austria. Pp 423–435. IAEA, Vienna Austria, 14–18th April 1997.
- McDermott, F., Frisia, S., Huang, Y., Longinelli, A., Spiro, B., Heaton, T.H.E., Hawkesworth, C.J., Borsato, A., Keppens, E., Fairchild, I.J., van der Borg, K., Verheyden, S., Selmo, E., 1999. Holocene climate variability in Europe: evidence from $\delta^{18}\text{O}$, textural and extension-rate variations in three speleothems. *Quaternary Science Reviews* 18, 1021–1038.
- Miorandi, R., Borsato, A., Frisia, S., Fairchild, I.J., Richter, D.K., in press. Epikarst hydrology and implications for stalagmite capture of climate changes at Grotta di Ernesto (N.E. Italy): results from long-term monitoring. *Hydrological Processes*.
- Nielson, H., 1974. Isotopic composition of the major contributors to atmospheric sulphur. *Tellus XXVI*, 211–221.
- Novák, M., Vile, M., Bottrell, S.H., Štěpánová, M., Jačková, I., Buzek, F., Přečková, E., Newton, R., 2005. Isotope systematics of sulfate-oxygen and sulfate-sulfur in six European peatlands. *Biogeochemistry* 76 (2), 187–213.
- Patris, N., Delmas, R.J., Legrand, M., De Angelis, M., Ferron, F.A., Stievenard, M., Jouzel, J., 2002. First sulphur isotope measurements in central Greenland ice cores along the preindustrial and industrial periods. *Journal of Geophysical Research* 107 (D11 4115) ACH 6-1-ACH 6-11.
- Pichlmayer, F., Schöner, W., Seibert, P., Stichler, W., Wagenbach, D., 1998. Stable isotope analysis for characterization of pollutants at high elevation alpine sites. *Atmospheric Environment* 32 (23), 4075–4085.
- Pretchel, A., Alewell, C., Armbruster, M., Bittersohl, J., Cullen, J.M., Evans, C.D., Helliwell, R., Kopáček, J., Marchetto, A., Matzner, E., Meesenburg, H., Moldan, F., Moritz, K., Vesely, J., Wright, R.F., 2001. Response of sulphur dynamics in European catchments to decreasing sulphate deposition. *Hydrology and Earth System Sciences* 5 (3), 311–325.
- Rees, C.E., Jenkins, W.J., Monster, J., 1978. The sulphur isotopic composition of ocean water sulphate. *Geochimica et Cosmochimica Acta* 42 (4), 377–381.
- Schwikowski, M., Dorscher, A., Gaggler, H.W., Schotterer, U., 1999. Anthropogenic versus natural sources of atmospheric sulphate from an Alpine Ice Core. *Tellus* 51B, 938–951.
- Smart, P.L., Friederich, H., 1986. Water movement and storage in the unsaturated zone of a maturely karstified aquifer, Mendip Hills, England. Proceedings of the Conference on Environmental Problems in Karst terrains and their solutions, October 28–30 1986. National Water Wells Association, Bowling Green, Kentucky, pp. 57–87.
- Smith, R.J., Pitcher, H., Wigley, T.M.L., 2001. Global and regional anthropogenic sulphur dioxide emissions. *Global and Planetary Change* 29, 99–119.
- Smith, C.L., Fairchild, I.J., Spötl, C., Frisia, S., Borsato, A., Moreton, S.G., Wynn, P.M., 2009. Chronology building using objective identification of annual signals in trace element profiles of stalagmites. *Quaternary Geochronology* 4 (1), 11–21.
- Spötl, C., Fairchild, I.J., Tooth, A.F., 2005. Cave air control on dripwater geochemistry, Obir Caves (Austria): implications for speleothem deposition in dynamically ventilated caves. *Geochimica et Cosmochimica Acta* 69 (10), 2451–2468.
- Vestreng, V., Myhre, G., Fagerli, H., Reis, S., Tarrasón, L., 2007. Twenty-five years of continuous sulphur dioxide emission reduction in Europe. *Atmospheric Chemistry and Physics* 7, 3663–3681.
- Wynn, P.M., Fairchild, I.J., Baker, A., Frisia, S., Borsato, A., Baldini, J., McDermott, F., 2008. Isotopic archives of sulphur in speleothems. *Geochimica et Cosmochimica Acta* 72, 2465–2477.
- Zhao, F.J., Knights, J.S., Hu, Z.Y., McGrath, S.P., 2003. Stable sulfur isotope ratio indicates long-term changes in sulfur deposition in the Broadbalk Experiment since 1845. *Journal of Environmental Quality* 32, 33–39.