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Bronze Age volcanic event recorded in stalagmites by combined isotope and trace element studies

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Stable isotope analyses of speleothems (carbonate deposits formed in caves) have been widely used to reconstruct paleoenvironmental conditions. Recent improvements in geochemical techniques have enabled us to analyze climate-influenced deposits at high temporal resolution so that hitherto unrecognized environmental conditions may be identified. Stable H, C and O isotope analyses on carbonate and inclusion water have been combined with multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) age dating and laser-ablation ICP-MS trace element analyses on a stalagmite from southern Hungary. The study reveals significant changes in chemical and isotopic compositions of the speleothem between approx. 3800 and 3500 years BP ('Before Present') indicating coupled changes in the temperature and precipitation regime under which the speleothem formed. Stable isotopic and trace element correlations within this time period correlate with similar studies of stalagmites of comparable age from the Alpine-Mediterranean region. Our studies suggest that traces of deposition of volcanic dust, possibly related to the Thera eruption of Santorini (Greece) ca. 1650 BC (~3650 BP), and environmental changes can be detected at a distance of several thousand kilometers. Copyright © 2009 John Wiley & Sons, Ltd.

One major cause of climate change on Earth is volcanism that injects chemical aerosols and gases into the atmosphere, thus affecting solar irradiation and heat loss.[1–3] Volcanism is thought to be a major factor in cataclysms like the Permo-Triassic and Cretaceous-Tertiary extinction events.[4,5] On a smaller scale, during the Quaternary, volcanism acted as a forcing factor for environmental change over short time periods, e.g. after the Toba, Tambora and Mount Pinatubo eruptions.[7–9] Greenhouse gas emission during magmatic degassing, as well as sulphate aerosol production during explosive eruptions, is known to cause perturbations in global temperature, but the significance of volcanic influence on climate in the longer term is still debated.[10]

At millennial resolution it has been shown that the entire Bronze Age (~5300 to ~3200 years BP 'Before Present') is

characterized by several climate swings as demonstrated in the archaeological and palynological record in the Carpathian Basin.[11] Climatic fluctuations at this time began with a cold and humid period followed by warmer conditions around 4000 years BP. In the Carpathian Basin, tell-type (i.e. built on mounds) human settlements were widespread in this time, but declined around 3500 years BP, perhaps because of a rapidly cooling climate that was also accompanied by progressively wet conditions. This period is characterized by changes in settlement structure, as the widespread distribution of tells (settlements established on mounds) turned into a concentrated pattern with frequent abandonment, attributed in part to environment deterioration. Although the temporal resolution is much lower than in the present study, archeological studies in Alpine areas have shown migrations of lake-dwelling communities in the Middle Bronze Age due to significant lake level changes.[12]

Tree-ring growth series may preserve volcanically induced climate proxies at annual resolution[13–15] but the lack of corresponding ring-width series further back in the past prevents the establishment of detailed studies on the behaviour of climate downturns possibly caused by violent eruptions.

Although volcanic signals like SO_4^{2-} time series variations, such as those detected in ice cores,[16] are not frequent in cave

carbonate deposits (speleothems),[17,18] these deposits have specific advantages: stalagmites are widespread in continental areas, they develop in relatively protected environments, practically free from re-deposition and alteration, and can be dated by absolute radiometric methods at relatively high precision.[19,20] The sulphur concentration within a stalagmite, however, is not only controlled by the sulphate content and variability of the atmosphere since it can be modified by several factors, e.g. enhanced weathering of surrounding rocks, storage in the soil zone and biogenic activity.[21]

Speleothems which record environmental change in the European Middle Bronze Age (~4000–3500 years BP) are of particular interest as this period was notable as a time of cultural change, thought to be related to climatic downturn after or related to volcanism. This is especially the case in the Mediterranean region, where the Santorini volcano eruption led to the collapse of the Minoan culture about 3650 years ago.[22] A strong growth depression in Swedish tree rings dated at 1637 ± 65 years BC (~3637 years BP) was also observed, thus raising the possibility of multiple volcanic eruptions causing sudden cooling.[23] High-resolution geochemical data published on speleothems are still scarce from this period. Recently published preliminary studies have reported significant isotopic and chemical variations related to volcanically induced climate changes attributed to the Thera eruption of Santorini (Greece).[24,25]

In this study, we conducted complex trace element and H, C, and O isotope analyses on a speleothem from Hungary (Fig. 1(a)) acquired at high spatial and temporal resolution using various mass spectrometric techniques. The full treatment of the geochemical data of the entire stalagmite record (together with Sr isotope data) will be published elsewhere, but in this paper we intend to show how isotopic and chemical compositions can detect climate variations during the Middle Bronze Age and thereby identify possible signs of the Santorini eruption. We present a new geochemical tool for correlation of stalagmite records over a range of several thousand kilometers.

EXPERIMENTAL

The age determinations were conducted at the Institute of Geological Sciences, University of Bern, Switzerland, using standard procedures.[26] Sample chips (0.1–0.2 g) were spiked with a mixed ^{229}Th–^{236}U and dissolved in HNO_3 and taken to dryness. U and Th were separated on anion columns using a 0.5 mL Dowex AG 1x8 resin (Dow Chemical Co., Midland, MI, USA). U and Th mass spectrometry was carried out on a multicollector inductively coupled plasma mass spectrometer (Nu Instruments, Oxford, UK) equipped with an ESI (Elemental Scientific Inc., Omaha, NE, USA) Apex desolvating system without membrane and using a self-aspirating nebulizer. The electron multiplier yield was calibrated every four samples by running a NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) U050 solution (a reference standard material, which has a certified ratio of ^{235}U/^{238}U = 0.05278). U measurements were made from 0.5 N HNO_3 solutions in static mode, where masses 236 and 234 were measured in parallel electron multipliers and 235 and 238 in Faraday cups. Th measure-

ments were made from 3 N HCl solutions in a two-cycle multicollector dynamic mode, where one electron multiplier, equipped with a wide-angle retarding potential (WARP) filter, alternatingly measured masses 229 and 230. Ages and errors presented with ^{230}Th(0) = 0.8·^{232}Th correction. Some U-Th data were verified by an additional age determination at the National Taiwan University, Taipei (see Supporting Information for details). The obtained ages are absolute ones and given as BP ('Before Present'), whereas archaeological ages are usually given as BC ('Before Christ').

Carbon and oxygen isotope compositions of drilled calcite samples at a spatial resolution of 1 cm were determined using the conventional H_3PO_4 digestion method[27] at 25°C and a Finnigan MAT delta S mass spectrometer at the Institute for Geochemical Research in Budapest, Hungary. Samples drilled at high spatial resolution (~0.5 mm) were analyzed using an automated carbonate preparation device (GAS-BENCH II) and a ThermoFinnigan delta plus XL continuous flow mass spectrometer at the University of Lausanne, Switzerland.[28] (Finnigan MAT and ThermoFinnigan are former brand names of Thermo Fisher Scientific Inc., Waltham, MA, USA). Standardization was conducted using laboratory calcite standards calibrated against the NBS-19 standard. The hydrogen isotope composition of inclusion-hosted water was determined by off-line thermal decrepitation and vacuum crushing followed by vacuum distillation purification of H_2O and conversion into H_2 by reaction with Zn alloy (produced at the Indiana University, Bloomington, IN, USA) at 480°C and 30 min. D/H ratios were measured in the evolved H_2 gas by continuous flow mass spectrometry using a GASBENCH II preparation device as inlet port to a ThermoFinnigan delta plus XP spectrometer at the Institute for Geochemical Research, Budapest, Hungray.[29] The results are expressed in the δ-notation ($\delta = (R_1/R_2 - 1) \times 1000$) where R_1 is the D/H, ^{13}C/^{12}C or ^{18}O/^{16}O ratio in the sample and R_2 the corresponding ratio of the standard (V-PDB for C and V-SMOW for H and O, in ‰). The reproducibilities for C and O isotope analyses are better than ±0.15‰. The analytical precision of δD analyses based on measurements of water standards and inclusion-bearing samples with 'known' isotopic compositions (conventionally analyzed before and at other laboratories) is better than 5‰.

Trace element compositions were analyzed by laser-ablation ICP-MS using an ELAN 6100 DRC ICP-MS instrument (Perkin-Elmer, Waltham, MA, USA) coupled with a excimer laser (193 nm, Geolas 200 M system; LAMBDA PHYSIK, Göttingen, Germany) at the University of Lausanne. The measurements were performed using the following settings: laser: 7 Hz, 28 kV, energy ~170 mJ, fluency ~13 J/cm^2; spot size 60 μm, acquisition time: gas blank ~30 s, data ~60 s. Helium was used as the carrier gas (flow rate of 1.1 L/min). Data were reduced using the CONVERT and LAMTRACE spreadsheets developed by S. E. Jackson (Macquarie University, Sydney, Australia). NIST612 glass was used as an external standard and electron microprobe measurements of Ca served as an internal standard. BCR-2 glass (certified reference material supplied by the US Geological Survey, Denver, CO, USA) was monitored during all analytical sessions and treated as unknowns during data reduction. The error is estimated to lie between 5 and 10% on a relative basis.
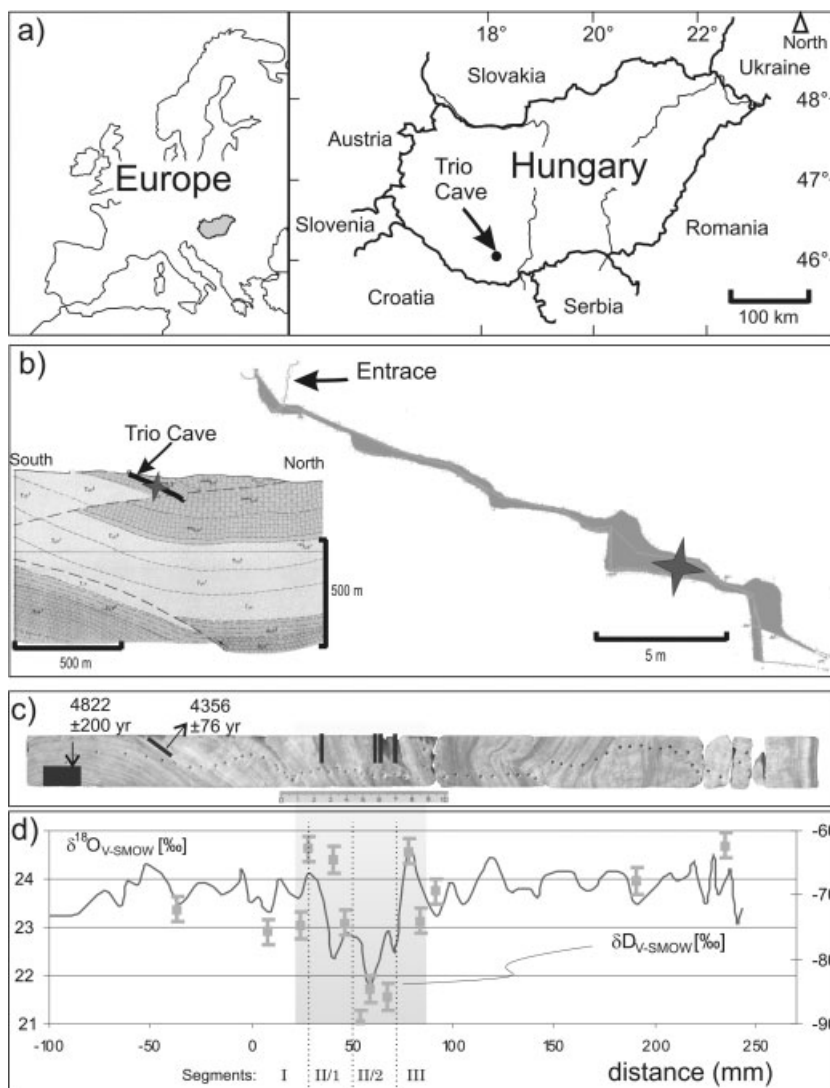
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Figure 1. (a) Location of Trio Cave in southern Hungary; (b) schematic cross-section of the Trio Cave and the surroundings with the sample location, indicated by cross (mapped and created by the SZKBE Cave Explorer Group in 2001–2002); (c) image of the drilled Trio stalagmite core. Positions of the U-Th age data reported in Fig. 2 are indicated by grey vertical bars, other data outside the distance range of Fig. 2 are given here; (d) stable H and O isotope compositions of the carbonate and the inclusion waters of the stalagmite core (indicated by curve and grey bars with errors, respectively). The section discussed in detail in this paper is indicated by the grey zone. Segments I–III are distinguished on the basis of isotope changes (see text and Fig. 2). The data are plotted against distance from the beginning of the section selected for this paper.

RESULTS AND DISCUSSION

Due to the large volume of data, the results are listed in the Supporting Information. A 42 cm long drill core from a stalagmite at the Trio Cave (Fig. 1(b)), southern Hungary, was analyzed. Based on preliminary U-series age determination data, this specimen began to form 4822 ± 200 years ago and was still actively growing when collected in 2001 AD. Following screening at low resolution (~1 cm; Fig. 1(c)), high-resolution C and O isotope analyses and high-precision U-Th age dating define a strong isotopic shift and systematic cyclicities in the ~3900–3200 years BP segment

(Figs. 2(a) and 2(b)). The isotope record of this section can be sub-divided into three segments (Figs. 1(c) and 2). Segment I defines the starting compositions of the stalagmite record. Segment II reflects a negative shift in $\delta^{18}O$ values (with segment II/2 marking the most negative $\delta^{18}O$ peak), and segment III represents a positive $\delta^{18}O$ trend including several positive peaks in $\delta^{18}O$ values.

The absence of $\delta^{13}C$-$\delta^{18}O$ correlations within the major $\delta^{18}O$ shift of segment II indicates that the isotopic changes are not related to a kinetic isotope fractionation process,[30,31] but rather to an external climatic forcing factor. This is supported by analyses on a single lamina of the early part of the
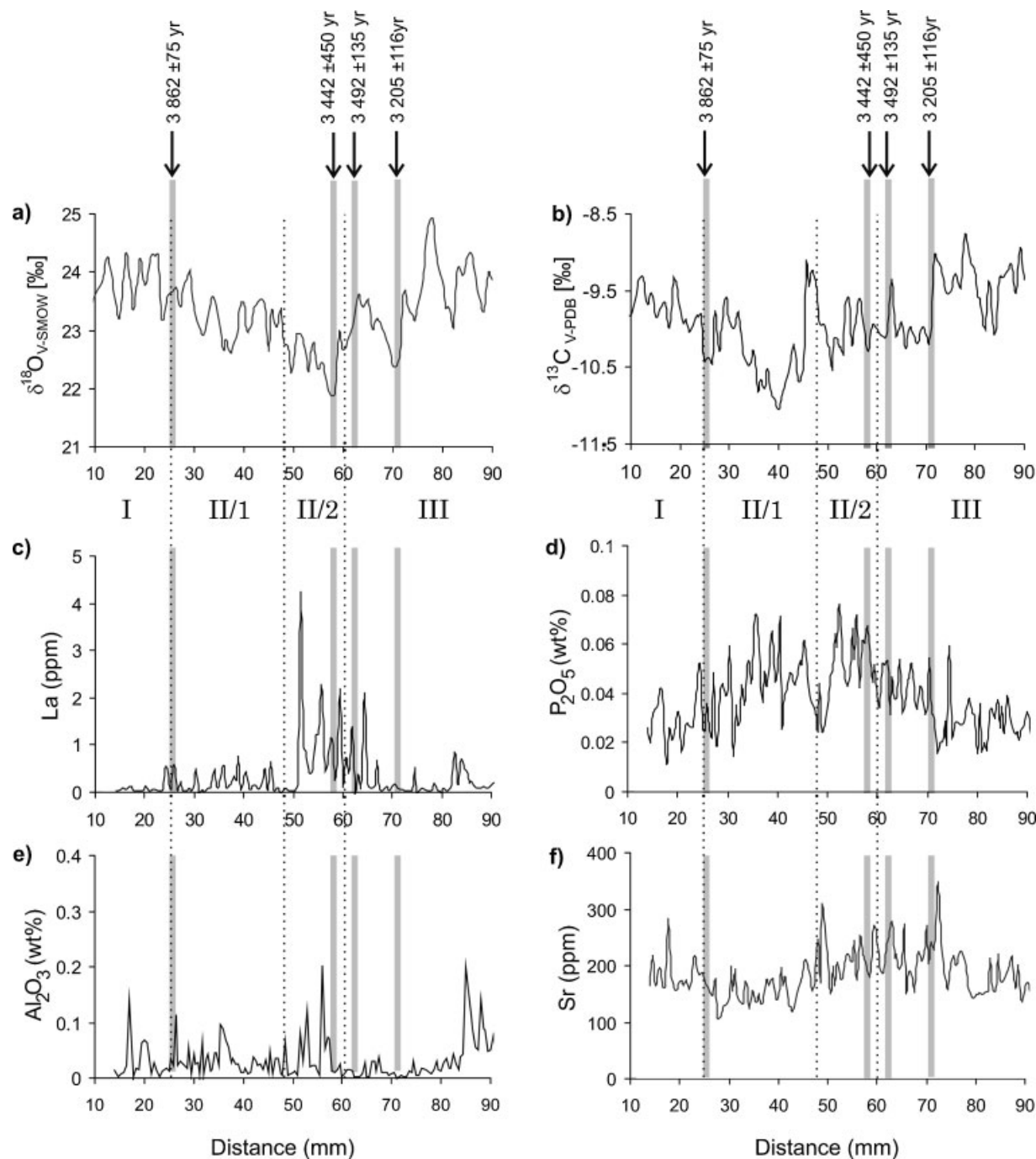
Figure 2. (a) Stable O isotope composition of the studied section; (b) stable C isotope compositions of the studied section (ca. 3900 to 3200 years BP) of the Trio stalagmite; (c) lanthanum, (d) phosphorus, (e) aluminium and (f) strontium contents of the studied section in the Trio stalagmite. Vertical grey bars show the position of the (MC-ICP-MS) U-Th data. All data are plotted against distance from the beginning of the selected section. Distinguished segments are marked by the numbers I, II, II/2 and III and separated by punctated lines (see text).

stalagmite where the selected layer could be analyzed at ~10 cm length. The $\delta^{13}C$ and $\delta^{18}O$ data showed no correlation in this lamina (determining a regression line with slope = 0.07 and R^2 = 0.01) indicating that carbonate precipitation took place in equilibrium.[30]

Before the detailed discussion of isotopic and trace element data, the effect of sampling bias should be addressed. Stalagmites are usually sampled along the growth axis in order to avoid fractionation that may occur as the dripwater flows down on the sides. This sampling protocol could not be

followed for the Trio stalagmite due to the strict protection, so it could be drilled only from the sides. The core shows (Fig. 1) an increasing dipping of laminae along the growth direction. However, all the laminae within the selected section part show the same dipping, so systematic variations within the section cannot be related to morphological changes.

As O isotope compositions depend on temperature and water composition, additional evidence for the role of these factors is needed. Information on water composition changes

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can be provided by fluid inclusions within the parent dripwaters entrapped during speleothem carbonate precipitation. D/H analysis of such inclusion water represents the isotopic composition of the paleoprecipitation at the cave site.[32–34] The average δD value (Fig. 1(c)) of segments I and II/1 is $-71‰$ (n = 6) and for section III is $-67‰$ (n = 5), whereas section II/2 contains H_2O with a δD value of $-87‰$ (n = 3).[29] This change in H-isotopic composition is in good agreement with the expected δD shift, on the basis of the observed $\delta^{18}O$ change (Fig. 2(a)), assuming that the variation in water composition following the Meteoric Water Line relationship[35] ($-2‰$ $\delta^{18}O$ shift would correspond to $-16‰$ δD change). As water δD and $\delta^{18}O$ values get lower with decreasing atmospheric temperature, the δD data support the premise that speleothem $\delta^{18}O$ values represent a climate-related phenomenon.

As a first-order interpretation, $\delta^{18}O_{calcite}$ changes can be related to a cooling period that produces lower $^{18}O/^{16}O$ ratios in the infiltrating meteoric water. A lower precipitation temperature would, however, induce larger calcite-water O isotope fractionation, shifting carbonate $\delta^{18}O$ values in a positive direction.[36,37] The resulting change in these opposing processes is about 0.35‰/°C. Furthermore, as the sampled sections encompass several years, the observed changes in ^{18}O may reflect variations in the relative amounts of winter and summer precipitation. More humid winters would produce lower $^{18}O/^{16}O$ ratios in the infiltrating water, whereas higher degree of evaporation would drive the $\delta^{18}O$ value of meteoric water in a positive direction.

Humidity can also be inferred from the $\delta^{13}C$ values (Fig. 2(b)). An increase in the biological activity of the soil could result in lower $^{13}C/^{12}C$ ratios of the dripwater, hence resulting in low $\delta^{13}C$ values in the precipitating carbonate.[38] Warm and humid climate would enhance the bioactivity in the soil, while dry climate and/or strong cooling would have the opposite effect.[39,40] It is not unrealistic to expect that these complex processes may also affect the trace element concentrations within the carbonate of the stalagmite. Phosphorus is usually regarded as a proxy element of soil activity, with high P contents in water (and in the stalagmites) from sources with high biogenic productivity.[41] The Si and Al content would indicate the significance of silicate rock weathering, whereas the Mg and Sr content depends on temperature and rate of precipitation, evaporation of dripwater solutions and carbonate precipitation along the infiltration pathways,[42] as well as on dissolution of surrounding rocks.[43]

As shown in Fig. 2(c), the speleothem P content varies with the $\delta^{13}C$ changes with good anti-correlation (elevated P contents at lower $\delta^{13}C$ values), suggesting an increase of biogenic activity during the period marked by the negative $\delta^{18}O$ shift. Cooling, as indicated by the $\delta^{18}O$ values, would cause a decline in biogenic activity under arid conditions; thus, the increasing biogenic activity observed here would suggest more humid conditions when associated with cooling. This period is followed by a decreasing biogenic signal in segment III with an overall positive $\delta^{18}O$ shift, indicating a climate change to warmer and more arid conditions.

Superficial weathering of silicate rocks would be reflected by Si, Al, Fe and Th contents in dripping waters, and, hence, in the precipitating carbonate. Monitoring of dripwater composition was not conducted in the present study as (i) strict protection of the cave does not allow frequent sampling, and (ii) it would correspond only to the recent part of the stalagmite and the long-term weathering behaviour of the area cannot be ascertained from the data. However, it is important to note that the stalagmite segment corresponding to the time period under consideration shows no systematic variation of these elements; see Al for example (Fig. 2(e)). Mg and Sr data (Fig. 2(f)) for this section of the Trio Cave stalagmite core exhibit only unsystematic variations and do not support a major change in the processes controlling the weathering zone mobility of these elements. In contrast, rare earth elements (REEs; here La, Ce, Pr, Nd) and Y, which behaves in a manner similar to the heavy REEs (from Eu to Lu by definition), exhibit large variations in concentration and display a systematic distribution across the three sections of the stalagmite core. The similar geochemical behaviour is supported by the fact that the Y contents show perfect linear correlations with the concentrations of La, Pr and Nd (with R^2 values of 0.94, 0.91 and 0.91, respectively). Ce is an exclusion in this case as it is decoupled from Y and the other REEs in the selected section (with R^2 values between 0.18 and 0.24) probably related to its sensitivity to redox conditions. Further discussions of this phenomenon will be given in another paper. In segment I, the REEs are at background level (<0.3 ppm), whereas in segment II, with the appearance of the first REE and Y peaks, they rise to 0.5 ppm and coincide with the onset of the shift in $\delta^{18}O$ values. The REE content rises abruptly by about an order of magnitude at the point where the $\delta^{18}O$ value is at its lowest in segment II/2 (Fig. 2(c)). Thereafter, the REE and Y contents gradually decrease to <1 ppm, with only minor fluctuations.

The causes of stepwise REE enrichment are considered to be particularly important in view of the changes in climate indicated by the speleothem isotopic compositions. Several mechanisms can explain the variations in REEs and Y, for example, weathering of local bedrock, which consists of Permian and Triassic sandstones and limestones. Limestone dissolution is an ongoing process in cave carbonate formation; thus, an increase in limestone-derived REE contents (due to enhanced dissolution and/or concentration rise during evaporation) would also be associated with an increase in Sr and Mg concentrations. Such a relationship cannot be found in the selected section, La shows no correlation with Sr and Mg (R^2 values <0.05); thus, increasing contribution of limestone-derived REEs as an explanation for the elevated REE contents can be excluded.

Weathering of sandstones or deposited silicious dust derived from continental areas may provide an appropriate source of REEs, so the behaviour of sandstone-related elements should be evaluated. A longer core section of about 20 cm (including the 9 cm section described in detail) was analyzed by LA-ICP-MS at a resolution of 0.6 mm in order to place any change in REEs into a longer temporal context (see Table 3 in Supporting Information). In general, Th is well correlated with Si and Al, both in the selected and the entire section (with R^2 values of 0.8-0.9), suggesting a detrital origin from siliceous rocks. In order to determine the origin of REEs, the concentrations of Th and La are plotted in
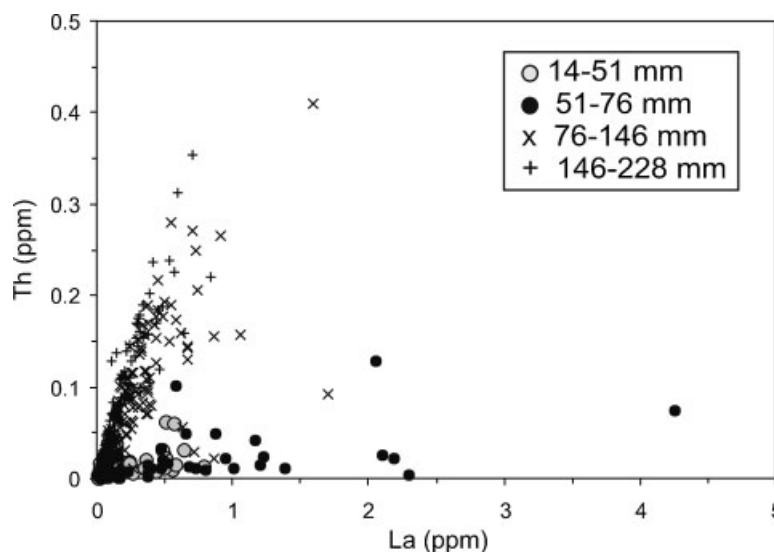
Figure 3. Th versus La contents (in ppm) in the Trio stalagmite.

Fig. 3. The data distribution indicates that the stalagmite section between 51 and 76 mm (ca. 3500–3200 years BP) differs significantly from the other part of the core (black dots in Fig. 3), making it imperative that a source of REEs separate from the local country rocks or silicious dust transported from continental areas be found. This is further supported by the fact that no systematic Sr-Mg-Si-Al-Th variations are associated with the changes in REEs in the 3900–3200 years BP section, so the effect of enhanced weathering and dissolution of the country rocks and siliceous continental dust as a source of REEs can be confidently excluded.

As major volcanic eruptions are known for this period in the Mediterranean region (the Avellino eruption of Mount-Vesuvius[44] and the Thera eruption of Santorini[22,45,46]), deposition of volcanic dust should be considered as a source of REEs. As tephra deposits (air-fall material of volcanic origin) are prone to rapid weathering, this can result in a release of REEs and thus provide a feasible source of material that can be transported as dissolved ions or as colloidal particles. Based on the U-Th age datings for the section, the age of the REE peak is about 3560 years BP, agreeing strongly with the age of 3660–3613 years BP for the Thera eruption.[22]

One of the major strengths of stalagmite records is their reproducibility. Their geochemical characteristics can be interpreted as reflecting regional or global climate change processes where comparable regional records from other stalagmites can be correlated at appropriate precision (called the 'replication test').[47] For a valid correlation of records, the geochemical data should be plotted against time. Based on the U-Th data, the age model in this study (calculation of growth rate for the given section) was established as follows. The obtained ages have a very good linear correlation with sampling distance ($R^2 = 0.99$) according to the following equation:

$$Age = -8.2386 \, (distance) + 3980,$$

where age is given in years BP, and distance is given in mm from the starting point of the core. The geochemical data were plotted versus the calculated ages in Fig. 4 that shows the $\delta^{18}O$, $\delta^{13}C$ and La content data obtained on the Trio

stalagmite in comparison with $\delta^{18}O$ data from speleothems of Austria (called 'COMNISPA', a record compiled from O isotope data obtained on several stalagmites collected in the Spannagel Cave)[48] and $\delta^{13}C$ and sulphur content data from a stalagmite from the Sofular Cave, Turkey, reported by Frisia *et al.*[25] The $\delta^{18}O$ patterns of the COMNISPA record and Trio stalagmite show strong similarities in the entire 5000 year long section, suggesting that the Trio stalagmite recorded regional climate processes. It is notable that the selected period of 3800 to 3300 years BP contains a strong negative $\delta^{18}O$ peak that can be identified in both records and correlated within 100 years. The observed similarities for the C isotope variation shows a strong positive peak at about 3600 years BP in both the Trio and the Sofular Caves with their calculated ages being within a decade of each other. Changes in the O isotope composition thus appear to reflect climate variations within a time scale of several hundred years, whereas the C isotope peak is not associated with appreciable $\delta^{18}O$ change and records a very rapid process limited to a few decades. The age of 3600 years BP fits the Santorini eruption within the usual age dating limit (∼50–100 years). The strong $\delta^{13}C$ shift can be produced by sudden decrease in soil and vegetation activity, also supported by the contemporaneous drop in the phosphorus content of the Trio stalagmite (between 46 and 52 mm; see Fig. 2).

The correlation of different records reveals further features that can be interpreted more confidently if obtained from more than a single site. Interestingly, the REE content shows a lag compared with the $\delta^{13}C$ peak, as it does to the sulphur content in the Sofular stalagmite.[25] This delay in the trace element change can be related to the deposition of volcanic material that affects the vegetation activity immediately, but whose erosion and weathering take time. The difference in the degree of delay between the two caves may be caused by the variation in annual precipitation and soil thickness or its filtering affect. The Trio Cave is situated in a valley of a forested area; thus, its expected filtering effect would be stronger than at Sofular Cave situated in an open landscape in Anatolia (Turkey), resulting in a longer transfer of trace elements.
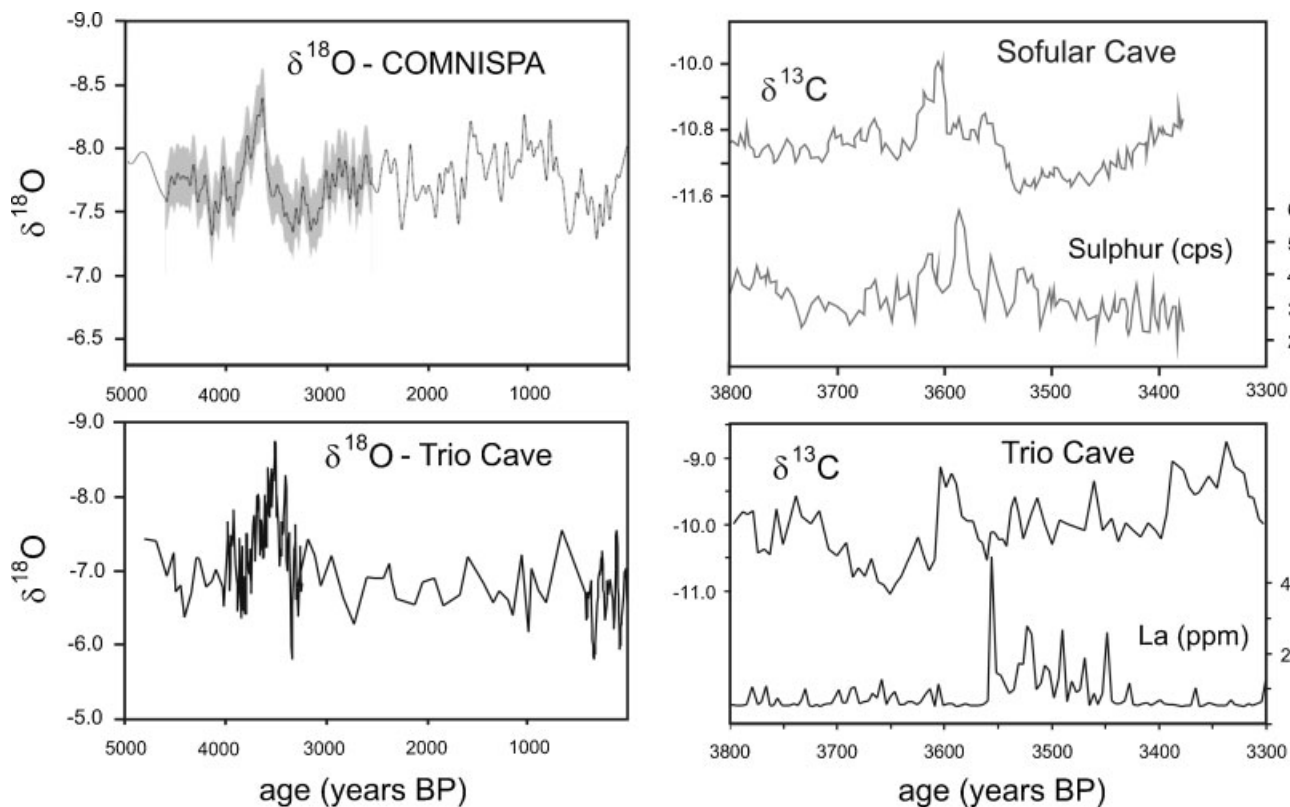
Figure 4. Stable oxygen and carbon isotope compositions (in ‰ relative to V-PDB), La content (in ppm) and sulphur content (in counts per second obtained by synchrotron radiation-based micro X-ray fluorescence analyses) versus time in the stalagmites of the Trio (this study), the Spannagel (COMNISPA record)[35] and Sofular[17] Caves.

CONCLUSIONS

Combined isotopic and trace element analyses of a stalagmite of the Middle Bronze Age period from the Trio Cave in Hungary record volcanic influence within a period of cooling and increased humidity followed by rapid warming and a more arid climate between 3900 and 3200 years BP. The observed climatic change is very similar to the millennial-scale climate variations attributed to changes in global volcanic activity. The cooling and humidity changes are mainly detected on the basis of oxygen isotope data, but variations in phosphorus content also reflect increase and decrease in soil activity spanning several hundred years. The combined REE and isotope data suggest that the Minoan volcanic activity in the Middle Bronze Age was superimposed upon already intensified climate changes that lasted for about 300 years. The signal for the volcanic influence was detected as a sharp carbon isotope peak and sudden elevations in concentrations of REEs. Both the oxygen and carbon isotope records can be confidently correlated with several contemporary speleothem records in the Alpine-Mediterranean region, thus lending support to the conclusions drawn from the study of the Trio stalagmite. As we have shown in this study, the application of high-resolution techniques (e.g. laser-ablation ICP-MS), with absolute dated studies of stable isotope and trace element variations in speleothems, offers a means to identify the influence of volcanic activity on short-term climate variations. The detailed study of an appropriately dated speleothem can provide a method for the identification of violent eruptions and any subsequent climate downturn, independently from other proxies.

SUPPORTING INFORMATION^Q3

Additional supporting information may be found in the online version of this article.

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