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Article

Keywords: tephrostratigraphy, volcanic ash, tephra, volcanism, Southern Andes, non-karst, speleothem, dating

Posted Date: April 14th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-350595/v1>

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Version of Record: A version of this preprint was published at Communications Earth & Environment on February 10th, 2022. See the published version at <https://doi.org/10.1038/s43247-022-00358-0>.

High-resolution stalagmite stratigraphy supports the Late Holocene tephrochronology of southernmost Patagonia

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Keywords: tephrostratigraphy, volcanic ash, tephra, volcanism, Southern Andes, non-karst, speleothem, dating

Abstract

Volcanic ash layers are important markers for the chronostratigraphy of paleoclimate and paleoenvironmental archives at the southern tip of South America. However, this requires that tephra are well-dated. We report geochemical data from the MA1 stalagmite formed in a non-karst cave near Mt. Burney volcano in southernmost Patagonia (~53°S). High-resolution LA-ICP-MS analyses, SEM imagery, and NanoSIMS enable to identify volcanogenic signals during the last 4.5 kyrs BP from sub-annual trace element variations and tephra particles in distinct laminae. The new $^{230}\text{Th}/\text{U}$ -chronology of MA1 provides precise dating of tephra from Mt. Burney (MB) and Aguilera (A) at 4216 $^{+93}_{-193}$ yrs BP (MB₂), 2291 $\pm$ 33 yrs BP (MB₃), 853 $^{+41}_{-60}$ yrs BP (MB₄) and 2978 $^{+91}_{-104}$ yrs BP (A₁). This unique high-resolution record of MA1 holds potential to date further eruptions from Southern Andean volcanoes for the tephrochronology in this critical region, and potentially also large-volume explosive volcanism off South America.

Introduction

Severe and long-lasting impact on regional ecosystems from explosive volcanic eruptions and ash (tephra) fallout has been observed in fragile environments such as the super-humid South Patagonian Andes^{1,2}. While geochemical fingerprinting links tephra glass shard compositions to their volcanic source and represents a valuable tool in tephrochronology³, the dating of distinct tephra layers enables a reconstruction of the regional history of volcanic activity and provides isochronous marker horizons for stratigraphic interpretations and correlation of paleoenvironmental archives over large geographical areas⁴. Despite intensive research and rapid advances in the development of tephrochronological methods in the last few decades, the accurate identification of distinct tephra layers and the precise synchronization of single volcanic events recorded in geological archives from different depositional environments remains challenging^{4,5}.

Accurate age constraints are particularly difficult for sedimentary archives in southernmost Patagonia. There, the ages of widespread Holocene tephra layers from Plinian eruptions from volcanoes of the Patagonian Andes⁶ in the southern segment of the Southern (41.5 – 46°S) and the Austral (49 – 55°S) Volcanic Zones were mainly deduced from ^{14}C -dated materials of terrestrial outcrops, peat and marine/lacustrine sediment cores^{3,5,7,8}. This tephrochronological framework constitutes a principal reference for the stratigraphy of most geological records used in paleoclimate/paleoenvironmental studies from this climatically unique and poorly explored region⁹.

Age uncertainties and problems with correlation of tephra layers in regional soils and sediment or peat core archives are due to variable composition, unclear stratigraphy and diverging chronologies based on ^{14}C -dated carbonates, bulk organic matter (OM) or single plant remains^{3,4}. In particular, ^{14}C -dated components of soils and sediments can have age offsets of hundreds of years due to reservoir effects caused by, e.g., the re-sedimentation and bioturbation of older OM or carbonate dissolution^{10,11}, which have serious implications for age models. Large errors in age determination of volcanic ash layers also occur from interpolation of bracketing ^{14}C -dates⁴ and/or age constraints based on estimated sedimentation/peat accumulation rates^{12,13}.

Further challenges include the correct identification of the source volcano by the characteristic physical/textural properties as well as the mineralogical and geochemical composition of tephra pumice and glass shards⁸. Site-dependent, potentially intense weathering processes in acidic peatland ecosystems¹⁴ can compromise geochemical fingerprinting methods for tephra correlation³. Chemical weathering over long periods strongly alters the composition of volcanic glass and embedded phenocrysts, leading to drastic changes of major and trace element concentrations^{15,16,17}.

Albeit their increasingly important role as high-resolution terrestrial archives for the reconstruction of past climate variations and environmental changes, only few speleothem records have so far contributed to regional tephrochronologies worldwide^{18,19,20,21,22}. This is due to the fact that an unequivocal detection of volcanic signals in speleothems is difficult and speleothems containing distinct layers with tephra glass shards or even small pumice particles have – to our knowledge – not yet been documented.

However, speleothems can be very useful for such studies because $^{230}\text{Th}/\text{U}$ -dating allows exceptionally accurate and precise dating and variations in chemical elements can be detected with up to (sub-) annual resolution. Therefore, speleothems have great potential for high precision dating of volcanic events comparable to ice core tephra records^{18,23}. Combined with stable isotope data ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) and other trace element proxies, speleothem records enable both the dating of volcanic activity and the evaluation of possible environmental and climate impacts following from the documented eruptions^{18,19,20,21}.

In this work, we analyze a non-karst speleothem (MA1 stalagmite²⁴) to better constrain the Late Holocene tephrostratigraphy in Southern Patagonia and provide evidence for soil-environmental changes related to tephra deposition under extreme climate conditions. This speleothem formed in a small cave ca. 40 km S of Mt. Burney volcano and recorded sub-annual trace element variations detected by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). These high-resolution compositional profiles were combined with a refined $^{230}\text{Th}/\text{U}$ -chronology age model constructed from published²⁴ and additional new $^{230}\text{Th}/\text{U}$ -dates. Based on this improved age model, our new LA-ICP-MS data, and a principal component analysis (PCA), we (i) detect pyroclastic particles incorporated into the stalagmite, (ii) identify and date the ash as MB₂ and MB₃ tephra of the Mt. Burney eruptions and document further volcanic signals from Mt. Burney and Aguilera. Furthermore, (iii) MA1 recorded the environmental response to changes in the hydrological/pedological regime caused by the eruptions and

their deposits. In addition, scanning electron microscopy (SEM) and nanoscale secondary ion mass spectrometry (NanoSIMS) of detrital components preserved in selected, distinct lamina were used to support the identification of MB₂ and MB₃ tephra. Within the context of the new data reported here, previously published stable isotope data ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) of MA1²⁴ provide additional constraints on short-term perturbations of the local surface hydrology following both eruptions.

Environmental context and characteristics of the MA1 stalagmite

The MA1 stalagmite was obtained from the Marcelo Arévalo (MA) cave, situated at 20 m a.s.l. in the Magellanic moorlands at 52°41.7'S/73°23.3'W²⁴ (Fig. 1a). The cave developed in a nearly vertical tectonic fracture zone cross-cutting a plutonic sequence of granitoids, orthogneiss and mafic dykes²⁵ (Fig. 1b). The hydrologic system in this fracture zone directly connects the cave with a small catchment (625 m²) at 80 m a.s.l. that is characterized by acidic, waterlogged peatland soils and surrounding bare rock outcrops²⁵ (Fig. 1b). The super-humid climate in this region is controlled by pronounced seasonal variations of the southern westerly wind belt^{26,27} (SWW) and a present annual precipitation of ~3,800 mm a⁻¹²⁸ (recorded at the automatic weather station Arévalo, Fig. 1b). Reconstructed annual precipitation during the Late Holocene reached up to 6,500 mm a⁻¹²⁴. Elevated drip rates (~150 – 250 cm³ d⁻¹) measured at the MA1 sampling site vary within the seasonal course²⁴. An estimated maximum delay of only 4 – 6 weeks between major rainfall events and increased drip rates²⁴ indicates a relatively high transmissivity of the fractured aquifer system due to a good connectivity of the cave with the local surface hydrology in combination with the extraordinary precipitation. MA1 shows a rather constant mean growth rate of 67 $\mu\text{m a}^{-1}$ (minor variations of 25 – 100 $\mu\text{m a}^{-1}$) and continuous growth over the last 4.5 kyrs BP²⁴.

Fig. 1

The cave site is located only 40 km S of the Mt. Burney volcano (52°19'S/73°22'W, Fig. 1a), the most active volcano of the Austral Volcanic Zone during the Late Quaternary⁵. Originating from this volcano, ten Holocene Plinian eruptions dispersed tephra layers across wide areas of southernmost South America³. Particularly after the large-volume MB₂ eruption, regional pristine ecosystems suffered a millennium-scale damage caused by a SO₂-induced acidification associated with the deposition of >10 cm of volcanic ash^{1,2}. In contrast, the tephra deposits from the significantly smaller MB₃ eruption are only a few millimeters thick^{12,13}.

Results

Chronology

We used StalAge²⁹ to construct a new age-depth model for the MA1 speleothem compared to the previous study of Schimpf et al.²⁴ (Fig. 2). It is based on 18 ²³⁰Th/U-ages (instead of 16) and a slightly modified correction factor for detrital Th according to Budsky et al.³⁰. The results of ²³⁰Th/U-dating, including the improved detritus correction, are shown in Table S1. The applied StalAge model for MA1 covers the entire 28 cm length along the growth axis of the speleothem, representing about 4.8 kyrs. For details of the ²³⁰Th/U age constraints, detritus correction and the construction of the age model, see the “Methods” section.

Fig. 2

Element concentrations determined by LA-ICP-MS

Concentrations of S, P, U, Si, Sr, and Zr – selected by virtue of the well-known composition of Mt. Burney tephra^{7,8,31} and the environmental impact after the deposition of MB₂ ash¹ – were measured on thin sections prepared along the entire length of MA1 (4.5 to 0.6 kyrs BP) and are presented in Figs. 3-5. Average elemental concentrations were determined from a total 59,200 LA-ICP-MS measurements for S (132 ppm), P (2212 ppm), U (2.4 ppm), Si (1397 ppm), Sr (197 ppm), and Zr (3.2 ppm). Against this background, we observe numerous high amplitude spikes identified as short (few months up to three years) and strong variations in the deposition of these elements. Such peak concentrations reached >10 ppm for U and Zr, >400 ppm for Sr, >1,000 ppm for S and P and easily exceeded 10,000 ppm in case of Si (Figs. 3-5). These high amplitude spikes are well correlated for S, P, U, Si, Sr, and Zr and appear highly irregular with respect to frequency and intensity along the profiles. Particular conspicuous spikes of S, P, U, Sr, and partly Zr, occur at 0.853, 2.291, 2.978 and 4.216 kyrs BP (Fig. 3). At 4.216 and 2.291 kyrs BP (highlighted by orange bars; Fig. 4), both peaks are followed by (i) a series of smaller, but equally discrete, short-term spikes for the same elements decreasing in height or by (ii) more extended periods characterized by consistently elevated concentrations from ~4.20 to 4.15 kyrs BP, respectively (gray bars; Fig. 4).

As would be expected for elements that are contributed from detrital silicate, Si should be closely related with Zr. Indeed, Fig. 5 shows that a large number of LA-ICP-MS measurements fall on a tight correlation trend that projects from the origin with a Si/Zr ratio of 3300 towards the composition of MB₂ glass with average values of 77 wt.% SiO₂ and 110 ppm Zr^{7,8}. This trend with this Si/Zr ratio therefore represents a mixing line between two endmembers: the Si- and Zr- rich MB₂ glass and the Si- and Zr-free, CaCO₃-rich matrix of the speleothem. More elevated concentrations of Zr and Si (Fig. 5a) are an artifact from the normalization to Ca in LA-ICP-MS measurements that include significant but unknown amounts of a non-carbonate component (i.e. tephra, which is lower in Ca compared to the carbonate). This artifact in the concentration data is (i) not avoidable and (ii) does not affect the characteristic Si/Zr ratio of the ash component. However, a large number of analyses fall off this correlation trend (Fig. 5) and can be attributed to silicate minerals derived from basement rocks. One additional component is thus identified as particular rich in Si (and low in Zr) and probably represents quartz, whereas a few data points tend towards high Zr and may be caused by traces of detrital zircon.

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Fig. 5

In order to further characterize elemental peaks of Si, Zr, S and other elements in the speleothem record and to provide for tests that these may represent volcanic signals, we analyzed the data set using a PCA^{22,32}. The first three principal components (PC) explained 80.7% of the variability within the entire data set (Figs. 6 and S1, and Table S2). High scores for PC-1 (44.4%), PC-2 (19.4%) and PC-3 (16.9%) reflected the correlated trace element peaks as discussed above and displayed in Figs. 3-5. PC-1 had high loadings of S, P, U and Si, whereas PC-2 loadings mirrored mainly Si and Sr. Zr was dominantly loaded on PC-3. High PC scores, particularly of PC-1, suggest distinct depositional events at 0.853, 2.291, 2.978 and 4.216 kyrs BP. However, all PCs show a high variability in score values from 4.20 to 4.15 kyrs BP and synchronous spikes from 2.27 to 2.17 kyrs BP.

Fig. 6

Detection of tephra particles by SEM and NanoSIMS

Images obtained from SEM of detrital siliciclastic components in laminae at 4.15 and 2.20 kyrs BP where PC scores and concentrations of Si and Zr are high are shown in Figs. 7a-c. Some layers were found to be particularly rich in fragments of pyroclastic material (Fig. S3), comprised of either vesicular glass shards (Fig. 7a; 2.20 kyrs BP) or phenocrysts glazed with a thin coating of volcanic glass (Figs. 7b-c; 4.15 kyrs BP). These images document the perfect preservation of micro-tephra that were included during the growth of the speleothem.

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206 Detritus-rich inclusions were further analyzed in-situ by NanoSIMS (Figs. 7d-e and S2). The $30 \times 30 \mu\text{m}$
 207 measurement spots focused on non-carbonate materials accumulated in lamina sections at ~3.92 and
 208 ~2.29 kyr BP. Elevated $^{28}\text{Si}^-$ and $^{16}\text{O}^-$ secondary ion counts indicate an enrichment of irregularly shaped,
 209 in part porous siliciclastic particles of 5 to 15 μm size which are framed by thin rims that are high in
 210 $^{27}\text{Al}^{16}\text{O}^-$ counts (Figs. 7d-e and S2a). $^{12}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$ demonstrate that these micron scale particles are
 211 embedded in a matrix of OM with dispersed Fe and Al as indicated by spots of $^{56}\text{Fe}^{16}\text{O}^-$ and $^{27}\text{Al}^{16}\text{O}^-$.
 212 NanoSIMS measurements on inclusions at ~3.50 and ~3.11 kyr BP did not detect intact siliciclastic
 213 particles (Figs. S2b-c). Spots with higher $^{28}\text{Si}^-$, $^{27}\text{Al}^{16}\text{O}^-$, and $^{56}\text{Fe}^{16}\text{O}^-$ counts appear as fine flaky
 214 structures. These structures occur scattered throughout the observed areas and correlate with high $^{12}\text{C}^-$,

$^{12}\text{C}^{14}\text{N}$, and ^{32}S signals from OM. Grains of bedrock-derived mineral detritus, such as quartz, were identified at ~0.73 kyrs BP by strong localized signals of ^{28}Si and absence of any other elements (Fig. S2d). However, in this case, thin $^{27}\text{Al}^{16}\text{O}$ -rims have not been observed.

Discussion

Identifying volcanic input by compositional spikes of characteristic elements in the MA1 record provides means for precise dating and the correlation of volcanic ash inputs into Patagonian soils and environmental archives⁹. In order to identify such volcanic signals, we need to consider the direct primary elemental deposition from tephra, volcanic volatiles and leached components. In addition, there may be a secondary response to tephra deposition on peatland soils that potentially affects nutrient cycling³³, chemical leaching^{15,16}, and soil C stocks^{34,35}. Pristine peatland ecosystems such as those of southern Patagonia may be particularly sensitive to such volcanic impacts with high tephra-loading and variable climate conditions^{1,36}. Finally, we will address the implications and improved age constraints of tephra signals that we detected in the MA1 speleothem.

The primary elemental deposition and leaching from tephra comes from a contribution of fine-grained glassy tephra particles and is identified by synchronous and sharp peaks of Zr and Si. These peaks indicate the accumulation of volcanic glass at and after 4.216 and 2.291 kyrs BP (Fig. 5) and identifies the ash component by its Si/Zr ratio of about 3300 which is similar to MB₂ glass (Fig. 5). These primary tephra signals also determine the high amplitude spikes of PCs 1 – 3 (Figs. 6 and S1). The presence of tephra fragments in the stalagmite is verified by SEM imaging in Figs. 7a-c. The structure of observed shards and vesicle-rich glass coatings on phenocrysts resemble characteristics of the well-documented Mt. Burney tephra^{1,7,8,13,31}. Indications of recurring tephra input over time spans of 60 yrs are found also directly after the 4.216 and 2.291 kyrs BP ashfall events by continued elevated Zr and Si contents at 4.20, 4.18, 4.14 and 2.26, 2.20, 2.19 kyrs BP (Fig. 5). This additional siliciclastic input is most likely caused by repeated periods of tephra reworking and deposition caused by distinct storm events^{9,26}. Owing to differences in rainfall²⁴ shown by variable $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ levels in (Figs. 3-4), a climate-induced influence on the hydrological soil-to-stalagmite transport is suggested, explaining a slightly dissimilar response to tephra fallout recorded by the MA1 stalagmite during 4.5 – 4.0 kyrs BP compared to 2.5 – 2.0 kyrs BP.

Micron-sized volcanic glass fragments with superficial alteration rims were observed by NanoSIMS analyses (Figs. 7d-e and S2a). Their texture differs significantly from bedrock-derived silicates (Fig. S2d). These images identify rims rich in $^{27}\text{Al}^{16}\text{O}$ around the glass particles indicating the formation of secondary alumino-silicates³⁷. This is consistent with recent studies that documented pronounced glass leaching and deposition of Al-(hydr)oxides related to tephra weathering in other humid acidic environments^{16,38,39}. The close textural relation between $^{27}\text{Al}^{16}\text{O}$ -enrichments and OM ($^{12}\text{C}^{14}\text{N}$)

surrounding the observed particles (Figs. 7d-e and S2a) suggests that the leaching processes likely occurred in-situ in the micro-chemical environment at the stalagmite surface and during the deposition of the tephra particles.

Apart from this in-situ alteration of glass shards and their incorporation into the growing stalagmite, there will also be secondary effects in soils as a response to volcanic fallout. Various volcanogenic chemical compounds dissolve rapidly in surface environments after the direct wet deposition of acid rain from the eruption plume and/or after leaching by water from freshly deposited tephra^{15,33}. Typical chemical compounds leached from pristine tephra are sulfates and a range of soluble salts containing other mobile and volatile metals³³. Here, we focus on S, P, Sr and U to trace solutes potentially derived from Mt. Burney tephra that has been identified here and for which the composition is well known^{7,8,31}.

While chemical signals indicate the prolonged chemical effect of tephra deposition (i.e. elevated Si, Sr and Zr in Figs. 3 and 5), pristine tephra particles are absent in speleothem lamina at ~3.50 and ~3.11 kyrs BP (Figs. S2b-c). During this time, Kilian et al.¹ documented a millennium-scale acidification phase in regional soils following the Plinian MB₂ eruption. This may have caused efficient chemical alteration of tephra and transport of leached elements from the catchment to the speleothem. Accordingly, we observe correlated patterns of ¹²C¹⁴N⁻, ²⁸Si⁻, ²⁷Al¹⁶O⁻, and ⁵⁶Fe¹⁶O⁻ counts in NanoSIMS images of the speleothem during this period (Figs. S2b-c), which indicate the accumulation of silicate weathering products together with OM^{37,40}. These residues are typical for the decomposition of glassy tephra in acidic soils and are likely comprised of organo-mineral complexes enriched in Al-/Fe-(hydroxides) and silica gels^{16,38,39}. The low pH of 3.9 – 5.4 in soils of the MA catchment²⁵ may also promote mobilization of water-soluble Sr and U from fresh volcanic glass^{17,33}. We therefore interpret the short-term release of Sr and U as a signal of tephra leaching in acidic waterlogged peat soils^{1,14} at 4.216 and 2.291 kyrs BP (Figs. 3-4). We associate the periodically increasing Sr and U concentrations in time periods following the eruptions with the storm phase-induced incorporation of leached elements from tephra in the catchment. The high peaks of Sr could additionally be explained by a contribution from plagioclase phenocrysts^{21,22} embedded in MA1 (e.g., mineral components in Figs. 7b-c), which are – next to volcanic glass – a dominant component of tephra from Mt. Burney^{7,31}.

PCA results (Figs. 6 and S1, Table S2) discriminate two different domains covered by element concentrations in MA1. PC-1 mainly reflects high concentrations of presumably volcanogenic SO₄²⁻ and PO₄³⁻^{15,18,22}. Second, we expect a simultaneous mobilization of S- and P-bearing species adsorbed to pedogenic OM^{41,42} due to the sudden perturbation of peat soil hydro-chemistry after ashfall^{1,2,36}. Accordingly, high amounts of detected ³²S⁻, ¹²C⁻ and ¹²C¹⁴N⁻ secondary ions counts (Figs. 7 and S2) imply a direct linkage between soil OM and S in the stalagmite^{43,44,45}, as OM is obviously not associated with the composition of fresh tephra³³. In addition, PC-1 implies a contribution of siliciclastic components in the form of fine-grained detrital materials in combination with intense leaching processes with mobilization, transport and deposition of mobile lithophile elements from rock substrate or tephra

in soils. PC-2 and PC-3 primarily mirror siliciclastic components without a concurrent deposition of volcanogenic SO_4^{2-} and PO_4^{3-} . According to Jamieson et al.²², volcanic signals in a speleothem do not automatically produce a clear corresponding chemical excursion in the stalagmite stratigraphy. However, in our particular case, all three PCs are indicative of volcanic impacts on the soil-to-stalagmite transfer and deposition system. During the observed periods, PC-1 main spikes (Fig. 6) coincide well with peaks of the lithophile elements (Si, Sr, Zr and U) as well as S and P concentrations (Figs. 3-5). Such high amplitude compositional spikes, significantly exceeding average concentrations, are comparable to characteristic volcanic signals observed in other speleothems^{18,20,21,22,23}. According to our reasoning above, these distinct compositional peaks suggest volcanic events at 4.216 and 2.291 kyrs BP (Figs. 3-6 and S1).

We also observe variations of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ signatures²⁴ by 1 to 1.5‰ in the record following these 4.216 and 2.291 kyrs BP events. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ first decrease for ca. 10 years followed by higher values lasting for ~20 yrs (Fig. 4). We interpret these isotopic changes as a combined effect of varying rainfall intensity and short-term perturbations of the hydro-chemical soil system within the catchment subsequent to tephra deposition²¹. Environmental changes such as variations in redox-pH conditions, water table fluctuations and plant decomposition may strongly affect the release of dissolved organic matter (DOM) from peat soils^{46,47}. DOM can percolate into cave drip waters and be recorded in $\delta^{13}\text{C}$ signatures of speleothems^{20,43,44,45}. The close relationship between the abundance of OM that derives from drip water DOM and $^{12}\text{C}^-$ and $^{12}\text{C}^{14}\text{N}^-$ signals in detritus-rich laminae of MA1 is shown by the NanoSIMS measurements⁴⁰ (Figs. 7d-e and S2). Therefore, the link between detrital and volcanic input in MA1 and the fundamental changes in soil chemistry and hydrology in the catchment is clearly documented.

Finally, an import of elements such as S and Sr in the MA catchment area can also occur by sea salt aerosols^{24,48,49}. However, sea salt contribution from the nearby Pacific Ocean through surface deposition and transfer to cave drip waters is responsible for overall elevated concentrations compared to more “continental” speleothems^{21,22,23,50}. Such speleothems contain concentrations of, i.e., Sr ranging between 10 and 20 ppm^{22,50}. Consistent and strong SWW-induced wind velocities and frequent storm events in the region^{9,26} cause a constant deposition of sea spray-derived elements. These elements are characterized by short residence times in waterlogged peatland soils¹⁴ and therefore we argue that the high annual precipitation^{9,28} leads to a persistent input and “excess” sea salt S and Sr signatures in the speleothem. Thus, sea salt-derived S and Sr must be of secondary importance for the distinct high amplitude spikes of these elements, because their deposition would not result in the documented compositional spikes and a close correlation that we observed with other mobile and immobile lithophile trace elements (e.g., Si and Zr, Figs. 3-5) would not be expected.

These data have implications for tephrochronology because the results of our data prove that the MA1 stalagmite recorded distinct volcanic events for which we can determine precise ages from the refined

age-depth model using the StalAge algorithm²⁹ with errors represented by 95% confidence limits (Fig. 2a).

Based on ²³⁰Th/U-ages, these eruptions can now be dated more precisely to 4216 ^{+93/-193} yrs BP (MB₂) and 2291 ± 33 yrs BP (MB₃). The ²³⁰Th/U-age for the MB₂ eruption is in good agreement with the ¹⁴C-age of 4200 ± 50 cal yrs BP published by Breuer et al.⁵¹, which is based on macro-plant remains included in the >10 cm thick MB₂ ash deposit. Our new MB₃ age falls into the lowermost range of bracketing ¹⁴C-ages presented by Biester et al.¹² and Kilian et al.¹³. At that time, the MB₃ eruption was only roughly dated to ~2020 ± 90 cal yrs BP^{12,13} (>1830 ± 40 and <2210 ± 90 cal yrs BP¹², >1980 ± 40 and <2060 ± 90 cal yrs BP¹³). This new age is therefore more precise than previous datings.

Following our arguments developed above, our trace element profiling and PCA analysis (Figs. 3, 5, 6 and S1), an additional volcanic event at 853 ^{+41/-60} yrs BP is clearly indicated by the data of this study. This eruption can be correlated to the MB₄ tephra deposit from Mt. Burney, which was only poorly dated by stratigraphic correlation (~800 yrs BP³). With a reported ¹⁴C-age between ~3067 and 3339 cal yrs BP⁷, the A₁ eruption from the remote Aguilera stratovolcano is one further potential candidate for a more precise dating. We found a matching volcanic signal in MA1 with a ²³⁰Th/U-age of 2978 ^{+91/-104} yrs BP. This is in accordance with the regional distribution of A₁ tephra⁷, which has also been discovered in lake sediments nearby the MA cave site¹³.

With this successful identification of volcanic eruptions, we propose that our high-resolution speleothem archive has probably documented the impact of further ashfall events from other, more distal volcanic centers of the Southern and Austral Volcanic Zones. In contrast to typical geochemical fingerprinting, trace element variations in MA1 enable precise age constraints for a refinement of existing tephrochronologies. For example, the peaks of S concentrations in MA1 (Figs. 3-4) likely recorded atmospheric signals of further volcanoes, such as Reclus and Cerro Hudson, and other high-magnitude volcanic events in the southern hemisphere off South America. This opens the possibility of correlation with Antarctic ice cores⁵² to evaluate large-scale southern hemispheric patterns of Late Holocene volcanism.

We conclude that the unique, sub-annually resolved speleothem LA-ICP-MS data presented here might constitute an important contribution to the Late Holocene tephrochronology of southernmost South America. This will allow a better understanding of the volcanic history in the region, and an improvement for the reconstruction of paleoclimate and paleoenvironmental conditions from regional geological archives. Besides well-preserved tephra layers, MA1 provides multiple climatically and environmentally important information due to its unique nature as a non-karst stalagmite with enclosed manifold detrital components. This information includes potential feedback signals to SWW dynamics and environmental impacts of regional volcanism back to ~4.8 kyrs BP, which document the evolution of one of the most remote and pristine ecosystems worldwide^{9,26}.

Methods

Chronology

Stalagmite MA1 was dated at the Heidelberg Academy of Sciences. Sample preparation and analytical methods were described in detail by Schimpf et al.²⁴. We included two additional samples (Lab. No. 3672 and 3436, Table S1) that were not considered in Schimpf et al.²⁴ due to their large content of detrital ²³²Th. Stalagmite MA1 generally contains high amounts of detrital Th. This is obvious from the ²³⁰Th/²³²Th activity ratios that range from 4.257 to 93.70 (Lab. No. 3672 and 3653, Table S1). However, these values are well below the limit of >200 suggesting insignificant detrital contamination⁵³. Detrital contamination of MA1 also results in age inversions (i.e., uncorrected ages that are not in stratigraphic order). For instance, the sample with Lab. No. 3435 at 268.5 mm distance from top is significantly older (5.128 kyrs BP) than the sample below at 274 mm distance from top (4.803 kyrs BP).

Schimpf et al.²⁴ assumed a ²³²Th/²³⁸U weight ratio of $4.8 \pm 50\%$ for the detritus, which resulted in a smooth age-depth relationship. This value agrees with the conventionally used value for the upper continental crust (3.8 ± 1.9^{54}). Here we used a different approach to account for detrital contamination, based on an algorithm recently published by Budsky et al.³⁰. This algorithm calculates corrected ages assuming a specific ²³²Th/²³⁸U weight ratio of the detritus and ²³⁰Th, ²³⁴U and ²³⁸U in secular equilibrium, and then determines the ²³²Th/²³⁸U weight ratio of the detritus, which results in a minimum sum of age inversions (in years). For stalagmite MA1, this approach results in a ²³²Th/²³⁸U weight ratio of the detritus of 3.69, which is close to the mean value of the upper continental crust⁵⁴ and in agreement within error with the value used by Schimpf et al.²⁴. As suggested by Budsky et al.³⁰, we assumed a conservative uncertainty of $\pm 50\%$ for the determined ²³²Th/²³⁸U ratio of the detritus. Fig. 2a shows a comparison of the uncorrected and the corrected ages.

The final age-depth model for MA1 (Fig. 2a) was calculated in *R*⁵⁵ using the Monte-Carlo-based StalAge algorithm²⁹, which has been specifically designed for speleothems. In contrast to the previously used Akima interpolation, StalAge provides 95% confidence limits, which allows to assess the uncertainty of the age model.

LA-ICP-MS data

The MA1 stalagmite was analyzed with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at GZG, University of Göttingen. LA-ICP-MS elemental analyses were performed as ablation tracks on 14 overlapping, 30 μ m thick and 40 – 50 mm long polished thin sections covering the growth axis of the stalagmite from 24 to 280 mm (distance from top, Fig. S3). The thin sections were the same as for electron microprobe analyses presented in Schimpf et al.²⁴. The ICP-MS used was a Perkin Elmer ELAN DRC II Q-ICP-MS coupled to a Lambda Physik COMPex 110 Argon Fluoride laser (193 nm) with a GeoLas optical bench by MikroLas and a small volume sample chamber. The

ablation setup was operating with a beam width of 120 μm , a repetition rate of 10 Hz for the laser pulses (dwell time 40 ms per isotope, 1.078 s per sweep) and a scan speed of 20 $\mu\text{m s}^{-1}$. Background data were taken before and after the measurements for 2 – 3 minutes. The measurements were calibrated to the standards NIST610 and NIST612 by bracketing analyses and the internal standard ^{43}Ca was used to convert the measurements into absolute concentrations. Matrix effects between NIST610/NIST612 and CaCO_3 were considered to contribute less than 10% error. Measured isotopes were ^{27}Al , ^{29}Si , ^{31}P , ^{34}S , ^{43}Ca , ^{88}Sr , ^{90}Zr and ^{238}U . Element concentrations have been stoichiometrically normalized to 400,000 ppm ^{43}Ca , assuming that the stalagmite is composed of 100% CaCO_3 . Background was subtracted and baseline drift corrected. For ablation spots on lamina with more than 10% detrital siliciclastic material (minerals/volcanic glass containing significantly lower Ca compared to speleothem CaCO_3), the internal normalization to ^{43}Ca will result in systematically higher values for lithophile elements. However, their elemental ratios (e.g., Si/Zr) will be unaffected.

The final LA-ICP-MS record was compiled by aligning the overlapping ablation tracks using a “wobble-matching” technique based on Al concentrations measured – taking small-scale variations of lamina thickness into account. It is characterized by sub-annual resolution of in total 59,200 LA-ICP-MS measurements covering a time span of 4212 years (4.809 – 0.597 kyr BP). Finally, the consistency of the LA-ICP-MS data set with already published ICP-MS drill core data²⁴ was ensured by matching averaged concentrations of the LA-ICP-MS measurements with the contents previously determined by ICP-MS. For this purpose we chose U as soluble, calcite-compatible element²⁴ and used the original drilling diameter of 1.5 mm in accordance with the exact distance from top for every single coring point to calculate the average of the LA-ICP-MS concentrations for comparison (~290 LA-ICP-MS measurements per drill core). LA-ICP-MS and ICP-MS U concentrations are in good agreement and correlate with $r = 0.68$ (Fig. S4).

The principal component analyses (PCA) for the assessment of speleothem high-resolution LA-ICP-MS data was done according to Orland et al.³² and Jamieson et al.²². The PCA was performed with Origin (version Pro 2019b) to further constrain the occurrence of signals derived from volcanic activity in MA1 and was calculated for the trace elements P, S, Sr, Si, Zr and U after z-score normalization.

SEM and NanoSIMS of incorporated detrital components

Stalagmite sections formed during and after the two Plinian eruption periods of the Mt. Burney volcano at 2.0 – 2.3 kyr BP and 3.8 – 4.2 kyr BP, and during the millennium-scale acidification phase (~3.50 and ~3.11 kyr BP) after the MB₂ eruption¹ include laminae rich in detrital components. Representative samples of these sections were taken from the identical blocks the thin sections were prepared of (examples in Fig. S3) and have been investigated with SEM and NanoSIMS. The samples contain the same detritus-rich laminae as analyzed by LA-ICP-MS. We chose NanoSIMS because this technique

allows to differentiate embedded inorganic (e.g., $^{28}\text{Si}^-$) and particularly organic (e.g., $^{12}\text{C}^{14}\text{N}^-$) components from ubiquitous, very low electrically conductive CaCO_3 ^{56,57}.

SEM imaging was conducted with a LEO 435VP and a JEOL JXA-89000 RL at the Geology Department of Trier University and the GZG, University of Göttingen. Replicate samples were analyzed after dissolution in 5 M ultra-pure HCl and an acidic acetate buffer solution⁵⁸ to extract incorporated detritus. An acceleration voltage of 15 kV was applied to produce high-resolution images in secondary electron and back-scattered electron mode.

Prior to NanoSIMS measurements, samples were documented by optical microscopy. NanoSIMS analyses were carried out at the Chair of Soil Science of the Technical University of Munich with a Cameca NanoSIMS 50L using a Cs^+ primary ion beam with an impact energy of 16 keV. The selected stalagmite samples were polished and coated with a conductive Au/Pd layer (ca. 30 nm, Polaron Emitech SC7640 sputter coater) to account for charging during the measurements. Charging was additionally compensated using the electron flood gun of the NanoSIMS. Contaminants and the Au/Pd coating layer were locally sputtered away using a high primary beam current (pre-sputtering/implantation), while the reactive Cs^+ ions were implanted into the sample. The secondary ion yields were enhanced until reaching a steady state. The primary beam (ca. 2 pA) was focused at a lateral resolution of ca. 120 nm and was scanned over the sample, with $^{12}\text{C}^-$, $^{16}\text{O}^-$, $^{12}\text{C}^{14}\text{N}^-$, $^{28}\text{Si}^-$, $^{32}\text{S}^-$, $^{27}\text{Al}^{16}\text{O}^-$, and $^{56}\text{Fe}^{16}\text{O}^-$ secondary ions collected on electron multipliers with an electronic dead time fixed at 44 ns. To accurately separate mass isobars, a suitable mass resolution was achieved with appropriate slits and apertures (D1_3, ES_3, AS_2). The secondary ions were recorded using a dwell time of 1 ms pixel⁻¹, with 256 × 256 pixels for a 30 × 30 μm field of view with 30 planes per scan. Single planes were corrected for dead time, drift and accumulated using ImageJ software⁵⁹ in combination with the Open-MIMS plugin⁶⁰.

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Data availability

The authors declare that the data supporting the findings of this work are included in the article and its Supplementary Information file. The LA-ICP-MS dataset analyzed during the current study is available in the PANGAEA data repository (<https://doi.org/10.1594/PANGAEA/...>). NanoSIMS and SEM data are available from the corresponding author on reasonable request.

Acknowledgements

Andreas Kronz (GZG), Johann Lugmeier and Gertraud Harrington (TUM) are acknowledged for technical assistance and analytical support. This work was funded by grants AR 367/4, Ki 456/10-11, KR 2061/1, MA 821/32 and Wo 362/18 of the German Research Foundation (DFG).

Author contributions

B.K. conceptualized this work together with R.K. and G.W., planned the NanoSIMS operations, compiled the data and performed the analyses. K.K. and K.S. provided the LA-ICP-MS analyses. NanoSIMS operations were enabled by C.W.M. and executed by C.M. D.Scho. established the refined chronology. Statistical analyses were performed by J.S. D.Schi. dated the MA1 stalagmite and ensured data consistency. R.K., G.W., S.T.-B. and H.W.A. shared supervision. B.K. wrote the manuscript, jointly with G.W. All authors contributed to the final version. R.K. acquired the funding, coordinated the field work, and was the driving force behind our research in Patagonia. His enthusiasm and contagious curiosity for a deeper understanding of this remote ecosystem will never be forgotten.

Conflict of interest

The authors declare no competing interest.

Figure captions

Fig. 1:

Location of the study area and site characteristics. **a**, The study site at the windward side of the southernmost Andes, ~40 km S of the Mt. Burney volcano. Inserted isopach lines indicate the thickness and distribution of tephra deposits from the MB₂ eruption⁷. In addition, Reclus and Aguilera volcanoes are shown. **b**, Marcelo Arévalo (MA) cave and its environmental context. The hydrological connection between the cave and its catchment is schematically illustrated. The background map in **a** was generated with GeoMapApp⁶¹.

Fig. 2:

New age-depth model of the MA1 stalagmite. **a**, StalAge²⁹ age-depth model, including the corresponding 95% confidence limits (thin red lines). Uncorrected ages and ages after detritus-correction³⁰ are shown with standard deviations as 2 σ -error bars (see Table S1 for details). **b**, Photo of MA1 including the 18 sampling points for ²³⁰Th/U-dating.

Fig. 3:

Stable isotope and LA-ICP-MS data of MA1 between 4.5 and 0.6 kyrs BP. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records²⁴ of the MA1 stalagmite combined with concentrations of S, P, U, Sr and Zr. ¹⁴C-ages of tephra layers from Late Holocene eruptions of volcanoes of the Southern and Austral Andean Volcanic Zone³ are indicated. Rectangles mark the two periods displayed in Fig. 4. Orange bars highlight newly dated Plinian eruptions of Mt. Burney at 4.216 and 2.291 kyrs BP, confirmed by PCA results (Figs. 6 and S1). Positions of lamina sections investigated by SEM and NanoSIMS (Figs. 7 and S2) are also shown.

Fig.4:

Stable isotope and LA-ICP-MS data of MA1 for time spans enclosing two Mt. Burney eruptions. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records²⁴ of the MA1 stalagmite combined with concentrations of S, P, U, Sr and Zr (**a**, 2.4 – 2.0 kyrs BP; **b**, 4.3 – 4.0 kyrs BP). ¹⁴C-ages of tephra layers from eruptions of Cerro Hudson and Mt. Burney³ are indicated. Orange bars highlight newly dated Plinian eruptions of Mt. Burney at 4.216 and 2.291 kyrs BP, confirmed by PCA results (Figs. 6 and S1). Light gray bars mark time spans characterized by an elevated incorporation of micron scale detrital volcanic glass/tephra following both eruptions. Positions of lamina sections investigated by SEM and NanoSIMS (Figs. 7 and S2) are also shown.

Fig. 5:

Variations and relationships of Si and Zr concentrations in MA1 determined by LA-ICP-MS. In the upper part, the whole record (**a**, 4.5 and 0.6 kyrs BP) is shown. Rectangles in **a** mark the time spans displayed in **b** (2.4 – 2.0 kyrs BP) and **c** (4.3 – 4.0 kyrs BP). Orange bars highlight newly dated eruptions

of Mt. Burney at 4.216 and 2.291 kyrs BP. The corresponding binary plots in the lower part indicate a high correlation of measurements on a mixing line between speleothem carbonate (CaCO_3) and a Si-/Zr-rich endmember with a Si/Zr ratio of 3300 (blue line). The most likely candidate for this Si-/Zr-rich endmember is MB_2 glass^{7,8}. Vectors pointing outwards from the mixing line towards quartz (SiO_2) and zircon (ZrSiO_4) endmembers are included.

Fig. 6:

Scores of principal component PC-1 of the PCA performed on LA-ICP-MS data (S, P, U, Si, Sr and Zr). **a**, PC-1 scores for the time span from 4.5 to 0.6 kyrs BP. Rectangles indicate the periods displayed in **b** (2.4 – 2.0 kyrs BP) and **c** (4.3 – 4.0 kyrs BP). Orange bars mark times in which PC-1 main spikes are synchronous with trace element peaks (Figs. 3-5; at 4.216 and 2.291 kyrs BP).

Fig. 7:

Fine-grained glass shards and Mt. Burney phenocrysts detected in laminae of MA1, formed after the two Mt. Burney eruptions at 4.216 and 2.291 kyrs BP. SEM images show a glass shard (**a**, 2.29 kyrs BP) and phenocrysts coated with residual, vesicle-rich volcanic glass (**b** and **c**, 4.15 kyrs BP) incorporated in MA1. NanoSIMS secondary ion mappings of detrital components in laminae at 3.92 and 2.29 kyrs BP are displayed in **d** and **e**.

Figures

Figure 1

Location of the study area and site characteristics. a, The study site at the windward side of the southernmost Andes, ~40 km S of the Mt. Burney volcano. Inserted isopach lines indicate the thickness and distribution of tephra deposits from the MB2 eruption⁷. In addition, Reclus and Aguilera volcanoes are shown. b, Marcelo Arévalo (MA) cave and its environmental context. The hydrological connection between the cave and its catchment is schematically illustrated. The background map in a was generated with GeoMapApp⁶¹.

Figure 2

New age-depth model of the MA1 stalagmite. a, StalAge29 age-depth model, including the corresponding 95% confidence limits (thin red lines). Uncorrected ages and ages after detritus-correction³⁰ are shown with standard deviations as 2σ -error bars (see Table S1 for details). b, Photo of MA1 including the 18 sampling points for $^{230}\text{Th}/\text{U}$ -dating.

Figure 3

Stable isotope and LA-ICP-MS data of MA1 between 4.5 and 0.6 kyr BP. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records²⁴ of the MA1 stalagmite combined with concentrations of S, P, U, Sr and Zr. ^{14}C -ages of tephra layers from Late Holocene eruptions of volcanoes of the Southern and Austral Andean Volcanic Zone³ are indicated. Rectangles mark the two periods displayed in Fig. 4. Orange bars highlight newly dated Plinian eruptions

of Mt. Burney at 4.216 and 2.291 kyrs BP, confirmed by PCA results (Figs. 6 and S1). Positions of lamina sections investigated by SEM and NanoSIMS (Figs. 7 and S2) are also shown.

Figure 4

Stable isotope and LA-ICP-MS data of MA1 for time spans enclosing two Mt. Burney eruptions. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records²⁴ of the MA1 stalagmite combined with concentrations of S, P, U, Sr and Zr (a, 2.4 – 2.0 kyrs BP; b, 4.3 – 4.0 kyrs BP). ¹⁴C-ages of tephra layers from eruptions of Cerro Hudson and Mt. Burney³

are indicated. Orange bars highlight newly dated Plinian eruptions of Mt. Burney at 4.216 and 2.291 kyrs BP, confirmed by PCA results (Figs. 6 and S1). Light gray bars mark time spans characterized by an elevated incorporation of micron scale detrital volcanic glass/tephra following both eruptions. Positions of lamina sections investigated by SEM and NanoSIMS (Figs. 7 and S2) are also shown.

Figure 5

Variations and relationships of Si and Zr concentrations in MA1 determined by LA-ICP-MS. In the upper part, the whole record (a, 4.5 and 0.6 kyrs BP) is shown. Rectangles in a mark the time spans displayed in b (2.4 – 2.0 kyrs BP) and c (4.3 – 4.0 kyrs BP). Orange bars highlight newly dated eruptions of Mt. Burney at 4.216 and 2.291 kyrs BP. The corresponding binary plots in the lower part indicate a high correlation of measurements on a mixing line between speleothem carbonate (CaCO₃) and a Si-/Zr-rich endmember with a Si/Zr ratio of 3300 (blue line). The most likely candidate for this Si-/Zr-rich endmember is MB2 glass^{7,8}. Vectors pointing outwards from the mixing line towards quartz (SiO₂) and zircon (ZrSiO₄) endmembers are included.

Figure 6

Scores of principal component PC-1 of the PCA performed on LA-ICP-MS data (S, P, U, Si, Sr and Zr). a, PC-1 scores for the time span from 4.5 to 0.6 kyrs BP. Rectangles indicate the periods displayed in b (2.4 – 2.0 kyrs BP) and c (4.3 – 4.0 kyrs BP). Orange bars mark times in which PC-1 main spikes are synchronous with trace element peaks (Figs. 3-5; at 4.216 and 2.291 kyrs BP).

Figure 7

Fine-grained glass shards and Mt. Burney phenocrysts detected in laminae of MA1, formed after the two Mt. Burney eruptions at 4.216 and 2.291 kyrs BP. SEM images show a glass shard (a, 2.29 kyrs BP) and phenocrysts coated with residual, vesicle-rich volcanic glass (b and c, 4.15 kyrs BP) incorporated in MA1. NanoSIMS secondary ion mappings of detrital components in laminae at 3.92 and 2.29 kyrs BP are displayed in d and e.

Supplementary Files

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- [SupplementaryInformationKlaesetal.2021.pdf](#)