

# **Historical eruptions of Lautaro Volcano and their impacts on lacustrine ecosystems in southern Argentina**

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## Abstract

Lacustrine sediment sequences were obtained from Lagunas Verde and Gemelas Este, two small lakes located east of the southern Patagonian Ice Field and close to the village of El Chaltén, in Argentinian Patagonia. Four tephra layers were identified in each of the short sediment sequences and characterised using individual glass-shard tephra chemistry to determine provenance. Bulk sediment geochemistry and diatom assemblages were analysed to understand the impact of the tephra deposits on the lake ecosystems. Age-depth models for the cores were established by  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  dating. Tephra deposits in Laguna Gemelas Este were dated to AD 1986-1998, 1943-1968, 1927-1955 and 1849-1892, and the tephra deposits in Laguna Verde were dated to AD 1940-1970, 1888-1934, 1871-1920, and 1536-1669, the latter interval determined by extrapolation. All tephras had similar geochemical composition and originated from volcanoes in the northern Austral Volcanic Zone. Tephra units were attributed to known historical eruptions and all but one, most likely, were from Lautaro Volcano ( $49^{\circ} 01' \text{S}$ ;  $73^{\circ} 33' \text{W}$ ). The age of the youngest tephra (AD 1986-1998) from Laguna Gemelas Este points to Viedma Volcano ( $49^{\circ} 22' \text{S}$ ;  $73^{\circ} 19' \text{W}$ ) as a possible source. Volcanic eruptions had a larger impact on Laguna Verde than on Laguna Gemelas Este, as expressed by changes in  $\delta^{15}\text{N}$  values and diatom communities during tephra deposition. These shifts are explained by perturbations of the nitrogen cycle in the lake, associated with shifts in lacustrine primary production. Primary producers may have been affected by increased water turbidity caused by the ash fall, and consequently, used less nitrogen. Diatom assemblages in Laguna Verde showed marked reductions in numbers of planktonic/tychoplanktonic taxa, in favour of epiphytic/benthic diatom taxa, when tephra was deposited. This contrasts with Laguna Gemelas Este, in which epiphytic/benthic diatom species were generally more abundant and decreases in abundances of planktonic/tychoplanktonic taxa were not as strongly linked to tephra layers as in Laguna Verde. At Laguna Gemelas Este, flatter relief, greater fetch and/or drier climate may have contributed to generally less ecosystem variability, resulting in seemingly less environmental response to volcanic eruptions than in Laguna Verde.

## Introduction

The subduction of the Antarctic plate (~49-53 °S) and the Scotia Microplate (~53-55 °S) beneath the South American continent induces volcanism in the Andean mountain range between 49 and 55 °S, referred to as the Austral Volcanic Zone (AVZ; Stern 2008). Volcanoes Lautaro and Fueguino represent the northernmost and southernmost volcanoes, respectively, of six known active volcanoes in the AVZ (Fig. 1A; Stern 2008). Late Glacial and Holocene eruption histories of the volcanoes in the AVZ have been reconstructed mainly using tephra layers deposited in soil outcrops, lake sediments, or peat sections (Kilian et al. 2003; Markgraf et al., 2003; Naranjo and Stern 2004; Stern 2004, 2008; Weller et al. 2015, 2017; Del Carlo et al. 2018). Explosive eruptions of the AVZ have also been documented in the last glacial, using long lake sediment records from Laguna Potrok Aike (51.97 °S 70.38 °W; Haberzettl et al. 2009; Wastegård et al. 2013).

Far less is known about recent, historical volcanic events in the AVZ. In particular, there is a considerable gap in knowledge regarding the historical volcanic frequency of centres in the northern Austral Volcanic Zone (NAVZ), which includes Volcanoes Lautaro, Viedma and Aguilera (Stern and Kilian 1996; Stern 2008; Fontjin et al. 2014). This is partly because of their location, which is difficult to reach, and generally ice-covered. Despite reports of historical eruptions (Lliboutry 1998; Martinic et al. 2008), few traces of them have been found in natural archives (Fontjin et al. 2014). The identification of tephra in natural archives could confirm historical reports and provide information about the explosivity of these eruptions, from the thickness and spatial distribution of the units. Moreover, previous geochemical fingerprints of NAVZ volcanoes (Stern and Kilian 1996; Stern 2008) are predominantly based on bulk tephra chemistry, instead of more accurate single-grain, glass-shard geochemistry, which has been rarely applied (Kastner et al. 2010). Closing this knowledge gap by studying lake sediment records and the individual glass-shard chemistry of tephra in the vicinity of these volcanoes was the first major aim of our study. Our second major aim was to establish the effect of historical volcanic deposition on these lake ecosystems by analysing paleoenvironmental variables in the sediment archives. The influence of volcanic ashfall on lake ecosystems has been debated in terms of changing pH, habitat, and nutrient availability (Lotter et al. 1995; Telford et al. 2004; Self et al. 2015). Such short-term disturbance of lacustrine systems by volcanic eruptions can be manifested in biological and geochemical sediment variables, but has rarely been documented in southernmost South America. One example, however, is the Lago Galletue (Chile) sediment record, in which a shift in diatom and chironomid assemblages and a decrease in organic matter content was ascribed to tephra from an eruption of Llaima Volcano (Cruces et al. 2006; Urrutia et al. 2007).

Our study was conducted in the NAVZ. The research area is close to the eastern margin of the Southern Patagonian Ice Field (SPI), and east of the Andean mountain ridge, with Mt. Fitz Roy (3406 m a.s.l.) being one of the most renowned mountain peaks in the region (Fig. 1B). The persistent southern hemisphere westerlies dominate the climate and provoke a strong humidity gradient on the leeward side

of the Andes where the study sites are located (Garreaud et al. 2013). This precipitation gradient is reflected in the vegetation distribution, with a dense *Nothofagus* forest in the west and Patagonian steppe to the east (Fig 1A, B). The influence of this humidity gradient on lacustrine habitats is of interest for ongoing paleolimnological studies. Additionally, the downwind position of lakes with respect to active volcanoes is beneficial for reconstructing eruption histories, as tephra is transported toward the sites. Nevertheless, the eruption history of NAVZ centres is still uncertain because of the remoteness of the area. After exploration of several regional lakes, the sediments of two small lakes, Laguna Gemelas Este (49.3849° S 72.8985° W, 880 m a.s.l.) and Laguna Verde (49.2090° S 72.9728° W, 560 m a.s.l.) were chosen for detailed investigation. Their climatic settings differ, but both contain continuous fine-grained sediment records with sufficient organic matter to facilitate investigations of tephra layers and the effects of volcanic ashfalls on Patagonian lake ecosystems.

The area surrounding the lakes belongs, in part, to Los Glaciares National Park. It was sparsely populated by indigenous people before European settlers arrived in the early 20<sup>th</sup> century (Madsen 1952). Construction of El Chaltén, the only village in the area, began in AD 1985 (Rodriguez 2009). Because of its remoteness and late settlement, reports about regional environmental trends and volcanic eruptions prior to that time are scarce. Although active volcanoes exist in the region, tephra records containing historical events are not yet established, mainly because of the inaccessibility of volcanic cones and the lack of studied sediment records (Fontjin et al. 2014). An exception to this is the 2000-year-long sediment record from Lago del Desierto (Fig. 1B), in which a tephra layer was ascribed to the AD 1959/60 eruption of Lautaro Volcano on the basis of the chronology (Kastner et al. 2010). Moreover, tephra layers of unknown age were reported from regional soils and attributed to Lautaro, Hudson and Monte Burney Volcanoes (Villegas et al. 2009). The area is also of great interest for paleoclimate and paleoenvironment reconstructions. Evidence of recent climate change is found in the accelerated shrinking of the SPI and adjacent glaciers, documented using tree-ring analysis, moraine dating, and remote sensing (Masiokas et al. 2009; Meier et al. 2018).

Our study is a first step to overcome the lack of limnogeological and volcanological data for the historical past in the NAVZ. The glass-shard chemical composition and age of tephra deposits in short sediment cores from Lagunas Verde and Gemelas Este were investigated and an attempt was made to attribute them to historical eruptions. The two lakes are comparable in size and morphometry, but located at two ends of a humidity gradient in the *Nothofagus* forest. Thus, results also provide insights into the behaviour of lake systems under different hydroclimate conditions and into the reaction of their nutrient cycles and diatom communities to short-term disturbances such as volcanic events.

## Materials and methods

### Sampling and scanning

Sediment cores were recovered in April 2017 with a percussion corer (Aquatic Research Instruments, USA) deployed from a rubber boat in 5.8 and 5.0 m of water in Laguna Verde and Laguna Gemelas Este, respectively. Limnological variables (pH, electric conductivity, water temperature) in lake surface waters were measured in the field with a Universal Pocket Meter (Multi 340i, WTW). The surface of the recovered sediment cores was fixed with floral foam, and core tubes were capped and transported to the lab where they were cut lengthwise. Sediment core GEM17-1 from Laguna Gemelas Este had a length of 37 cm, and sediment core VER17-1 from Laguna Verde had a length of 84 cm. The smoothed surface of one core half was photographed and scanned with an X-ray-fluorescence (XRF) core scanner (ITRAX, Cox Analytics) equipped with a Mo-tube. Elemental “concentrations” are in counts per second (cps) and were divided by coherence (coh) for standardisation (Hahn et al. 2014). Colour and lithologic variations were described before the cores were subsampled at one-cm intervals according to standard procedures (Ohlendorf et al. 2011). Volumetric samples (11.9 cm<sup>3</sup>) were weighed before and after lyophilisation to obtain water content and dry bulk density (DBD) used for calculation of cumulative bulk dry mass. Sediment colours were determined with a Munsell soil colour chart on the fresh, non-oxidised sediment surface after core opening (Munsell Color 2000).

#### Bulk organic matter stable isotope geochemistry

Lyophilised samples were carefully homogenised with a spatula and sieved at 250 µm to obtain the fine sediment fraction, free of larger organic and minerogenic particles. An amount of the fine sediment fraction, sufficient to provide about 30 µg of nitrogen (typically 3-40 mg dry matter), was weighed into tin capsules for total nitrogen content (TN, in wt%) and stable isotope ( $\delta^{15}\text{N}_{\text{TN}}$ ) determinations. Likewise, an amount of the fine sediment fraction sufficient to yield about 100 µg of organic carbon (typically 1-20 mg dry matter) was weighed in tin capsules for total organic carbon content (TOC, in wt%) and stable isotope ( $\delta^{13}\text{C}_{\text{TOC}}$ ) analyses. These samples were decalcified by acid fumigation with 32% HCl for 16 hours in an empty desiccator (Harris et al. 2001) before folding and analysis. The packed samples were combusted at 1080 °C in an elemental analyser (EuroEA, Eurovector) with automated sample supply linked to an isotope ratio mass spectrometer (Isoprime, Micromass). Peak integration was used to determine TN and TOC concentrations and for calibration against elemental standards. The TOC/TN is presented as the molar ratio. All isotope results are reported in ‰ in standard  $\delta$  notation, according to the equation

$$\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \cdot 1000 \quad (1)$$

where R is the isotope ratio ( $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$ ) of the sample and an international standard (VPDB for carbon, AIR for nitrogen), respectively. Calibrated laboratory standards were used to ensure the quality of analyses and to relate the raw values to the isotopic reference scales. Although  $\delta^{15}\text{N}_{\text{TN}}$  measurements

of Laguna Verde tephra layers were near the detection limit of the instrument, no signs of disturbance were recorded in the chromatographs and values were reproducible.

#### Radiometric dating

Activities of  $^{137}\text{Cs}$ ,  $^{40}\text{K}$ ,  $^{210}\text{Pb}$ , and  $^{226}\text{Ra}$  were determined by gamma spectrometry with a High-Purity-Germanium Well Detector. Excess  $^{210}\text{Pb}$  data were obtained by subtracting  $^{226}\text{Ra}$  from total  $^{210}\text{Pb}$  activity (Appleby 2001). A constant-flux-constant-sedimentation (CFCS) model was used for  $^{210}\text{Pb}$  age determination (Sanchez-Cabeza and Ruiz-Fernández 2012). To approach the requirements for the CFCS model, all 1-cm-thick slices containing tephra layers were removed prior to age calculations. Additionally, negative and zero  $^{210}\text{Pb}$  activities were excluded from the age models, and one and two outliers were discarded from the base of the GEM17-1 and VER17-1 records, respectively. The  $^{210}\text{Pb}$  activity at the sediment surface ( $C_0$ ), the age and dry-mass sedimentation rates were determined from linear regression of log excess  $^{210}\text{Pb}$  activity versus cumulative bulk dry mass, using a half-life for  $^{210}\text{Pb}$  of 22.23 years (Sanchez-Cabeza and Ruiz-Fernández 2012). Lower and upper age estimates were determined from the sediment samples neighbouring the tephra layers, maximum and minimum errors were calculated by considering the slope error obtained in the aforementioned linear regression. Decay-corrected  $^{137}\text{Cs}$  activities were calculated using a half-life of 30.07 years (Ribeiro Guevara and Arribére 2002).

#### Compositional analysis of tephra deposits

Tephra layers were identified visually, using Ca peaks from XRF scans, and with DBD anomalies. Tephra samples were wet-sieved using demineralised water and a 25- $\mu\text{m}$  nylon mesh to reduce the presence of very fine-grained material, inappropriate for chemical analysis. The remaining sample was oven-dried at 50 °C and mounted in a multi-hole resin disc using Specifix-20 Epoxy resin (Froggatt and Gosson 1982). Once set, ground and polished, the disc was coated in carbon for chemical analysis (Lowe 2011).

The major elemental properties of individual glass shards in the sample were analysed at the Research Laboratory for Archaeology and the History of Art, University of Oxford, using a wavelength-dispersive JEOL JXA-8600 electron microprobe (EMP), equipped with four spectrometers. Where the abundance of glass shards was sufficient, thirty glass shards were analysed in each sample. All analyses were conducted with a 6-nA beam current, 15-kV accelerating voltage and a 10- $\mu\text{m}$  beam diameter. To minimise element loss, sodium was analysed first. Elemental peaks were collected for 30 seconds (s), except for Na (12 s), P (60 s), Cl (50) and Mn (40 s), and for half of the total peak time on the background, either side of the peak. The machine was calibrated for each element using primary standards (minerals) prior to analysis. Also, to verify the calibration, Max Planck Institute (MPI-DING) reference glasses

were analysed at the beginning, middle and end of analytical runs (StHs6-80/G, ATHO-G, GOR132-G). Mean values for these were within 2 standard deviations of the published standard values (Jochum et al. 2006). During analysis, minerals, vesicles, and resin were avoided. To account for secondary hydration, data were normalised to 100 wt%.

## Diatom analyses

An aliquot of each sample was dried at 80 °C, oxidized with H<sub>2</sub>O<sub>2</sub> (30 vol%), and heated in a microwave oven for 2 minutes to eliminate organic material (Battarbee 1986). When removal of clay from the sediments was necessary, the samples were also treated following Bates et al. (1978). Samples were then rinsed repeatedly with distilled water until they reached neutral pH. Permanent slides were mounted using Naphrax®. A minimum of 400 valves per slide were counted to calculate relative abundances in percent and numbers of individuals per gram of dry sediment. Observations were made using a Reichert-Jung Polivar binocular optical microscope equipped with an immersion objective (Plan Apo 100X, NA 1.32) and differential interference contrast optics. The works of Frenguelli (1923, 1942), Metzeltin and Lange-Bertalot (1998, 2007), Rumrich et al. (2000), and Metzeltin et al. (2005) were used to identify diatom taxa.

## Results

### Sites and limnology

Laguna Verde is located in a humid forest with approximately 930 mm average annual precipitation (Estancia Huemules meteorological station, period 2007-2016, 1.4 km SE of the lake; Fig. 1C). The lake has an area of 0.029 km<sup>2</sup>, is fed by a small inflowing creek, and is located in a basin surrounded by dense forest of *Nothofagus pumilio*. The catchment area is mountainous and has slope angles up to 40° on the western side of the lake. The lake's maximum diameter is 305 m and its maximum water depth is 5.8 m. It is surrounded by bulrush (*Schoenoplectus* sp.) and hosts few aquatic macrophytes (*Potamogeton* sp., aquatic mosses). During three visits in April (2015, 2017, 2018), electric conductivities of 20-30 µS cm<sup>-1</sup>, pH values of 6.8-7.4 and temperatures of 5.2-10.2 °C were measured in the surface water.

Laguna Gemelas Este is located just above the lower tree line, which is 1 km west of the lake. The lower tree line is at an altitude of 550-650 m a.s.l. and caused by insufficient rainfall for tree growth. A meteorological station in the steppe close to the lower tree line and 5.4 km NNE from the lake receives about 305 mm average annual precipitation (Río de las Vueltas meteorological station, period 1993-2016, Fig. 1C). The name Lagunas Gemelas ("twin lakes" in Spanish) refers to two adjacent lakes, a shallow western and a deeper eastern lake. Here we report data from the eastern lake, referred to as Laguna Gemelas Este. It has no surficial inflow, an area of 0.04 km<sup>2</sup>, a maximum diameter of 310 m, a



maximum depth of 5.2 m, and is surrounded by a patchy forest of *Nothofagus pumilio* close to the steppe-forest ecotone. A few aquatic macrophytes (aquatic mosses, *Isoetes* sp., *Myriophyllum* sp.) grow in the lake. Surface water had electric conductivities of 16-20  $\mu\text{S cm}^{-1}$ , pH values of 7.2-7.7 and temperatures of 3.2-7.9 °C measured in April of the years 2015-2018.

## Sedimentology and bulk-sediment geochemistry

In cores from both lakes, macroscopically visible tephra layers are characterized by high Ca content (given as Ca  $\text{coh}^{-1}$ ), high DBD, and low contents of TOC and TN (Fig. 2 A, B). Tephra layers showing these characteristics occurred at 4-5, 10-15, 17-22 and below 36 cm in GEM17-1. Ca contents are missing for the latter tephra at the core base because of analytical difficulties, but a high DBD value indicates it is a tephra, as does visual identification (Fig. 2A). Similarly, tephras were detected at 5-11, 16-18, 20-28, and 54-58 cm in VER17-1. The four tephras of GEM17-1 were labelled GT1-GT4 from top to bottom, the four of VER17-1 were labelled VT1-VT4.

Sediment core GEM17-1 from Laguna Gemelas Este consists of brownish-grey (Munsell colours 2.5Y5/3, 2.5Y4/3, 2.5Y4/2), organic-rich mud intercalated with silty-to-sandy, greyish (2.5Y7/1) tephra layers (Fig. 2A). The upper part of GEM17-1 has high TOC (4-13 wt%) and TN (0.3-1.3 wt%) contents outside of tephra layers and can be classified as diatomaceous biogenic mud. The lower part (>32 cm depth) contains less TOC and TN, possibly because of a higher admixture of minerogenic components. The dark colour of a layer at 27-28 cm also appears to be of minerogenic, not organic origin, as TOC and TN do not increase. TOC/TN ratios generally vary between 6 and 24, with an exceptionally high TOC/TN ratio of 54 at 30.5 cm depth.  $\delta^{13}\text{C}_{\text{TOC}}$  values range between -22 and -18‰ and  $\delta^{15}\text{N}_{\text{TN}}$  between 1 and 4‰. During deposition of tephras GT1 and GT3, but not GT2, the carbon isotopic composition changes. The  $\delta^{13}\text{C}_{\text{TOC}}$  values are as much as 2.6‰ lower in GT3 and 1.6‰ higher in GT1 than in sediment surrounding the tephra.

Sediment core VER17-1 from Laguna Verde consists of laminated, clayey, olive-grey mud (5Y4/2, 5Y 5/2, 5Y6/2) intercalated with four greyish to violet-greyish (5Y6/1, 7.5YR6/2), sandy tephras (Fig. 2B). Outside of the tephra layers, VER17-1 exhibited overall lower TOC (1.1-8.0 wt%) and TN contents (0.1-1.1 wt%) than GEM17-1. TOC/TN ratios range from 6 to 24. Highest TOC/TN values were reached at the base of VT3 and between VT2 and VT1. The latter peak is coincident with a TOC maximum. A second TOC maximum occurs immediately above VT4, this time coinciding with a TN maximum, increased  $\delta^{13}\text{C}_{\text{TOC}}$  values and a blackish layer.  $\delta^{15}\text{N}_{\text{TN}}$  values decrease by as much as 5.2‰ in each tephra layer, compared to tephra-free sections, exhibiting  $\delta^{15}\text{N}_{\text{TN}}$  values between -0.5 and 2.0‰.

## Radiometric dating and tephra stratigraphy

<sup>137</sup>Cs data exhibit a double peak in GEM17-1 at 1.5 (82.0 Bq kg<sup>-1</sup>) and 5.5 cm (69.2 Bq kg<sup>-1</sup>), while <sup>210</sup>Pb activities show a distinct minimum centred at 3-5 cm sediment depth, coinciding with the low <sup>137</sup>Cs between the two peaks (Fig. 3A). The <sup>137</sup>Cs and <sup>210</sup>Pb minima are related to thin tephra layer GT1, which diluted the radioisotopes. In contrast to GEM17-1, the <sup>137</sup>Cs record of VER17-1 exhibits only a single peak with a maximum at 2-3 cm sediment depth and a steady exponential decrease of <sup>210</sup>Pb between 0 and 5 cm depth (Fig. 3B), suggesting that GT1 has no counterpart in VER17-1.

The lake sediment records were dated using excess <sup>210</sup>Pb. Tephra layers were first removed for calculation of cumulative dry mass, leading to a result of steadily increasing dry mass values with depth (Fig. 3). Exponential regressions (CFCS model) resulted in mean dry-mass sedimentation rates of 51 mg cm<sup>-2</sup> a<sup>-1</sup> (R<sup>2</sup>=0.85) and 34 mg cm<sup>-2</sup> a<sup>-1</sup> (R<sup>2</sup>=0.91) and extrapolated C<sub>0</sub> values of 168 Bq kg<sup>-1</sup> and 171 Bq kg<sup>-1</sup> for GEM17-1 and VER17-1, respectively.

The <sup>210</sup>Pb chronologies enable estimation of the timing of tephra deposition. For GEM17-1, the resulting age ranges were AD 1986-1998 for GT1, AD 1943-1968 for GT2, AD 1927-1955 for GT3, and AD 1849-1892 for GT4, including the error ranges (Fig. 3A). The age ranges of VER17-1 were AD 1940-1970 for VT1, AD 1888-1934 for VT2, and AD 1871-1920 for VT3 (Fig. 3B). VT4 is outside of the dated depth range because of the short half-life of <sup>210</sup>Pb. Extrapolation of the exponential regression obtained from the CFCS model, however, resulted in an estimated deposition age of AD 1536-1669.

#### Geochemical composition of tephra deposits

The geochemical properties of seven tephra layers (GT1, GT2, GT3, and VT1, VT2, VT3, VT4) were analysed. GT4 was not analysed because little material was available. The analysis of glass was made difficult by the high abundance of minerals. VT1 was noted as being a particularly mineral-poor sample in comparison to other analysed samples and was characterised by a greater abundance of colourless cusped and fluted glass shards. There is no compositional difference between tephra layers (Table 1; Fig. 4). All identified tephra deposits are rhyolitic and the major elemental glass-shard chemistry suggests a similar eruptive source. Across all samples, the average silica content is 75.30 ± 1.08 wt%. The average potassium concentration is 3.37 ± 0.23 wt%, and the averaged calcium and titanium contents are 1.87 ± 0.43 wt% and 0.30 ± 0.08 wt%, respectively (Table 1).

#### Diatoms

For sediment core GEM17-1, diatom assemblages in all samples were analysed, except for three (16-17, 21-22 and 24-25 cm) that lacked enough material for analyses. Overall, the diatoms were well preserved, and exhibited a maximum concentration of 70 · 10<sup>6</sup> valves g<sup>-1</sup> dry sediment at 7-8 cm depth (Fig. 5A). The total abundance was highly variable, with frequently lower concentrations if volcanic eruptions occurred. Lowest concentrations were found in the samples prior to and at the base of GT2. Only one

planktonic/tychoplanktonic taxon, *Aulacoseira* sp. 1, was found and its relative abundance fluctuates widely in the record. The taxon is most abundant in the samples between GT3 and GT4. Minimum values of *Aulacoseira* sp. 1 occur in the upper part of the core, but do not always coincide with the tephra layers. The most abundant benthic/epiphytic taxa were *Psammothidium marginulatum*, *Encyonema sileciacum*, *Nitzschia fonticola*, *Pinnularia* aff. *appendiculata*, *Sellaphora tridentula*, *Sellaphora* sp. 1, *Staurosirella* sp. 12 and *Staurosirella* sp. 8. Some benthic/epiphytic taxa, such as *Psammothidium marginulatum*, *Pinnularia* aff. *appendiculata*, and *Sellaphora tridentula* show relative abundance peaks within one or more tephra layers. *Nitzschia fonticola* reaches continuously high relative abundances after the deposition of GT3. (Fig. 5A).

The VER17-1 sediment core has an overall high diatom concentration, except when tephra layers are present. Lowest diatom abundances occurred in tephra layers VT1-VT4. The middle section of tephra VT1 (8-9 cm depth in the tephra between 5 and 11 cm) did not contain any diatoms. Diatom concentration reached its maximum value at 32 cm depth ( $410 \cdot 10^6$  valves  $\text{g}^{-1}$  of dry sediment) and decreased again below. This sediment core is characterised by dominance of two *Aulacoseira* species (*Aulacoseira* sp. 1 and sp. 2), that occur in generally high relative abundances over the whole sequence, except for tephra layers, where they almost disappear, leading to short periods with dominance of benthic/epiphytic diatoms such as *Encyonema sileciacum*, *Nitzschia frustulum* var. *minutula*, small fragilarioids, *Sellaphora* sp. 1 and *Tabellaria flocculosa* (Fig. 5B).

## Discussion

### Regional history of explosive volcanic eruptions

Analysis of volcanic ash layers identified in the AVZ is often limited to bulk chemistry (Stern, 2008; Weller et al., 2015, 2017). This is problematic because bulk chemical analysis can be influenced by the abundance of minerals in the sample. It is therefore preferable to utilise individual-grain, glass-shard analysis to correlate between records (Fontijn et al., 2016; Del Carlo et al., 2018). There are, however, limited comparative chemical data because of the remote and often ice-covered locations of AVZ centres (and particularly NAVZ centres), and the lack of glass-shard analyses.

AVZ deposits are rich in silica, but have variable potassium as a consequence of magma variations along the volcanic arc, and as such, potassium is a useful indicator of their source (Kilian et al. 2003). For example, the widespread R<sub>1</sub> unit from Reclus Volcano has average SiO<sub>2</sub> and K<sub>2</sub>O contents of 77.60 wt% and 2.60 wt% in its glass, respectively (Del Carlo et al. 2018). Comparatively, the widespread MB1 unit from Mt Burney Volcano has a slightly higher average SiO<sub>2</sub> content (78.31 wt%) and slightly lower average K<sub>2</sub>O (2.01 wt%) in its glass (Del Carlo et al., 2018). The A<sub>1</sub> unit from Aguilera Volcano has average SiO<sub>2</sub> and K<sub>2</sub>O contents of 75.81 wt% and 4.14 wt% in its glass, respectively (Stern, 2008). By comparison, bulk tephra and pumice analyses of the same A<sub>1</sub> unit yielded

much lower SiO<sub>2</sub> content (65.34 wt%) and K<sub>2</sub>O content (2.26 wt%) (Stern, 2008). Analysis of glass in deposits attributed to Lautaro Volcano indicates SiO<sub>2</sub> and K<sub>2</sub>O contents of ~75 wt% and ~3.3 wt%, respectively (Kastner et al., 2010), whereas bulk chemical analysis points to lower SiO<sub>2</sub> and K<sub>2</sub>O contents of 65.72 wt% and 2.05 wt%, respectively (Motoki et al., 2006). The pumice in the bulk sample is reported to contain minerals such as hornblende and orthopyroxene (Motoki et al. 2006), which may have altered the analyses when compared to glass data by Kastner et al. (2010). There are no available chemical data, bulk or glass-shard, for tephra from Viedma Volcano.

The geochemical signatures of all tephra layers investigated in this study are similar, and thus indicate the same eruptive source. With respect to tephra identified from AVZ volcanoes like Monte Burney, Reclus and Aguilera (Stern 2008), the samples in GEM17-1 and VER17-1 have intermediate potassium concentrations, with an average value across all samples of 3.4 wt%. The chemical composition of volcanic deposits is in line with NAVZ deposits, as identified by Stern (2008) and Del Carlo et al. (2018). The closest volcanoes with known historical activity are Lautaro, Viedma, and possibly Aguilera (Fig. 1A, B; references in Fontijn et al. 2014). The geochemical signatures of tephra layers investigated here are congruent with those of pure glass shards from the Lago del Desierto sediment record, where a tephra was tentatively ascribed to the 1959/60 eruption of Lautaro (Kastner et al. 2010). It is, however, important to note that: i) the compositional fields of Austral Volcanic Zone volcanic centres are still relatively poorly defined, ii) there are no glass-chemistry data for Viedma Volcano, which is nearby Lautaro Volcano, iii) the high abundance of minerals in the investigated tephra resulted in a low number of chemical analyses, and iv) there is still chronological uncertainty for this historical period. As such, assignment of these layers to a historical eruptive age, based solely on the major elemental glass-shard chemistry, is not yet possible.

The chemical affinity of the deposits identified from Lagunas Gemelas Este and Verde display a similar compositional trend to that of Aguilera Volcano, but with a slightly lower potassium content (Stern 2008). As no comparable glass-shard chemistry of tephra from Lautaro, Viedma and Aguilera Volcanoes exist for comparison, assignment of these tephra in our records is based mainly on geographical and chronological evidence. We hypothesise that all but one of the tephra deposits identified in the Lagunas Gemelas Este and Verde sediment sequences originated from Lautaro Volcano, for the following reasons: 1) Lautaro Volcano is closer to the coring locations than any other AVZ volcano, except for Viedma Volcano; 2) Lautaro was the most frequently erupting NAVZ volcano in the region during the recent past (Lliboutry 1998; Motoki et al. 2006; Martinic 2008; Siebert et al. 2010; Fontijn et al. 2014) and is 42 km WNW from Laguna Verde and 60 km WNW from Laguna Gemelas Este. As winds in this area frequently blow from a northwesterly direction (Garreaud et al. 2009), tephra of Lautaro's eruptions very likely would have arrived in the area of investigation. Several confirmed eruptions have been reported from Lautaro Volcano at: AD 1978/79, 1972, 1959-60, 1945, 1933, 1883, 1878/79, and 1876 (Table 2). The only known historical eruption of Viedma Volcano was in AD 1988 (Kilian 1990; Siebert et al. 2010). Another historical eruption occurred in AD 1886. Burmeister (1891)

described widespread ash fall in the Santa Cruz Valley and other areas in Patagonia in that year, pointing to an eruption of one of the volcanoes in the NAVZ at that time. Fontjin et al. (2014) erroneously dated the eruption to AD 1891 and attributed it to Aguilera, but any other NAVZ volcano is possible. The independently dated Laguna Gemelas Este and Laguna Verde sequences indicate that the timing of the tephra units best fits the reported historical eruptions of Lautaro. This strongly suggests that Lautaro Volcano was the main source of tephra layers identified in Laguna Gemelas Este and Laguna Verde, except for GT1 (Fig. 6). The source of GT1 remains uncertain because the  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  chronologies disagree at this point in the sequence.

$^{137}\text{Cs}$  is exclusively related to anthropogenic radioactive fallout from atmospheric nuclear weapons tests and nuclear accidents. Globally significant  $^{137}\text{Cs}$  fallout started in AD 1954, reached a first maximum in AD 1959-1960, and an absolute maximum in AD 1963-1964 (Appleby 2001). In Argentina, however, maximum fallout occurred in AD 1964-1966, whereas peaks in AD 1970-1972 and AD 1974 were related to tropospheric fallout from south Pacific atmospheric nuclear weapons testing (Ribeiro Guevara and Arribére 2002). The bimodal  $^{137}\text{Cs}$  distribution in GEM17-1 suggests that GT1 diluted the  $^{137}\text{Cs}$  peak. Thus, the ashfall happened around or after maximum  $^{137}\text{Cs}$  deposition, i.e. around the 1960s-1970s or later.  $^{210}\text{Pb}$  gives a more precise date for the deposition of GT1 and relates it to the 1990s. The absence of this thin tephra layer in the  $^{137}\text{Cs}$  record of Laguna Verde might be explained by the position of this lake outside of the fallout lobe of that specific eruption. As no major eruption was reported from Lautaro Volcano in the 1990s, the tephra most likely originated from the eruption in 1988 of Viedma Volcano, which is 28 km west of the lake (Fig. 1B). It is also possible that the  $^{210}\text{Pb}$  dating is in error at this point in the sequence, and the  $^{137}\text{Cs}$  may be more accurate; in that case, the deposit would likely be from the Lautaro eruption of 1978/79, because the decay-corrected  $^{137}\text{Cs}$  nonetheless indicates a post-maximum fallout date for GT1 (Fig. 3A).

The similar  $^{210}\text{Pb}$  age ranges of GT2 and VT1 imply that they very likely represent the same eruptive event that happened between the 1940s and 1970s.  $^{210}\text{Pb}$  ages of VT2 and GT3 correspond less clearly in age, pointing to the same or two different eruptions in the first half of the last century. Finally, VT3 is  $^{210}\text{Pb}$ -dated to the end of the 19<sup>th</sup> or beginning of the 20<sup>th</sup> century. Although their assignment to Lautaro Volcano is preliminary, to the best of our knowledge these tephra records represent the first evidence of frequent eruptions and widespread tephra deposition from this volcano in recently deposited lake sediments. The  $^{210}\text{Pb}$  age ranges for tephra deposition of GT2-4 and VT1-3 fit well with historically documented eruption dates, but cannot provide accurate, annually resolved ages for the tephra layers. Among the historical eruptions reported so far, the most likely candidates for matches with our sedimentary tephra deposits, because of their elevated volcanic explosivity indices (VEI; Newhall and Self 1982), are the Lautaro eruptions of AD 1959-60 (GT2, VT1), AD 1933 (GT3, VT2), and AD 1876 or 1878/79 (GT4, VT3) (Table 2; Fig. 6). The eruptions of AD 1883 from Lautaro Volcano (Martinic 2016) or the eruption of AD 1886 (Burmeister 1891) from an unidentified volcano in the NAVZ, are also possible candidates for the tephtras deposited around the end of the 19<sup>th</sup> century (Table 2; Fig. 6).

## Impact of volcanic eruptions (tephra deposition) and hydroclimate on lake ecosystems

After volcanic eruptions, volcanic ash can be remobilised by wind erosion over several years in Patagonia (Wilson et al. 2011). Therefore, organic matter and biogenic particles contained in the tephra layers could represent not only material deposited immediately (weeks to months) after the eruption, but even for several years thereafter.

The influence of volcanic eruptions and tephra deposition varied between the two study lakes. No clear organic-geochemical changes common to all tephra layers were observed in GEM17-1. In contrast,  $\delta^{15}\text{N}_{\text{TN}}$  shifted to values 2.1‰ lower, on average, in the tephra layers of VER17-1, compared to normal sediments (Fig. 7), whereas neither TOC/TN nor  $\delta^{13}\text{C}_{\text{TOC}}$  show comparable shifts (Fig. 2). Since the TOC and TN content of tephra layers is lower in VER17-1 compared to GEM17-1, any impact of tephra should be more detectable in VER17-1. As the shift is evident mainly in the nitrogen isotope ratios, the input of allochthonous organic matter with low  $\delta^{15}\text{N}$  values during volcanic eruptions can be excluded as an explanation for the  $\delta^{15}\text{N}_{\text{TN}}$  shifts in VER17-1. Rather, greater inputs of allochthonous organic nitrogen from terrestrial plant sources may lead to increased TOC/TN ratios (Meyers and Lallier-Vergés 1999), but this is not observed for the tephra layers of VER17-1. Deposition of higher amounts of soil organic matter, with comparatively low TOC/TN ratios (11-17; Mayr et al. 2009), during ashfalls can also be excluded, as Patagonian soils have comparatively high  $\delta^{15}\text{N}$  values (2-9‰; Mayr et al. 2009). The most likely explanation therefore is a disturbance of the lacustrine nitrogen cycle provoked by each eruption and lasting for the duration of the specific eruption, i.e. weeks to months. Massively higher turbidity during volcanic activity, caused by ash fallout, could have led to light limitation and decreased nitrogen assimilation in the lacustrine ecosystem (Finlay and Kendall 2007). Lower nitrogen consumption by primary producers, such as diatoms, is associated with more negative  $\delta^{15}\text{N}$  values in their biomass because of less nitrate utilization (Waser et al. 1998). Because organic matter content is generally very low in the tephra layers, however, low  $\delta^{15}\text{N}$  values therein more likely originate from inorganic nitrogen. Inorganic nitrogen concentration may have remained relatively high because of reduced primary production, and became bound as ammonium in the minerogenic fraction of the tephra.

Diatom assemblages show repeated breakdowns of planktonic/tychoplanktonic communities during tephra deposition. This was more evident in Laguna Verde than in Laguna Gemelas Este (Fig. 5A, B). As for species composition, assemblages from Laguna Verde were completely dominated by *Aulacoseira* spp. except in the tephra layers, whereas in Laguna Gemelas Este there were different species with shifting relative abundances along the core. *Aulacoseira* spp. have highly silicified valves and form thread-like colonies that require high water turbulence to remain suspended in the photic zone of the lake (Fernandez et al. 2013; Recasens et al. 2015). A decrease of *Aulacoseira* spp. only occurs during tephra deposition in VER17-1, denoting its sensitivity to volcanic ashfall. Ashfall could have

increased turbidity in the water column, increased light attenuation and reduced the depth of the photic zone. This would have diminished the development of planktonic/tychoplanktonic taxa, while non-planktonic taxa were less limited by reduced light conditions.

In Laguna Gemelas Este, epiphytic/benthic diatoms frequently dominated, and there is greater variability between planktonic/tychoplanktonic species and epiphytic/benthic ones. Diatoms have been shown to be sensitive to tephra impacts, which cause water turbidity, alter habitats, change water chemistry and nutrient availability. In response, the diatoms display changes in their abundance and/or assemblage composition (Barker et al 2000; Egan et al 2018). Lake systems, however, are variable, complex, and affected by a wide range of environmental factors (Telford et al. 2004). A clear link between changes in the diatom record and tephra deposition, as seems to be the case in Laguna Verde, is less clear in GEM17-1, and only obvious for GT2-GT4, but not for GT1 (Fig. 5A). The less clear pattern in GEM17-1 is mainly a consequence of generally higher variability between planktonic/tychoplanktonic species and epiphytic/benthic diatoms at Laguna Gemelas Este than at Laguna Verde. This higher variability can be explained by factors other than tephra deposition. First, samples with low occurrence of *Aulacoseira* sp. 1 may represent times of low lake level, as lower water level restricts their tychoplanktonic habitat and expands the areal coverage of benthic habitats. Second, Fey et al. (2009) studied Patagonian Laguna Las Vizcachas and suggested that higher amounts of epiphytic taxa could point to stronger wind-induced lateral water movements, by transporting littoral diatoms from their nearshore habitat to the lake centre. Third, less intense wind-induced turbulence could also disadvantage *Aulacoseira*, in comparison to benthic/epiphytic taxa, as the taxon is favoured by wind-induced lake turbulence (Giles et al. 2018). In summary, factors influencing diatom assemblages are more complex at Laguna Gemelas Este than at Laguna Verde, perhaps because it is situated in a more wind-exposed topographic location than is Laguna Verde.

Effects of volcanic eruptions are possibly less pronounced in the GEM17-1 record because of its more distal position in the fallout lobe, indicated by finer-grained and thinner tephra layers than those identified in VER17-1. Another possible cause for less tephra having entered Laguna Gemelas Este is the less humid climate and the flatter relief, compared to conditions at Laguna Verde. Mean angle of the slopes west of Laguna Verde is 27° and can reach values >40°, whereas Laguna Gemelas Este is located on a hillock with a slope of <2°. Thus, tephra eroded by surface runoff more easily enters Laguna Verde than Laguna Gemelas Este, even more so because the latter lacks surficial inflows, in contrast to the former.

Different hydrologic settings may have had an effect on the stable isotope values of the two sediment records as well. At the drier Laguna Gemelas Este site,  $\delta^{13}\text{C}_{\text{TOC}}$  and  $\delta^{15}\text{N}_{\text{TN}}$  were, on average, 5.2‰ and 1.3‰ higher, respectively, than at the more humid site, Laguna Verde (excluding tephra deposits). Surface sediments from 72 lakes along a climate gradient in western Chile showed a significant increase of  $\delta^{13}\text{C}_{\text{TOC}}$  and  $\delta^{15}\text{N}_{\text{TN}}$  with decreasing mean annual precipitation (Contreras et al. 2018). The causes for such humidity-dependent isotope differences could be manifold, including

different ratios of allochthonous-to-autochthonous organic matter and differences in nutrient fluxes (Mayr et al. 2009; Fan et al. 2017; Contreras et al. 2018) and cannot be disentangled without better knowledge of the carbon and nitrogen cycles in the lakes.

## Conclusions

This study was a first step toward detecting and analysing tephtras of historic volcanic eruptions from Lautaro Volcano, and eventually Viedma Volcano, with the ultimate goal being to better understand the impacts of volcanic ashfall on lake ecosystems in the area of El Chaltén. We found that Lautaro tephtras are regionally widespread and can be used as time markers once the tephrochronologic framework is completed. We also demonstrated that the effects of ashfall can differ between lake ecosystems at similar distances from the volcano centre, probably as a consequence of different limnological conditions imposed by different climate and geomorphological settings. Ongoing studies will shed further light on the regional distribution of observed tephtras and improve their tephrochronological value by studying additional lake sites and sediment variables. These data will be helpful for understanding the eruptive history of AVZ centres and provide insights into the environmental impacts of volcanic events on lacustrine ecosystems.

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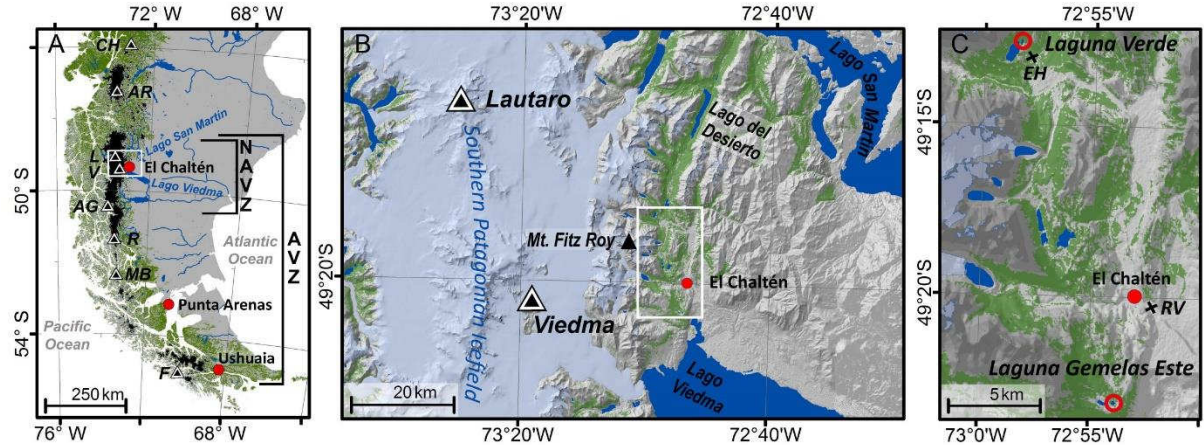
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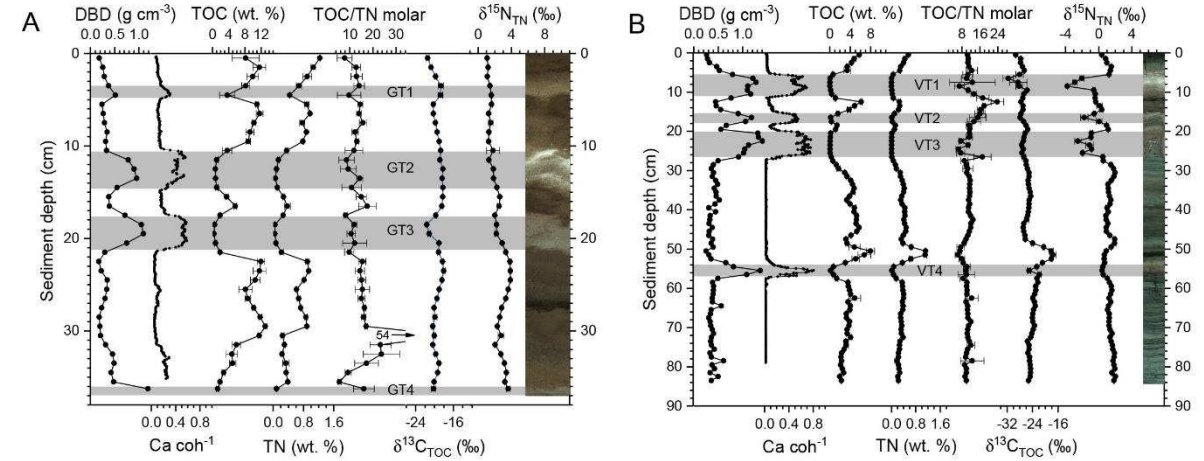
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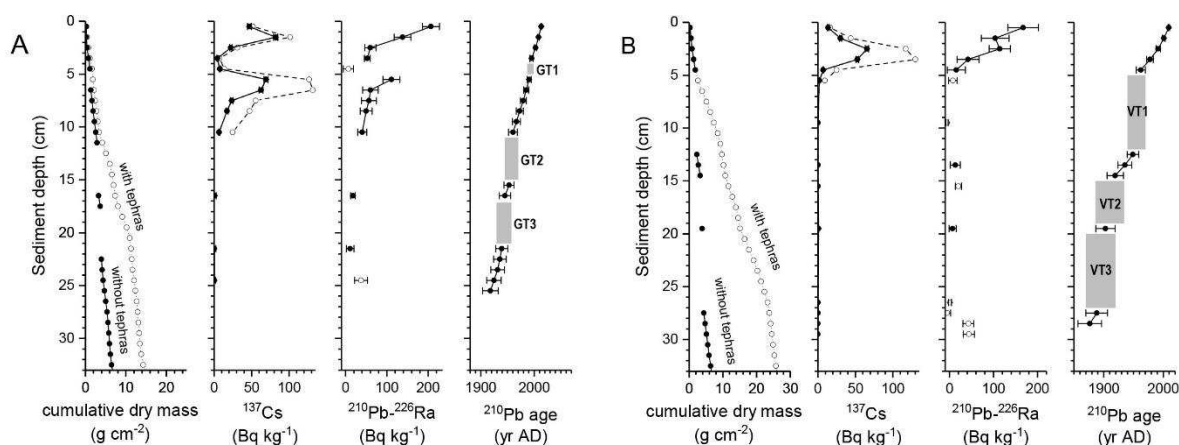
Figures



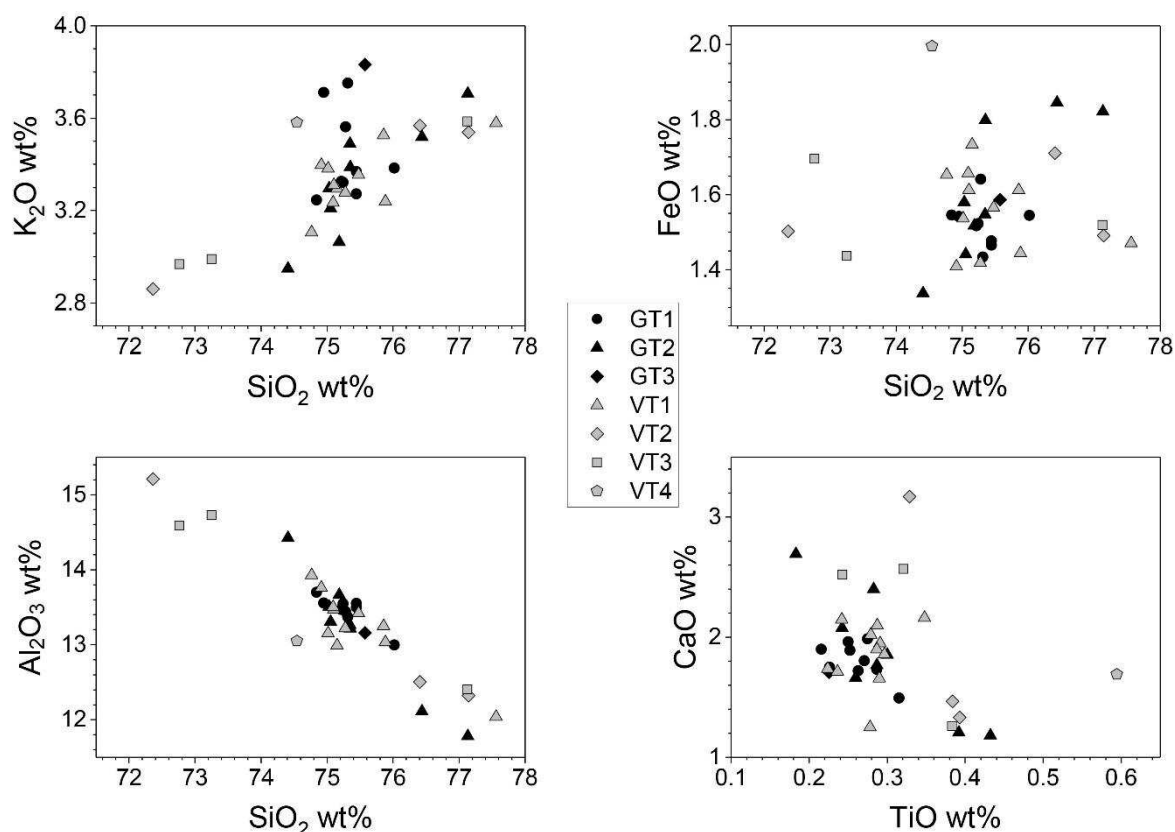
**Fig. 1** (A) Map of southern South America showing the research area (box) and major active volcanoes: Cerro Hudson (CH), Arenales (AR), Lautaro (L), Viedma (V), Aguilera (AG), Reclús (R), Monte Burney (MB), Fuego (F). The extension of the Austral Volcanic zone (AFZ) and northern Austral Volcanic Zone (NAVZ) is indicated. (B) Southern Patagonian Ice Field, subglacial Lautaro and Viedma Volcanoes, and the research area next to El Chaltén. The forested area is in green. (C) Locations of Lagunas Verde and Gemelas Este in the area around El Chaltén. Crosses mark the meteorological stations at Estancia Huemules (EH) and Río de las Vueltas (RV). Base map: SRTM, LP DACC NASA Version 3, forested area: Hansen et al. (2013), water bodies: Messenger et al. (2016), glaciated area: Meier et al. (2018)



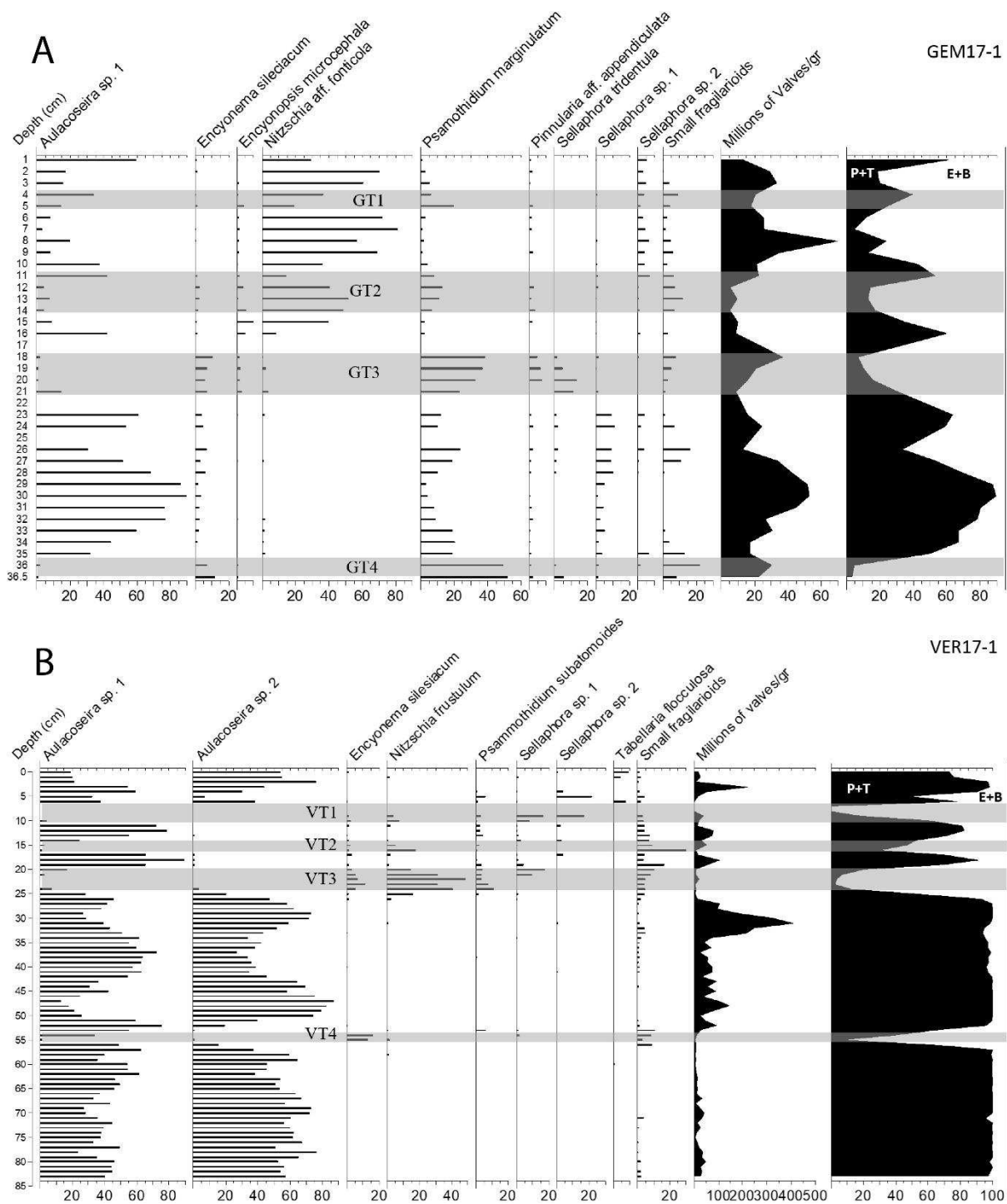
**Fig. 2** Geochemical and stable isotope records and core photographs of GEM17-1 (A) and VER17-1 (B). Grey bars highlight tephra layers readily recognizable by their Ca/coh records. Error bars of organic geochemical data represent standard deviations of 2-3 analyses



**Fig. 3** Cumulative dry mass, activities of <sup>137</sup>Cs (solid symbols: original data, open symbols: decay-corrected data), excess <sup>210</sup>Pb, and <sup>210</sup>Pb ages of the upper 35 cm of GEM17-1 (A) and VER17-1 (B). Dates given represent mean <sup>210</sup>Pb ages, bars represent maximum and minimum possible ages. Excess <sup>210</sup>Pb values used for the age models are given with solid symbols. The maximum and minimum age ranges of tephra layers are shown as grey bars

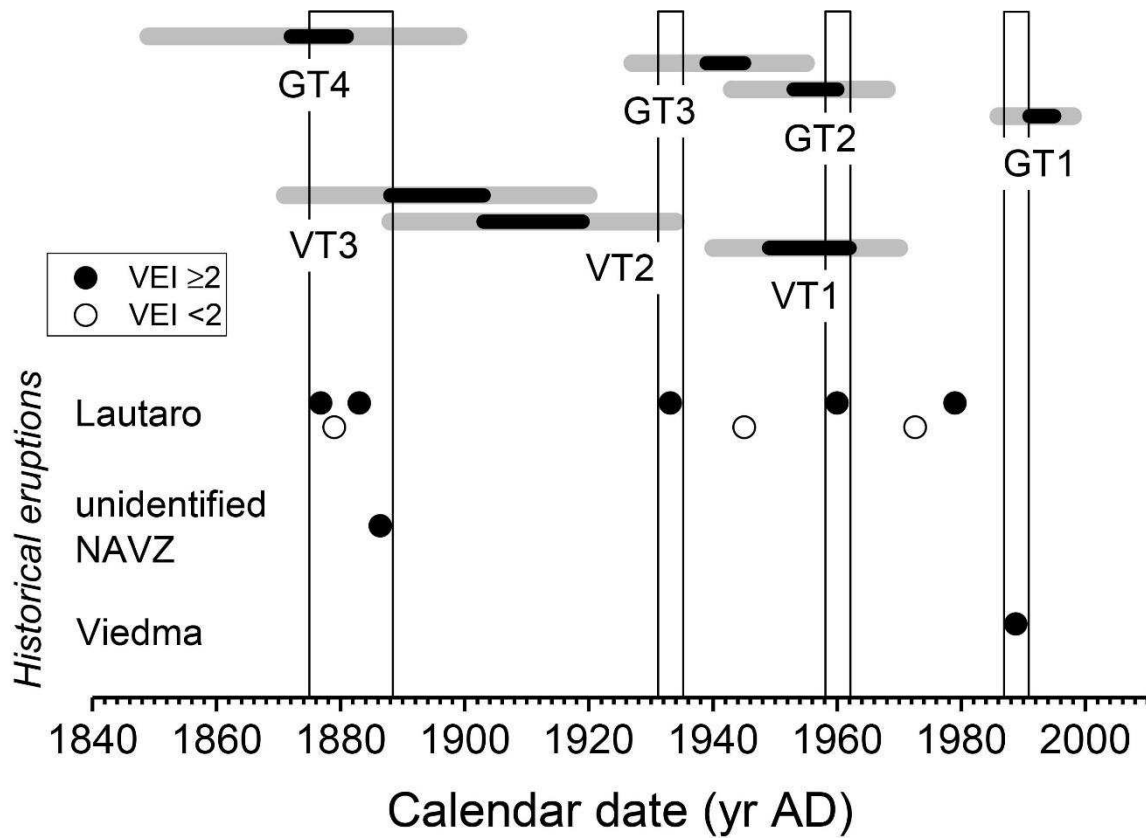


**Fig. 4** Variation diagrams of glass-chemical data identified from tephra layers in GEM17-1 (GT1-3) and VER17-1 (VT1-4) sediment cores. Each data point represents one analysed glass shard. For average chemical composition of tephras, see Table 1

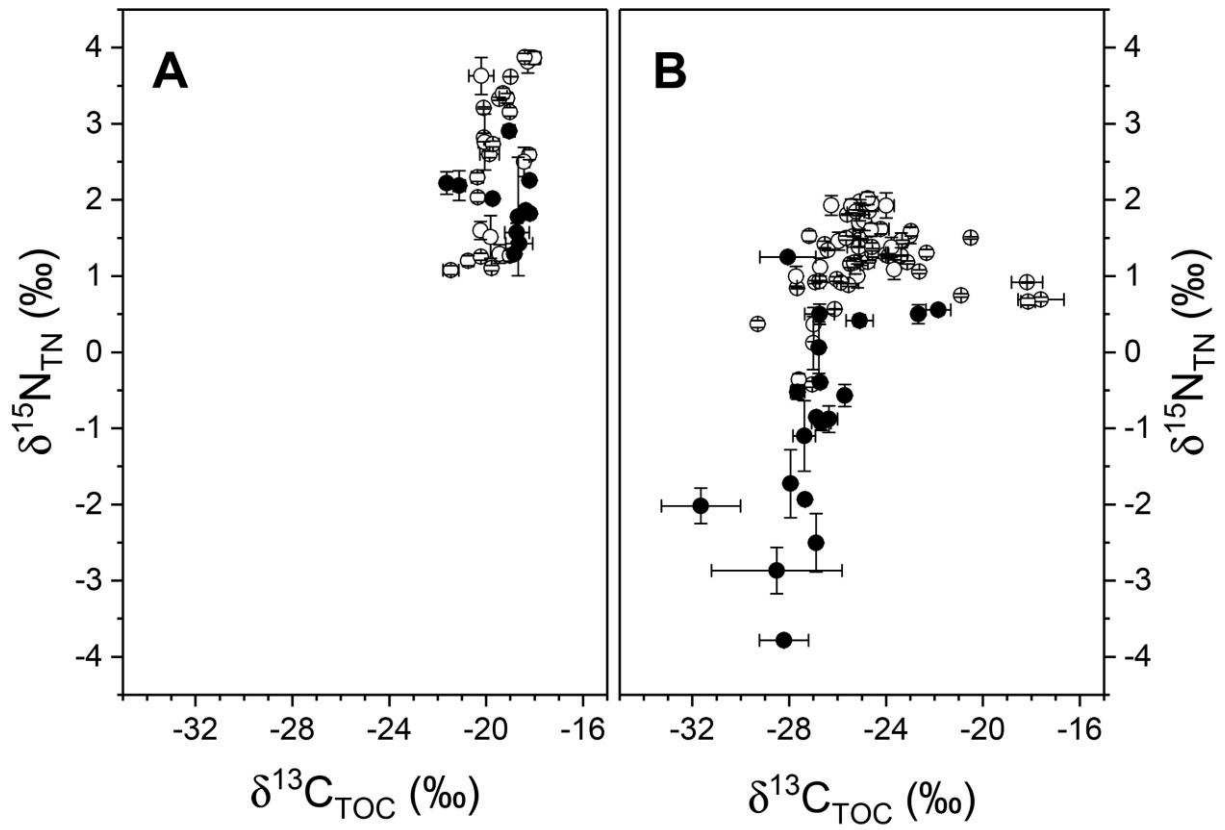


**Fig. 5** Assemblages of the most important diatom taxa (in percent), total diatom concentration (log scale) and percentage of benthic and epiphytic (B+E) versus planktonic and tychoplanktonic (P+T) diatom taxa in cores GEM17-1 (A) and VER17-1 (B). Only taxa that occurred with an abundance >5% in at least 2 samples are shown





**Fig. 6** Schematic timeline of historical eruptive events of Lautaro, Viedma, and an eruption of an unidentified NAVZ volcano as recorded in the literature (Table 2), against tephra layers identified in Lagunas Verde (VT1-3) and Gemelas Este (GT1-4), which were chronologically constrained using  $^{210}\text{Pb}$  measurements. Filled circles represent high-explosivity events and open circles low-explosivity events. Ages are presented using the lower and upper age estimates by black bars, and maximum and minimum errors as grey lines. Vertical bars highlight the historical volcanic eruptions most likely present in the lacustrine tephra records with a volcanic explosivity index (VEI)  $\geq 2$



**Fig. 7**  $\delta^{15}\text{N}_{\text{TN}}$  versus  $\delta^{13}\text{C}_{\text{TOC}}$  values for GEM17-1 (A) and VER17-1 (B). Sediment layers containing tephra (black circles) are optically distinguished from those without tephra (open circles). In VER17-1  $\delta^{15}\text{N}_{\text{TN}}$  values in the tephra are lower than in the rest of the sediment which is not the case for GEM17-1

**Table 1** Individual glass-shard major elemental composition (means and standard deviations) from seven tephras identified in GEM17-1 (GT1-3) and VER17-1 (VT1-4)

Label		SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O	Cl	Total
GT1	avg	75.31	0.26	13.46	1.52	0.03	0.29	1.80	3.66	3.44	0.04	0.19	96.86
n=9	sdev	0.34	0.03	0.20	0.06	0.03	0.04	0.15	0.16	0.19	0.02	0.03	1.96
GT2	avg	75.49	0.30	13.16	1.61	0.03	0.28	1.86	3.70	3.33	0.07	0.18	97.48
n=8	sdev	0.87	0.08	0.85	0.19	0.04	0.06	0.53	0.15	0.25	0.04	0.02	1.52
GT3	avg	75.57	0.23	13.16	1.59	0.05	0.20	1.71	3.51	3.83	0.07	0.09	98.11
n=1													
VT1	avg	75.46	0.28	13.25	1.56	0.04	0.26	1.86	3.73	3.34	0.05	0.18	97.46
n=11	sdev	0.78	0.03	0.49	0.11	0.04	0.07	0.27	0.28	0.13	0.03	0.03	1.61
VT2	avg	75.30	0.37	13.35	1.57	0.03	0.19	1.99	3.68	3.32	0.05	0.15	96.94
n=3	sdev	2.57	0.03	1.62	0.12	0.03	0.05	1.03	0.44	0.40	0.05	0.02	1.15
VT3	avg	74.38	0.32	13.91	1.55	0.04	0.28	2.12	3.96	3.18	0.12	0.15	97.54
n=3	sdev	2.39	0.07	1.30	0.13	0.03	0.17	0.74	0.72	0.35	0.09	0.04	2.51
VT4	avg	74.55	0.59	13.05	2.00	0.00	0.40	1.69	3.92	3.58	0.16	0.06	98.92
n=1													

**Table 2** Historic eruptions in the NAVZ. VEI was obtained from the Global Volcanism Program (2013), except for the eruptions of 1883 and 1886, which were estimated from historic descriptions, as referenced

Volcano	Year of eruption	VEI	Reference
Viedma	1988	2	Kilian (1990)
Lautaro	1978/79	2	Lliboutry (1998)
Lautaro	1972	1	Lliboutry (1998)
Lautaro	1959/60	2	Martinic (1988)
Lautaro	1945	1	Lliboutry (1998)
Lautaro	1933	2	Martinic 1988
Unidentified, NAVZ	1886	≥2	Burmeister (1891)
Lautaro	1883	≥2	Martinic 2016
Lautaro	1878/79	?	Martinic 2008
Lautaro	1876	2	Martinic 1988