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Towards a late Quaternary tephrochronological framework for the southernmost part of South America – the Laguna Potrok Aike tephra record

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A B S T R A C T

A total of 18 tephra samples have been analysed from the composite sediment sequence from Site 2 of the Laguna Potrok Aike ICDP expedition 5022 from southern Patagonia, Argentina, which extends back to ca 51 ka cal BP. Analyses of the volcanic glass show that all layers but one are rhyolitic in composition, with SiO_2 contents ranging between ca 74.5 and 78 wt% and suggest an origin in the Austral Andean Volcanic Zone (AVZ; 49–55°S). Nonetheless, two main data clusters occur, one group with K_2O contents between ca 1.5 and 2.0 wt%, indicating an origin in the Mt. Burney volcanic area, and one group with K_2O contents between ca 2.7 and 3.9 wt%, tentatively correlated with Viedma/Lautaro and the Aguilera volcanoes in the northern part of the AVZ. The early Holocene Tephra, MB_1 and the late Pleistocene Reclus R_1 tephra occur in the upper part of the sequence. Periods with significant tephra deposition occurred between ca 51–44 ka cal BP, and ca 31–25 ka cal BP, with a decrease in tephra layer frequency between these two periods.

1. Introduction

The stratigraphic and chronological investigation of sedimentary ash layers has undergone rapid development during the last decades, partly due to the advancements in identifying and extracting small amounts of volcanic glass shards and minerals from various deposits, but also because the analytical precision and accuracy of chemical measurements have improved considerably (Turney, 1998; Pearce et al., 2011; Hayward, 2012). Identification of source volcanoes and related sedimentary pyroclastic deposits are usually based on major element chemistry of glass shards or mineral phases, which in some cases may be sufficient for regional and local correlations of volcanic ash sequences and eruptive events (Lowe, 2011).

The Austral Andean Volcanic Zone (AVZ; 49–55°S) in South America is the southernmost volcanic province of the Andes. It contains several large and very active volcanoes, including Hudson, Reclus, Aguilera and Mt. Burney, and widespread ash layers originating from these volcanic fields have been found in several peat bogs, sedimentary outcrops or lake sediment sequences (Auer, 1974; Kilian et al., 2003; Markgraf et al., 2003; McCulloch et al., 2005; Haberzettl et al., 2007; Stern, 2008). To some extent ash layers from different volcanoes could be distinguished in-between and source-related through comparison of chemical and isotopic data, e.g., SiO_2 vs. K_2O, or Rb vs. $^{87}Sr/^{86}Sr$, respectively (Stern, 2008). However, since some volcanic fields show remarkably stable chemical compositions over time, as is the case for many Andean volcanoes (Stern and Kilian, 1996), for secure source classification and tephra correlations more sophisticated discriminating methods are needed, involving for example laser ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) analyses of minor and trace elements from both glass shards and related mineral species of an ash layer.

The oldest of the ash layers reported so far is the late Pleistocene Reclus R_1 tephra, dated to ca 12,685 ± 260 ^{14}C years BP. Two widespread tephras from Mt. Burney, dated to ca 8425 ± 500 and 3820 ± 390 ^{14}C years BP, respectively, the Hudson H_1 tephra (ca 6850 ± 160 ^{14}C years) and the Aguilera A_1 eruption

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(3000 ± 100 ^{14}C years BP) are important stratigraphic marker horizons for regional Holocene records (Stern, 2008). However, whereas the late Pleistocene and Holocene tephrochronology of the southernmost part of Patagonia is relatively well known, tephra records older than ca 15 ka cal BP are sparse (Haberzettl et al., 2007, 2008).

In this paper we describe the tephrostratigraphy of the composite Profile from Site 2 of the ICDP expedition 5022 (hereafter 5022-2CP) 'Potrok Aike Maar Lake Sediment Archive Drilling Project', PASADO; (Zolitschka et al., 2009, 2013). Seven cores were recovered from two main coring sites in the lake centre, recovering the uppermost ca 100 m of the lacustrine sediment infill (Fig. 1). The sedimentary record reaches back to ca 51 ka cal BP (Kliem et al., 2013b) providing an exceptionally high-resolution for a lacustrine sedimentary sequence from this region. The lithostratigraphy of the 5022-2CP sediment record is presented by Kliem et al. (2013b), and chronological constraints are provided by radiocarbon age estimates, supported by magnetostratigraphy (Fig. 2). Moreover, volcanic ash layers identified in both lake sediment cores and sediment outcrops in the vicinity of the lake, are used for local correlations providing important stratigraphic tie-points. For example, the previously investigated core PTA03/06 from the northern lake shoulder of Laguna Potrok Aike (Haberzettl et al., 2008) has been correlated with the 5022-2CP record using three characteristic tephra layers with ages between ca 44 and 51 ka cal BP as marker horizons (Gebhardt et al., 2012; Kliem et al., 2013a). Here we provide, however, the first detailed report on the tephrostratigraphy and chemical composition of the visible ash layers identified in the 106 m long 5022-2CP sedimentary profile. The majority of the tephra layers discussed here have not been presented elsewhere. The tentative identification of source volcanoes is based on major element chemistry of glass shards, but we emphasize that for absolute correlations, future studies must rely also on more sophisticated discriminating methods based on

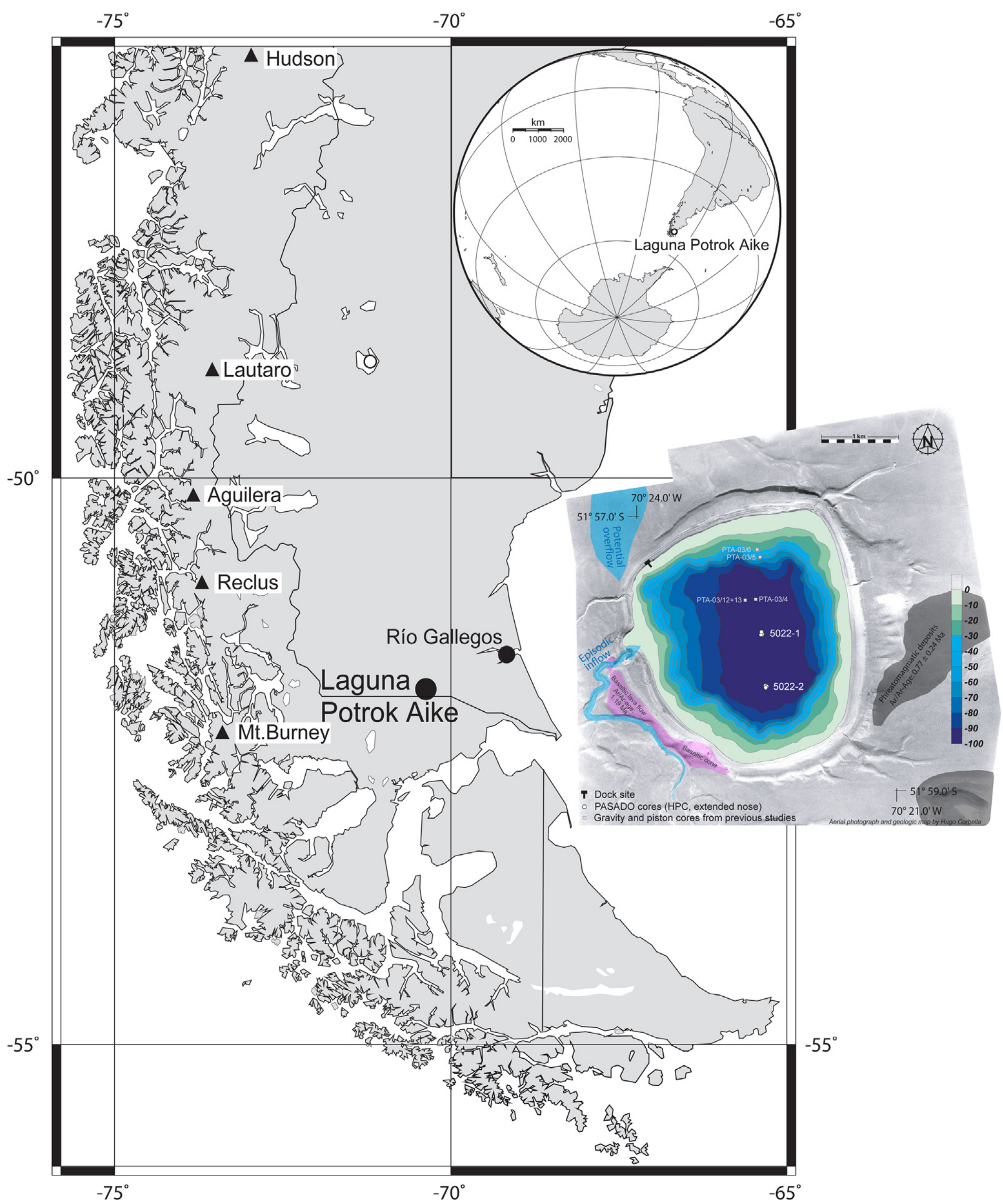

Fig. 1. Map of southernmost Patagonia showing the location of Laguna Potrok Aike and volcanoes referred to in the text.

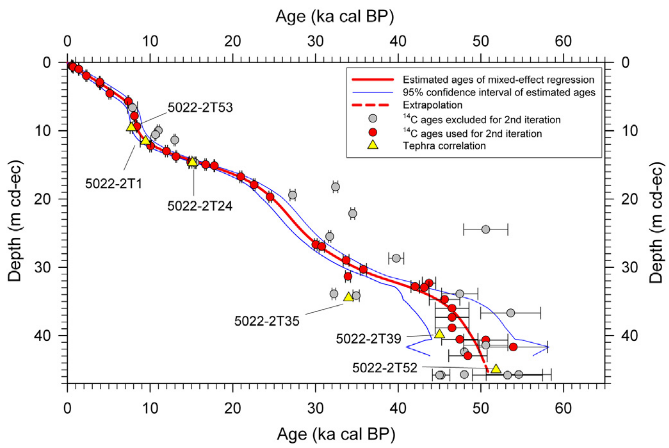

Fig. 2. Age–depth of the 5022-2CP record model from (Kliem et al., 2013b).

minor and trace elements from both glass shards and mineral species.

2. Materials and methods

Laguna Potrok Aike (113 m a.s.l., 51°57.789′S, 70°22.754′W) is located in the western part of the Pali Aike Volcanic Field (PAVF) of southernmost Patagonia (Argentina). This tectonovolcanic region is characterized by extensive backarc volcanism with widespread scoria cones, plateau lavas and maars (Mazzarini and D'Orazio, 2003). An Ar/Ar age estimate of 0.77 ± 0.24 Ma for the phreatomagmatic pyroclastic suite outcropping on the eastern side of the maar is regarded as reflecting the initial stage of maar formation (Zolitschka et al., 2006). Currently, Laguna Potrok Aike is 100 m deep with a maximum diameter of 3.5 km, and a surface area of 7.74 km^2. The regional climate as well the lake hydrology is strongly affected by the Southern Hemisphere Westerlies, the main regional atmospheric circulation pattern.

Sediment cores were recovered mainly with a hydraulic piston corer during austral spring of 2008 within the framework of the ICDP lake drilling expedition 5022 (PASADO). This expedition was carried out with the GLAD800, a containerized barge system equipped with a drill rig and operated by the non-profit organization DOSECC (Drilling, Observation and Sampling of the Earths Continental Crust). Based on lithologic characterization and after macroscopic correlation a composite profile was assembled from Site 2. This key composite record (5022-2CP) is based on three parallel holes with a total recovery rate of 95.2% and covers the last 51 ka cal BP (Gebhardt et al., 2012; Kliem et al., 2013a).

Twenty-four visible ash layers were identified in the 5022-2CP record. Most of these tephras stand out as silt- to fine sand-sized whitish or greyish layers, from millimetres up to a maximum of 145 cm in thickness, contrasting markedly against the embedding dark lacustrine sediments consisting mainly of grey clays and sandy silts. Apart from glass and pumice, many if not all tephra layers also contain various accessory volcanic minerals, with plagioclase as the most abundant phase in most layers.

In total 18 volcanic glass samples were analysed for their main element chemical composition using the electron microprobe facilities of the Tephrochronology Analytical Unit at the University of Edinburgh, UK (Table 1). Analyses were performed on polished thin-sections on a five-spectrometer Cameca SX-100 electron microprobe for concentrations of ten major oxides. Ten elements were analysed with an accelerating voltage of 15 keV, a beam current of 2 nA for the major elements and 80 nA for the minor elements and a beam diameter of 5 μm (for operating conditions, see also Hayward, 2012). Standard calibration blocks were used for calibration, and glass standards to assess the accuracy during analyses. Only analyses above 94 wt% are included in the means (cf. Table 2).

3. Tephrostratigraphy: results and data interpretation

All individual glass shard chemical analyses are shown as biplots of major oxides, particularly SiO_2 vs. K_2O, following the conventional practice in identifying tephras from the volcanoes of the AVZ based on their chemical affinities (e.g. Kilian et al., 2003; Stern, 2008). As a result of this data, all ash layers identified in the 5022-2CP sediment record are rhyolitic except the 5022-2T35 layer, which has two components with a dominating dacitic one (Fig. 3a). Generally, the rhyolitic tephras can be subdivided into two groups, one with SiO_2 contents ranging between ca 73 and 79 wt% and K_2O between ca 1.5 and 2.0 wt%, and another with SiO_2 between 76 and 78 wt% and K_2O between 2.7 and 3.9 wt% (Fig. 3a).

The first group correlates with published analyses of tephras and eruptives from Mt. Burney (Kilian et al., 2003; Stern, 2008), which is also indicated by concentrations of other main oxides, e.g. FeO_{tot} between 1.1 and 2.0 wt% and TiO_2 between 0.15 and 0.37 wt%, respectively (Fig. 2b; Table 2). However, for the second group it is more difficult to distinguish between the source volcanoes. On the one hand the three northernmost volcanoes in the AVZ (Aguilera, Viedma, Lautaro) are chemically similar and only a few datasets exist with information on their chemical composition (Stern, 2008; Kastner et al., 2010). The Reclus volcano on the other hand has an intermediate chemical composition between Mt. Burney and the northern volcanoes (Stern, 2008).

3.1. *Tephra layer 5022-2T1 (12.32–12.34 m)*

The uppermost of the analysed tephra layers is clearly distinguished from the surrounding dark sediment by its white colour and sharp upper and lower boundaries (Fig. 4). The SiO_2 vs. K_2O data comparison (Fig. 2a) shows that the most likely source is the Mt. Burney volcano, although the Si contents (77.6–78.4 wt%) are slightly higher and CaO and FeO_{tot} are significantly lower than for all other Mt. Burney derived tephras presented in our record (Table 2). Plagioclase is also abundant. This layer is correlated with the early Holocene Tephra, MB_1 from Mt. Burney (e.g. Kilian et al., 2003; Stern, 2008) that has previously been described from Laguna Potrok Aike (Haberzettl et al., 2007, 2008). The MB_1 tephra is of early Holocene age but the exact date of this eruption is not well constrained independently. It has recently been radiocarbon dated to 8425 ± 500 ^{14}C years BP (8851–9949 cal BP; Stern, 2008), and a calibrated age of 9000–9175 cal BP was reported by Kilian et al. (2003). The age–depth model of the 5022-2CP record (Kliem et al., 2013b) suggests a slightly higher depositional age of ca 9545 cal BP (2σ range 8851–10,238 cal BP). However, this age overlaps within the age ranges suggested by Stern (2008). Haberzettl et al., 2007 concluded that the fallout of the MB_1 tephra generated intense erosion in the Laguna Potrok Aike catchment as well as sediment remobilization in the lake basin.

3.2. *Tephra layers 5022-2T2 (16.04–16.05 m), 5022-2T3 (16.48 m) and 5022-2T4 (16.78–16.79 m)*

A distinct feature in the upper part of the 5022-2CP sedimentary record is the presence of a 145-cm thick sediment section consisting of a highly altered and multi-layered volcanic ash bed intercalated with brown laminations of fine sand with

Table 1
Analysed tephras from the Laguna Potrok Aike (5022-2CP) record. All samples between PAS-2T4 and PAS-2T23 are from a 145-cm thick sediment section consisting of highly altered and multi-layered volcanic ash beds intercalated with brown laminations of fine sand with organic macro remains, including the Reclus R_1 tephra. Some tephras have not yet been analysed (e.g. PAS-2T25) and other samples were considered to be insignificant and were not analysed. Ages (midpoints and 2σ ranges) refer to the age–depth model of Kliem et al. (2013b). All tephra-layer thicknesses are approximated.

Tephra sample	Depth (m)	Thickness	Age (cal BP), 2σ range	Source volcano	Correlation	Comments
PAS-2T1	12.32–12.34	18 mm	9545 (8851–10,238)	Mt. Burney	MB_1	
PAS-2T2	16.04–16.05	10 mm	–	Reclus	R_1	Reworked
PAS-2T3	16.48	4 mm	–	Reclus	R_1	Reworked
PAS-2T4	16.78–16.79	5 mm	16,379 (15,780–16,978)	Reclus	R_1	Upper part of R_1 or reworked
PAS-2T26	21.98	4 mm	20,628 (19,915–21,341)	Mt. Burney		Possibly reworked
PAS-2T27	28.23–28.34	110 mm	25,072 (23,879–26,265)	Mt. Burney		Possibly reworked
PAS-2T30	30.15–30.49	340 mm	26,198 (24,999–27,398)	Mt. Burney		
PAS-2T31	33.13–33.19	60 mm	28,204 (26,991–29,416)	Viedma/Lautaro?		
PAS-2T32	38.04–38.06	20 mm	30,640 (29,349–31,932)	Mt. Burney		Possibly reworked
PAS-2T33	38.70–38.73	36 mm	31,272 (29,954–32,590)	Mt. Burney		
PAS-2T35	55.93–55.97	40 mm	44,437 (40,656–48,219)	Viedma/Lautaro?		2 glass components
PAS-2T36	57.03	3 mm	45,322 (41,082–49,563)	Mt. Burney		
PAS-2T37	63.33–63.40	70 mm	47,073 (42,400–51,747)	Aguilera?		
PAS-2T38	67.94–67.99	50 mm	48,280 (43,558–53,003)	Mt. Burney		
PAS-2T39	72.06–72.15	90 mm	48,742 (43,835–53,649)	Mt. Burney		
PAS-2T40	76.51–76.52	>15 mm[a]	49,612 (41,555–57,669)	Viedma/Lautaro?		
PAS-2T48	94.09–94.10	15 mm	50,758 (44,485–57,030)	Mt. Burney		Possibly reworked
PAS-2T52	95.38–95.39	15 mm	50,854 (44,581–57,126)	Mt. Burney		

[a] Upper boundary not known due to a coring gap.

organic macro remains. A similar sediment unit has also been reported in previous cores from Laguna Potrok Aike (Haberzettl et al., 2007). Already published chemical analyses of glass shards from the lower part of this unit suggest that this particular ash sample correlates with the Reclus R_1 tephra (Haberzettl et al., 2007).

For the present study three additional samples were analysed, one from the 5022-2T4 layer (16.78–16.79 m) and two from ca 5 mm-thick layers (5022-2T2 and 5022-2T3) found above the 5022-2T4 layer, at 16.04–16.05 and 16.48 m depth, respectively. Chemical analyses indicate that the three layers have identical chemical compositions, with K_2O between 2.5 and 2.8 wt% and SiO_2 between 76.8 and 78.0 wt%. These values closely overlap with results of previous analyses of the Reclus R_1 tephra (Kilian et al., 2003; Haberzettl et al., 2007; Stern, 2008). Based on this data, it is very likely that the upper two tephra layers (5022-2T2 and 5022-2T3) are reworked from the main Reclus tephra bed, either from the catchment or within the lake basin. Nonetheless, it is not yet clearly documented whether most of the interbedded tephra from this sediment package represents indeed reworking of the main volcanic ash-fallout, or alternatively may be taken as evidence for multiple eruptive events within a short time span.

During the last years several attempts have been made to date the Reclus tephra applying the radiocarbon method with results ranging between ca 12,000 and 13,000 ^{14}C years BP. The most detailed efforts so far are from the Strait of Magellan (McCulloch et al., 2005) where a weighted pooled mean age of 12,638 $\pm$ 60 ^{14}C years BP (14,348–15,507 cal BP) was derived from high-resolution dating of peat samples bracketing the Reclus tephra at two sites. A similar approach was undertaken by Sagredo et al. (2011) in the Última Esperanza area in Chilean Patagonia, where a weighted mean of eight radiocarbon dates yielded an age range between 14.5 and 15.0 ka cal BP for a tephra layer also correlated with the Reclus tephra. Although there is very good chronological agreement between these studies, the age ranges reported are significantly younger compared to the ca 16,380 cal BP age derived from the 5022-2CP age–depth model (Kliem et al., 2013b). This apparent discrepancy indicates either that the 5022-2CP age–depth model is not well constrained over this part of the sequence or, alternatively, the eruptive history of this volcano (and the related volcanic field) is far from being understood.

3.3. Tephra layers 5022-2T26 (21.98 m), 5022-2T27 (28.23–28.34 m), 5022-2T30 (30.15–30.49 m)

Three layers showing chemical compositions similar to a Mt. Burney source were found at 21.98 m, 28.23–28.34 m and 30.15–30.49 m depth, respectively. The main element geochemistry is identical between the two lower layers, while some shards in the upper thin layer (5022-2T26) have elevated concentrations for CaO, Na_2O and Al_2O_3, very likely indicating contamination from mineral (plagioclase?) phenocrysts present in the glass shards, although such mineral inclusions were not observed during microprobe analyses.

The 5022-2T27 tephra has unconformable boundaries with the overlying and underlying sediment, and it is possible that the whole layer is redeposited, perhaps from a shore wash-out of the lowermost 5022-2T30 layer that shows a similar chemical composition. Indeed, the 5022-2T30 layer is one of the thickest tephras in the entire sequence and its undulating lower boundary suggests downward particle migration due to density-induced settling of particles (Beierle and Bond, 2002). The 5022-2T30 layer displays all characteristic values of Mt. Burney tephras, e.g. K_2O around 1.7 wt% and SiO_2 around 76.7 wt%. Moreover, this layer represents a new, previously unreported eruptive event from Mt. Burney in the later part of Marine Isotope Stage (MIS) 3. Our present interpretation is that the 5022-2T27 tephra may be a reworked layer from this large eruption at ca 26.2 ka cal BP, although additional investigations are needed for fully clarifying these assertions. It is also possible that the 5022-2T26 layer may represent a previously unrecognized minor eruptive event from Mt. Burney.

3.4. Tephra layer 5022-2T31 (33.13–33.19 m)

This layer has an undulating lower boundary and a sharp, erosive upper boundary. Chemical analyses provide results distinctly different from Mt. Burney tephras, with K_2O values between 2.7 and 3.1 wt%. Na_2O is lower than in the Mt. Burney tephras (ca 3.9–4.2 wt%) and TiO_2 is lower than in any other of the analysed layers (0.07–0.09 wt%; Fig. 2b). K_2O is higher than in the Reclus R_1 tephra and, interestingly, the chemical data suggest a possible origin in the Viedma or Lautaro volcanoes, although the scarcity of glass chemical data from these volcanoes makes this

Table 2
Major element composition of tephra layers from the 5022-2CP record from Laguna Potrok Aike shown as mean oxide concentrations (wt %); (a) raw data; (b) normalised to 100%; (c) standards. One standard deviation is given in parentheses. Ten elements were analysed by a Cameca SX-100 wavelength dispersive electron microprobe with five spectrometers, an accelerating voltage of 15 keV, beam current of 2 nA for the major elements and 80 nA for the minor elements and a beam diameter of 5 μm. Standard calibration blocks were used for calibration and glass standards were used to assess the accuracy during analyses. Only analyses above 94% are included in the means. n = number of analyses. Two secondary standards (BHVO2g and Lipari obsidian) were analysed at regular intervals to monitor instrumental drift and assess the accuracy and precision of the analyses.

(a)

Sample	n	SiO_2	TiO_2	Al_2O_3	FeO_{tot}	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Total
PAS-2T1	11	75.66 (0.82)	0.14 (0.01)	12.38 (0.25)	1.04 (0.11)	0.04 (0.01)	0.24 (0.02)	1.20 (0.09)	4.41 (0.42)	1.87 (0.13)	0.03 (0.00)	97.02 (1.13)
PAS-2T2	32	74.17 (0.96)	0.11 (0.01)	12.38 (0.33)	1.19 (0.10)	0.04 (0.01)	0.21 (0.03)	1.44 (0.08)	3.83 (0.13)	2.53 (0.09)	0.03 (0.01)	95.93 (1.30)
PAS-2T3	9	74.66 (0.79)	0.11 (0.01)	12.28 (0.29)	1.20 (0.07)	0.04 (0.01)	0.22 (0.03)	1.43 (0.09)	3.81 (0.10)	2.52 (0.19)	0.03 (0.01)	96.29 (0.97)
PAS-2T4	12	77.59 (0.25)	0.11 (0.01)	12.78 (0.24)	1.18 (0.07)	0.04 (0.01)	0.21 (0.02)	1.54 (0.09)	3.91 (0.12)	2.61 (0.09)	0.03 (0.01)	96.29 (0.97)
PAS-2T26	7	72.29 (2.18)	0.33 (0.03)	13.79 (1.43)	1.39 (0.11)	0.04 (0.01)	0.21 (0.05)	2.37 (0.64)	4.97 (0.50)	1.50 (0.21)	0.05 (0.01)	96.93 (0.93)
PAS-2T27	21	73.52 (1.17)	0.27 (0.03)	12.55 (0.29)	1.48 (0.14)	0.05 (0.01)	0.38 (0.05)	1.87 (0.15)	4.58 (0.14)	1.59 (0.06)	0.04 (0.01)	96.32 (1.01)
PAS-2T30	6	73.91 (0.73)	0.25 (0.01)	12.39 (0.21)	1.43 (0.06)	0.04 (0.01)	0.36 (0.02)	1.78 (0.08)	4.49 (0.07)	1.64 (0.08)	0.03 (0.00)	96.31 (1.02)
PAS-2T31	13	73.64 (0.55)	0.08 (0.01)	12.48 (0.24)	0.99 (0.11)	0.05 (0.01)	0.19 (0.04)	1.17 (0.04)	3.86 (0.08)	2.80 (0.12)	0.03 (0.00)	95.29 (0.78)
PAS-2T32	22	74.06 (1.25)	0.25 (0.02)	12.65 (0.31)	1.49 (0.12)	0.04 (0.00)	0.36 (0.03)	1.85 (0.12)	4.48 (0.15)	1.63 (0.08)	0.04 (0.01)	96.85 (1.41)
PAS-2T33	15	73.79 (0.58)	0.25 (0.02)	12.66 (0.23)	1.42 (0.14)	0.04 (0.01)	0.35 (0.05)	1.88 (0.14)	4.48 (0.10)	1.67 (0.08)	0.04 (0.01)	96.57 (0.64)
PAS-2T35A	9	68.70 (1.34)	0.52 (0.05)	14.74 (0.86)	2.73 (0.13)	0.05 (0.01)	0.84 (0.15)	3.07 (0.12)	4.23 (0.13)	2.38 (0.06)	0.10 (0.01)	97.36 (1.83)
PAS-2T35B	2	73.76 (0.26)	0.12 (0.02)	12.38 (0.86)	1.23 (0.30)	0.04 (0.03)	0.29 (0.13)	1.38 (0.08)	3.58 (0.37)	3.22 (0.14)	0.03 (0.01)	96.03 (1.37)
PAS-2T36	9	73.83 (1.21)	0.23 (0.02)	12.24 (0.43)	1.24 (0.17)	0.04 (0.00)	0.30 (0.06)	1.57 (0.22)	4.38 (0.15)	1.65 (0.08)	0.03 (0.01)	95.52 (1.02)
PAS-2T37	13	74.43 (0.35)	0.09 (0.01)	12.27 (0.29)	0.73 (0.11)	0.02 (0.01)	0.10 (0.02)	1.06 (0.09)	3.71 (0.11)	3.33 (0.18)	0.01 (0.01)	95.75 (0.55)
PAS-2T38	9	72.77 (0.92)	0.32 (0.02)	12.44 (0.22)	1.68 (0.10)	0.04 (0.01)	0.41 (0.03)	1.99 (0.09)	4.35 (0.22)	1.67 (0.08)	0.05 (0.01)	95.72 (1.26)
PAS-2T39	24	71.64 (0.75)	0.35 (0.02)	12.93 (0.27)	1.92 (0.10)	0.05 (0.01)	0.52 (0.03)	2.31 (0.10)	4.51 (0.13)	1.60 (0.07)	0.05 (0.01)	95.88 (0.94)
PAS-2T40	6	73.64 (0.77)	0.08 (0.02)	12.55 (0.17)	1.07 (0.11)	0.04 (0.01)	0.20 (0.01)	1.24 (0.12)	3.81 (0.16)	2.77 (0.13)	0.03 (0.01)	95.44 (0.89)
PAS-2T48	10	73.53 (0.21)	0.25 (0.02)	12.60 (0.44)	1.43 (0.11)	0.04 (0.01)	0.36 (0.03)	1.79 (0.09)	4.48 (0.07)	1.63 (0.05)	0.04 (0.01)	96.14 (0.60)
PAS-2T52	14	73.57 (0.93)	0.25 (0.02)	12.63 (0.23)	1.42 (0.10)	0.04 (0.01)	0.38 (0.03)	1.84 (0.14)	4.55 (0.17)	1.60 (0.07)	0.04 (0.01)	96.33 (1.15)

(b)

Sample	n	SiO_2	TiO_2	Al_2O_3	FeO_{tot}	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Source
PAS-2T1	11	77.98 (0.34)	0.15 (0.01)	12.76 (0.21)	1.07 (0.11)	0.04 (0.01)	0.25 (0.02)	1.24 (0.09)	4.54 (0.40)	1.93 (0.16)	0.03 (0.00)	Mt. Burney
PAS-2T2	32	77.32 (0.28)	0.11 (0.01)	12.90 (0.22)	1.24 (0.11)	0.04 (0.01)	0.22 (0.03)	1.50 (0.08)	3.99 (0.12)	2.64 (0.09)	0.03 (0.01)	Reclus (reworked)
PAS-2T3	9	77.53 (0.31)	0.11 (0.01)	12.76 (0.27)	1.24 (0.08)	0.04 (0.01)	0.23 (0.03)	1.48 (0.10)	3.96 (0.08)	2.61 (0.09)	0.03 (0.00)	Reclus (reworked)
PAS-2T4	12	77.59 (0.25)	0.11 (0.01)	12.78 (0.24)	1.18 (0.07)	0.04 (0.01)	0.21 (0.02)	1.54 (0.09)	3.91 (0.12)	2.61 (0.09)	0.03 (0.01)	Reclus
PAS-2T26	7	74.30 (1.94)	0.34 (0.02)	14.17 (1.23)	1.43 (0.10)	0.04 (0.01)	0.21 (0.05)	2.44 (0.64)	5.10 (0.44)	1.54 (0.21)	0.05 (0.01)	Mt. Burney
PAS-2T27	21	76.32 (0.74)	0.28 (0.03)	13.03 (0.29)	1.54 (0.15)	0.05 (0.01)	0.40 (0.05)	1.94 (0.16)	4.76 (0.14)	1.65 (0.06)	0.04 (0.01)	Mt. Burney (reworked ?)
PAS-2T30	6	76.74 (0.24)	0.26 (0.01)	12.87 (0.10)	1.48 (0.06)	0.05 (0.01)	0.37 (0.03)	1.70 (0.08)	4.66 (0.04)	1.70 (0.08)	0.03 (0.00)	Mt. Burney
PAS-2T31	13	77.28 (0.22)	0.08 (0.01)	13.09 (0.16)	1.04 (0.11)	0.05 (0.01)	0.20 (0.04)	1.23 (0.04)	4.05 (0.09)	2.94 (0.13)	0.03 (0.00)	Viedma/Lautaro?
PAS-2T32	22	76.48 (0.44)	0.26 (0.02)	13.06 (0.27)	1.54 (0.13)	0.04 (0.00)	0.37 (0.04)	1.91 (0.13)	4.63 (0.14)	1.68 (0.09)	0.04 (0.01)	Mt. Burney (reworked?)
PAS-2T33	15	76.40 (0.42)	0.26 (0.02)	13.11 (0.22)	1.47 (0.14)	0.04 (0.01)	0.36 (0.05)	1.95 (0.14)	4.64 (0.10)	1.73 (0.08)	0.04 (0.01)	Mt. Burney
PAS-2T35A	9	70.56 (0.23)	0.54 (0.05)	15.14 (0.14)	2.80 (0.11)	0.05 (0.00)	0.87 (0.15)	3.15 (0.10)	4.35 (0.12)	2.44 (0.08)	0.11 (0.01)	Viedma/Lautaro?
PAS-2T35B	2	76.82 (1.36)	0.12 (0.02)	12.89 (0.71)	1.28 (0.29)	0.05 (0.03)	0.30 (0.13)	1.44 (0.07)	3.72 (0.33)	3.36 (0.19)	0.03 (0.01)	Viedma/Lautaro?
PAS-2T36	9	77.29 (0.81)	0.25 (0.02)	12.82 (0.44)	1.29 (0.18)	0.04 (0.00)	0.31 (0.06)	1.73 (0.08)	4.59 (0.15)	1.73 (0.08)	0.04 (0.01)	Mt. Burney
PAS-2T37	13	77.49 (0.55)	0.10 (0.02)	12.94 (0.34)	0.82 (0.15)	0.02 (0.01)	0.12 (0.03)	1.17 (0.14)	3.92 (0.13)	3.41 (0.20)	0.01 (0.01)	Aguilera?
PAS-2T38	9	76.03 (0.32)	0.33 (0.02)	13.00 (0.13)	1.75 (0.10)	0.05 (0.01)	0.43 (0.03)	2.08 (0.09)	4.54 (0.21)	1.75 (0.08)	0.05 (0.01)	Mt. Burney
PAS-2T39	24	74.72 (0.28)	0.37 (0.02)	13.48 (0.22)	2.00 (0.11)	0.05 (0.01)	0.54 (0.04)	2.41 (0.10)	4.70 (0.14)	1.67 (0.07)	0.05 (0.01)	Mt. Burney
PAS-2T40	6	77.16 (0.12)	0.09 (0.02)	13.15 (0.17)	1.12 (0.12)	0.05 (0.01)	0.21 (0.01)	1.30 (0.12)	3.99 (0.14)	2.90 (0.14)	0.03 (0.01)	Viedma/Lautaro?
PAS-2T48	10	76.49 (0.50)	0.26 (0.02)	13.10 (0.38)	1.48 (0.11)	0.04 (0.01)	0.37 (0.03)	1.86 (0.09)	4.66 (0.06)	1.69 (0.06)	0.04 (0.01)	Mt. Burney (reworked?)
PAS-2T52	14	76.37 (0.46)	0.26 (0.02)	13.11 (0.22)	1.47 (0.10)	0.04 (0.01)	0.39 (0.03)	1.91 (0.13)	4.72 (0.15)	1.67 (0.08)	0.04 (0.01)	Mt. Burney

(c)

Sample	n	SiO_2	TiO_2	Al_2O_3	FeO_{tot}	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Mean
Lipari	9	74.378 (0.813)	0.078 (0.004)	12.968 (0.151)	1.510 (0.089)	0.072 (0.009)	0.036 (0.007)	0.738 (0.018)	4.141 (0.047)	5.093 (0.129)	0.005 (0.004)	99.020 (1.039)
BHV0-2G	15	49.978 (0.444)	2.775 (0.008)	13.493 (0.124)	10.964 (0.271)	0.171 (0.009)	7.251 (0.107)	11.318 (0.167)	2.271 (0.108)	0.516 (0.030)	0.261 (0.010)	98.996 (0.597)
Lipari[a]		74.1 (1.4)	0.074 (0.02)	13.1 (0.5)	1.55 (0.05)	0.065 (0.031)	0.041 (0.022)	0.73 (0.06)	4.07 (0.22)	5.11 (0.27)	0.010 (0.02).	100.03

[a] Recommended values for the Lipari glass standard from Kuehn et al. (2011).

correlation uncertain. We suggest that the 5022-2T31 tephra deposited roughly around 28.2 ka cal BP (Table 1) represents an eruption of one on the northern volcanoes of the AVZ, possibly Lautaro or Viedma. However, recent analyses of the 1959/60 eruption of the Lautaro volcano (Kastner et al., 2010) indicate slightly higher K_2O concentrations for similar SiO_2 concentrations compared to those reported in our study. Nevertheless, as the full temporal and spatial variability of the products of the northern volcanoes of the AVZ is unknown, more work on proximal and distal material is needed before secure correlations can be established.

3.5. Tephra layers 5022-2T32 (38.04–38.06 m) and 5022-2T33 (38.70–38.73 m)

These two tephra layers are separated by only 64 cm and in consequence their estimated ages overlap, given the high sediment accumulation rates that characterise the Laguna Potrok Aike record.

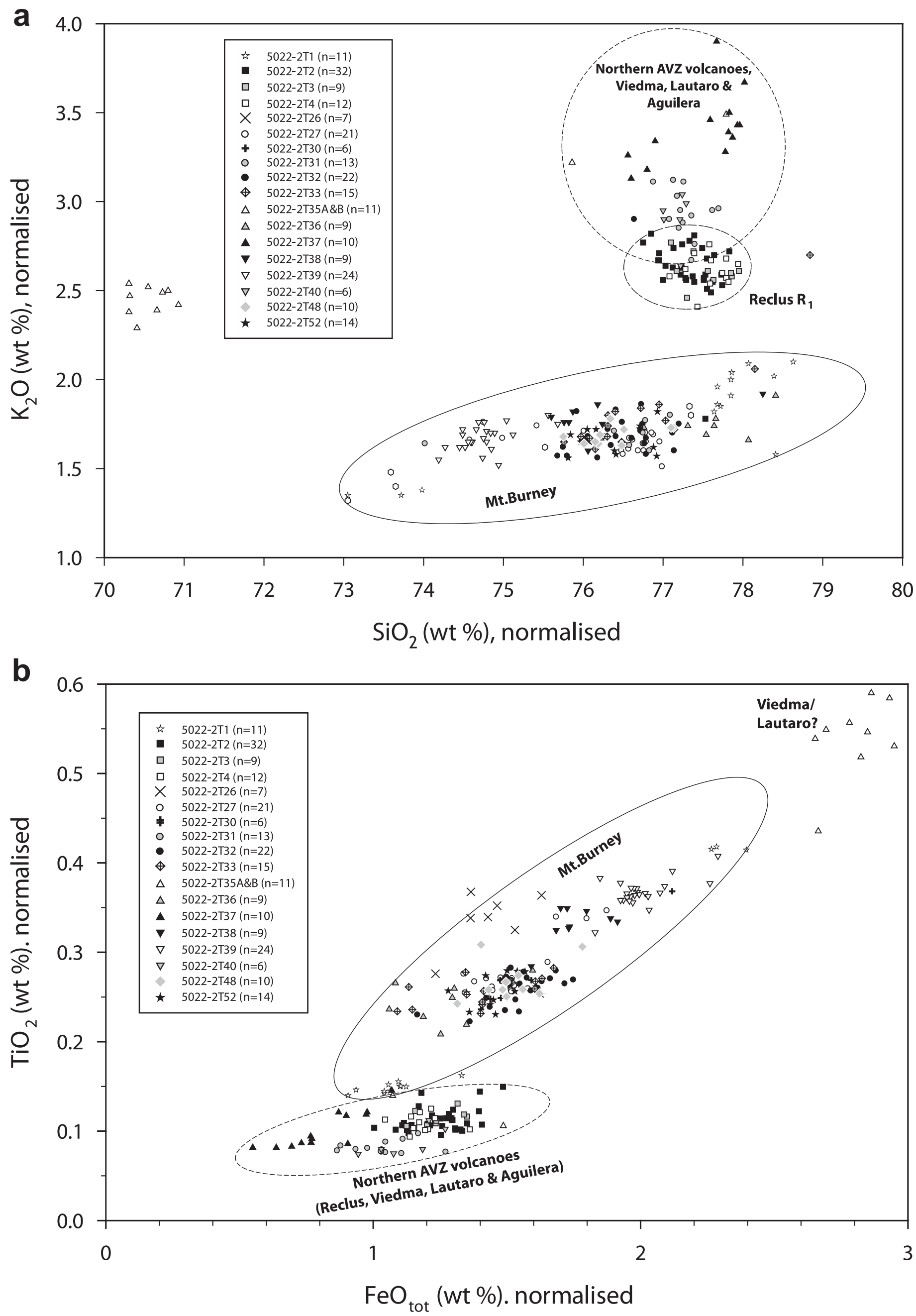

Fig. 3. Biplots showing (a) SiO_2 vs. K_2O and (b) FeO_{tot} vs. TiO_2 for single glass shards from Laguna Potrok Aike, normalised to 100%. Geochemical envelopes are based on the present investigation but overlap for the most parts with previous investigations of tephras from the AVZ (e.g. Kilian et al., 2003; Haberzettl et al., 2008; Stern, 2008).

Moreover, the lower layer has all characteristics of primary tephra fallout, such as a sharp basal and a more gradual upper contact. Thin whitish layers occur up to 3 cm above the main tephra layer, indicating slight reworking following its initial sedimentation. The upper tephra layer is stratigraphically less distinct with an undulating lower boundary. The chemistry of both ashes is identical and displays clear chemical compositions consistent with the other Mt. Burney tephras, e.g. K_2O around 1.7 wt% and SiO_2 around 76.4 wt%. We suggest that the lower layer represents a new, previously unreported eruption from Mt. Burney in the later part of MIS 3, around 31 ka cal BP. Nonetheless, we find it unlikely that two major eruptions of this volcano occurred within a few hundred years, although more observations are needed for disproving this hypothesis. For the moment, however, we interpret the tephra layer 5022-2T32 as being a product of reworking from the underlying 5022-2T33 tephra.

3.6. Tephra layer 5022-2T35 (55.93–55.97 m)

This is one of the most distinct tephras in the Laguna Potrok Aike sediment record (Fig. 4) and the youngest in a sequence of major tephra deposits – and in consequence intensive volcanic activity in the source region – identified between ca 44 and 51 ka cal BP. The interval between 5022-2T33 and 5022-2T35 represents a time period of ca 12,000 years and is the longest interval in the Laguna Potrok Aike sequence without sedimentation of visible volcanic ashes. The 5022-2T35 layer is fining upwards over a sharp lower boundary and it is the only tephra in the Laguna Potrok Aike record

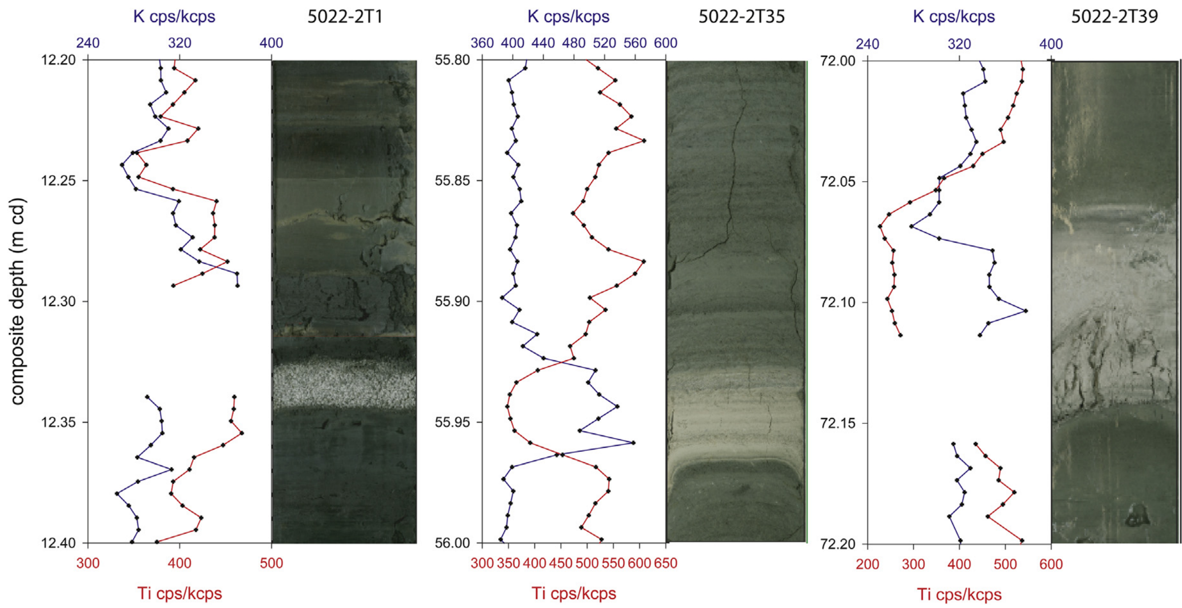

Fig. 4. Photographs of the 5022-2T1, 5022-2T35 and 5022-2T39 tephras with K and Ti counts from XRF core scanning. Tephra layers from Laguna Potrok Aike are often associated with negative peaks in Ti and positive peaks in K. Missing data in some parts of the sections are due to the highly porous, waterlogged and coarse-grained nature of the tephra layers. For details, see (Hahn et al., submitted for publication).

with a dacitic composition. It has been identified previously in the PTA03-6 core from the northern lake shoulder (Haberzettl et al., 2008), and based on the glass chemical data, the authors noted the presence of two chemically distinct end-members in this tephra layer, of which a dacitic A component dominates quantitatively over the rhyolitic glass type B, the latter was tentatively linked with Reclus volcanic activity. Both chemically distinct glass shard components also occur in the record from 5022-2CP reported here, although only two analyses of the rhyolitic glass type B were made. In our opinion, the correlation with the Reclus volcano is, however, not straightforward. The K_2O values are higher than in the Reclus R_1 tephra and the analyses of both components fall closer to the fields expected for Viedma and Lautaro volcanoes (cf. Stern, 2008). Nevertheless, because compositional variations in the latter volcanoes are not well defined yet, more information is needed before a secure correlation can be established for the dacitic and rhyolitic components identified in the 5022-2T35 tephra layer. The mixed composition may, however, establish the role of this ash layer as a distinctive marker in other sediments of similar age throughout Patagonia and possibly beyond.

3.7. *Tephra layer 5022-2T36 (57.03 m)*

This ca 3 mm thick and undulating layer directly overlies a ca 5 mm thick sandy layer and was initially considered as a potentially reworked ash. The chemical analysis suggests that the eruptive region of this tephra is Mt. Burney. However, the values obtained for some elements differ slightly compared with the other tephras from Mt. Burney identified in the lower part of the sequence. For example, FeO_{tot} and MgO are lower, which may indicate that the 5022-2T36 is indeed primary ash fallout, or at least, a previously unrecognized minor eruptive event from Mt. Burney.

3.8. *Tephra layer 5022-2T37 (63.33–63.40 m)*

This distinct ash layer has sharp upper and lower boundaries and is geochemically distinct from all other analysed layers in the Laguna Potrok Aike sequence. K_2O ranges between 3.1 and 3.9 wt% and Na_2O is only marginally higher at 3.7–4.1 wt%. This suggests an origin in one of the northern volcanoes of the AVZ. As noted above, only a few analyses are available on glass from Viedma, Lautaro and Aguilera volcanoes. We tentatively correlate this tephra with Aguilera because of the high K_2O concentrations (cf. Stern, 2008); however, more data from this volcano is needed before a secure correlation can be established.

3.9. *Tephra layer 5022-2T38 (67.94–67.99 m)*

This layer has a sharp, erosive upper and a more diffuse lower boundary. Major oxide chemistry indicates affinities with the Mt. Burney volcano, but CaO and FeO_{tot} are higher (ca 2.10 wt% and 1.75 wt%, respectively) than in any other volcanic ash from this volcano, except the 5022-2T39 layer (Table 2). We suggest that the 5022-2T38 layer represents a new, previously unreported eruption from Mt. Burney in the early part of MIS 3 (Table 1).

3.10. *Tephra layer 5022-2T39 (72.06–72.15 m)*

This layer stands out as one of the most distinct tephras in the Laguna Potrok Aike sediment sequence (Fig. 4). The SiO_2 vs. K_2O diagram indicates an origin from the Mt. Burney volcano, but the layer is chemically distinct from all other tephras from this volcano and has CaO values of ca 2.40 wt% and FeO_{tot} around 2.00 wt% (Table 2; Fig. 2b). A tephra with similar geochemical composition and age was previously reported by Haberzettl et al. (2008) in core PTA03/06 from a depth of 643 cm. We conclude that these tephra horizons represent the same ash bed originating from Mt. Burney.

3.11. *Tephra layer 5022-2T40 (76.51–76.52 m)*

The thickness of this ash layer cannot be given exactly at the coring location. A coring gap, approximately of 8 cm thickness, affected both the upper part of the tephra and the overlying sediments. The lower boundary is diffuse and the chemical composition indicates an origin in one of the northern volcanoes of the AVZ (Fig. 2a). It is chemically very similar to ash layer 5022-2T31 and we consider that 5022-2T40 is a product of a previously unknown eruption of one of the northern volcanoes of the AVZ, possibly Viedma or Lautaro.

Several tephra layers have been observed in the core sections between ca 77.00 and 79.30 m depth, but none of them has been chemically analysed so far. The lowermost layer is exceptionally thick and homogenous, extending over 70 cm between 78.60 and 79.30 m depth. It very likely represents primary ash fallout, although its lower boundary cannot be examined due to a coring gap and sediment loss. Another well-marked tephra and possibly a primary ash fallout as well was found between 77.60 and 77.78 m depth, whilst the upper three thinner tephra layers occurring between 76.98 and 77.52 m depth might represent reworked material given their structure and the undulating nature of their contacts with under- and overlying sediments. Nevertheless, taking into consideration that chemical data from tephra 5022-2T40 at 76.51–76.52 m depth points to an origin in the northernmost volcanoes of the AVZ, which are chemically quite similar (Stern, 2008; Kastner et al., 2010), it would be interesting to obtain reliable chemical data at least for the unanalysed thick, possibly primary fallout ash layers occurring between 77.00 and 79.30 m depth.

3.12. Tephra layers 5022-2T48 (94.09–94.10 m) and 5022-2T52 (95.38–95.39 m)

The two lowermost analysed tephra layers are both derived from Mt. Burney eruption(s) and provide geochemical compositions closely resembling the values obtained for tephra layers 5022-2T30 and 5022-2T33 (Table 2). The 5022-2T48 and 5022-2T52 tephras are separated stratigraphically by only 130 cm. Their inferred depositional ages slightly overlap, particularly if one takes into account the large uncertainty of the age–depth model in this part of the sequence (Table 1). Although the age overlap cannot be taken as evidence of reworking, it is also possible that the upper 15 mm thick tephra layer represents a reworked counterpart of the stratigraphically lower 5022-2T52 ash event. Moreover, both ash layers can be correlated chemically with the Mt. Burney derived tephra found at 859 cm depth in the northern lake shoulder core PTA03/06 (Haberzettl et al., 2007, 2008).

4. Discussion and conclusions

The tephrostratigraphic record from Laguna Potrok Aike provides an unprecedented view on the explosive volcanism in the AVZ, from early MIS 3 to the Holocene. Several of the thickest late Pleistocene and Holocene layers were already known from a recent investigation of another sediment sequence from Laguna Potrok Aike (Haberzettl et al., 2007, 2008), but the older part of the sediment record extending back to 51 ka cal BP provides new data on several ash layers, that will very likely act as important marker horizons providing that they are identified in other records. Although significant effort has been focused in this respect, the age–depth model of the 5022-2CP is not yet precise enough, especially in the lower part of the sequence (Kliem et al., 2013b), to allow exact correlation with other sedimentary tephra archives from the southern hemisphere, for example ice-core records from Antarctica and marine sediment cores from the southern oceans. Indeed, recent eruptions from Andean volcanoes suggest that fine volcanic products might have been occasionally spread over wide areas, including the southern Atlantic and Indian Oceans (Prata et al., 2012). For example, even the moderate-sized eruption of the Puyehue-Cordón Caulle volcano in Central Chile in 2011 (VEI 4) caused air travel disruption as far as Australia and New Zealand (Klüser et al., 2012). Most ice-core records from Antarctica contain extensive evidence for volcanic eruptions, including macroscopic tephra layers, primarily of local origin, but numerous cryptotephras and volcanic aerosol spikes that could be linked to more regional or global eruptive events are also present (Castellano et al., 2005; Narcisi et al., 2005, 2010). However, data survey has not yet resulted in any potential match between the tephras identified in the Laguna Potrok Aike record and those reported from Antarctic ice. Most volcanic ash layers reported so far from the Antarctic ice records have compositions with affinities mainly to volcanic fields within Antarctica and neighbouring volcanic islands (Narcisi et al., 2005; Dunbar and Kurbatov, 2011). Only a few of them may have an Andean origin, although the correlation of the supposed Andean tephras with known eruptions or sedimentary ash layers in records from the South American continent were not yet unequivocally achieved (Kurbatov et al., 2006). Nevertheless, with a better constrained age–depth model for the older part of the Laguna Potrok Aike record it would be possible to suggest a narrower temporal range in searching the Antarctic ice cores for cryptotephra layers that might provide potential tie-lines between the South American continent and Antarctica. However, one of the most critical issues regarding the value of the Laguna Potrok Aike data in providing a regional tephrostratigraphic record is the occurrence of several reworked tephra units, most notably the mixed ash unit between ca 16.84 and 18.24 m depth. Although chemical analyses of this volcanic ash-sediment suite suggest an origin in the Reclus volcanism (Haberzettl et al., 2007), it is advisable that for future tephra studies of sedimentary records from Patagonia, sedimentological, chemical or isotopic methods that allow distinguishing reworked tephra products should rigorously be applied (Lowe, 2011).

Overall, the tephra record from Laguna Potrok Aike presented in this study is dominated by volcanic products from Mt. Burney, and although some of these layers might represent reworked volcanic ashes (even though evidence for reworking is not always convincing), at least eight layers are at present considered as primary fallout from recurrent eruptions of this volcano over the last ca 51 ka cal BP (Table 1). In general however, the chemical composition of glass particles from Mt. Burney eruptions is similar and complicates the use of the major element concentrations as a discriminating tool, although slight variations observed in some major element ratios help separating between various tephra layers and, supposedly, different eruptive events (Fig. 2). Whether these slight chemical differences relate to changing chemical compositions between different eruptions or reflect chemical zonation during the course of one more powerful (and possibly longer-lasting) eruption, cannot be assessed based on presented data, since in most cases only one sample aliquot from each ash occurrence has been analysed. It is possible, however, that with the advent of more sophisticated discriminating analyses of minor and trace elements from both glass shards and mineral phases such data would allow separating eruptive events from Mt. Burney with more confidence.

Four tephra layers have affinities with the northern volcanoes of the AVZ, namely Aguilera, Viedma and Lautaro (Stern and Kilian, 1996; Stern, 2008). As noted previously, the full temporal, spatial and chemical variability of the volcanic products of the northern volcanoes of the AVZ is not known, and more work on proximal and distal ashes is needed before more firm correlations can be made.

The lack of volcanic products from Hudson volcano in the record from Laguna Potrok Aike is somehow surprising. The Holocene H_1 tephra (ca 6850 ± 160 ^{14}C years) has been identified previously in the sediments (Haberzettl et al., 2007), but no older depositional event associated with this highly active volcano has been detected. This may be due to its relatively large distance from Laguna Potrok Aike on the one hand, or because of the fact that very thin tephra layers as well as cryptotephras may have been overlooked in the 100 m thick sediment sequence investigated in this study. However, no tephra layers from Hudson older than the early Holocene have been reported, not even in areas proximal to the volcano (Naranjo and Stern, 1998). Nevertheless, a recent report on several macro- and cryptotephras found in marine sediments offshore southern Chile from the late Pleistocene and the Holocene propose the Hudson as the most likely volcanic source for these ash layers (Carel et al., 2011).

The tephra layer frequency of the Laguna Potrok Aike sequence can potentially be used to infer the frequency of large volcanic eruptions in the AVZ. However, at this stage we refrain in doing this to avoid bias induced by the large number of possibly reworked layers. However, we assert that if only stratigraphically certain primary ash fallout deposits are included, two periods with significant tephra deposition occurred between ca 51–44 ka cal BP and 31–25 ka cal BP (Table 1), respectively, with a decrease in tephra layer frequency between both periods. Whether this pattern represents a real change in volcanic activity in the AVZ, is too early to deduce based only on data from Laguna Potrok Aike, but a link between volcanic activity, glaciation and millennial-scale rapid environmental change has often been discussed (Bay et al., 2004; Nowell et al., 2006; Huybers and Langmuir, 2009; Tuffen, 2010).

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