Tephrochronology of the upper Río Cisnes valley (44°S), southern Chile

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ABSTRACT. Based on their petrography and chemistry, 18 tephra analyzed from two lake and bog cores and one outcrop in the upper Río Cisnes valley are believed to have been derived from nine different eruptions of the Mentolat volcano, four of the Melimoyu volcano, and one from the Hudson volcano. Some of these tephra correlate chronologically and petrochemically with previously documented large eruptions of these volcanoes, including the Late-Glacial Ho eruption of Hudson (17,340 cal yrs BP), the mid-Holocene MEN1 eruption of Mentolat (7,710 cal yrs BP), and the Late-Holocene MEL2 eruption of Melimoyu (1,680 cal yrs BP). A Melimoyu-derived tephra from the outcrop occurs in glacial-lacustrine sediments and is considered to pre-date the Last Glacial Maximum (>19,670 cal yrs BP). The data suggest that none of the tephra were produced by explosive eruptions of the Maca, Cay and Yanteles volcanoes.

Keywords: Tephra, Tephrochronology, Tephrostratigraphy, Volcanism, Andes, Chile.

RESUMEN. Tefrocronología en curso superior del valle del río Cisne (44°S), Chile Austral. Dieciocho tefras provenientes de testigos de un lago y un mallín, junto a un perfil expuesto en el alto valle del río Cisnes fueron caracterizadas sobre la base de su petrografía y química y corresponderían a nueve diferentes erupciones del volcán Mentolat, cuatro del volcán Melimoyu y una del volcán Hudson. Algunas de estas tefras se correlacionan cronológica y petroquímicamente con grandes erupciones de estos volcanes previamente documentadas, incluyendo la erupción Ho del volcán Hudson (Tardiglacial, 17.340 años cal. AP), la erupción MEN1 del volcán Mentolat (Holoceno medio, 7.710 años cal. AP) y la erupción MEL2 del volcán Melimoyu (Holoceno tardío, 1.680 años cal. AP). Una tefra perteneciente a la erupción del volcán Melimoyu, hallada en un perfil expuesto en un contexto de depósitos glaciolacustres, tiene una edad (>19.670 años cal. AP) que precede al término del Último Máximo Glacial en Patagonia Central. Los datos sugieren que ninguna de las tefras fueron producidas por erupciones explosivas de los volcanes Maca, Cay y Yanteles.

Palabras clave: Tefra, Tefrocronología, Tefrostratigrafía, Volcanismo, Andes, Chile.

1. Introduction

Tephra layers in sediment cores from lakes and bogs provide information on the history of explosive volcanic eruptions from nearby volcanoes, and thus a basis for evaluating the possibilities for and potential effects of future eruptions. The identification, petrochemical description and correlation of synchronous volcanic tephra layers over large geographic areas and in different environmental settings also provides a stratigraphic correlation tool for a broad range of disciplines (Lowe, 2011; Fontijn *et al.*, 2014), including archaeology (Prieto *et al.*, 2013), palaeoclimatology and palaeogeomorphology (García *et al.*, 2015, this volume).

Here we characterize both petrochemically and chronologically multiple Late-Glacial and Holocene tephra layers in two sediment cores from the area of the upper Río Cisnes valley (Figs. 1 and 2); one core from Lago Shaman (Fig. 3; de Porras *et al.*, 2012), and one core from Mallín El Embudo (Fig. 4; de Porras *et al.*, 2014). With this information we attempt to correlate tephra layers between the cores and to other previously described tephra in the region, and identify for each layer their possible source volcano, which potentially include the Yanteles, Melimoyu, Mentolat, Maca, Cay and Hudson stratovolcanoes, as well as numerous small monogenetic cones located between Puyuhuapi and Palena (Fig. 1). We also describe one sample of tephra that outcrops in glacial-lacustrine sediments, and pre-dates the Last Glacial Maximum.

2. Background

Bedrock geology in the upper Río Cisnes valley consists of plutons of the Patagonia batholith and Lower



FIG. 1. Regional map showing the location, in the box, of the area of Alto Río Cisnes (Fig. 2) from which tephra samples were studied, and both stratovolcanoes (larger triangles) and the Puyuhuapi and Palena groups of minor monogenetic mafic eruptive cones (MEC: smaller solid triangles) in the southern SSVZ (Stern, 2004; Stern et al., 2007).



FIG. 2. Map of the location of the Lago Shaman and Mallín El Embudo cores in relation to the LGM moraine complexes along the Chile-Argentina border and the frontal moraine formed during a Late-Glacial glacial advance in the upper Río Cisnes valley (de Porras *et al.*, 2012, 2014). Also shown is the location at Las Barrancas of the Late-Glacial glacial-lacustrine sediments containing the outcrop of the >19,670 BP tephra sample Cisnes 263A.

Cretaceous sediments overlain by Quaternary deposits, which include the materials examined in this study. de Porras et al. (2012, 2014) describe in some detail the environmental setting of the two cores. Lago Shaman is located in the semi-arid forest-steppe ecotone just west of the Chile-Argentina border, which at this latitude corresponds to a moraine complex formed during the last Late-Glacial Maximum (LGM; Fig. 2). This area became ice free at or soon after 19,000 BP, and the deepest organic layer dated, from 599 cm depth in the 613 cm long Lago Shaman core (LS0604A; Fig. 3), yields an age of 18,950 cal yrs BP (Table 1). In contrast, the Mallín El Embudo core is located in a wetter forested area ~35 km to the southwest of Lago Shaman (Fig. 2), west of a small frontal moraine interpreted to have formed by a Late-Glacial glacial advance before approximately 13,000 BP (de Porras et al., 2014). The oldest age obtained, from 809 cm deep in this 844 cm long composite core (EE0110A and B; Fig 4) was 12,997 cal yrs BP.

These two cores were collected with the purpose of providing a pollen record and its implications for the changing climate in this region since the end of the last glaciation (de Porras et al., 2012, 2014), as well as a charcoal record and its implication for the history of fires caused possibly by climate change, volcanic activity and/or the human occupation of the valley, which dates back to 11,500 BP (Méndez and Reyes, 2008; Méndez et al., 2009; Reyes et al., 2009). Both cores contain clastic layers which are in most cases tephra (Figs. 3 and 4). The Lago Shaman core contains more numerous tephra, which may possibly reflect the fact that Lago Shaman occurs in an open arid area with no vegetation to interfere with tephra fall and wind redistribution of tephra, while Mallín El Embudo occurs in a wetter environment with forest cover. One other tephra sample (Cisnes 263A; Fig. 5) was also collected from an outcrop of glacial-lacustrine sediment at Las Barrancas (Fig. 2). It occurs \sim 3 meters below the contact, dated as



FIG. 3. X-ray image of Lago Shaman core (de Porras *et al.*, 2012). Bright white layers are either sand or tephra and darker areas are organic rich sediments.

19,670 cal yrs BP, between these and overlying fluvial sediments (Fig. 5).

Previous tephrochronologic studies in this area of the southern Southern Volcanic Zone (SSVZ) of the Andes include those of Naranjo and Stern (1998, 2004), Mella *et al.* (2012) and Weller *et al.* (2014). These studies indicate that all the potential source volcanoes for the tephra in the upper Río Cisnes valley (Yanteles, Melimoyu, Maca, Cay and Husdon) have had Holocene explosive eruptions producing locally or regionally distributed tephra falls (Naranjo and Stern, 1998, 2004; Mella *et al.*, 2012; Weller *et al.*,



FIG. 4. X-ray image of Mallin El Embudo core (de Porras *et al.*, 2014). Bright white layers are either sand or tephra and darker areas are organic rich sediments.

2014). Melimoyu, Mentolat and Hudson have summit craters/calderas possibly formed in association with these events. Melimoyu and Hudson are two of the largest volcanic edifices in the SSVZ (Völker *et al.*, 2012). Also the many small monogenetic cones in the region have produced basaltic scoria deposits as well as lava flows (López-Escobar *et al.*, 1995a; Gutiérrez *et al.*, 2005; Watt *et al.*, 2013; Vargas *et al.*, 2013), but the potential regional extent of distribution of tephra from these generally small volume mafic eruptions is uncertain

The previously published interpretations of the source volcanoes of tephra in the SSVZ were made in part on the basis of tephra major element chemistry compared with published whole rock chemistry of samples of lavas from the volcanoes of the SSVZ (Naranjo and Stern, 2004; Weller *et al.*, 2014). In a similar fashion, the possible sources of seven of the tephra in the Lago Shaman core were made on the basis of bulk tephra trace-element chemistry compared to published whole-rock trace-element

analysis of lava samples from the SSVZ volcanoes to the west of the core site (de Porras *et al.*, 2012). These trace-element data suggest Melimoyu, Mentolat and Hudson volcanoes as the sources for these seven tephra (de Porras *et al.*, 2012; Weller *et al.*, 2014).

Since spatial coverage is still too restricted to allow for the construction of tephra isopach maps, which is the most conclusive way to identify source volcanoes for tephra, this paper also employs the geochemical approach of comparing tephra chemistry with the published data concerning the volcanic rocks associated with the different SSVZ centers (Fig. 6) to identify possible tephra source volcanoes of the tephra. Information concerning the chemistry of the magmas erupted from the volcanic centers in the SSVZ has been published by Stern et al. (1976), Futa and Stern (1988), López-Escobar et al. (1993, 1995a), D'Orazio et al. (2003), Gutiérrez et al. (2005), Kratzmann et al. (2009, 2010), Watt et al. (2013) and Weller et al. (2014). Samples from SVZ volcanoes in south-central Chile, and specifically the SSVZ

TABLE 1. DEPTH IN CM OF TEPHRA AND ¹⁴C AGE DATES IN CAL YRS BP FROM THE LAGO SHAMAN (DE PORRAS *ET AL.*, 2012) AND MALLÍN EL EMBUDO (DE PORRAS *ET AL.*, 2014) CORES.

Lago Shaman							
tephra depth cm		~age*	Source*	eruption*	age*		
а	64-70	1,440	Melimoyu	MEL2	1,680		
	85	1,827±40	-	-	-		
b	94	2,140	Mentolat	-	-		
с	104	2,490	Mentolat	-	-		
	122	3,111±40	-	-	-		
d	160	3,720	Mentolat	-	-		
e	170	3,880	Mentolat	-	-		
	195	4,275±50	-	-	-		
f	207	4,610	Melimoyu	-	-		
g	255	8,280	Melimoyu	-	-		
	260	8,357±40	-	-	-		
h	261	8,400	Mentolat	-	-		
i	270	8,800	Mentolat	MEN1	7,710		
	316	10,824±70	-	-	-		
m	326	11,140	Mentolat	-	-		
	392	13,241±40	-	-	-		
	489	18,474±100	-	-	-		
q	533	18,665	Mentolat	-	-		
v	570	18,820	Hudson	Но	17,340		
у	598	18,940	Mentolat	MENo	>17,340		
	599	18,951±50	-	-	-		
Mallín El Embudo							
tephra	depth cm	~age*	source	eruption*	age*		
	25	94±20	-	-	-		
	154	1,453±30	-	-	-		
	162	1,743±40	-	-	-		
а	173-179	2,090	Melimoyu	MEL2	1,680		
	266	4,492±40	-	-	-		
b	255-278	4,810	Melimoyu	-	-		
h	549	9,010	Mentolat	MEN1	7,710		
	585	9567±30	-	-	-		
	699	11179±30	-	-	-		
	740	11,302±69	-	-	-		
j	746	11,450	Mentolat	-	-		
	809	12,997±35	-	-	-		
CIS 263-A	-	>19,670	Melimoyu	-	-		

*Measured ¹⁴C age dates in cal yrs BP; ~ages for tephra interpolated from measured ages; possible sources based on tephra chemistry (Table 3); ages of previously documented eruptions from Naranjo and Stern (2004) and Weller *et al.* (2014).



FIG. 5. A. Photo of the ~6 cm thick Cisnes 263A tephra in glacial-lacustrine sediment formed during the last glaciation; B. This tephra occurs ~3 meters below the contact, dated as 19,670 cal yrs BP, between the glacial-lacustrine clay and overlying fluvial sediments.

volcanoes, fall into different and distinguishable chemical groups (Fig. 6). Two of these groups have previously been termed Type-1, or Low Abundance, and Type-2, or High Abundance magmas (Hickey *et al.*, 1986, 1989, 2003; López-Escobar *et al.*, 1993, 1995a, 1995b). These two different magma types are distinguished by their different concentrations of the incompatible elements K_2O (Fig. 6a), Rb, Ti, Ba. Zr, Sr, Y, Nb and La, as well as La/Yb and Ba/ La ratios, over a large range of SiO₂ contents from basalts to dacites. In the SSVZ, Maca, Cay and Yanteles stratovolcanoes (Fig. 6), and the Palena group of monogenetic cones are Type-1 or Low Abundance volcanoes (López-Escobar *et al.*, 1993, 1995a; D'Orazio *et al.*, 2003; Gutiérrez *et al.*, 2005; Carel *et al.*, 2011; Watt *et al.*, 2013), while Hudson and Melimoyu volcanoes (Fig. 6) and the Puyuhaipi group of monogenetic cones are Type-2 or High



FIG. 6. A. SiO₂ versus K₂O for samples of both lavas and tephra from Yanteles, Melimoyu, Maca, Cay and Hudson volcanoes (Futa and Stern, 1988; López-Escobar et al., 1993; Naranjo and Stern, 1998, 2004; D'Orazio et al., 2003; Gutiérrez et al., 2005; Kratzmann et al., 2009, 2010), illustrating the separation of these samples into what have previously been termed High, Low and Very Low Abundance magma types (Hickey et al., 1986, 1989, 2003; López-Escobar et al., 1993, 1995a, 1995b; Sellés et al., 2004; Watt et al., 2011). Line separating the fields of High-, Medium-, and Low-K convergent plate boundary magmas are from Peccerillo and Taylor (1976); B. Ti versus Rb for the SSVZ volcanoes and each individual tephra from the upper Río Cisnes valley (Table 3); C. Sr versus Ba for the SSVZ volcanoes and tephra from the upper Río Cisnes valley (Table 3);

tephra	components	Glass color	Vesicles	Microlites Plag		
a	Gl>Plag>Cpx>Opx	Brown	Few, round			
b	Plag>Gl>Opx>Cpx>Amph>>Ol	Clear	Abund, round	-		
с	Plag>Gl>Opx>Cpx>Amph>>Ol	Clear	Abund, round	-		
d	Plag>Gl>Opx>Cpx>Amph>>Ol	Clear	Abund, round	-		
e	Plag>Gl>Opx>Cpx>Amph>>Ol	Clear	Abund, round	-		
f	Gl>Plag>Cpx>Opx>Ol	Brown	Few, round	Plag		
g	Gl>Plag>Cpx>Opx	Brown	Few, round	Plag		
h	Plag>Gl>Opx>Cpx>Amph>>Ol	Clear	Abund, round	-		
i	Plag>Gl>Opx>Cpx>Amph>>Ol	Clear	Abund, round	-		
m	Plag>Gl>Opx>Cpx>Amph>>Ol	Clear	Abund, round	-		
q	Plag>Gl>Opx>Cpx>Amph>>Ol	Clear	Abund, round	-		
v	Gl>>Plag>Opx	Brown to Tan	Abund, stretched	-		
У	Plag>Gl>Opx>Cpx>Amph>>Ol	Clear	Clear Abund, round			
Mallín El Embu	do					
tephra	components	Glass color	Vesicles	Microlites		
a	Gl>Plag>Cpx>Opx	brown	Few, round	Plag		
b	Gl>Plag>Cpx>Opx>Ol	brown	Few, round	Plag		
h	Plag>Gl>Opx>Cpx>Amph	Clear	Abund, round	-		
j	Plag>Gl>OPx>Cpx>Amph	Clear	Abund, round	-		
CIS 263-A	Gl>Plag>Cpx>Opx	brown	Few, round	Plag		

TABLE 2. MAIN PETROGRAPHIC FEATURES OF THE TEPHRA FROM THE UPPER RÍO CISNES VALLEY.

Gl: glass; Plag: plagioclase; Cpx: clinopyroxene; Opx: orthopyroxene; Amph: amphibole; Ol: olivine; Abund: abundant.

Abundance centers (López-Escobar *et al.*, 1993, 1995a; Naranjo and Stern, 1998, 2004; Kratzmann *et al.*, 2009, 2010; Carel *et al.*, 2011). The Palena and Puyuhuapi group basalts are not plotted in figure 6 because they both contain abundant olivine and lack orthopyroxene and amphibole, and are therefore petrologically distinct from the tephra in the upper Río Cisnes valley described below (Table 2).

Although samples from different Type-1 Low Abundance volcanoes are generally similar to each other, a specific exception in this southern part of the SSVZ is the Mentolat volcano, which at any given SiO₂ content has lower K₂O (Fig. 6a; López-Escobar *et al.*, 1993; Naranjo and Stern, 2004; Watt *et al.*, 2011), Rb, Ti (Fig. 6b), Sr, Ba (Fig. 6c) and La/Yb (Watt *et al.*, 2011), similar to other unusually or Very Low Abundance samples from Nevado de Longaví (Sellés *et al.*, 2004), Calbuco (López-Escobar *et al.*, 1995b) and Huequi (Watt *et al.*, 2011) volcanoes further to the north. Like Mentolat, all these other Very Low Abundance centers are characterized by the presence of amphibole in their eruptive products (López-Escobar *et al.*, 1993, 1995b; Sellés *et al.*, 2004; Watt *et al.*, 2011).

3. Methods

X-ray images of the cores (Figs. 3 and 4) were taken to allow for better visual identification of the tephra deposits and to provide a means of stratigraphic correlation of the tephra layers between the cores. The white layers in these images, arbitrarily termed a though z in the Lago Shaman core (Fig. 3) and a, b, g, h and j in the Mallín El Embudo core (Fig. 4), are the denser lithologies, often tephra deposits, but in some cases sand, and the darker layers are less dense organic-rich lacustrine sediments. The chronology of the tephra in the trenches and cores is constrained by AMS radiocarbon dates of organic material in the overlying and underlying sediments (Fig. 7; Table 1; de Porras *et al.*, 2012, 2014). Radiocarbon dates were converted to calendar years before present (cal yrs BP) using the CALIB 5.01 program (Stuiver *et al.*, 1998).

The tephra samples were washed to remove any organic matter, and then dried and sieved to remove any coarse fraction material not volcanic in origin. After cleaning, the bulk tephra samples were mounted on petrographic slides and examined under a petrographic microscope in order to identify petrographic characteristics such as tephra glass color and morphology (Fig. 8) and the proportion and identity of mineral phases (Table 2). Trace-element data for bulk tephra samples were determined using an ELAN D CR ICP-MS (Table 3; Saadat and Stern, 2011). Trace-element compositions are considered accurate to $\pm 5\%$ at the level of concentrations in these samples, based on repeated analysis of standard rock samples of known composition (Saadat and Stern, 2011).

4. Results

A summary of some of the most obvious petrographic features of each of 13 tephra samples from the Lago Shaman core, four from the Mallín El Embudo core, and one other outcrop sample (Cisnes 263A), are presented in Table 2 and tephra trace-element chemistry are presented in Table 3. The chemical and petrologic characteristics of each tephra, and the reasons for suggesting a possible source volcano, are discussed below in chronological order from the youngest to the oldest.

4.1. Tephra 'a' from both cores

The youngest tephra in both cores, tephra 'a' (Figs. 3 and 4; Tables 1-3), is approximately 6 cm thick in each core and in both consists dominantly of identical appearing brown glass with a few round and only rarely stretched vesicles and containing



FIG. 7. Age versus depth in the core of the different tephra analyzed from the Lago Shaman and Mallín El Embudo cores. Also shown are the ages for tephra MEL2 from Melimoyu (Naranjo and Stern, 2004) which may correlate with tephra 'a' in both cores, MEN1 from Mentolat (Naranjo and Stern, 2004; Stern *et al.*, 2013) which may correlate with tephras 'i' in Lago Shaman and 'h' in Mallín El Embudo, and Ho from Hudson which correlates with tephra 'v' in Lago Shaman (Weller *et al.*, 2014).



FIG. 8. Photomicrographs (2.2x2 mm) showing glass color and morphology and proportion relative to phenocrysts of: A. Tephra 'a' from Lago Shaman, containing abundant dark brown glass with only a few round vesicles and occasional plagioclase microlites (Table 2), suggested to be derived from Melimoyu volcano (Table 1); B. Tephra 'c' from Lago Shaman, containing clear glass with round vesicles, and abundant plagioclase and orthopyroxene phenocrysts (Table 2), suggested to be derived from Mentolat volcano; C. Tephra 'v' from Lago Shaman, with abundant brown to tan glass containing stretched vesicles, correlated with tephra derived from the Late-Glacial Ho eruption of the Hudson volcano (Weller *et al.*, 2014); and D. Tephra Cisnes 263A, with abundant dark brown glass containing only a few rounded vesicles (Table 2), suggested to be derived from the Melimoyu volcano.

occasional plagioclase microlites (Fig. 8A). Phenocrysts of plagioclase, which are the most abundant along with both clinopyroxene and orthopyroxene, are similar in size to the glass shards. The samples from both cores have nearly identical chemistry, which is similar to the High Abundance types of rocks erupted in the southern SVZ by the Hudson and Melimoyu volcanoes (Fig. 6) and Puyuhuapi cones (López-Escobar et al., 1993, 1995a). However, olivine is abundant in and orthopyroxene has not been reported from the Puyuhuapi group basalt samples (López-Escobar et al., 1995a), and Hudson tephra glasses are typically stretched-vesicle-rich and microlite-poor (Fig. 8C). Also Hudson, located over 200 km to the southwest of Lago Shaman (Fig. 1), had no known large eruption in the time period 1,440

to 2,090 BP when the tephras 'a' were deposited (Table 1). The proximity of the core to the Melimoyu volcano suggests that this is the most likely source for these two chemically High Abundance type tephra 'a' samples. Their ages have been estimated as ~1,440 BP (<1,827±40 cal yrs BP) in the Lago Shaman core and $\sim 2,090$ BP ($>1,743\pm40$ cal yrs BP) in the Mallín El Embudo core (Table 1), and they may possibly represent two separate events, but their near identical appearance, thickness and chemistry suggest they formed from the same eruption, despite the difference in their estimated ages. Naranjo and Stern (2004) documented a relatively large explosive eruption of the Melimoyu volcano (MEL2) at 1,680±100 cal yrs BP (Table 1; Fig. 7), essentially splitting the difference between the interpolated age

Core	Shaman													Embudo)			Cis-263A
Lab #	CS5054	CS5055	CS5056	CS5057	CS5058	CS5059	CS5060	CS5061	CS5062	CS5063	CS5064	CS5065	CS5066	CS5051	CS 3817	CS5052	CS5053	CS 3847
tephra	a	b	c	d	e	f	g	h	i	m	q	v	У	а	b	h	j	
~age	1,440	2,140	2,490	3,720	3,880	4,610	8,280	8,400	8,800	11,140	18,665	18,820	18,940	2,090	3,940	9,010	11,450	>19,000
source	Mel	Men	Men	Men	Men	Mel	Mel	Men	Men	Men	Men	Hudson	Men	Mel	Mel	Men	Men	Mel
Ti	8,813	5,632	5,281	5,863	4,992	7,298	8,202	5,669	4,378	5,380	4,964	7,366	5,723	8,647	6,911	4,252	5,041	8,569
Mn	1,036	569	1,425	1,266	1,297	965	1,054	946	905	956	850	890	773	1,065	914	1,070	1,006	1,304
Rb	34	16	12	13	11	59	55	23	21	21	20	44	20	32	56	22	17	34
Sr	508	431	457	449	440	422	429	471	377	418	381	399	449	492	398	393	430	478
Y	28	23	15	16	17	35	37	24	17	17	17	29	19	27	33	21	23	35
Zr	224	98	51	91	67	249	275	116	99	79	96	213	68	213	322	117	91	224
Nb	16	6	4	4	3	18	17	8	5	4	3	10	3	17	16	7	5	13
Cs	1.6	0.5	0.5	0.5	0.4	2.4	2.1	0.7	0.9	0.8	0.7	1.0	0.7	1.2	2.5	0.9	0.9	1.2
Ba	486	199	134	191	147	604	503	288	248	267	218	480	225	487	624	298	264	568
Hf	6.6	2.3	1.7	2.4	2.0	6.6	6.5	3.4	2.8	2.3	2.3	6.9	1.8	6.5	6.6	3.8	3.5	5.9
Pb	8.4	3.4	3.0	4.9	3.2	12.2	13.0	6.7	6.7	8.9	6.3	8.8	8.8	8.6	11.7	8.2	9.5	8.0
Th	6.8	2.6	1.2	2.0	1.8	8.0	7.6	2.9	2.6	2.1	1.7	4.6	1.7	7.1	7.7	2.4	2.8	6.1
U	1.0	0.4	0.2	0.3	0.3	1.9	1.9	0.6	1.0	0.6	0.7	1.3	0.9	0.8	2.3	0.7	0.8	1.2
La	28.4	9.76	6.16	10.1	8.37	38.8	33.8	12.8	11.1	10.5	11.9	28.0	10.9	26.5	32.8	14.7	10.6	36.1
Ce	64.7	21.3	15.5	23.4	20.9	79.8	75.8	29.6	26.2	24.0	27.8	63.2	24.8	61.0	73.0	34.1	25.5	76.2
Pr	7.99	2.62	2.18	2.91	2.37	8.81	9.33	3.76	3.30	3.90	3.57	7.61	3.08	7.68	8.05	4.53	4.38	8.50
Nd	31.9	11.7	10.4	14.2	11.8	38.5	37.2	18.8	14.1	16.3	15.4	31.1	14.1	30.3	32.8	19.7	18.6	37.1
Sm	7.11	2.65	2.82	3.39	2.95	6.91	8.13	4.34	3.36	3.43	3.53	6.49	3.38	6.44	7.01	4.78	4.31	8.21
Eu	2.02	0.93	1.19	1.15	1.19	2.24	2.29	1.46	0.90	1.10	1.06	1.79	1.18	2.01	2.03	1.58	1.44	2.69
Gd	8.07	3.20	3.21	3.86	3.56	9.02	9.50	4.93	3.93	4.25	3.80	7.37	3.82	7.66	8.12	5.82	5.19	9.49
Tb	0.97	0.43	0.41	0.48	0.52	1.18	1.18	0.62	0.48	0.55	0.46	0.88	0.47	1.01	1.02	0.77	0.85	1.23
Dy	5.84	2.55	2.98	3.14	3.37	7.85	7.10	4.59	3.12	3.72	3.16	5.24	2.96	5.54	6.53	4.53	4.64	6.47
Но	1.09	0.45	0.58	0.64	0.66	1.25	1.37	0.69	0.53	0.58	0.53	0.94	0.55	1.08	1.16	0.95	0.90	1.26
Er	3.52	1.54	1.82	2.03	1.86	4.18	4.17	2.36	1.79	2.00	1.89	3.12	1.79	3.16	3.61	2.89	2.72	3.77
Tm	0.42	0.18	0.23	0.28	0.27	0.51	0.57	0.30	0.21	0.27	0.21	0.38	0.19	0.46	0.47	0.41	0.38	0.50
Yb	3.03	1.24	1.72	1.74	1.65	3.56	3.97	2.25	1.90	1.99	1.96	2.97	1.73	2.95	3.16	2.35	2.25	3.39
Lu	0.41	0.17	0.23	0.26	0.26	0.59	0.52	0.25	0.20	0.20	0.22	0.35	0.19	0.39	0.51	0.39	0.34	0.45

TABLE 3. TRACE-ELEMENT CONTENTS IN PARTS-PER-MILLLION (PPM) OF BULK TEPHRA SAMPLES FROM THE LAGO SHAMAN AND MALLIN EL EMBUDO CORES AND AN OUTCROP OF GLACIAL-LACUSTRINE SEDIMENT.

estimations for tephra 'a' in these two cores, and we tentatively attribute both these tephra layers to this same MEL2 eruption (de Porras *et al.*, 2012). We suggest that the different ages are due either to near surface contamination of the samples dated or uncertainties in the interpolated estimates.

4.2. Tephras 'b, c, d and e' from Lago Shaman

These tephras are all only 1 cm thick or less. They all have chemistry similar to Very Low Abundance types of rocks erupted in the southern SVZ from the Mentolat volcano, and they all have very similar petrographic appearance, with clear glass shards containing rounded but not stretched vesicles (Fig. 8B), and a large proportion of phenocryst phases including plagioclase, two pyroxenes, brown amphiboles and minor olivine. Both their chemistry and petrography, which are essentially identical to Mentolat derived tephra MEN1 (Naranjo and Stern, 2004), which has also been observed in cores from near Coyhaique (Weller et al., 2014) and Cochrane (Stern et al., 2013), are consistent with their being derived from the Mentolat volcano. Mella et al. (2012) dated tephra related to an explosive eruption of Mentolat volcano between 2,615±90 and 4,340±60 cal yrs BP, and either tephra 'd' or 'e' in the Lago Shaman core could have been produced by this same eruption. These tephra do not appear in the Mallín El Embudo core.

4.3. Tephra 'b' in Mallín El Embudo and 'f' in Lago Shaman

Tephra 'b' in Mallín El Embudo and 'f' in Lago Shaman both occur as diffuse layers mixed with organic sediment over a zone of between 10-20 cm thickness (Figs. 3 and 4). Both have nearly identical chemistry similar to High Abundance type rocks erupted from Melimoyu and Hudson volcanoes (Fig. 6), and both consist of dark brown glass with only a few generally round vesicles and occasional plagioclase microlites similar to the two samples of tephra 'a'. Plagioclase phenocrysts are abundant and both orthopyroxene and clinopyoxene crystals also occur, along with minor olivine. The presence of orthopyroxene and their high Rb, Ba, and La contents and relatively low Sr and Ti contents (Fig. 6) distinguishes them from Puyuhaupi basalts (López-Escobar et al., 1995a). Although they were

previously attributed to the H2 eruption of the Hudson volcano based on their chemistry (de Porras *et al.*, 2012, 2014), the lack of vesicles and the plagioclase microlites in the glass distinguishes them from typical Hudson H2 samples, and the constraints on their age (4,600 to 4,800 cal yrs BP) suggest they are older than the ~3,900 cal yrs BP age of the H2 eruption (Naranjo and Stern, 1998). Therefore we now attribute these tephra to a mid-Holocene eruption of the Melimoyu volcano not previously recognized in outcrop in this region.

4.4. Tephra 'g' from Lago Shaman

Tephra 'g' from Lago Shaman has petrography (brown glass; Table 2) and High Abundance chemistry (Fig. 6; Table 2) similar to tephra 'a' and 'f' from this core, and we suggest the Melimoyu volcano as its source.

4.5. Tephras 'h' from both cores and 'i' from Lago Shaman

These tephra have Very Low Abundances chemistry (Fig. 6) and petrography (clear glass, abundant phenocrysts including amphibole; Table 2) similar tephra 'b, c, d and e' from Lago Shaman, and MEN1 from cores near Coyhaique and Cochrane (Stern et al., 2013). They are attributed to explosive eruptions of the Mentolat volcano. Tephra 'i' from Lago Shaman and 'h' from Mallín El Embudo are both similar in age and coarser grained than tephra 'h' from Lago Shaman, and we consider them to be deposited from the same eruption. This eruption may correspond to the MEN1 eruption, although the ~7,710±120 cal yrs BP age of the MEN1 eruption (Naranjo and Stern, 2004; Stern et al., 2013) is somewhat younger than the approximate ages (8,800 and 9,010 cal yrs BP, respectively; Table 1) of these two tephra (Fig. 7).

4.6. Tephras 'm' from Shaman and 'j' from Mallín El Embudo

These two tephra have similar age and Very Low Abundance type chemistry to each other, and are also similar petrologically (clear glass, phenocryst-rich with amphiboles; Table 2) to other tephra in these cores and elsewhere derived from the Mentolat volcano.

4.7. Tephra 'q' from Lago Shaman

This Late-Glacial age tephra has similar Very Low Abundance chemistry (Fig. 6) and petrography (clear glass, abundant phenocrysts with amphibole; Table 2) to other tephra in these cores and elsewhere derived from the Mentolat volcano.

4.8. Tephra 'v' from Lago Shaman

Tephra 'v' from Lago Shaman occurs as a 2 cm thick layer of brown to tan glass with abundant stretched vesicle (Fig. 8C). The glass lacks microlites and the tephra contains only rare phenocrysts of plagioclase and orthopyroxene. The chemistry of this tephra layer is characteristic of a High Abundance type samples and identical to that of Hudson Ho tephra (Weller et al., 2014). The age determined in the Lago Shaman core is ~18,820 BP, while that determined for Ho in multiple cores from near Coyhaique is 17,340±90 cal yrs BP (Table 1; Weller et al., 2014). Tephra from the Ho eruption was distributed to the northwest of the volcano, and the 2 cm thickness of tephra 'v' in the Lago Shaman core is consistent with the isopachs of Ho tephra estimated by Weller et al. (2014).

4.9. Tephra 'y' from Lago Shaman

This Late-Glacial age tephra has similar petrography (clear glass, abundant phenocrysts with amphiboles; Table 2) and Very Low Abundance chemistry to other tephra in these cores and elsewhere derived from the Mentolat volcano. A Late-Glacial tephra MENo derived from Mentolat volcano has also been described from sediment cores taken from lakes near Coyhaique (Weller *et al.*, 2014).

4.10. Cisnes 263A

This 6 cm thick dark colored tephra contains brown glass with a small amount of rounded vesicle (Fig. 8D) and phenocrysts of plagioclase and two pyroxenes. Its High Abundance type chemistry is identical to that of tephra 'a' from the two cores and its source volcano in likely to have been the Melimoyu volcano. It is the first pre-Late-Glacial Maximum age tephra reported in this region of the southern Andes.

5. Discussion and Conclusions

In general, the 17 tephra from the Lago Shaman and Mallín El Embudo cores fall into two easily distinguishable groups; one with abundant brown glass with a few rounded vesicles (Fig. 8A), a smaller proportion of plagioclase and pyroxene phenocrysts, and High Abundance type chemistry (Fig. 6; Table 3), and another group with clear glass with rounded vesicles (Fig. 8B), abundant phenocrysts of plagioclase, pyroxenes, brown amphibole and minor olivine, and Very Low Abundance type chemistry (Fig. 6; Table 3). We attribute the first group to eruptions of the Melimoyu volcano and the second to eruptions of the Mentolat volcano. One tephra (v) from Lago Shaman has tan to brown glass with abundant stretched vesicles (Fig. 8C), few phenocrysts and High Abundance chemistry (Fig. 6), and this tephra is attributed to the large Late-Glacial age Ho eruption of the Hudson volcano (Weller et al., 2014). The glacial age tephra from the outcrop (CIS-263A) is similar to those with brown glass (Fig. 8D) and High Abundance chemistry (Fig. 6) and is attributed to an eruption of the Melimoyu volcano.

Based on their petrography, chemistry and age, we conclude that the 17 tephra analyzed from the Lago Shaman and Mallín El Embudo cores have been derived from nine different eruptions of the Mentolat volcano, three of the Melimoyu volcano, and one from the Hudson volcano. Although, there is still not enough spatial coverage to constrain isopach maps for the eruptions that produced all the tephra, some of these tephra do appear to correspond chronologically and petrochemically to some of the larger eruptions identified previously by Naranjo and Stern (1998, 2004), Mella et al. (2012), Stern et al. (2013) and Weller et al. (2014), while others occurred at times when no such large eruption has been previously identified. Tephras 'a' in the two cores may correspond to Late-Holocene eruption MEL2 of Melimoyu (Table 1) previously documented by Naranjo and Stern (2004). Either tephra 'd' or 'e' in the Lago Shaman core may have formed from a Late-Holocene explosive eruption of Mentolat documented by Mella et al. (2012). Tephra 'b' in Mallín El Embudo and 'f' in Lago Shaman do not result from the H2 eruption of Hudson as previously suggested (de Porras et al., 2012, 2014), but rather from a mid-Holocene eruption of the Melimoyu

volcano not previously described. Tephras 'i' from the Lago Shaman core and 'h' from the Mallín El Embudo core may have been deposited during the mid-Holocene MEN1 eruption of Mentolat (Table 1; Naranjo and Stern, 2004; Stern *et al.*, 2013). Tephra 'v' in Lago Shaman was produced by the Late-Glacial Ho eruption of Hudson (Table 1; Weller *et al.*, 2014). Tephra 'y' in the Lago Shaman core may correspond to the Late-Glacial MENo eruption of Mentolat documented in cores from lakes near Coyhaique (Weller *et al.*, 2014). The one pre-Late-Glacial Maximum tephra Cisnes 263A also formed from an eruption of Melimoyu volcano.

This information confirms the repeated episodic explosive eruption of the Mentolat and Melimoyu volcanoes beginning from, in the case of Mentolat the earliest Late-Glacial period at approximately >17340 cal yrs BP, and in the case of Melimoyu before the Last Glacial Maximum at >19,670 BP. The petrochemical data suggest that the eruptive products of each of these two volcanoes has been relatively constant in character over this time period, although they differ significantly from each other despite being located within only 70 km of each other along strike on the volcanic front of the SSVZ arc.

The data also suggest that none of the tephra in these cores were the products of the eruption of the small monogenetic basaltic cones near Puyuhuapi and Palena (Fig. 1), as these basalts have abundant olivine and lack orthopyroxene and amphibole. The eruption of the small monogenetic basalt cones in the Palena and Puyuhuapi group may have been too small to generate regional tephra falls. Nor is there any unambiguous indication of tephra in the upper Río Cisne valley being derived from the Maca, Cay and/or Yanteles volcanoes, which are Low Abundance type centers (Fig. 6). One tephra (MAC1) observed close to Puerto Aisén has been attributed to an explosive eruption of Maca (Naranjo and Stern, 2004), and Mella et al. (2012) attribute another tephra observed in this area to Cay volcano, but neither of these volcanoes have summit craters/ calderas as do Hudson, Mentolat and Melimoyu, and they may have had more effusive and less explosive eruptive histories.

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