



Characterization of tephras dispersed by the recent eruptions of volcanoes Calbuco (1961), Chaitén (2008) and Cordón Caulle Complex (1960 and 2011), in Northern Patagonia



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ABSTRACT

Pyroclastic materials dispersed in recent volcanic eruptions in Northern Patagonia were analysed in order to characterize the volcanic provenance by the geochemical fingerprint. The volcanic products studied were dispersed by eruptions of volcanoes Calbuco in 1961, Chaitén in 2008, and Cordón Caulle Volcanic Complex (CCVC) in 1960 and 2011. The geochemical characterization was based on the determination of 35 major and trace elements by Instrumental Neutron Activation Analysis, including geochemical tracer such as Rare Earth Elements (REE). The study of the pyroclastic products also included the morphological analysis by petrographic and scanning electron microscopy, and the mineralogical characterization by X-ray diffraction.

Geochemical tracers determined in the glass fraction of the dispersed pyroclastic materials allowed a clear discrimination of the three volcanoes that gave origin to the tephras, the three of them with different evolution degree. Tephras from 1960 and 2011 CCVC eruptions showed the same geochemical signature. The geochemical parameters providing the differential characterization are the normalized REE and multi-element patterns, the Eu anomaly, the heavy to light and medium to light REE normalized ratios, and the Cs, Sc, Rb, Ta and Th concentrations. The bulk glassy fraction showed the same composition for each volcanic eruption in samples collected even in distant sites (from 100 to 220 km in Chaitén, 2008, and from 80 to 650 km in CCVC 2011), attesting to be the most reliable material for correlation purposes.

According to the mineralogy, cristobalite was found in volcano Chaitén tephra as an indicator of such origin. Arsenic, an element of environmental interest, exhibited concentrations ranging from 6 to 16 $\mu\text{g g}^{-1}$, with the highest values corresponding to Puyehue–Cordón Caulle and Chaitén products.

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1. Introduction

Tephra studies have developed increasingly during the last decades as a valuable tool in different fields; e.g. for tephrostratigraphical and tephrochronological purposes, or to develop paleolimnological correlations. The large volume of pyroclastic material produced by volcanic eruptions can be dispersed over hundreds of kilometres providing key extended chronostratigraphic markers. Tephrostratigraphical and tephrochronological

applications require tephra layers to be analysed in detail including physical and chemical characteristics, considering the typical morphological features, mineralogical assemblages and geochemical examination (Westgate and Gorton, 1981; Lowe, 2011). The geochemical characterization may provide a fingerprint which enables to identify the provenance volcano, allowing the association of terrestrial and lacustrine tephra deposits with specific volcanic events, providing key data for this kind of studies (Clift and Fitton, 1998; Ortega-Guerrero and Newton, 1998; Wade et al., 2005; Steinhauser et al., 2007; Daga et al., 2008).

Northern Patagonia is located near the Southern Volcanic Zone (SVZ) of the Andean Range, an active volcanic region with high historic eruptive frequency and high impact all over the Argentinean Patagonia (Naranjo et al., 1993; Inbar et al., 1995; Petit-Breuilh

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Sepúlveda, 2004; Stern, 2004; Martin et al., 2009; Alfano et al., 2011; Wilson et al., 2011; Collini et al., 2013). Previous works on outcrops and lacustrine sedimentary sequences from Patagonian–Andean zone allowed the identification and characterization of distal tephra deposits from different volcanic sources affecting the area during post-glacial times, particularly those from the most recent eruption records (Naranjo and Stern, 2004; Singer et al., 2008; Daga et al., 2006, 2008, 2010, 2012; Iglesias et al., 2011; Durant et al., 2012), showing that the predominant atmospheric conditions at these latitudes favour the tephra records in the SVZ easternward territory (Fig. 1). The high SVZ eruptive frequency sometimes makes it difficult to identify clearly the volcanic provenance due to deposits superposition from eruptions close in time.

The characterization of tephras dispersed in recent eruptions, with volcanic provenance undoubtedly identified, provides key information for tephrochronological correlations in recent and ancient sequences.

The aim of this work is to contribute to the knowledge of tephras that have been affecting Patagonian territory for thousands of years, providing a geochemical fingerprint of the products dispersed by recent volcanic events of Cordón Caulle Volcanic Complex (1960 and 2011), and Calbuco (1961) and Chaitén (2008) volcanoes, allowing the identification of each tephra provenance by analysing samples of volcanic products clearly related to these eruptions. The geochemical characterization consists in the analysis of 35 major and trace elements by Instrumental Neutron Activation

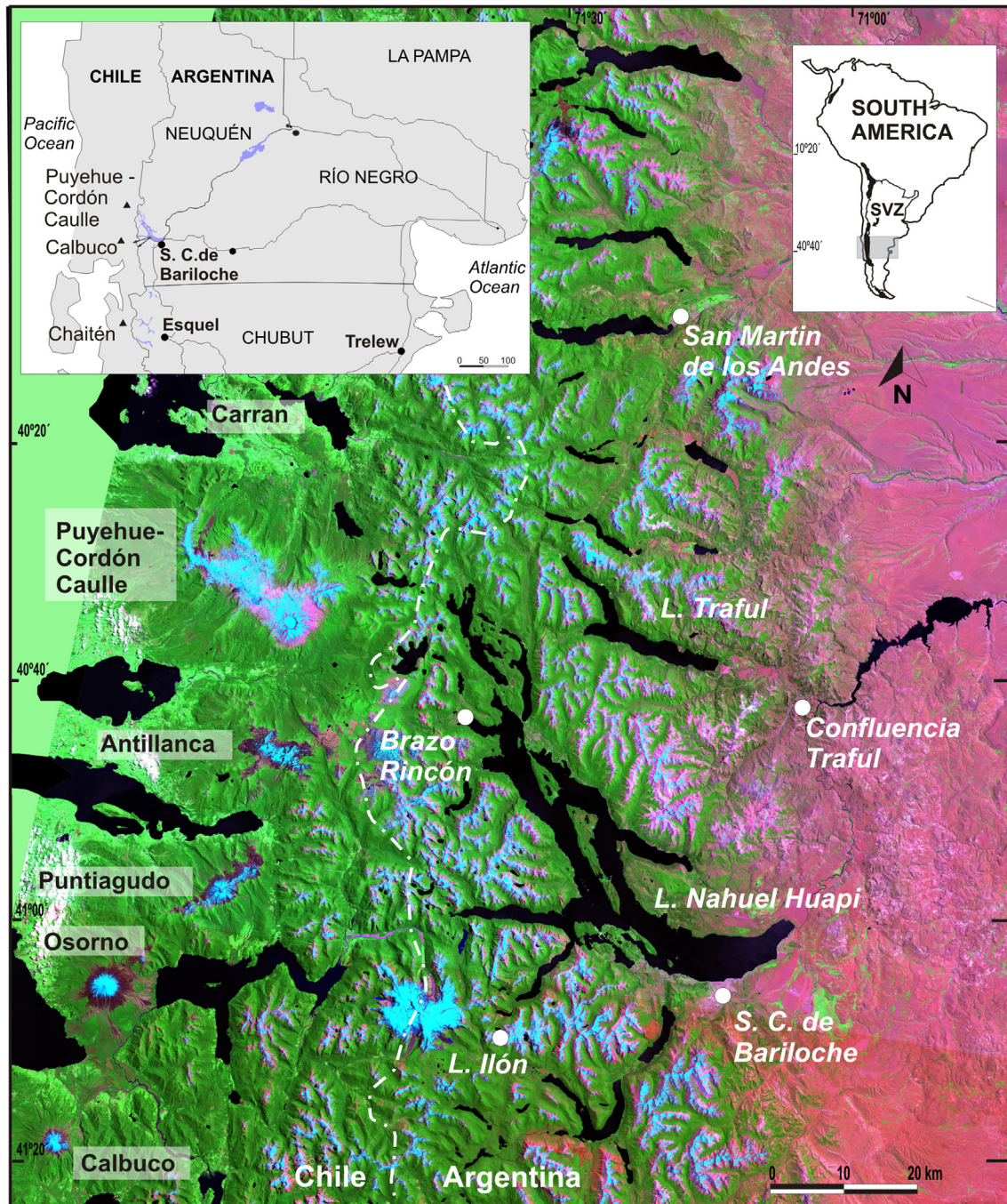


Fig. 1. Location of the volcanic centres (▲) in the Southern Volcanic Zone (SVZ) that dispersed the pyroclastic products analysed in this study (volcanoes Calbuco and Chaitén, Cordón Caulle Volcanic Complex), and tephra sampling sites (Table 1). North Patagonia Andean Range, South America.

Analysis (INAA), complemented by a morphological and a mineralogical characterization. The studied elements include potential pollutants, namely antimony (Sb), arsenic (As), barium (Ba), bromine (Br), cobalt (Co), chromium (Cr), thorium (Th), uranium (U), and zinc (Zn), valuable data for environmental studies providing that volcanic ashes are a well known source of pollutants.

2. The volcanic eruptions

The Andes mountains of Northern Patagonia are located in the SVZ (Fig. 1). The SVZ is the result of the subduction of the Nazca plate under the South American plate, which generates an active volcanic arc extending from 33°S to 46°S. This arc includes several active volcanic centres since the Miocene (Gerlach et al., 1988; López-Escobar et al., 1995; Stern, 2004).

The Cordón Caulle Volcanic Complex (CCVC; 2236 m above sea level; 40°30'S, 72°12'W) runs in a NW–SE direction between the Cordillera Nevada caldera in the NW and Puyehue stratovolcano in the SE, composing the Puyehue–Cordón Caulle Volcanic Complex (Gerlach et al., 1988; Fig. 1). This system includes various fissure vents with aligned domes and pyroclastic cones, with abundance of silicic magma types, unique among the mostly bimodal centres along the SVZ, where basalts widely predominate over more silica-rich rocks (Lara et al., 2004). The latest eruptions from CCVC generated mainly rhyodacitic and rhyolitic products (Lara et al., 2006; Castro et al., 2013). The CCVC 1960 eruption began on May 24th, 38 h after the main shock of the largest instrumentally recorded earthquake (M 9.5, Valdivia, Chile), with an explosive subplinian phase (VEI = 3) and an eruptive column of about 8 km high, together with the emission of water vapour from vents along the fissure system (Lara et al., 2006). The dispersion plume direction was SE, generating 10 cm thick white pumice deposits at 30–40 km from the source and transporting pyroclastic products to the Argentinean side, to Nahuel Huapi National Park (González-Ferrán, 1995; Petit-Breuilh Sepúlveda, 2004; Lara et al., 2006). On June 4th, 2011, the CCVC began an eruptive process with a new explosive subplinian phase (VEI = 3–4; Cardona et al., 2012) and the generation of an eruptive column made of gases and volcanic ash 11–13 km high and 5 km wide (Cardona et al., 2012; Aguilera et al., 2012). The eruption dispersed volcanic products to the SE of the volcano, impacting mainly on La Angostura and San Carlos de Bariloche cities as well as small towns across the Patagonian steppe, reaching the Atlantic Ocean coast in just one day (Fig. 1). During the following days, the dispersion of the volcanic plume had variable directions but it moved mostly to the East side of the Andean mountains due to the West–East dominant direction of winds at this latitude.

Chaitén volcano (1112 m above sea level; 42°50'S, 72°39'W; Fig. 1) is considered one of the eight polygenetic volcanoes of the southernmost part of the SVZ, located 12 km west from the larger Michinmahuida volcano (Naranjo and Stern, 2004). Although there are references to historic reports of volcanic events during the 18th and 19th centuries (Petit-Breuilh Sepúlveda, 2004), works previous to the 2008 eruption considered that Chaitén had been dormant, dating the last violent eruption 9370 y BP, with pyroclastic flows and ash fall deposits containing a yellow rhyolite pumice capped by a thin layer of dark mafic scoria (Naranjo and Stern, 2004). It was not until the 2008 explosive eruption that research started to develop in this uninhabited and unexplored area of the Chilean territory. Recent reports with new field and analytical data indicate that Chaitén volcano is much more active than previously reported, with several explosive eruptions during the Holocene, being the most recent in the middle of the 17th century (Watt et al., 2013; Amigo et al., 2013; Lara et al., 2013). The Chaitén volcano plinian eruption started on May 2nd, 2008, generating an eruptive column close to 21 km high (Lara, 2009). The event had immediate social and economic impact along Southern Chile and Argentina, with an

ash cloud blown from SE to NE of the volcano across the Andes, affecting a vast region and reaching the Argentinean Atlantic coast (Fig. 1) (Watt et al., 2009; Durant et al., 2012). Although Chaitén volcano was included among more than 120 active centres in the zone, it was not considered of high priority level due to the lack of historical eruptive records, and no seismic monitoring system was installed prior to the eruption (Basualto et al., 2008; Lara, 2009; Castro and Dingwell, 2009). The exposures of the last major eruptions are limited, probably due to the extensive erosion over the last 9000 years (Naranjo and Stern, 2004); fresh stratigraphic sequences were exposed due to erosion processes during 2008 eruption, allowing the identification of the new eruptive events related to Chaitén and neighbour volcanoes (Amigo et al., 2013).

Calbuco volcano (2003 m above sea level; 41°20'S, 72°35'W; Fig. 1) is a Late Pleistocene–Holocene active composite stratovolcano, having erupted mainly andesite over 150,000 years. The most recent activity consisted of a plinian eruption in 1893–1894, and a young historic dome–cone and lava flows developed during the 1917, 1929, and 1961 eruptions (López-Escobar et al., 1995). The Calbuco 1961 explosive eruption started on March 10, with a short and violent explosive phase and the formation of a 12 km high eruptive column. The dispersed pyroclastic products covered the volcano eastern areas with a few millimetres thick tephra deposit, reaching San Carlos de Bariloche city (Fig. 1) (González-Ferrán, 1995; Petit-Breuilh Sepúlveda, 2004).

Tephra falls from these volcanoes have affected large areas, spreading over hundreds of kilometres from the sources to the Patagonian and Pampean regions, reaching the Atlantic Ocean and neighbouring countries, favoured by the dominant westerly winds of these latitudes (Fig. 1). The geographical dispersion of these eruptive products turn these deposits into valuable marker layers for correlation purpose for time scales where the dating methods are scarce, but a comprehensive geochemical characterization of recent tephra dispersed in Argentinean territory has been undertaken only in a few cases (Villarosa et al., 2001; Daga et al., 2006, 2008, 2010, 2012; Iglesias et al., 2011).

3. Material and methods

3.1. Tephra samples

The tephra studied, coarse (63–2000 µm) and fine ashes (<63 µm), are composed of variable proportions of vitric or glassy particles (shards, including pumice and scoria, derived from vesiculated juvenile magma), crystals and crystal fragments, and lithic pyroclasts. Glass shards have proved to be the most suitable component in geochemical characterization for source identification (Ortega-Guerrero and Newton, 1998; Daga et al., 2008; Albert et al., 2012). The morphology of all components identified and the whole rock mineralogy will be described further on, but the geochemical analysis will be focused on the glassy products (Table 1).

3.1.1. Cordón Caulle Volcanic Complex

Volcanic ash from the 1960 event were manually collected in San Carlos de Bariloche (Fig. 1) immediately after the CCVC eruption on May 24th, 1960 (sample CC1960-Ba), and stored in the Museo de la Patagonia (Patagonia Museum), San Carlos de Bariloche, Argentina. This sample corresponds to coarse ash, with particles <200 µm. A well preserved tephra layer corresponding also to CCVC 1960 eruption – recovered from a sedimentary sequence extracted from Brazo Rincón, Lake Nahuel Huapi, near to the volcano (Fig. 1, Table 1) – is considered here (sample CC1960-BR) although the INAA results were reported in a previous work (Daga et al., 2006). This tephra corresponds to coarse ash; the geochemical composition was determined on coarse glass particles (250–500 µm).

Table 1
Tephra samples studied, dispersed by volcanoes Calbuco 1961 and Chaitén 2008, and by Cordon Caulle Volcanic Complex 1960 and 2011, North Patagonia, South America.

Sample code	Event	Sampling site ^a			Sample source	Grain size ^c (μm)	Grain size ^d (μm)	Sampling date
		Site	Coordinates	Distance ^b km/direction				
CC1960-Ba	CCVC ^e 1960	S. C. de Bariloche	41°06'S, 71°25'W	100/SE	Ash fallout ^f	<200	50–100 ^g	1960
CC1960-BR	(40°30'S, 72°10'W)	Brazo Rincón	40°44'S, 71°46'W	40/SE	Sediment core	<500	250–500 ^g	–
CC2011-Ba4	CCVC ^e 2011	S. C. de Bariloche	41°06'S, 71°25'W	100/SE	Ash fallout	<1500	<63 ^h	June 4th, 2011
CC2011-Ba6	(40°30'S, 72°10'W)	S. C. de Bariloche	41°06'S, 71°25'W	100/SE	Ash fallout	<150	<63 ^h	June 6th, 2011
CC2011-CT		Confluencia Traful	40°43'S, 71°05'W	90/E	Ash fallout	<150	<63 ^h	June 6th, 2011
CC2011-SMA		San Martín de los Andes	40°09'S, 71°20'W	80/NE	Ash fallout	<1500	<63 ^h	June 6th, 2011
CC2011-AC		Atlantic Coast: Trelew	43°15'S, 65°18'W	650/SE	Ash fallout	<150	<63 ^h	June 5th, 2011
Ch2008-Ba	v. Chaitén 2008	Esquel	42°54'S, 71°18'W	100/E	Ash fallout	<150	<63 ^h	May 2nd, 2008
Ch2008-Es	(42°50'S, 72°39'W)	S. C. de Bariloche	41°06'S, 71°25'W	220/NE	Ash fallout	<150	<63 ^h	May 8th, 2008
Ca1961	v. Calbuco 1961 (41°20'S, 72°35'W)	Laguna Ilón	41°11'S, 71°44'W	75/ENE	Sediment core	<1500	250–500 ⁱ	–

^a See Fig. 1.

^b Distance and direction from the source to the sampling site; see Fig. 1.

^c Grain size of the tephra sample collected.

^d Grain size of glassy material used for geochemical characterization.

^e Cordon Caulle Volcanic Complex.

^f Material stored in the Museo de la Patagonia (Patagonic Museum), S. C. de Bariloche, Argentina; the museum records describe that the material was collected immediately after the Cordon Caulle Volcanic Complex eruption in May 24th, 1960. Pumice particles with geochemical characterization coinciding with glass shards (Daga et al., 2006).

^g Separated and cleaned glass shards (Daga et al., 2006).

^h Material sieved through 63 μm mesh size, composed mostly by glass shards according to the microscope observations and X-ray diffraction patterns.

ⁱ Isolated and cleaned glass shards (Daga et al., 2008).

Tephra samples from CCVC 2011 eruption were collected in San Carlos de Bariloche, San Martín de los Andes, and Trelew on the Atlantic Ocean coast (Fig. 1, Table 1), in plastic and glass containers during ash fallout. Also, tephra samples were collected in the Traful river region (Fig. 1, Table 1) immediately after deposition, from dry surface deposits. Only the sample from San Carlos de Bariloche, June 4th (CC2011-Ba4) was affected by rainwater action during the first hours of collection. As it can be observed later from the results of the analysis, there is no significant difference in the composition between the wet and dry samples (Table 2a).

Samples collected in San Carlos de Bariloche on June 4th, 2011 (CC2011-Ba4), and in San Martín de los Andes (CC2011-SMA) correspond to coarse ash (particles reaching 1500 μm) (Fig. 2a). On the contrary, samples collected in Trelew (CC2011-AC), in San Carlos de Bariloche on June 6th, 2011 (CC2011-Ba6), and in Traful river (CC2011-CT) correspond to fine ash with few coarse particles reaching 150 μm (Fig. 2b).

3.1.2. Chaitén volcano

Tephra samples were collected in Esquel immediately after the Chaitén volcano eruption (Ch2008-Es) on May 2nd, 2008, from dry surface deposits, and in San Carlos de Bariloche on May 8th (Ch2008-Ba), in plastic containers from direct ash fallout (Fig. 1, Table 1). In all cases the volcanic products were undoubtedly generated by the Chaitén volcano eruption. Samples collected from Chaitén 2008 eruption correspond to coarse–fine ash, with particles smaller than 150 μm (Fig. 2e and f).

3.1.3. Calbuco volcano

A tephra sample from Calbuco 1961 eruption (Ca1961) was obtained from a well preserved tephra layer recovered from a sedimentary sequence extracted from Lake Ilón, situated 70 km to the ENE of the volcano (Fig. 1, Table 1). The tephra layer was associated to the 1961 eruption (Daga et al., 2008). It corresponds to a coarse ash deposit, with some fragments reaching 1500 μm.

3.2. Sample conditioning

The fallout samples were first dried at room temperature, and oven dried afterwards at 105 °C until constant weight. The volcanic ashes

recovered from lacustrine sequences were freeze-dried until constant weight before sieving. Dried bulk samples were used to morphological and whole rock mineralogical descriptions (next section). On the other hand, for the geochemical characterization of the glass fraction, all ash fallout samples and those collected immediately after ash deposition were sieved through a 63 μm mesh, and the finest fraction was used. The <63 μm fraction obtained after sieving was composed mainly of glass shards in all cases. In the case of the volcanic ashes recovered from lacustrine sequences, the largest glassy fraction (250–500 μm) was considered for the geochemical characterization because this size involves shorter transport distances, thus avoiding potential mixing during the sedimentation process from simultaneous sources (e.g. volcano PCCVC and Calbuco had eruptions in 1960 and 1961 respectively, considered simultaneous in sedimentary records).

3.3. Morphological and mineralogical characterization

Previous to any treatment, bulk samples were analysed with a binocular magnifying glass to identify the macroscopic characteristics and to classify the typical kind of particles in each sample. Samples were also mounted on a holder and coated with Au for observations with a Philips 515 scanning electron microscopy (SEM) at an acceleration voltage of 10 kV.

The qualitative mineralogy of powdered bulk samples was analysed by X-ray diffraction (XRD), using a Philips PW3719 X-ray diffractometer, operating with 40 kV accelerating voltage and 40 mA current, and collecting data between 3 and 60 2θ, by the Grupo de Caracterización de Materiales (Centro Atómico Bariloche). The phase identification was achieved by using data processing software for XRD files. After sieving, qualitative characterization of the finest particles (<63 μm size) was performed using a binocular magnifying glass and a petrographic microscope.

3.4. Elemental analysis

The geochemical characterization of the glass fractions was performed by INAA. This nuclear technique, not involving any chemical treatment, is particularly suitable for the characterization of pyroclastic material because it allows the simultaneous determination of the total concentration of elements with very different

Table 2a
Elemental composition and geological parameters of the volcanic ashes (glassy fraction), Cordón Caulle Volcanic Complex.

	1960 Event		2011 Event				
	CC1960-Ba ^a	CC1960-BR ^{b,c}	CC2011-Ba4 ^a	CC2011-Ba6 ^a	CC2011-CT ^a	CC2011-SMA ^a	CC2011-AC ^a
Al (wt%)	8.16 ± 0.37	7.64 ± 0.33	7.56 ± 0.30	7.78 ± 0.32	7.73 ± 0.29	7.35 ± 0.29	7.29 ± 0.28
Ca (wt%)	1.41 ± 0.39	–	1.95 ± 0.31	1.23 ± 0.31	1.69 ± 0.32	1.26 ± 0.53	2.11 ± 0.49
Cl (wt%)	–	–	0.225 ± 0.030	0.280 ± 0.029	0.263 ± 0.030	0.190 ± 0.027	0.216 ± 0.029
Fe (wt%)	2.72 ± 0.17	2.75 ± 0.16	3.37 ± 0.17	2.76 ± 0.15	2.84 ± 0.15	2.77 ± 0.15	3.13 ± 0.17
K (wt%)	2.56 ± 0.79	2.30 ± 0.45	2.73 ± 0.31	2.75 ± 0.24	2.79 ± 0.22	2.56 ± 0.25	2.45 ± 0.26
Mg (wt%)	<0.4	0.46 ± 0.30	0.55 ± 0.13	0.31 ± 0.19	0.40 ± 0.18	0.46 ± 0.18	0.55 ± 0.13
Mn (µg g ⁻¹)	845 ± 28	880 ± 29	903 ± 28	865 ± 25	875 ± 27	839 ± 29	854 ± 26
Na (wt%)	4.20 ± 0.17	4.12 ± 0.17	3.88 ± 0.15	4.22 ± 0.15	4.15 ± 0.15	4.04 ± 0.14	3.78 ± 0.13
Ti (wt%)	0.375 ± 0.098	0.339 ± 0.071	0.386 ± 0.072	0.413 ± 0.065	0.378 ± 0.063	0.278 ± 0.055	0.359 ± 0.058
As (µg g ⁻¹)	13.6 ± 1.1	15.1 ± 1.1	15.0 ± 1.0	14.9 ± 1.0	15.3 ± 1.0	15.0 ± 1.0	15.7 ± 1.1
Ba (µg g ⁻¹)	800 ± 97	812 ± 82	765 ± 62	814 ± 68	812 ± 69	784 ± 67	790 ± 68
Br (µg g ⁻¹)	6.34 ± 0.68	5.27 ± 0.64	4.76 ± 0.44	4.92 ± 0.39	4.60 ± 0.40	4.48 ± 0.32	4.43 ± 0.49
Co (µg g ⁻¹)	3.63 ± 0.22	3.51 ± 0.15	6.25 ± 0.20	3.13 ± 0.11	3.56 ± 0.12	3.27 ± 0.11	5.41 ± 0.18
Cr (µg g ⁻¹)	<1	1.37 ± 0.80	9.10 ± 0.95	2.24 ± 0.64	3.03 ± 0.53	2.59 ± 0.56	6.55 ± 0.65
Cs (µg g ⁻¹)	4.64 ± 0.35	4.97 ± 0.64	5.00 ± 0.31	5.16 ± 0.30	5.15 ± 0.32	5.05 ± 0.30	5.00 ± 0.32
Hf (µg g ⁻¹)	8.98 ± 0.57	10.23 ± 0.53	10.02 ± 0.43	11.03 ± 0.48	10.62 ± 0.45	10.68 ± 0.45	10.06 ± 0.45
Rb (µg g ⁻¹)	72.5 ± 6.8	78.4 ± 5.3	77.3 ± 4.3	78.5 ± 4.4	79.2 ± 4.5	78.5 ± 4.6	76.0 ± 4.4
Sb (µg g ⁻¹)	1.09 ± 0.17	0.96 ± 0.13	1.02 ± 0.10	0.99 ± 0.11	1.04 ± 0.10	0.99 ± 0.10	1.07 ± 0.12
Sc (µg g ⁻¹)	12.32 ± 0.47	12.80 ± 0.44	15.78 ± 0.41	12.85 ± 0.32	13.42 ± 0.38	13.01 ± 0.32	14.56 ± 0.41
Sr (µg g ⁻¹)	284 ± 61	123 ± 35	225 ± 49	180 ± 33	193 ± 49	169 ± 29	202 ± 30
Ta (µg g ⁻¹)	0.557 ± 0.060	0.601 ± 0.048	0.573 ± 0.036	0.577 ± 0.036	0.603 ± 0.041	0.589 ± 0.040	0.576 ± 0.038
Th (µg g ⁻¹)	8.72 ± 0.60	9.47 ± 0.56	9.26 ± 0.42	9.28 ± 0.42	9.78 ± 0.51	9.58 ± 0.45	9.21 ± 0.49
U (µg g ⁻¹)	2.10 ± 0.36	2.50 ± 0.34	2.67 ± 0.22	2.51 ± 0.23	2.55 ± 0.25	2.84 ± 0.28	3.06 ± 0.33
V (µg g ⁻¹)	–	4.7 ± 1.9	33.0 ± 6.5	9.3 ± 2.9	11.3 ± 2.8	11.5 ± 2.7	26.3 ± 6.2
Zn (µg g ⁻¹)	74.9 ± 8.6	74.1 ± 8.2	104.6 ± 6.2	95.4 ± 5.7	99.5 ± 6.1	98.4 ± 6.1	98.1 ± 6.2
Zr (µg g ⁻¹)	443 ± 81	422 ± 53	464 ± 47	436 ± 32	458 ± 35	454 ± 43	456 ± 38
La (µg g ⁻¹)	31.4 ± 1.1	35.5 ± 1.1	36.96 ± 0.95	37.73 ± 0.95	37.58 ± 0.96	37.33 ± 0.95	35.56 ± 0.98
Ce (µg g ⁻¹)	72.9 ± 5.4	81.7 ± 5.1	88.0 ± 4.4	93.6 ± 4.8	91.8 ± 4.6	91.8 ± 4.6	90.3 ± 4.8
Nd (µg g ⁻¹)	43.2 ± 4.0	45.6 ± 3.5	44.8 ± 3.2	44.5 ± 4.3	46.2 ± 3.6	44.5 ± 2.9	44.5 ± 3.4
Sm (µg g ⁻¹)	9.32 ± 0.70	9.42 ± 0.65	9.43 ± 0.51	9.48 ± 0.52	9.66 ± 0.57	9.41 ± 0.52	9.39 ± 0.56
Eu (µg g ⁻¹)	1.695 ± 0.093	1.705 ± 0.085	1.823 ± 0.074	1.759 ± 0.071	1.841 ± 0.074	1.776 ± 0.072	1.773 ± 0.070
Tb (µg g ⁻¹)	1.43 ± 0.11	1.489 ± 0.098	1.456 ± 0.081	1.447 ± 0.080	1.471 ± 0.085	1.438 ± 0.083	1.435 ± 0.082
Dy (µg g ⁻¹)	9.48 ± 0.86	9.60 ± 0.87	9.36 ± 0.88	10.23 ± 0.95	9.67 ± 0.89	9.45 ± 0.92	9.14 ± 0.84
Yb (µg g ⁻¹)	5.79 ± 0.52	6.60 ± 0.57	6.86 ± 0.55	7.01 ± 0.57	7.17 ± 0.61	6.98 ± 0.55	6.73 ± 0.58
Lu (µg g ⁻¹)	0.781 ± 0.056	0.898 ± 0.059	0.939 ± 0.051	1.048 ± 0.072	0.955 ± 0.054	0.947 ± 0.048	0.957 ± 0.073
Eu anomaly ^d	0.562	0.554	0.597	0.575	0.575	0.585	0.585
La _N /Sm _N ^e	2.12	2.37	2.47	2.50	2.45	2.38	2.38
La _N /Lu _N ^e	4.18	4.11	4.09	3.74	4.09	4.09	3.86

^a Volcanic ash samples collected after the event from direct fallout, composed of glass shards.

^b Volcanic ash preserved in lacustrine sedimentary sequences samples.

^c Daga et al., 2006.

^d Normalized to Chondrite (Boynton, 1984); formula for calculation in Daga et al., (2008).

^e Normalized to Chondrite (Boynton, 1984).

chemical properties (e.g. lanthanides, actinides, alkali and transition metals, halogens), in major and trace levels, without any matrix effect (e.g. scoria, glass or pumice). Sample masses analysed ranged from 1 to 100 mg. They were irradiated in the RA-6 nuclear reactor, Centro Atómico Bariloche, Argentina; a short term irradiation (2–10 min) in a predominantly thermal neutron flux, and a long term one (10–24 h) in a mixed flux (thermal–epithermal–fast). The absolute parametric method was used to determine the elemental concentrations (Daga et al., 2006, 2008). The elements determined were: major Al, Ca, Fe, Mg, Mn, Na, K, and Ti; Rare Earths La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu, and other relevant trace elements Sb, As, Ba, Br, Cs, Co, Cr, Hf, Rb, Sc, Sr, Ta, Th, U, V, W, Zn, and Zr. Corrections for spectral interferences were performed when necessary. Corrections due to contributions of ²³⁵U fission products, and ²⁷Al(n,p)²⁷Mg, ⁵⁴Fe(n,α)⁵¹Cr, and ¹⁷⁶Yb(n,γ)¹⁷⁷Yb–¹⁷⁷Lu reactions were also included. Analytical errors were computed as the propagation of the uncertainties associated with the nuclear parameters, the efficiency of the gamma-ray detection system, the neutron flux determinations, and the area of the specific emission considered, as well as the sample mass, relevant only for lower masses. Analytical errors differ for each element and sample

analysed, since they depend on the nuclear parameters of each element, on the irradiation conditions, and on the composition of the sample, varying from 5 to 15% in most cases. Certified Reference Materials NIST Buffalo River Sediment and IAEA SL1 Lake Sediment were analysed together with the samples for analytical quality control; the results are reported in table SD1. Measured concentrations coincide with certified values within the uncertainties.

4. Results and discussion

4.1. Morphology

After previous macroscopic description under binocular magnifying glass, morphological analysis was based on SEM images observation (Fig. 2) considering the description of particle shapes, superficial texture and vesicularity.

4.1.1. Cordón Caulle Volcanic Complex

Samples from CCVC showed two different grain sizes, coarse and fine ashes (Fig. 2), with morphological differences associated to the grain size. The sample CC2011-Ba4 collected on June 4th, 2011

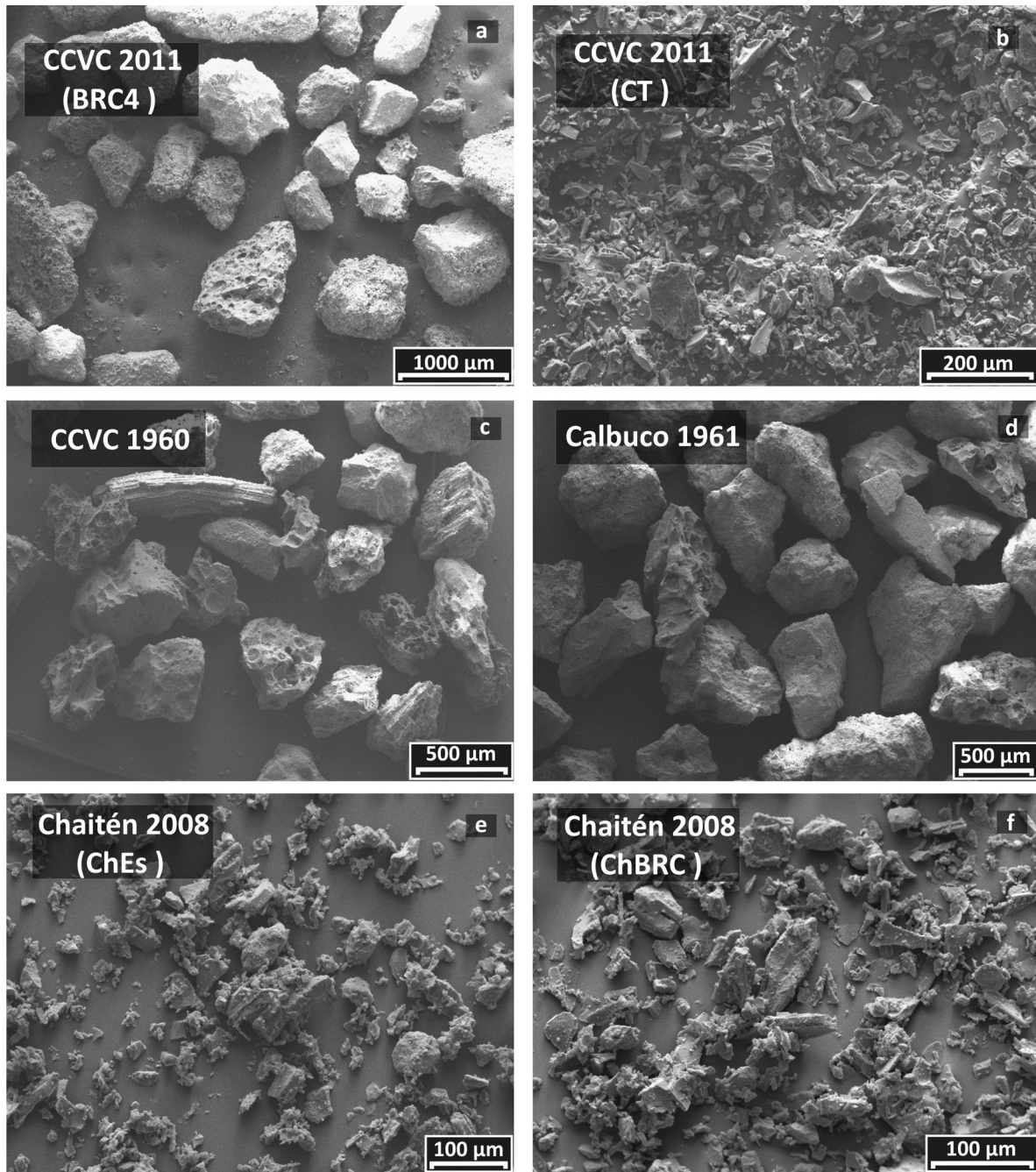


Fig. 2. Scanning Electron Microscopy (SEM) images of the pyroclastic products dispersed by Calbuco and Chaitén volcanoes, and by Cordón Caulle Volcanic Complex.

(Table 1), corresponds to coarse ash (maximum particle size of 1500 μm) and represents the material ejected during the first eruptive phase (Cardona et al., 2012). It was composed predominantly of highly vesicular and fluidal white pumice particles and, in less proportion, of grey and brown pumice fragments, dark scoria, crystals and crystal fragments, and lithics (Fig. 2a). Highly vesicular white pumice vary from irregular or subrounded shapes due to very small spherical to subspherical vesicles separated by thin glass walls, to stretched shapes given by elongated and tubular, sub-parallel vesicles conferring strong fluidal forms; others show distortion of vesicles and highly irregular shapes. Grey and brown pumice are morphologically similar to white pumice while scoria clasts are irregularly shaped, with moderate to low vesicularity, moderate vesicle diameter, thick walls, and glassy to

microcrystalline surface textures. Crystals, mainly pyroxenes and plagioclase, have euhedral shapes and are coated by glassy rims; lithics are irregular blocky shaped. The scarce finer material of this sample corresponds to fine ash composed mainly of colourless curved, Y-shaped, and flat plate glassy shards formed by the fragmentation of larger fragile pumiceous glassy fragments. The same features were observed in sample CC2011-SMA, collected in San Martín de los Andes on June 6th. On the contrary, samples CC2011-Ba6 and CC2011-CT, both also collected on June 6th, 2011 (Table 1) correspond to fine ash, mainly composed of colourless glass shards (platelike, curved, angular Y-shape shards) as remains of wall vesicles rupture, coexisting with scarce coarser and irregular vesicular and fluidal spongy glassy particles, with maximum size of 150 μm (Fig. 2b). Sample CC2011-AC showed the same morphological

features, being sampled on June 5th but in a site located 650 km from the source, suffering a density and grain size fractionation with distance. We can remark from the direct observation and from satellite images of the CCVC 2011 eruption that the coarse ash was dispersed during the first eruptive phase (June 4th and 5th, 2011) in SE direction, reaching as far as 100 km from the source at least, and at the beginning of the second eruptive phase (Cardona et al., 2012) to the NE, in San Martín de los Andes direction (Fig. 1). The material decreased the grain size with the distance, and the finest ashes travelled around the world high in the atmosphere. The plume drifted in the following days generating complex sedimentation patterns with samples of different grain size and morphology corresponding to the same day, or similar features in samples from hundreds of km of distance (Table 1, Fig. 2).

The pyroclastic material recovered from the sedimentary sequence extracted in Brazo Rincón (Fig. 1) from the layer corresponding to the CCVC 1960 eruption, (sample CC1960-BR, Table 1; BR1 glass shards in Daga et al., 2006) is granulometrically and morphologically similar to CC2011-Ba4, corresponding to coarse

ash composed mainly of highly vesicular white pumice and less amounts of brown pumice particles, scoria fragments, crystals and lithics (Fig. 2c), with a small population of fine ash (mainly glass shards). All components have the same morphological features as coarse ash from CCVC 2011 eruption products. The material recovered from the sedimentary sequence was accumulated after sedimentation at the lake bottom, whereby the particles fell through the water column after floating for unknown periods of time, involving differential settling not actually representing the eruptive sequence.

4.1.2. Chaitén volcano

Although Chaitén 2008 tephra deposits vary from layers of lapilli and blocks (juvenile and lithic material) to extremely fine-grained ash in the proximal-medial areas from the volcano (Alfano et al., 2011), the longer distance dispersed material were fine ashes dominated by colourless glass shards with platelike, curved, and blocky shapes, with little participation of whitish spongy coarser glassy fragments with a maximum size of 150 μm (Fig. 2e and f). Samples collected in Esquel and San Carlos de Bariloche (Ch2008-Es and Ch2008-Ba; Table 1) have similar grain size and particle characteristics (Fig. 2e and f), and also similar composition (Table 2b). These samples were collected in sites located at 100 and 220 km from the volcano (Fig. 1), with a 6-day time interval, corresponding to different eruptive phases, with no distance effects in the morphology or in the composition. Ruggieri et al. (2011) associated the fine particles sampled on May 3rd with the distance to the source and the plinian eruption, but grain size studies showed mean fine particle size up to 530 km from the volcano during the May 2nd to 5th phase, while during the May 6th to 7th phase the deposit was coarser close to the volcano with decreasing grain size with distance (Durant et al., 2012). This supports the observation of similar grain size in samples from May 2nd from Esquel city and ashes fallen in Bariloche on May 8th. The great power involved in the explosion of a plinian eruption is capable of generating the high fragmentation and the long distance direct dispersion observed, generating also complex distribution patterns mainly in volcano proximity according to grain size and morphology.

4.1.3. Calbuco volcano

This coarse ash (sample Ca1961) is composed mainly of brown glass shards, dark scoriaceous fragments and, in less proportion, white pumice and blocky lithic fragments (Fig. 2d). The juvenile glassy particles mainly correspond to highly irregular shapes with high vesicularity degree and vesicles varying from spherical to elongated, coalescent in some cases; vesicles are observed partially in the external surface whereas part of the fragments exposed a smooth, fluid-form glassy surface; in some cases, only the smooth curved surface is observed. Less amount of blocky glassy shards are observed, with irregular and curvilinear fracture surfaces in some cases. The scoriaceous fragments have irregular to subrounded shapes, high vesicularity and mainly small subspherical bubbles with moderate to thick glass walls. Pumice particles are highly vesicular fragments with small bubbles and thin glass walls varying from subspherical to elongate in shapes, giving irregular and stretched particle shapes, respectively. This tephra sample, as well as CC1960-BR, was recovered from a sedimentary sequence not allowing to obtain further information about the eruptive sequence.

4.2. Mineralogy

The mineral assemblage of a tephra could be used as a correlation parameter when it is distinctive or unusual (Westgate

Table 2b

Elemental composition and geological parameters of the volcanic ashes (glassy fraction). Volcano Calbuco 1961 and Chaitén 2008.

	Volcano Calbuco 1961	Volcano Chaitén 2008	
	Ca1961 ^a	Ch2008-Es ^b	Ch2008-Ba ^b
Al (wt%)	8.67 ± 0.37	7.45 ± 0.28	7.41 ± 0.29
Ca (wt%)	6.42 ± 0.59	1.06 ± 0.18	1.31 ± 0.21
Cl (wt%)	–	0.103 ± 0.020	0.112 ± 0.022
Fe (wt%)	8.09 ± 0.57	1.059 ± 0.059	1.053 ± 0.060
K (wt%)	0.52 ± 0.12	2.54 ± 0.13	2.63 ± 0.20
Mg (wt%)	3.37 ± 0.33	<1	<1
Mn ($\mu\text{g g}^{-1}$)	1539 ± 52	440 ± 14	443 ± 14
Na (wt%)	2.609 ± 0.098	3.16 ± 0.13	3.15 ± 0.13
Ti (wt%)	0.777 ± 0.093	0.108 ± 0.038	<0.2
As ($\mu\text{g g}^{-1}$)	5.67 ± 0.71	13.17 ± 0.86	11.03 ± 0.74
Ba ($\mu\text{g g}^{-1}$)	181 ± 33	750 ± 63	751 ± 64
Br ($\mu\text{g g}^{-1}$)	1.04 ± 0.39	1.61 ± 0.15	1.59 ± 0.22
Co ($\mu\text{g g}^{-1}$)	38.0 ± 2.0	1.410 ± 0.050	1.470 ± 0.056
Cr ($\mu\text{g g}^{-1}$)	110.2 ± 8.4	0.72 ± 0.29	<1
Cs ($\mu\text{g g}^{-1}$)	1.27 ± 0.16	8.07 ± 0.47	8.07 ± 0.48
Hf ($\mu\text{g g}^{-1}$)	2.21 ± 0.21	3.81 ± 0.17	3.77 ± 0.19
Rb ($\mu\text{g g}^{-1}$)	20.0 ± 4.4	123.3 ± 7.0	123.5 ± 7.3
Sb ($\mu\text{g g}^{-1}$)	0.335 ± 0.090	0.949 ± 0.089	0.893 ± 0.087
Sc ($\mu\text{g g}^{-1}$)	39.4 ± 2.0	2.491 ± 0.070	2.460 ± 0.073
Sr ($\mu\text{g g}^{-1}$)	406 ± 80	180 ± 25	179 ± 24
Ta ($\mu\text{g g}^{-1}$)	0.158 ± 0.030	0.870 ± 0.056	0.861 ± 0.056
Th ($\mu\text{g g}^{-1}$)	1.19 ± 0.11	13.52 ± 0.72	13.52 ± 0.78
U ($\mu\text{g g}^{-1}$)	0.333 ± 0.083	3.85 ± 0.36	4.15 ± 0.39
V ($\mu\text{g g}^{-1}$)	351 ± 21	3.8 ± 2.1	4.6 ± 2.1
Zn ($\mu\text{g g}^{-1}$)	129 ± 10	45.7 ± 2.8	41.1 ± 2.5
Zr ($\mu\text{g g}^{-1}$)	154 ± 57	181 ± 15	186 ± 15
La ($\mu\text{g g}^{-1}$)	7.01 ± 0.37	29.00 ± 0.77	29.09 ± 0.79
Ce ($\mu\text{g g}^{-1}$)	18.4 ± 1.6	56.1 ± 3.1	56.6 ± 3.4
Nd ($\mu\text{g g}^{-1}$)	13.0 ± 1.6	16.6 ± 2.2	17.9 ± 2.0
Sm ($\mu\text{g g}^{-1}$)	3.56 ± 0.34	3.01 ± 0.21	3.07 ± 0.22
Eu ($\mu\text{g g}^{-1}$)	1.099 ± 0.071	0.581 ± 0.023	0.576 ± 0.024
Tb ($\mu\text{g g}^{-1}$)	0.73 ± 0.11	0.356 ± 0.024	0.357 ± 0.022
Dy ($\mu\text{g g}^{-1}$)	4.60 ± 0.54	1.88 ± 0.23	1.66 ± 0.27
Yb ($\mu\text{g g}^{-1}$)	2.38 ± 0.21	1.56 ± 0.13	1.55 ± 0.13
Lu ($\mu\text{g g}^{-1}$)	0.301 ± 0.029	0.171 ± 0.012	0.161 ± 0.012
Eu anomaly ^c	0.867	0.651	0.636
La _N /Sm _N ^d	1.24	6.06	5.96
La _N /Lu _N ^d	2.42	17.6	18.8

^a Volcanic ash preserved in lacustrine sedimentary sequences samples.

^b Volcanic ash samples collected after the event from direct fallout, composed of glass shards.

^c Normalized to Chondrite (Boynton, 1984); formula for calculation in Daga et al., (2008).

^d Normalized to Chondrite (Boynton, 1984).

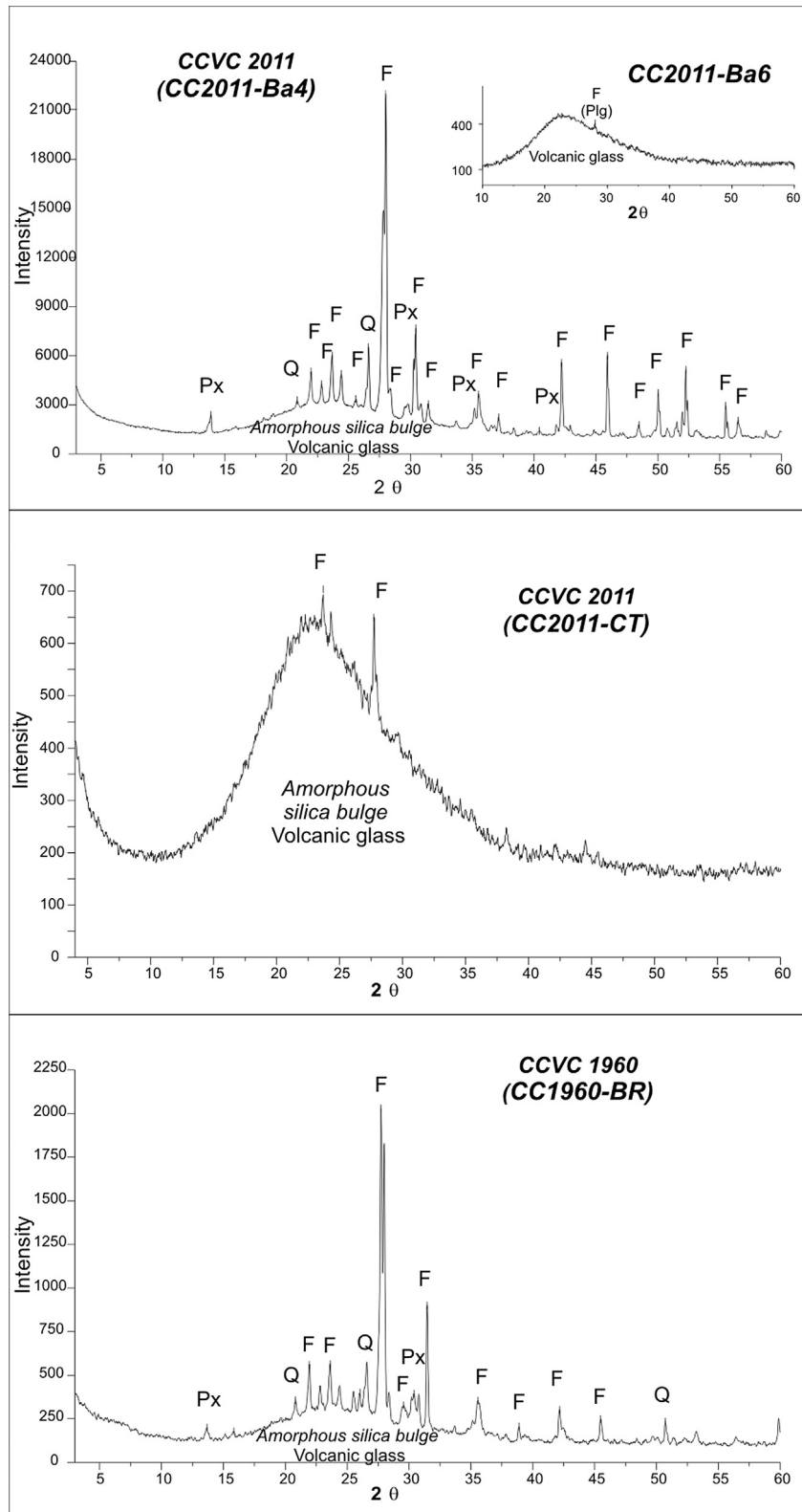


Fig. 3. Whole rock X-ray diffraction patterns of the pyroclastic products dispersed by Cordón Caulle Volcanic Complex, 1960 and 2011 eruptions. F: feldspar (mainly plagioclase feldspar); Px: pyroxene; Q: quartz.

and Gorton, 1981; Lowe, 2011). The mineralogical characterization is also relevant to assess the risk to human health of the volcanic ashes dispersed, given that it is proved that some minerals are harmful when breathing (e.g. cristobalite;

Horwell et al., 2010). Figs. 3 and 4 show the most representative whole rock diffraction patterns for bulk samples of the tephra studied, allowing a qualitative mineralogical characterization.

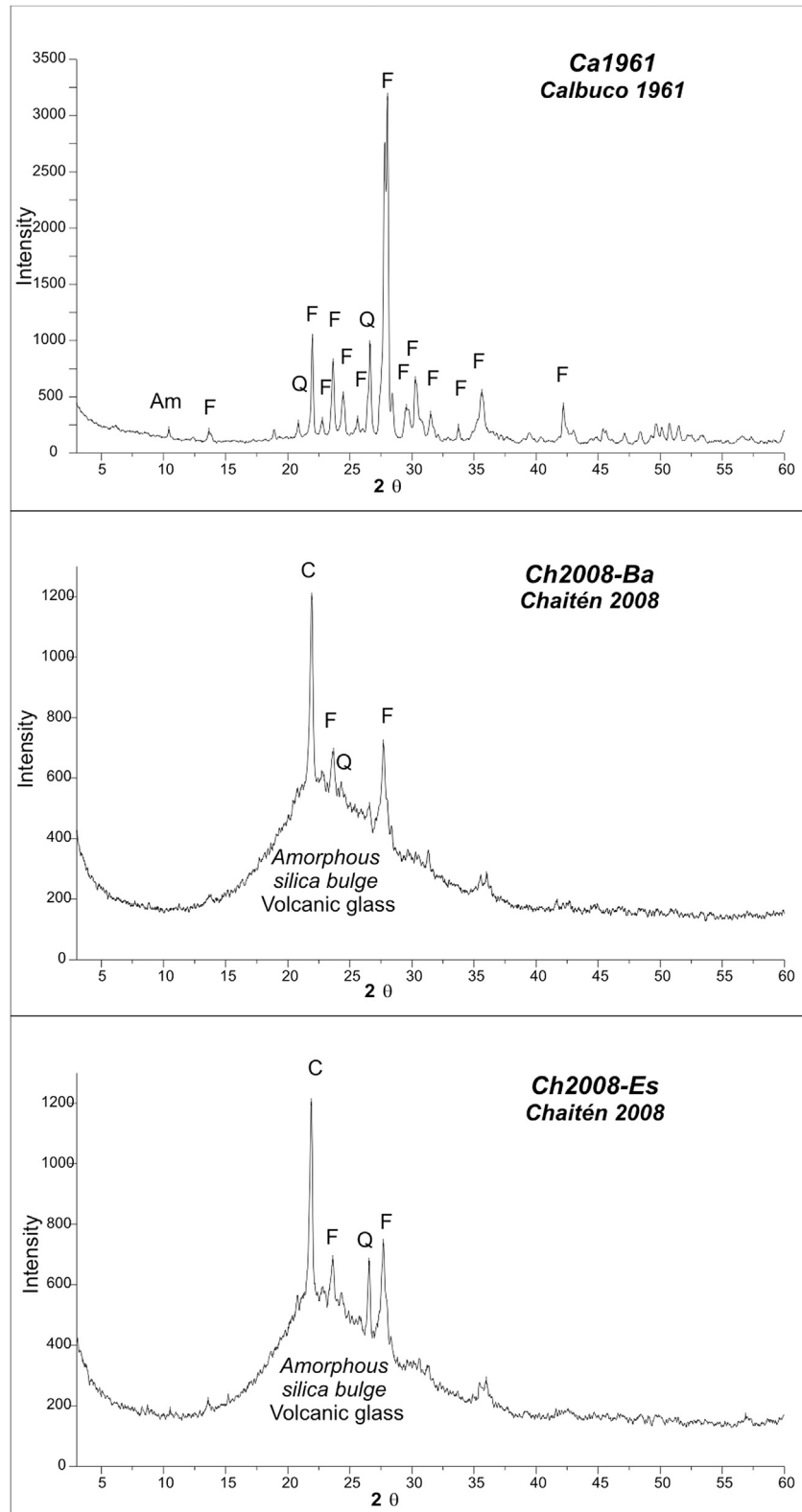


Fig. 4. Whole rock X-ray diffraction patterns of the pyroclastic products dispersed by volcano Calbuco 1961 and volcano Chaitén 2008 eruptions. Am: amphibol; C: cristobalite; F: feldspar (mainly plagioclase feldspar); Q: quartz.

4.2.1. Cordón Caulle Volcanic Complex

Coarse fallout ashes from 1960 and 2011 CCVC eruptions show similar mineralogy (CC2011-Ba4 and CC1960-BR in Fig. 3), with

identification of volcanic glass and mineral phases as plagioclase feldspar, pyroxene and quartz (Fig. 3); Fe–Ti oxides and apatite as accessory minerals were also identified under petrographic

microscope. A similar mineralogy was reported for previous CCVC eruptions (Gerlach et al., 1988); quartz was not reported for recent eruptive products, and could correspond here to the lithic fraction. The finer ash from CCVC 2011 eruption (<63 μm), used for geochemical characterization, is mainly composed of volcanic glass (similar to CC2011-Ba6 and CC2011-CT in Fig. 3).

4.2.2. Chaitén volcano

These ashes showed higher abundance of volcanic glass over the mineral phases, represented by cristobalite, plagioclase feldspar and quartz (Fig. 4). The <63 μm fraction, used for geochemical characterization, is composed mainly of volcanic glass. Cristobalite determinations, relevant due to the potential impact on human health, coincide with previous reports (Reich et al., 2009; Horwell et al., 2010).

4.2.3. Calbuco volcano

Even though the glassy fraction was identified, this tephra showed scarce volcanic glass compared with the mineral phases (Fig. 4). The crystal phases are represented by plagioclase feldspar, pyroxene, amphibole, and quartz, similar to the mineralogy reported by López-Escobar et al. (1995). In this case, glass shards isolated under microscope were used for the geochemical characterization for consistency in the type of material used to compare with the products of the other volcanoes.

4.3. Geochemical characterization

The vitric fraction geochemical composition of the products dispersed by the three volcanoes considered is presented in Tables 2a and b for comparison of the different tephra provenance. The fractionation degree of a light REE (LREE; La) to a middle REE (MREE; Sm), and to a heavy REE (HREE; Lu), normalized to chondrite (Boynton, 1984), and the Eu anomaly are also reported in Tables 2a and b because these parameters are analysed to identify the tephra source. REE Chondrite-normalized patterns (Boynton, 1984) and the multi-element diagram (normalized to primitive mantle of Wood et al., 1979) are shown in Figs. 5 and 6 respectively

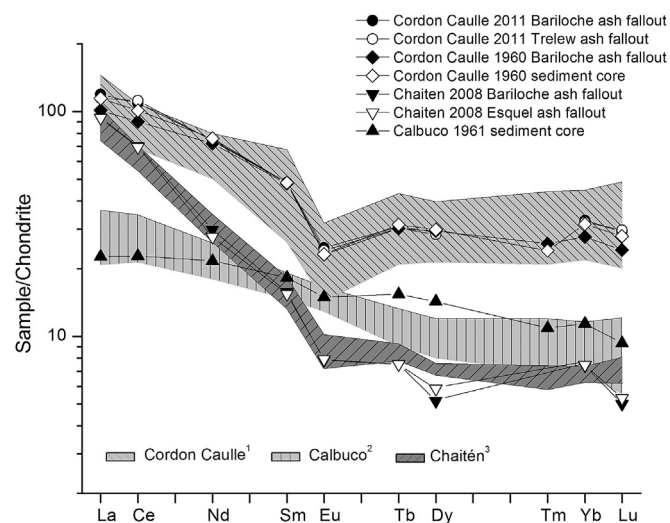


Fig. 5. Rare earth elements diagram of the glassy pyroclastic products dispersed by Calbuco and Chaitén volcanoes, and by Cordon Cauille Volcanic Complex. Elemental concentrations of glassy components normalized to Chondrite values of Boynton (1984). In shadow, the bulk rock composition corresponding to older and under study events reported in the literature: (1) Gerlach et al., 1988; (2) López-Escobar et al., 1995; (3) Naranjo and Stern, 2004; (3) Stern et al., 2008; (3) Ruggieri et al., 2011; (3) Amigo et al., 2013.

(shadow areas represent data reported in the literature for whole rock samples from previous and currently under study eruptions, showing good agreement with the results obtained in this work).

Chaitén volcano glassy products showed the highest $\text{LREE}_N/\text{MREE}_N$ (6.0–6.1) and $\text{LREE}_N/\text{HREE}_N$ ratios (17.6–18.8), and the most depleted HREE pattern; CCVC glassy products are the most enriched in LREE, MREE, and HREE, with low LREE/HREE ratios (3.7–4.2). On the other hand, Calbuco glassy products are the most depleted in LREE but more enriched in HREE than Chaitén's, resulting in the lowest LREE/HREE ratio (2.4). Normalized LREE/MREE and LREE/HREE ratios show similar values for CCVC 1960 and 2011 events (Fig. 5; Table 2a), supporting that both represent CCVC source. The glassy products of the three volcanoes have negative Eu anomaly (computed as in Daga et al., 2008), larger in CCVC, slightly lower for Chaitén volcano, and closer to the unit for Calbuco (Tables 2a and b), associated with different degrees of plagioclase fractionation.

The normalized to primitive mantle patterns (Fig. 6) with elements ordered with increasing incompatibility from right to left, result in a distinctive pattern for all subduction-related magmas (Wilson, 1989). The glassy products show an enrichment of Large Ion Lithophile Elements (LILE) (e.g. Rb, Ba, K, Zr, and Th and LREE) for the three volcanoes, with low abundances of High Field Strength Elements (HFSE), Ta and Ti, and HREE, relative to primitive mantle (Fig. 6).

The variations in REE and spider patterns slopes (Figs. 5 and 6; Tables 2a and b) clearly distinguish the three different arc volcanic sources, consistent with non-related suites of volcanic rocks, resulting in normalized abundances increasing in different degree (Wilson, 1989). The patterns are similar for CCVC 1960 and 2011 events representing the same volcanic provenance.

Between the most incompatible elements, Rb, Cs, Th, and Ta concentrations allow the discrimination of the tephra undoubtedly dispersed during the eruptions described, with increasing values associated to the differentiation degree, with lower values for Calbuco volcano, intermediate for CCVC, and higher for Chaitén products (Tables 2a and b). Less incompatible elements Zr, Hf, and Ti also allow the distinction of the three volcanoes in the tephra geochemical signature, but showing the opposite trend for Ti, and intermediate concentrations for Zr and Hf in Chaitén volcano (Tables 2a and b).

The concentration of compatible transitional metals Co, Cr, Sc, and V also allow the discrimination of the tephra, with the opposite trend respect to the incompatible elements described above, according with the evolution degree of each volcano and consistent with the expected fractionation trends. The lowest concentrations were observed in Chaitén ashes, slightly higher values in CCVC products (although significant concentration differences can be observed among sampling sites and events), and concentrations increased 25 \times to over 100 \times in Calbuco glasses (Tables 2a and b).

4.4. Environmental implications

Explosive volcanic eruptions impact the environment in different time and spatial scales, being a source of elemental pollutants. The immediate effects can be observed in air, water, and biota in the proximity of the source (Cronin et al., 1998; Dongarrà and Varrica, 1998; Delmelle, 2003; Stewart et al., 2006; Jones and Gislason, 2008; Wilson et al., 2010). After the impact of the initial fallout, the prolonged exposure of the pyroclastic products to weathering may cause the slow release of pollutants from the structure of constituent mineral phases and glassy matrix to soils and waters (Queirolo et al., 2000; Robinson et al., 2006; Martin et al., 2009; Nicolli et al., 2010; Ruggieri et al., 2011). Earlier

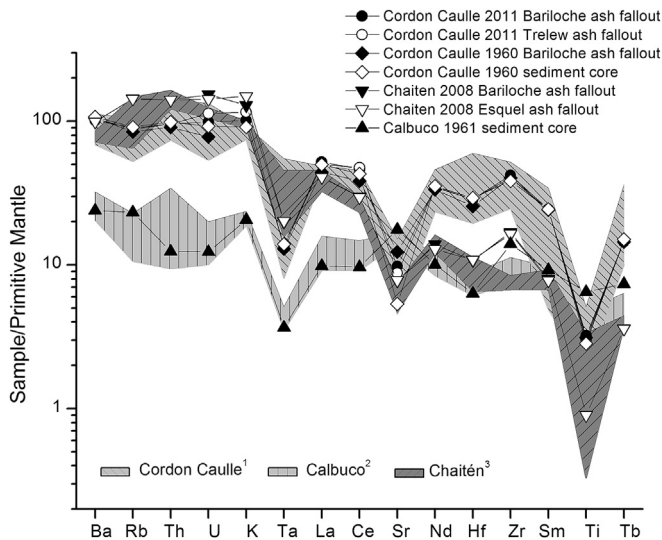


Fig. 6. Incompatible elements diagram of the glassy pyroclastic products dispersed by Calbuco and Chaitén volcanoes, and by Córdón Cauille Volcanic Complex. Elemental concentrations of glassy components normalized to primitive mantle values of Wood et al. (1979). In shadow, the bulk rock composition corresponding to older and under study events reported in the literature: ⁽¹⁾Gerlach et al., 1988; ⁽²⁾López-Escobar et al., 1995; ⁽³⁾Naranjo and Stern, 2004; ⁽³⁾Stern et al., 2008; ⁽³⁾Ruggieri et al., 2011; ⁽³⁾Amigo et al., 2013.

effects in recent Calbuco and CCVC eruptions, associated with gas emissions and the direct impact of particulate dispersed in air, could not be evaluated due to the lack of complete monitoring setup, while in Chaitén 2008 event early detection of environmental changes in the concentration of some elements were recorded (Martin et al., 2009; Durant et al., 2012). Ash fallout affected mainly Argentinean territory, and particularly for Chaitén volcano 2008 and CCVC 2011 events, the dispersion plumes had a main axis NW–SE, reaching the Atlantic coast in both cases, and even farther (Fig. 1), covering areas with contrasting environmental conditions.

The concentration of potential pollutants elements determined in glassy products from recent Calbuco, Chaitén and CCVC eruptions, namely Al, As, Ba, Br, Ca, Co, Cr, Cs, Fe, K, Mn, Mo, Na, Sb, Sc, Sr, Th, Ti, U, V, and Zn are reported (Tables 2a and b). Particular attention should be given to the semi-volatile As, Br, and Sb, which can be associated considering their affinity of fluid or gas phases, or forming sulphate and/or halide volatile compounds at magmatic temperatures (White, 2013; Moune et al., 2006), being adsorbed onto ash particles (Delmelle et al., 2007; Ruggieri et al., 2011). Bioindication of air pollution during CCVC 2011 eruption showed evidence of As, Br, and Sb gaseous releases (Bubach et al., 2012). These elements, especially As, are potential toxic trace elements for the environment (Stewart et al., 2006). The evaluation of the long term environmental impact of dispersed tephra can be assessed by leaching tests, but only Chaitén 2008 products were studied (Martin et al., 2009; Ruggieri et al., 2011, 2012; Durant et al., 2012). They found several trace elements with significant load in water batch leaching tests, including As, Ba, Co, Cr, Fe, Mn, Rb, Sb, Sr, Ti, and Zn, some of them potentially toxic in drinking waters (Ruggieri et al., 2011). Ruggieri et al. (2012) demonstrated that the main environmental impact of Chaitén volcano 2008 ashes was the elemental pollutants released from particle surface during the initial exposure in water bodies, whereas leaching associated with weathering processes and glass dissolution occurs in lower rates. Arsenic was found between the most mobile elements in leaching tests in Chaitén volcano 2008 ashes, releasing $\sim 6.59 \cdot 10^5$ kg to the environment in the first ash–water interaction (Ruggieri et al.,

2012). The mass of dispersed pyroclastic materials was estimated in $4.9 \cdot 10^{11}$ kg (Alfano et al., 2011). Considering the concentrations determined in the present work (Tables 2a and b), the estimated amount of semi-volatile pollutants dispersed by the Chaitén 2008 eruption in Argentinean territory mainly, were: $6 \cdot 10^6$ kg of As, $5 \cdot 10^5$ kg of Sb, and $8 \cdot 10^5$ kg of Br. Therefore, As released in the first ash–water interaction was 11% approximately of the total As dispersed.

4.5. Implications for tephrochronology

Basic background for tephrochronology is a detailed and accurate characterization of the tephra layer to be found in terrestrial settings or in lacustrine sequences, allowing the correlation with a particular tephra provenance, or with another dated tephra. Geochemical characterization is generally the main tool for source identification, particularly in ancient sequences where ashes primary features could not be well preserved, or sedimentation and after deposition processes exert their influence on the pyroclastic material. Therefore, the geochemical information obtained from volcanic ash samples from direct fallout or from lake deposits, both with clear dispersion source correlation, allows a precise characterization of the tephra provenance in this region, improving the tephrochronological framework in the Patagonia Andean Range, where this data is scarce.

The geochemical parameters normalized LREE/MREE and LREE/HREE ratios, and the Eu anomaly, and the concentration of the compatible elements Sc, Ta and Th, and the incompatible Cs and Rb (Tables 2a and b), are the clearest fingerprint of each source, Calbuco, Chaitén and CCVC, allowing the discrimination of the tephra provenance. As well, the normalized REE and incompatible element patterns (Figs. 5 and 6) are also characteristic features for the three volcanoes, as expected, due to the different petrogenetic evolution. The relatively flat REE pattern of the Calbuco volcano is in agreement with the more basic composition, corresponding to the less evolved magmatic system, while the steep slope of REE pattern of Chaitén volcano represents the most evolved rhyolitic magmatic complex from the three systems (López-Escobar et al., 1993; Naranjo and Stern, 2004; Muñoz et al., 2008; Amigo et al., 2013). New data from eruptions previous to Chaitén 2008 event demonstrate a remarkable homogenous geochemical composition for at least four events during the Holocene (Amigo et al., 2013; Lara et al., 2013; Watt et al., 2013), transforming these products also in valuable deposits for correlation purposes. The CCVC showed the highest REE contents but a lower LREE/HREE ratio than Chaitén, responding to the less fractionation degree from a less evolved dacitic–rhyodacitic composition (Gerlach et al., 1988; Singer et al., 2008; Castro et al., 2013) than Chaitén. Even Puyehue-CCVC shows a wider rock suite, with basaltic to rhyolitic products erupted since Late Pleistocene, the most recent eruptions correspond to Córdón Cauille rhyodacites to rhyolites (Gerlach et al., 1988). Ashes from 1960 and 2011 eruptions correspond to such silicic products, showing more evolved magmas relative to volcano Calbuco products, both in the central SVZ.

The geochemistry of the glassy fraction proved to be the best correlation data for tephrochronological purposes, whereas the morphological observations and the qualitative mineralogy of the tephra analysed contribute to the distinction between the dispersion sources and also between different eruptive moments. Coarse ashes from both CCVC events (CC2011-Ba4 and CC1960-BR, Table 1) showed the same components, with highly vesicular pumice, relatively high contents of euhedral to subhedral crystalline phases (plagioclase feldspar, pyroxene, Fe–Ti oxides and apatite as accessory phases), and scarce fine grain-sized glassy particles (Fig. 2a and c). For the 2011 eruption, where it was

possible to compare different eruptive moments at the same location, the coarse described ashes from the first explosive phase contrasted with the finer grain-sized ashes poor in free crystal phases ejected after this initial phase. Highly irregular platelike and Y-shape glass shards prevailed in this fine material (Fig. 2b), showing the continuity of the eruption explosiveness, but with mineral phases only as very fine crystal size or microcrystals within the predominant glassy matrix (Fig. 3, samples CC2011-Ba4 and CC2011-Ba6). On the other hand, mineralogy showed the typical density fractionation with the distance to the volcanic centre, observed in tephra samples collected at different locations after deposition from the volcanic cloud moving NW to SE. This is the case of crystal rich sample CC2011-Ba4 compared with glassy rich sample CC2011-AC (Fig. 3).

In spite of the whole rock mineralogical differentiation, the geochemistry of the glassy fraction showed agreement for the same explosive phase. Sample CC2011-Ba4, collected within 5 h after the initial explosion, and sample CC2011-AC, collected on June 5th –and corresponding to the same plume after travelling 630 km from the source–, showed higher Co, Cr, Fe, Sc and V concentrations when compared with samples CC2011-Ba6, CC2011-SMA and CC2011-CT, dispersed during the second eruptive phase (Table 1). Also, variations in Cr and V concentrations were observed in previous works on CCVC 1960 materials (Daga et al., 2006). The Co, Cr, Fe, Sc and V concentration of CCVC 1960 glassy products (samples CC1960-Ba and CC1960-BR) coincide with the concentration of the 2011 products ejected in the second eruptive phase (samples CC2011-Ba6, CC2011-SMA and CC2011-CT; Table 2a). The eruptive pulses following the initial one did not show relevant fractionation in the fine particulate with the distance. Recent studies on CCVC 1960 tephra showed that slight compositional variations are associated with differences in type and amount of phenocrystals and micro-lites within the glass matrix (Daga et al., 2012). It is to remark that the geochemical information regarding compatible elements should be considered carefully for a tephrochronological framework due to the variability in the concentrations associated with the eruptive sequence.

Calbuco tephra is characterized by the morphological features of the glassy particles, mainly due to the smooth fluid-form glassy surfaces in the glass particles, together with poorly vesicular irregular blocky glassy fragments. This feature has been associated with explosive eruptions with magma/water interactions (Wohletz, 1983), and can be considered a characteristic type of particles of the 1961 Calbuco eruption provenance comparing with CCVC and Chaitén volcano products.

Regarding morphology and grain size, and mainly mineralogy, Chaitén 2008 ashes have distinctive features. Fallout ashes recovered at 100 and 250 km from the source showed very fine grain-sized glassy shards, with no relevant fractionation with the distance (also observed in the elemental composition; Table 2b). This is in agreement with the reported mean particle size remarkably consistent and invariable beyond 100 km from the volcano (Durant et al., 2012), reflecting several phases of an explosive plinian rhyolitic eruption with generation of fine ashes. This seems to be a characteristic feature, but morphologically these fine ashes are not easily distinguished from CCVC distal products. Cristobalite, determined also in previous works, is the most characteristic, and a not common, mineral phase of this volcano, which was determined ranging from 2 wt % (during plinian phase) to 13–19 wt % (during dome growth) (Horwell et al., 2010).

4.6. Concluding remarks

Argentinean territory has received the impact of, at least, 60 active volcanic centres from the SVZ in historical times. The

dominant westerlies at these latitudes and the high eruptive frequency make crucial the accurate geochemical characterization of each tephra deposits for a consistent association with the volcanic provenance, regarding a tephrochronological framework. The available information about the volcanoes in the SVZ is focused on studies about evolution and petrology of the most important volcanic complexes, but both close and distal tephra characterization is limited in this zone, although increasing research was observed in recent years. Furthermore, the historical volcanic eruptions are not well known, and written records are available only since the middle of 16th century. Particularly, Chaitén volcano eruptive record was poor until field works carried out after the 2008 eruption. The geochemical and mineralogical characteristics of the products dispersed by the Chaitén 2008 eruption is unique for this source compared with neighbour volcanoes, turning therefore this tephra into a useful time marker layer to be identified across large distances and over a wide range of depositional environments, together with the recently identified eruptions from Chaitén during the Holocene.

The latitudes spanned by the tephra sources considered here, 40°30'S–42°50'S, correspond to the limit between the Central and Southern Volcanic Zones. This region is characterized by a greater abundance of basic volcanic rocks (basalts and basaltic andesites), although silicic rocks (including rhyolites) occur at several volcanoes (Hickey et al., 1984). Southern to 41°30' on the SVZ, rhyolites occur only at Chaitén volcano (López-Escobar et al., 1993). Thus the compositional diversity of the three tephtras analysed here turn the ancient and recent deposits of these volcanoes into valuable chronostratigraphic markers with wide geographical dispersion, mainly for the more evolved magmatic systems Chaitén and CCVC. Given the Calbuco volcano characteristics, a less silicic magmatic system than CCVC and Chaitén, a smaller areal dispersion of its tephtras is expected, but with influence in both Chilean and Argentinean territory. These aspects confirm the importance of the tephrochronology as a tool for dating and for correlation purposes, and emphasizes the need to develop more related works, particularly for recent times where other dating methods showed limited results.

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