Contribution of volcanic ashes to the regional geochemical balance: the 2008 eruption of Chaitén volcano, Southern Chile

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Abstract

The environmental geochemical behaviour of the rhyolitic ashes from the 2008 eruption of Chaitén volcano, Southern Chile, has been studied. After the bulk characterisation, the potential contribution to the regional geochemical fluxes was examined using: i) single batch leaching tests to provide a rapid screening of the implied major and trace elements; and ii) column experiments to evaluate the temporal mobility of leached elements. The environmental concerns of these ashes are related to the fine grained component present in each sample (independent of distance from the source), in particular the presence of cristobalite, and the geochemical hazards posed by ash-water interaction. Leaching experiments show the fast dissolution of surface salts and aerosols, which dominates over glass dissolution during the first steps of the ash-water interaction. Chaitén ashes could transfer to the environment more

than 1×10^{10} g or 10,000 metric tonnes (mt) of Cl, S, Ca, Na, Si, and K; between 1,000 and 10,000 mt of F, Mg, and Al; between 100 and 1,000 mt of As, Pb, P, Fe, Sr, Zn, Mn, and Br; between 10 and 100 mt of Ba, Li, Ti, Ni, Nb, Cu, Rb, Zr, V, Mo, Co, and Sc; and less than 10 mt of Cr, Sb, Ce, Ga, Cs, and Y. These results show the fertilizing potential of the ashes (e.g., providing Ca and Fe) but also the input of potentially toxic trace elements (e.g., F and As) in the regional geochemical mass balance. The Chaitén results evidence lower potentials for poisoning and fertilizing than low silica ashes due to the lower contents released of practically all elements.

Keywords: volcanic ash, batch leaching, column leaching, trace elements, Chaitén.

1. Introduction

During an explosive eruption, as the Chaitén volcano in 2008 in Chile, pyroclastic materials and gases are expelled from a volcanic vent into the atmosphere, which can form a plume up to several kilometres of altitude. A volcanic plume is a heterogeneous environment in which gases (principally water, carbon dioxide, sulphur dioxide, hydrogen, hydrogen sulphide, carbon monoxide and hydrogen chloride), aerosols and silicate ash particles coexist and interact in several ways (Delmelle et al., 2007). In this environment, ash particles act as adsorption sites for co-erupted condensing magmatic volatiles (Allard et al., 2000; Witham et al., 2005). As result, volcanic ash is composed of fine grained rock, mineral fragments and glass shards, with acids, salts and adsorbed gases coating particulate surfaces, with many being highly soluble and easily leachable (Frogner et al., 2001; Witham et al., 2005). There are a lot of factors controlling the adsorption and deposition of volatile compounds onto

tephra and its later release when interact with water, but the main factor is likely the volatility of elements at magmatic conditions (Aiuppa et al., 2008; Armienta et al., 2002; Obenholzner et al., 2003). These highly mobile compounds are one of the most important concerns of ash fall because some of them have an elevated potential toxicity (Jones and Gislason, 2008).

After deposition, the adsorbed compounds on ash can disperse into the environment. The dispersal rate depends on the nature of association of the compounds with the ash, but also the substrate where the ash is deposited, e.g., deposition straight onto a water body will have a much faster impact than deposition onto a previous layer of ash (Witham et al., 2005). Interaction of tephra with water dissolves soluble accumulations on particle surfaces resulting in changes of local water chemistry and, hence, quality (Jones and Gislason, 2008; Stewart et al., 2006; Witham et al., 2005). On the other hand, deposition of volcanic ash may provide an external nutrient source for primary production in ocean surface waters, in particular through iron fertilisation (Duggen et al., 2010).

Rhyolitic eruptions are relatively rare and the 2008 eruption of Chaitén volcano provides an opportunity to assess the environmental concerns related to the geochemistry of rhyolitic ash. After bulk characterisation of the Chaitén ashes, the aims of this paper are: firstly provide useful information on the implied potential toxic trace elements (PTTEs) during ash-water interaction through a rapid screening by single batch leaching tests (SBLTs); secondly, to evaluate this release as a function of time, giving information on the potential mobility of the leached compounds using a column leaching test; and thirdly

estimate the environmentally available fraction of major and trace elements of the Chaitén eruption.

2. Eruption of Chaitén volcano

The Chaitén volcano (42° 50' 21.94" S 72° 39' 5.38" W; 962 m a.s.l.) is a small elliptical (3x4 km in diameter) post-glacial caldera, located 10 km northeast of Chaitén town in the Gulf of Corcovado, in southern Chile. It is situated in the Southern Volcanic Zone (SVZ: 33–56° S) of the Andes which includes at least 60 historically and potentially active volcanic centres in Chile and Argentina (Naranjo and Stern, 2004; Stern, 2004) (Fig. 1).

The first historical eruption of Chaitén began on May 2008 (Lara, 2009) being the most explosive one in the Andes since Hudson, Chile, in 1991, and the first explosive rhyolitic eruption since Novarupta, Alaska, in 1912 (Watt et al., 2009). The Chaitén volcano activity started with a Plinian phase producing a 13-16 km high plume, followed by an extrusion of a lava dome (Alfano et al., 2011; Castro and Dingwell, 2009; Lara, 2009; Watt et al., 2009). The Plinian eruptive phase was preceded by several volcanotectonic seismic events. The dispersal of tephra during the first week of the eruption affected a vast continental region (with ash deposited over an area of $>2 \times 10^5 \text{ km}^2$), from Chile to the Atlantic coast of Argentina (~600 km from the source) (Folch et al., 2008; Watt et al., 2009). The paroxysmal phase occurred on May 6th (VEI 4 – Magnitude 4.5) when the plume came to 19 km altitude (Alfano et al., 2011), detected by satellite AIRS imagery near South Africa (Gangale et al., 2010).

The total ash deposit volume was estimated in 0.5-1.5 km³ (May 2008-January 2009 (Alfano et al., 2011). The eruption caused the evacuation of more

than five thousand people from a 70 km radius area (town of Chaitén and Futaleufú village), and disrupted water supplies and storm water, sewerage systems, agriculture, tourism, aviation and human and animal health in proximal and distal areas (Alfano et al., 2011; Carn et al., 2009; Martin et al., 2009; Watt et al., 2009).

3. Materials and methods

3.1 Sampling

Four volcanic ashes were sampled during the 2008 eruption of the Chaitén volcano in different sites of the affected zone following the recommended procedures (IVHHN, 2012; Witham et al., 2005). Table 1 and Figure 1 show the location and details. Samples were collected by a plastic shovel. Fieldwork was conducted during the first phase of the eruption in the case of CHA-G, CHA-E, and CHA-1F samples. CHA-1F ash was collected on a plastic surface in the main square of Chaitén village (10 km southeast from the vent). The CHA-G and CHA-E samples were collected in Esquel village (106 km west from the vent). The former correspond to a very pristine ash sampled over a vehicle during the first tephra fall out, while CHA-E was sampled on a building surface. Finally, CHA-2R was sampled on the ground at 60 km from the vent. It was not pristine because was affected by rainwater. Samples were collected and transported to the laboratory in polyethylene bags. They were dried in an oven at 40 °C and stored in polyethylene containers.

3.2 SEM-EDX and XRD analyses

Ash samples were mounted on carbon stubs and coated with carbon before the study in a FEI Quanta 200 ESEM FEG scanning electron microscope (SEM) equipped with an Energy Dispersive X-Ray (EDX) system for semi-quantitative chemical analysis (minimum spot size, 5 μm ; working distance, 10 mm; accelerating voltage, 20 kV). Samples were carefully examined by SEM at different magnifications for morphological features and analysed by EDX to know the chemical composition of glass shards and other mineral phases.

The mineralogical characterization was made by X-ray diffraction (XRD) analysis. Samples were powdered in an agate mortar and the diffractograms were obtained using a Bruker D-5005 instrument (Cu K- α 1 radiation, $\lambda = 1.5406$ Å, at 40 kV and 40 mA), collecting data between 4 to 6° of 2θ , with a scan step of 0.05° and a step duration of 3 s. Diffractogram evaluation was carried out using the DIFFRAC software.

3.3 Grain size analysis and porosity

Samples were analysed using a Malvern Mastersizer 2000 laser diffractometer following the recommended procedures (IVHHN, 2012). This technique measures particles within the range of 0.1–1000 μm using Mie theory. The optical properties of the particles are used to calculate their grain size expressed as a spherical equivalent size related to the volume of the particle (absorption, 0.1; refractive index, 1.526; measurement time, 20 s; obscuration, 5–20%; and pump speed, 2500 rpm). All samples were disaggregated with an ultrasonic probe in water prior to measurement (Hydro MU system). Samples were dried in an oven at 40 °C for 24 h before the analysis. Results are the average of three measurement cycles per sample.

3.4 Bulk composition

Concentrations of major elements in ash samples were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Optima 3100 X, Perkin Elmer), and trace elements by High Resolution-Inductively Coupled Plasma-Mass Spectrometry (HR-ICP-MS, Element XR, Thermo Scientific). Whole-rock analysis by ICPs was performed on a split (0.1 g) of each sample. This was digested with $\text{HNO}_3\text{:HClO}_4\text{:HF}$ (2.5:2.5:5 ml, v/v), doubly evaporated to incipient dryness with addition of HNO_3 , and finally made up to 100 ml with 1 % (v/v) HNO_3 . The precision and accuracy of analytical determinations were monitored using reference materials of the Geological Survey of Japan (rhyolite JR-3 and basalt JB-3) (Imai et al., 1995; Terashima et al., 1993). Loss on ignition (LOI) was determined on 1 g sample at 1,000 °C.

3.5 Leaching experiments

Leaching experiments were performed on unground and unsieved ashes. Several leaching tests can be used for simulation of the geochemical release from ash. The simplest type is the one-stage leaching procedure or single batch leaching tests (SBLT) (Duggen et al., 2010; Ruggieri, 2011; Ruggieri et al., 2011; Ruggieri et al., 2010). This was conducted with deionised water as leachant because allows a rapid screening of the potentially hazardous species leached from the ashes (IVHHN, 2012; Witham et al., 2005). After the exhaustive literature search of leaching protocols of this review, Witham et al. (2005) proposed recommendations for batch experiments based on the most common used methodologies rather than the optimal conditions. The present

procedure use optimized methods which have been developed through logical experiment design, careful measurement, and statistical analysis (Ruggieri, 2011). One (1.0000) gram of ash was mixed with 10 ml Milli-Q Plus ultrapure water type ($18.2 \Omega \text{ cm}^{-1}$) in 14x100 mm polypropylene test tubes. After 4 h of shaking at 20 rpm at room temperature, the water leachates, previous centrifugation, were filtered through Polyvinylidene Difluoride (PVDF) syringe filters with tube tip (Whatmann, 25 mm diameter and $0.45 \mu\text{m}$ pore size). Finally, the volume was made up to 100 ml in 1% (v/v) HNO_3 . The water leachate pH and the specific conductivity (SC) were monitored in duplicate batches immediately after ash–water mixing (pH_0 and SC_0) and at the end of the experiment (pH_f and SC_f), without filtering by means of specific electrodes (Crison Multimeter MM40).

A vertical column (Teledyne ISCO Ref. 69-3873-140) of 8 cm height and a cross-sectional area of 2.25 cm^2 was filled with 10.0000 g of CHA-1F ash. Loading of column was carried out gradually, under mild shaking in order to compact the ash. This filling process prevents the entrapment of air bubbles and a grain size fractionation. A silica filter with average pore size of $60 \text{ \AA}$ was attached at the column inlet and outlet. A peristaltic pump (Minipuls 3, Gilson) at the head of the column assured the constant and stable deionised water (Milli-Q Plus type, $18.2 \text{ M}\Omega \text{ cm}^{-1}$) flow from top to bottom at 0.24 ml min^{-1} (15 rpm). A fraction collector (FC 204, Gilson) at the column outlet took samples from the leaching solution in 14x100 mm polypropylene test tubes. We have employed the drop mode collection, counting 400 drops per tube of aqueous solutions from the column outlet. One litre of percolate solution was collected in 3 days resulting in a set of 100 tube samples. A subset of 40 samples was analysed for

major and trace elements, preparing acidified (1% HNO₃) dilutions of 1:5 ml, v/v, for ICP-OES and 1:10 ml, v/v, ICP-MS with Milli-Q Plus type deionised water. Another subset of 25 samples was removed for pH determination (Crison Multimeter MM40). Samples were stored at 4 °C until analysis.

In addition to the elements analysed in the whole-rock analysis, Cl, S, B, F, Br, and Hg concentrations were analysed in batch and column samples. Given the physico-chemical characteristics of the samples studied, the Cl, Br, and S concentrations were assumed as Cl⁻, Br⁻, and SO₄²⁻, respectively. The methods to determine major and trace elements using ICP-MS analysis were described previously (Fernandez-Turiel et al., 2000). Fluoride concentrations were determined in the water batch experiments using an ion selective electrode (ISE) for fluoride (Orion, Thermo Scientific).

4. Results and discussion

4.1 Morphological and mineralogical properties

Ash characterisation based on SEM and XRD analyses showed that glass is the main constituent of Chaitén ashes, which appears to be accompanied by plagioclase, mainly andesine, quartz, and cristobalite (Table 1). Other authors have also observed the occurrence of cristobalite in the 2008 Chaitén eruption ashes, which is present as highly crystalline silica nanofibers in the breathable ash fraction (<4 µm aerodynamic diameter) (Horwell et al., 2010; Reich et al., 2009). XRD patterns of studied ashes indicate more cristobalite content in CHA-2R sample. This sample was collected on August 15th 2008 and corresponds to

ash erupted following a dome collapse, confirming that the rhyolitic dome formed cristobalite in substantial quantities (Horwell et al., 2010).

General and detailed SEM images of studied ashes are reported in Figure 2. Low vesicular spongy glass clasts coexist with equant blocky glass shapes, and rarer Y-shard, platelike, curved and angular shards (wall vesicles breakage remains). The largest particles (5-200 μm) occur with a greater amount of fine-grained material ($\sim 1 \mu\text{m}$). Sporadic fragments, where the flattening of vesicles results in a very elongated form, were depicted, i.e., in CHA-1F, with highly elongate pipe-like vesicles parallel to the long axis of the pyroclast, indicating the flow direction. Also random highly vesicular spongy clast, i.e., in CHA-G and CHA-E, were observed and, occasionally, fractured surfaces and open-vesicle networks. The morphological differences of glass particles among samples are probably related to the distinct phases of Chaitén eruption.

4.2 Grain size analysis

The grain size distribution of the volcanic ash is of critical importance to discuss the associated environmental hazard. Particles with smaller diameters tend to have a higher surface area to mass ratio than larger particles and, then, they are more efficient scavengers of volatiles for the same tephra volume. Moreover, airborne particles with low grain size could be re-mobilised and dispersed from ash deposits by human activity and wind causing damage in the surrounding environment (Witham et al., 2005).

Results were obtained as volume percentages of grain size fractions and, then, they were converted into cumulative volume (%) distributions to assess the percentage of material in each fraction (Figure 3). The content of $<10 \mu\text{m}$

fraction is similar in all samples, independently of the distance to the Chaitén volcano (Figure 3). These results corroborate those reported by Horwell et al. (2008). The grain size distribution in the Chaitén ash samples suggests a possible evolution during the 2008 eruption passing from a clear bimodal distribution in the first initial phase (sample CHA-G) to a more homogeneous distribution only a few days later (samples CHA-1F and CHA-E). Moreover, the sample CHA-2R collected on August 2008 (after dome collapse) presents the same distribution of the sample collected during the first fallout.

4.3 Bulk composition

Chaitén ashes are rhyolites following the Total Alkali Silica (TAS) diagram for the classification of volcanic rocks (Le Bas et al., 1986). The major and trace element contents are generally in the range expected for a rhyolite (Tables 1 and 2).

4.4 SBLTs with deionised water

The ash–water interaction in SBLTs should be taken as a model of a typical field scenario in which ash-water interaction produces the release of the most soluble constituents. The dissolution of volcanic glass in natural conditions occurs at rates several orders of magnitude lower than in ash-leachate dissolution according to several experimental works (Gislason and Oelkers, 2003; Jones and Gislason, 2008; Witham et al., 2005; Wolff-Boenisch et al., 2004). These works found that the dissolution of glasses and other compounds occurring in volcanic ashes is remarkable even within the 4 h considered here.

These results could be interpreted as typical for a very early stage of weathering.

4.4.1 pH and specific conductivity

The pH of leachates is slightly acidic immediately after the ash-water interaction and before the agitation begins low pH continues. After 4 h of shaking, the leachates are slightly basic ranging the pH from 7.85 to 9.07 (Table 2). The values of pH in seawater leachates of Chaitén ash were also basic, close to 8, at the end of such experiments (Wall-Palmer et al., 2011). Basic pH values were also observed in the early and most explosive ash of the 2010 Eyjafjallajökull eruption and acidic pH with the later and more typical ash of this eruption (Gislason et al., 2011). The reason the Eyjafjallajökull ash varied from basic to acidic through its eruptive cycle was because the initial eruption interacted with the overlying glacier, so the phreatomagmatism stripped any adsorbed acids prior to deposition. Towards the end after the glacier had been melted through, the acids started appearing on the ash surfaces. Reactions of minerals with water and their thermodynamic fundamentals highlighted as pH changes are very common when mineral phases are in contact with water (Holdren and Speyer, 1985). The pH increase is due to both a fast and large dissolution of alkaline compounds and a release into solution of hydroxyl ions from the oxo-groups present on the particle ash surfaces (Oelkers and Gislason, 2001; Oelkers et al., 2009), whereas the acidic conditions are associated with acidic gas condensates on the ash particles (Gislason et al., 2011).

Specific conductivity (SC) increases after 4 h of ash-water interaction (Table 2). SC is a good approximation to the concentration of total dissolved solids (TDS) and the ionic constituents in solution, and, therefore, amount of readily soluble material on ash particle surfaces. In the Chaitén ashes the final SC_f values were ≥ 2 times higher than the initial SC_0 .

4.4.2 Leachate composition

Geochemical data of water leaching tests are presented as mg kg^{-1} (major elements) and $\mu\text{g kg}^{-1}$ (trace elements) (Table 3). The results of the elements Be, B, Ge, Se, REE (except Ce), Ta, Hg, Tl, Bi, Th and U are not in the Table 3 because their concentrations in SBLTs leachates were lower than the limit of detection. The elements with higher concentrations ($> 1 \text{ mg kg}^{-1}$) in ash leachates were Cl, S, F, Ca, Mg, Na, K, Si and Al, within the ranges observed in other leachates of the Chaitén ashes (Durant et al., 2011) (Table 3). These results are in agreement with contents of previous works on volcanic ashes of different compositions (Delmelle et al., 2000; Delmelle et al., 2007).

The Cl/S ratios are $\sim 2\text{-}3$ for samples CHA-G and CHA-1F whereas are lower ($\sim 0.6\text{-}1$) in the other samples. These ratios are lower than those observed by Durant et al. (2011) because the S concentrations are higher in the present work. Taking into account the Cl/S ratios observed here, the S content in the eruptive gases should be higher than the indicated in that work. Despite these discrepancies, both results indicate the role of S content in the Chaitén eruption was less important than in other historical Andean eruptions and this was probably related to the rhyolitic nature of the former magma and the comparatively low-silica character of the others.

The trace elements with higher concentrations in the water leachates of pristine ashes (e.g., Ni, Cu, As, Sr, Ba, and Pb) are usually combined with halogens and sulphates forming salts and/or acid droplets coating the ash-particle surfaces. The latter process involves the partial dissolution of the ash through reactions with the acidic gases (i.e., mainly SO₂, HCl, and HF) and aerosols (i.e., H₂SO₄) from the plume, followed by precipitation at the ash-liquid interface being responsible of the enrichment of elements with low volatility (lithophilic elements as Ba and Sr) (Delmelle et al., 2007). This is supported by volcanic gas measurements that indicate lithophilic element enrichment in the gaseous and particulate phases emitted during magma degassing processes in volcanic eruptions (Bundschuh et al., 2004; Hinkley, 1994; Hinkley, 1991; Hinkley et al., 1999; Symonds et al., 1992; Symonds et al., 1987).

The higher concentrations of trace elements observed in the leachates were of As, Pb, P, Fe, Sr, Zn, Mn and Br, while Ba, Li, Ti, Ni, Nb and Cu occurred in lower but significant contents. The trend is quite similar among the studied samples and comparable to previous studies on the ashes from the Chaitén eruption (Durant et al., 2011). The sample CHA-G presents an unusual high concentration of As, accompanied for some other elements as Pb or Li. These high contents of As-Pb were also observed in other leachates of ashes from the early eruption phases of Chaitén (sample CH0805_33 in Durant et al., 2011).

Some of the before mentioned elements have been observed in surface waters and related to the Chaitén eruption (Martin et al., 2009). However, the relationship with the eruption was based on the assumption that the surface waters were not affected by the entry of Ca from ash. This statement is questioned for the results obtained in the present work and those of Durant et

al. (2011) and therefore the presence of such elements could also be linked to other processes. On the other hand, the lack of extensive temporal data on water quality in the region makes difficult to estimate the input from the volcanic eruptions. Thus, laboratory leaching experiments represents a valuable source of information for assess these impacts.

For SBLTs, the relative mass leached fractions (RMLF) were calculated (Table 3). A RMLF of an element is defined as the leached fraction, expressed as % (element/solid by weight) determined by the SBLT over the total concentration in the ash (element/solid by weight) (Georgakopoulos et al., 2002a; Georgakopoulos et al., 2002b; Papastergios et al., 2009). For example, if we have $38.4 \mu\text{g g}^{-1}$ of As in the bulk ash and we have observed $3009 \mu\text{g kg}^{-1}$ in the leachate, 7.84 % of As have been released to the leachate in the ash-water interaction (i.e., $\text{RMLF}_{\text{As}} = 7.84 \%$). Thus, a RMLF is a 'proxy' as source of element mobility information for volcanic ashes. Although Se, Ag, Te, Pt, Au, Th, U and rare earth elements (REE) were analysed in SBLTs, their RMLFs could not be defined because their concentrations were below or very close to the respective detection limits in the leachates. RMLFs were not determined for Cl, SO_4 , B, F, Br, and Hg because these elements were not analysed in bulk ashes.

A preliminary grouping of elements may be realised according their RMLFs (Ruggieri et al., 2011), so we have the following classification (elements are listed in decreasing order of RMLFs):

- High mobile elements ($\text{RMLF} > 5\%$): As and Pb are in this group but only for sample CHA-G.

- Moderate mobile elements (RMLF between 0.5 and 5%): Mo, Ni, Co, Zn, Ca, Sb, Nb, Cu, and (in samples CHA-E, CHA-1F and CHA-2R) Pb and As.
- Low mobile elements (RMLF <0.5%): Li, V, Na, Mg, Sr, P, K, Zr, Cs, Rb, Cr, Ga, Mn, Ba, Y, Ce, Ti, Si, Al, and Fe,

These classes are arbitrarily defined but, despite the differences observed among samples, allow a first approach to the main trends on the mobility of the considered elements. These results show a low degree of mobility in all cases being remarkable the low mobility of major elements. The exception is calcium showing a moderate mobility in the four samples (RMLF 0.7-1.0%). In the case of iron, which has been studied in seawater leachates due to its fertilizer potential in oceans (Duggen et al., 2007; Duggen et al., 2010; Olgun et al., 2011), the RMLF < 0.009 % is extremely low and clearly below the value of Olgun et al. (0.1 %), but comparable to the values determined from concentrations observed in other leachates with deionized water of Chaitén ashes (Durant et al., 2011). The differences in the leaching methods (deionised water vs. seawater, reaction times, and solid/liquid ratio) could explain these low values due to adsorption of released Fe or precipitation through oxidation of the soluble Fe (II) to less soluble Fe (III).

4.5 Column experiment with CHA-1F sample

The results are reported as breakthrough curves of major and trace element concentration vs. accumulated volume of the percolate solution; experimental values of pH variation are also reported (Figures 4-6). Only selected elements

are reported here due to negligible concentrations in the other cases (e.g., REEs < 0.01 µg l⁻¹).

4.5.1 pH and hydrolysis

The pH value rises quickly upon leachant contacts with CHA-1F ash (Figure 4). This general feature observed in rocks (e.g., granites) has been commonly reported for volcanic ash leachates, also when seawater was used as leachant (Jones and Gislason, 2008; Rango et al., 2010; Ruggieri et al., 2011; Ruggieri et al., 2010; Smith et al., 1982; Smith et al., 1983; Stefansdottir and Gislason, 2005). After this early pH increase, the trend consists of a practically continuous pH decrease. The maximum value of pH (7.75) is close to the lower pH observed in the SBLTs (7.85; Table 2), but the lower pH (~6) is quite different due to the dissimilarities of the experiments (flow-through column vs. batch).

The initial increase corresponds to that observed in SBLTs and it is likely due to both a fast and large dissolution of alkaline compounds and a release into solution of hydroxyl ions from the oxo-groups present on the particle ash surfaces (Gislason et al., 2011; Oelkers and Gislason, 2001; Oelkers et al., 2009). This early ash-leachate release occurs in the first minutes of contact with water (Duggen et al., 2007; Olgun et al., 2011).

Early stages of the contact of many silicate minerals with water are usually highlighted by pH changes (Luce et al., 1972; Petrovic et al., 1976). In the case of amorphous silica, the main constituent of volcanic glass, H⁺ and (OH)⁻ diffuse in the three spatial dimensions, even through the solid surface, changing pH. In these active interfaces, the (OH)⁻ are linked to Si and the H⁺ to O, promoting the dissociation of water. This explains because the suspended solids in natural

waters are often negatively charged at pH close to neutrality (6-8) (Oelkers et al., 2009).

Although only at the beginning of the process, these negative charges surrounding the solid tend to attract H^+ , raising the pH of the closest solution until the equilibrium is obtained. Thereafter, the slower processes of dissolution, hydrolysis, and buffering power of the solid phase by progressive acid-base interaction proceed, decreasing the pH (Toscano et al., 2008). However, in a volcanic ash the process is more complex due to the occurrence of other silicates of Na, Ca, K and Mg (i.e., alkali feldspars). According to several studies on aluminosilicate dissolution, the process develops in three stages: (1) virtually instantaneous exchange of the alkaline ion (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) by H^+ (or as H_3O^+), i.e., with increase of pH; (2) generation and fast growth of a residual layer poor in these alkalis and rich in Si; and (3) interaction of feldspar-solution through the residual layer and beginning of an incongruent dissolution (process necessarily slower, at pH lower than in previous steps) (Oelkers and Gislason, 2001; Oelkers et al., 2009; Schott and Oelkers, 1995). The first stage involves a reversible reaction where H^+ forms the feldspar $HAISi_3O_8$ when Na^+ is released. At the end of the second stage, a layer of this compound is developed by incongruent dissolution. The third stage, the slow one, controls the process of aqueous dissolution. These processes (together with volcanic glass dissolution) explain the pH variation observed in the column leaching experiment.

4.5.2 Silica and aluminium dissolution

Chaitén ash could be defined as formed by amorphous-crystalline silicates (including volcanic glass and quartz) and minor amount of aluminosilicates (i.e.,

principally alkali feldspars). The rate of silicate glass dissolution in the aqueous phase can be reasonably described in terms of pH and aluminium dependencies, although the presence of other components (e.g., fluoride and sulphate) in the system may dramatically favour this process (Flaathen and Gislason, 2007; Frogner-Kockum et al., 2006; Wolff-Boenisch et al., 2004). It is well established that the solubility of amorphous silica is higher than for crystalline silica (quartz) (Alexander et al., 1954). In any case, the different forms of silica have the same fundamental structure. They are highly polymerized chains of SiO_4 in which the silicate group (Si-O-Si) is the reactive group. This group could be broken by water in two steps by: (1) the absorption of water near a Si-O-Si group; and (2) the formation of a new Si-O bond with the oxygen of the adsorbed water and the cleavage of the Si-O-Si group (Schott and Oelkers, 1995). Dissolution is associated with the latter step, which at 25 °C involves the equilibrium between the solid phase and a monomeric form of silica (Si(OH)_4) in solution (Alexander et al., 1954). The increase in total dissolved silicon at basic pH agrees with these processes (Figure 4).

Although in the studied rhyolitic samples the content of crystalline phases is relatively low, their presence could affect the leaching behaviour of elements associated with them. The structure of aluminosilicates (e.g., alkali feldspar) contains exchangeable cations (e.g., Na^+ , Ca^{2+}) along two hydrolysable sites in the polymer: silicate groups (Si-O-Si) and aluminate groups (Al-O-Si). As explained above their dissolution can be considered as a three step process. Here it is briefly explained in terms of Al concentration. The first step is the relatively rapid equilibrium between hydrogen and alkali ions on the mineral surface (causing an increase of pH) (Wollast and Chou, 1992). The second step

is the reversible exchange of hydrogen with aluminium on the mineral surface involving the breaking of Al-O bonds of Al-O-Si groups and leaving the surface of the minerals enriched in silica both at acidic (Casey et al., 1991; Casey et al., 1989) and basic conditions (Hellmann et al., 1990). The final and rate limiting step of these compound dissolutions is the hydrolysis of Si-O-Si bonds. These processes are subtle but apparent at the experiment scale when comparing the plots of pH, Al and Si in Figures 4 and 5.

4.5.3 Other major and trace element behaviours

The geochemical composition of leachates in the column experiments was predominantly controlled by dissolution of coatings on the ash particle surfaces and incongruent dissolution of glass. Therefore, we should discriminate between the elements rapidly released from the ash surface coatings and those related to more complex processes as particle dissolution.

The higher initial concentrations depicted for Cl ($\sim 300 \text{ mg l}^{-1}$) and SO_4 ($\sim 50 \text{ mg l}^{-1}$) in CHA-1F experiment confirm the presence of soluble compounds rapidly leachable (as chlorides and sulphates mainly of Ca, Mg and Na) onto pristine ash particle surfaces. Sharp variations in concentrations of these elements occur at the beginning of the experiment (Figure 4). The rapid release of alkali ions (i.e., Ca^{2+} , Mg^{2+} , Na^{+}) was accompanied by the increase of pH (i.e., rapid consumption of H^{+}), which suggest a rapid equilibration between hydrogen and alkali ions on the silicate surface (Rango et al., 2010). The same trend was reported for Li, B, Mn, Zn, Br, Rb, Sr, Mo, and Ba (Figures 5 and 6), indicating soluble salts of these elements on the surfaces which were formed in the plume of the volcanic eruption through gas-particle interaction or the partial

dissolution of the ash with gases (i.e., mainly SO₂, HCl, and HF) and aerosols (i.e., H₂SO₄), followed by precipitation at the ash-liquid interface, especially for elements with a low volatility in magma (lithophilic elements) (Delmelle et al., 2007).

On the other hand, elements as Si, Al, P, V, Fe, and As show a smooth decreasing variation in their concentration. This trend enhances their relationship to glass dissolution processes being associated with the beginning of the incongruent dissolution of volcanic glass (i.e., the reactive phase) by cation-exchange processes (Rango et al., 2010).

4.5.4 Comparison of column experiments between Chaitén and other ash compositions

Chaitén eruption is important because it is the only rhyolitic eruption in practically the last 100 years, so the geochemical data here are important when considering the environmental impact of previous rhyolitic eruptions, some of which have been extremely large. When compare the total mass released in Chaitén column leachate with other eruptions in the range of basaltic-andesite to dacite ash compositions (Jones and Gislason, 2008), the trend of the Chaitén ash is more like the ashes of Lascar, Montserrat, and Santiaguito eruptions, especially respect to Lascar (Table 4). The main differences with the other ashes are related to the lower values in Cl/S and Cl/F ratios and the lower contents released by practically all elements.

Despite the methodological differences between the column and the batch tests applied to the Chaitén samples, both produce results quite similar in orders of magnitude. The main differences could be associated with variations

in the reaction kinetic rates of both types of experiments, enriching the column leachates in Cl, Si, Al, Ca, V, Zn, Ga, As, Sr, and Sb concentrations whereas decrease the S, K, Cs, and Ba contents.

The results of the comparison of Chaitén ash with ashes of different compositions confirm that, independently of the ash composition, the dissolution of surface salts and aerosols dominates over glass dissolution during the first steps of the ash-water interaction. In addition, as preliminary remark that must be confirmed studying other ashes before to be generalized, such comparison points out the higher potentials for poisoning and fertilising of the ashes of less evolved low silica magmas (e.g., Hekla). Thus, the ashes of the most evolved high-silica magmas seem to have less geochemical hazard than those of the low-silica magmas.

5. Contribution to the regional geochemical balance

The water leached contents by SBLTs may be considered as the environmentally available amount (EAA) of each element studied, i.e., these values could be used to predict the element amount easily transferable to the environment through the water pathway from ashes. For a given element, knowing its EAA, the erupted volume and density of the ash, the total contribution (TC) of an eruption to the regional geochemical balance is calculated multiplying the EAA by the eruption mass (M); where M is determined multiplying the erupted volume by the ash density.

The application of the above equations to the studied ashes is presented in Table 5. We consider a minimum bulk volume of 0.5 km³ for the ash deposit, assuming a bulk density of 1,250 kg m³ (Alfano et al., 2011). This estimate

allows the modelling of the total contribution of Chaitén eruption. This is a first approach due to the weights of each one of the studied samples in the deposits are unknown. Despite the restrictions introduced by the uncertainties of the model, taking as reference the average TC values (Table 5), Chaitén ashes could transfer to the environment more than 1×10^{10} g or 10,000 metric tonnes (mt) of Cl, S, Ca, Na, Si, and K; between 1,000 and 10,000 mt of F, Mg, and Al; between 100 and 1,000 mt of As, Pb, P, Fe, Sr, Zn, Mn, and Br; between 10 and 100 mt of Ba, Li, Ti, Ni, Nb, Cu, Rb, Zr, V, Mo, Co, and Sc; and less than 10 mt of Cr, Sb, Ce, Ga, Cs, and Y.

Some of the trace elements available from these ashes are macro- and micronutrients (e.g., Mn, P, and Fe), evidencing the fertilising potential of the ashes (Duggen et al., 2010; Frogner et al., 2001; Niemeier et al., 2009). Although the total contributions of such elements are relatively low in the Chaitén ashes, their deposition could provide an external critical nutrient source in low nutrient areas, e.g. in southern areas of the Pacific and the Southern Ocean (Duggen et al., 2010).

Many other elements studied are potentially toxic trace elements (PTTEs), and some of them are included in the drinking water guidelines (ANMAT, 2010; INN, 2006; WHO, 2008) due to their potential toxicity even at very low concentrations and must be especially monitored in the environmental assessment of these ash fall deposits. The results obtained indicate that the PTTEs release and acidification by ash-water interaction could affect very fast (some hours to one day) the water quality in both terrestrial and marine ecosystems with important effects on the living organisms. This setting could be the reason of the low production of mussels in Chiloé Island, near to the

Chaitén volcano, as consequence of the toxic effects of ash leachates on the phytoplankton population during the eruption (Wall-Palmer et al., 2011). After the early ash-water interaction the chemical hazard decays drastically and, in general, surface water bodies that only received ash fall (rather than mudflow or pyroclastic flow deposits) undergone little modification of their chemical composition as was evidenced in the 1980 eruption of Mount St. Helens (Lee, 1996).

The Chaitén ash deposits are a major reservoir of some geogenic PTTEs. For example, Al and F could be an important hazard because Al-F complexation in acidic conditions may increase the solubility of these elements and could be toxic to both plants and animals, contributing to symptoms of illness related to Al toxicity and fluorosis (Frogner-Kockum et al., 2006). This hazard is only likely in terrestrial ecosystems because is mitigated in marine water due to their high buffering capacity or alkalinity. The cases of As and Pb are also remarkable and contribute to consider these ash deposits as a major reservoir of geogenic PTTEs. From an environmental point of view, the amount of available water interacting with ash deposits is a key factor controlling ash leaching and weathering. Thus, high precipitation rates as those observed in Southern Andes weather the ashes quickly and generating fertile soils, whereas the ashes affected by low precipitation rates as in Central Andes and La Puna will be weathered over a longer period of time (hundreds of thousands years) (Ruggieri, 2010).

6. Conclusions

The environmental concerns of these ashes are related to the fine grained component present in each sample (independent of distance from the source), in particular the presence of cristobalite, and the geochemical hazards posed by ash-water interaction.

Water-SBLTs evidence rapid release of major components, mainly SO_4 , Cl, Ca and Na from the ash particle surfaces but also some trace elements as F, As and Pb. Column leaching experiment discriminates between elements weakly associated with the ash particle surfaces and those involved in more complex chemical reactions. Many elements were removed at the beginning of the experiment (i.e., Ca, Mg, Na, K, Cl, SO_4 , F, Li, V, Mn, Br, Rb, Sr, Mo, Ba, and Pb). Some element concentrations (i.e., B, V, Fe, and As) do not show a very sharp decrease during the leaching time, suggesting their release is associated with glass dissolution. Thus, the interaction of ash and water mobilizes most of the environmentally available fraction of the ash very quickly while the later weathering is considerably slower. Therefore, the main impact of ash deposition is just after initial exposure to seawater (Duggen et al., 2007; Jones and Gislason, 2008; Stefansdottir and Gislason, 2005). The geochemical behaviour, along with its easy physical mobilization (by air and water), dictates the ephemeral character of ash deposits and the rarity of its preservation.

Water ash leachate data were also used as a basis to model the contribution of the Chaitén ashes to the regional geochemical mass balance. Despite the restrictions introduced by the uncertainties of the model, taking as reference the average TC values, Chaitén ashes could transfer to the environment more than 1×10^{10} g or 10,000 metric tonnes (mt) of Ca, Na, S, and Cl; between 1,000 and 10,000 mt of Si, K, F, Mg, and Al; between 100 and 1,000 mt of As, Pb and P;

between 10 and 100 mt of Fe, Sr, Zn, Mn, Br, Ba, Li, Ti, Ni, Nb, Cu, Rb, Zr, and V; and less than 10 mt of Mo, Sc, Cr, Sb, Ce, Ga, Cs, Co, and Y.

Some of the implied elements are macro- and micronutrients (e.g., Ca, Fe, Mn, and P), evidencing the fertilizing potential of the ashes, but others are potentially toxic and must be monitored in the environmental assessment of these ash fall deposits, especially in water for humans and livestock.

The dissolution of surface salts and aerosols dominates over glass dissolution during the first steps of the ash-water interaction in rhyolitic ashes as well as in the lower silica content ashes. However, the latter have higher potentials for poisoning and fertilizing due to release higher contents of practically all elements. The opposite occurs only exceptionally and for specific elements, an example is the case of the arsenic in the Chaitén ash which is enriched in relation to the other lower silica ashes considered.

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Figure captions

Figure 1. Location of the sampling sites of the Chaitén ashes.

Figure 2. SEM images of the studied ashes from 2008 Chaitén eruption.

Figure 3. Average results (3 runs) of grain size distributions expressed as volume percentages of grain size (top) and cumulative volume (bottom) of Chaitén ashes.

Figure 4. Behaviour of pH and concentrations of Ca, Mg, Na, K, Si, Cl, and SO₄ in the column leaching experiment of CHA-1F sample.

Figure 5. Variation of the concentrations of Li, B, Al, P, V, Fe, Mn and Zn in the column leaching experiment of CHA-1F sample.

Figure 6. Variation of the concentrations of As, Br, Rb, Sr, Mo and Ba in the column leaching experiment of CHA-1F sample.

Table captions

Table 1. Information on Chaitén volcanic ashes. Mineral composition: ***, common; **, frequent; *, scarce. Major oxides expressed as %, m/m; trace elements as mg kg⁻¹. LOI, Loss On Ignition.

	CHA-G	CHA-E	CHA-1F	CHA-2R
Collection date	03-May-08	08-May-08	10-May-08	15-Aug-08
Location	Esquel	Esquel	Chaitén	-
Longitude	71°20'45.56"W	71°18'27.78"W	72°42'18.68"W	72°38'45.09"W
Latitude	42°54'29.94"S	42°54'30.63"S	42°55'9.04"S	42°57'16.01"S
Distance from the vent	106 km	106 km	10.5 km	60 km
Pristine	yes	yes	yes	no
Glass	***	***	***	***
Andesine	**	**	*	**
Quartz	**	*	*	**
Cristobalite	*	*	*	**
SiO ₂	72.06	73.41	73.62	72.35
Al ₂ O ₃	14.66	14.42	14.41	14.61
Fe ₂ O ₃ total	1.88	1.59	1.57	1.88
MnO	0.07	0.07	0.07	0.07
MgO	0.60	0.36	0.35	0.56
CaO	1.99	1.62	1.57	2.04
Na ₂ O	4.18	4.20	4.07	4.08
K ₂ O	2.89	3.02	3.02	2.79
TiO ₂	0.20	0.17	0.16	0.21
P ₂ O ₅	0.08	0.10	0.08	0.09
LOI	1.65	0.96	1.06	1.43
Total	100.26	99.92	99.98	100.11

Table 1 Continuation..

Element	CHA-G	CHA-E	CHA-1F	CHA-2R
Li	41.1	45.5	48.4	46.1
Be	1.62	1.65	1.76	1.76
V	13.8	5.7	5.1	13.0
Cr	19.0	16.3	13.8	18.9
Co	2.57	1.52	1.41	2.81
Ni	4.31	1.56	1.67	3.68
Cu	8.5	5.9	6.4	10.5
Zn	51.2	53.3	51.0	54.1
Ga	14.1	14.0	14.1	14.5
Ge	1.07	1.13	1.21	1.21
As	38.4	15.1	18.1	47.8
Rb	99	103	105	98
Sr	167	154	151	173
Y	11.2	11.0	11.2	11.3
Zr	93	100	104	93
Nb	7.17	7.27	7.37	7.17
Mo	1.02	0.80	0.91	0.75
Sn	2.41	2.83	3.01	2.43
Sb	1.51	1.01	1.08	1.80
Cs	6.42	6.73	6.66	6.12
Ba	617	634	626	596
La	24.4	24.5	24.3	23.2
Ce	46.5	46.4	45.7	44.3
Pr	4.97	4.93	4.84	4.77
Nd	16.5	16.4	16.1	15.8
Sm	2.83	2.60	2.61	2.60
Eu	0.66	0.61	0.61	0.64
Gd	2.98	2.88	2.87	2.90
Tb	0.43	0.40	0.39	0.41
Dy	2.38	2.28	2.24	2.28
Ho	0.43	0.41	0.39	0.41
Er	1.37	1.30	1.25	1.26
Tm	0.20	0.19	0.19	0.19
Yb	1.44	1.36	1.37	1.31
Lu	0.23	0.22	0.22	0.21
Hf	3.18	3.40	3.42	3.98
Ta	0.68	1.13	1.28	1.95
Tl	0.64	0.67	0.65	0.65
Pb	22.4	25.6	20.7	19.6
Bi	0.30	0.27	0.24	0.28
Th	13.0	13.3	13.1	11.7
U	3.26	3.35	3.31	2.85

Table 2. The pH and the specific conductivity (SC) was monitored in duplicate batches in water ash leachates of Chaitén ashes at the beginning (pH_0 and SC_0), immediately after ash–water mixing, and at the end of the experiment (pH_f and SC_f), without filtering. SC is expressed in $\mu\text{S cm}^{-1}$ (1 g ash in 10 ml deionised water).

	CHA-G	CHA-E	CHA-1F	CHA-2R
pH_0	5.30	4.47	4.54	4.98
pH_f	9.07	7.85	8.64	8.60
SC_0	109	24	52	48
SC_f	184	86	96	94

Table 3. Total mass of elements leached in water and the respective relative mass leached fractions (RMLF); nd, RMLFs not determined (elements not analysed in bulk ash or in concentrations lower than the limit of detection in the leachate) (1 g ash in 10 ml deionised water). Comparison with the ranges observed in deionized water leachates (1:25 solid/liquid ratio) by Durant et al. (2011). <LoD, lower than limit of detection.

	CHA-G		CHA-E		CHA-1F		CHA-2R		Chaitén leachates min-max (# data) Durant et al. (2011)
	mg kg ⁻¹	RMLF %	mg kg ⁻¹	RMLF %	mg kg ⁻¹	RMLF %	mg kg ⁻¹	RMLF %	mg kg ⁻¹
Cl	126	nd	35	nd	148	nd	17	nd	53.18-344.25 (32)
S	66.1	nd	35.7	nd	51.1	nd	27.4	nd	3.85-92.35 (32)
F	10.30	nd	2.73	nd	6.80	nd	7.01	nd	3.78-28.35 (32)
Si	28.1	0.008	24	0.007	18.4	0.005	20.4	0.006	4.21-23.03 (28)
Al	5.25	0.007	6.49	0.008	4.95	0.006	4.82	0.006	<LoD-4.59 (32)
Mg	7.14	0.20	4.84	0.22	6.57	0.31	5.49	0.16	3.89-28.44 (32)
Ca	138	0.97	105	0.91	80	0.71	130	0.89	25.25-176.34 (32)
Na	88.0	0.28	29.5	0.09	64.2	0.21	28.8	0.10	21.61-94.49 (32)
K	21.4	0.09	14.0	0.06	14.2	0.06	18.2	0.08	1.95-53.93 (32)
P	0.43	0.12	1.25	0.29	0.37	0.11	0.40	0.10	
	µg kg ⁻¹	RMLF %	µg kg ⁻¹	RMLF %	µg kg ⁻¹	RMLF %	µg kg ⁻¹	RMLF %	µg kg ⁻¹
Li	185.0	0.45	75.8	0.17	95.5	0.2	88.4	0.19	
B	<LoD	nd	<LoD	nd	<LoD	nd	<LoD	nd	
Sc	27.6	nd	24.6	nd	21.1	nd	22.3	nd	
Ti	104	0.009	93	0.009	94	0.010	99	0.008	
V	59.8	0.43	17.3	0.30	10.2	0.20	35.0	0.27	
Cr	7.81	0.04	6.72	0.04	7.24	0.05	8.58	0.05	<LoD-4.00 (27)
Fe	48	0.00037	2.67	0.00002	<LoD	nd	1150	0.00875	5.58-1,496.65 (27)
Mn	145	0.027	110	0.020	473	0.087	209	0.039	94.49-3,272.11 (28)
Co	29.9	1.16	<LoD	nd	<LoD	nd	<LoD	nd	0.41-4.66 (28)
Ni	65.7	1.52	31.8	2.04	49.0	2.93	28.2	0.77	1.41-13.50 (28)
Cu	41.9	0.49	47.5	0.81	39.5	0.62	37.2	0.35	14.62-144.88 (28)
Zn	509	0.99	49.4	0.09	168	0.33	295	0.55	<LoD-523.99 (28)
Ga	4.86	0.03	2.67	0.02	4.19	0.03	3.49	0.02	
As	3009	7.84	130	0.86	352	1.94	726	1.52	<LoD-1,356.83 (28)
Br	252	nd	195	nd	198	nd	165	nd	
Rb	48.9	0.05	24.6	0.02	26.7	0.03	41.6	0.04	
Sr	296	0.18	409	0.27	146	0.1	182	0.11	
Y	1.14	0.01	1.88	0.02	<LoD	nd	1.90	0.02	
Zr	58.3	0.06	37.8	0.04	14.1	0.01	14.3	0.02	
Nb	39.8	0.56	40.3	0.55	46.9	0.64	47.4	0.66	
Mo	44.6	4.37	9.0	1.13	16.1	1.77	31.9	4.25	
Sb	9.33	0.62	2.37	0.23	4.48	0.41	8.38	0.47	
Cs	3.33	0.05	1.58	0.02	2.10	0.03	2.20	0.04	
Ba	90.3	0.01	201.0	0.03	85.2	0.01	107.0	0.02	
Ce	4.09	0.009	6.13	0.013	4.19	0.009	5.29	0.012	
Pb	2015	9.00	257	1.00	348	1.68	155	0.79	<LoD-2,072.21 (28)

Table 4. Total mass of elements leached in the water column experiment of the Chaitén ashes (sample CHA-1F). Results are compared with CHA-1F SBLT values and studies carried out on ashes of different compositions from another eruptions; nd, not determined; <LoD, lower than limit of detection; <sf, below significant figures. Concentrations expressed as mg kg⁻¹. Data of other eruptions after Jones and Gislason (2008).

Volcano	Hekla	Galeras	Sakura-jima	Lascar	Montserrat	Santiaguito	Santiaguito	Mount St. Helens	Chaitén (CHA-1F)	
Eruption year	2000	2005	1994	2004	2003	1998	1968	1980	2008	
Classification	Basaltic-Andesite	Andesite	Andesite	Dacite	Andesite	Andesite	Dacite	Dacite	Rhyolite	
Leaching test	column	column	column	column	column	column	column	column	column	batch
Cl	3293.58	1779.74	131.18	70.91	1769.10	205.63	177.27	329.71	477	148
S	11515.23	17770.42	3030.32	1.73	2.17	1.02	14.68	1782.54	20.5	51.1
F	3123.91	170.09	5.67	1.89	5.67	3.78	7.56	7.56	nd	6.80
Si	390.39	22.47	5.62	11.23	14.04	22.47	11.23	8.43	88.1	18.4
Al	909.28	164.59	5.40	2.70	8.09	8.09	<sf	2.70	16.31	4.95
Mg	240.62	692.69	4.86	2.43	269.79	9.72	17.01	9.72	12.33	6.57
Ca	1310.55	23589.91	24.05	84.16	513.00	84.16	216.42	76.15	189	80
Na	1938.04	1078.22	43.68	34.48	606.93	177.02	140.24	41.38	79.4	64.2
K	211.05	156.33	7.82	3.91	50.81	15.63	27.36	7.82	5.8	14.2
P	67.52	0.62	0.31	1.86	0.62	2.79	7.12	4.03	0.38	0.37
Li	0.49	1.25	<sf	0.07	0.28	0.14	0.14	<sf	0.12	0.10
B	3.35	5.73	<sf	0.43	3.89	1.41	0.97	0.22	0.80	<LoD
Sc									nd	0.02
Ti	18.67	<sf	<sf	<sf	<sf	<sf	<sf	<sf	<LoD	0.09
V	0.20	<LoD	<LoD	0.15	<LoD	0.05	<sf	<sf	0.03	0.01
Cr	0.10	0.05	0.31	0.16	0.21	0.21	0.52	0.21	<LoD	0.01
Fe	605.92	6.70	1.68	0.56	2.23	0.56	1.68	2.23	1.81	<LoD
Mn	36.81	39.01	<sf	<sf	39.56	1.10	1.65	0.55	1.31	0.47
Co	0.29	1.30	<sf	<sf	0.29	0.06	0.06	0.06	<LoD	<LoD
Ni	0.53	1.53	0.23	0.12	0.53	0.29	0.29	0.82	<LoD	0.05
Cu	0.70	1.97	1.14	0.25	2.73	0.06	0.32	0.19	<LoD	0.04
Zn	6.54	5.23	2.62	0.65	3.27	<sf	1.96	3.27	0.58	0.17
Ga									0.01	0.00
As	0.07	0.07	0.07	0.07	<sf	0.07	0.15	0.07	1.52	0.35
Br	4.79	5.59	<sf	<sf	7.19	2.40	2.40	3.20	0.34	0.20
Rb									0.03	0.03
Sr	7.01	35.05	<sf	0.88	0.88	0.88	0.88	<sf	0.52	0.15
Y									<LoD	<LoD
Zr									0.01	0.01
Nb									<LoD	0.05
Mo	<sf	<sf	<LoD	<LoD	<sf	<sf	<sf	<sf	0.02	0.02
Sb									0.04	0.00
Cs									<LoD	0.00
Ba	4.81	0.69	<sf	0.14	<sf	0.14	1.51	<sf	0.05	0.09
Ce									<LoD	0.00
Pb	<LoD	<LoD	<sf	0.21	0.21	0.21	0.21	0.21	0.01	0.35
Cl/S	0.3	0.1	0.04	41.0	816.7	202.3	12.1	0.2	23.2	2.9
Cl/F	1.1	10.5	23.1	37.5	312.0	54.4	23.4	43.6	nd	21.8

Table 5. Total contribution (TC) to the regional geochemical balance of selected elements from ashes of the 2008 Chaitén eruption, expressed in megagrams (Mg) or metric tonnes (mt); nd, not determined. Decreasing order in basis to average values.

	CHA-G	CHA-E	CHA-1F	CHA-2R	Average
	Mg (=mt)	Mg (=mt)	Mg (=mt)	Mg (=mt)	Mg (=mt)
Ca	86250	65625	49938	81250	70766
Cl	78750	21938	92500	10500	50922
Na	55000	18438	40125	18000	32891
S	41302	22320	31915	17105	28160
Si	17563	15000	11500	12750	14203
K	13375	8750	8875	11375	10594
F	6438	1707	4252	4382	4195
Mg	4463	3025	4106	3431	3756
Al	3282	4054	3096	3013	3361
As	1881	81	220	454	659
Pb	1259	161	218	97	434
P	267	782	233	253	384
Fe	30	2	0.6	719	188
Sr	185	256	91	114	161
Zn	318	31	105	184	160
Mn	91	69	296	131	146
Br	158	122	124	103	127
Ba	56	126	53	67	76
Li	116	47	60	55	69
Ti	65	58	59	62	61
Ni	41	20	31	18	27
Nb	25	25	29	30	27
Cu	26	30	25	23	26
Rb	31	15	17	26	22
Zr	36	24	9	9	19
V	37	11	6	22	19
Mo	28	6	10	20	16
Co	19	nd	nd	nd	nd
Sc	17	15	13	14	15
Cr	4.9	4.2	4.5	5.4	4.7
Sb	5.8	1.5	2.8	5.2	3.8
Ce	2.6	3.8	2.6	3.3	3.1
Ga	3.0	1.7	2.6	2.2	2.4
Cs	2.1	1.0	1.3	1.4	1.4
Y	0.7	1.2	nd	1.2	nd

Table 4

Volume of percolate solution ml

Volume of percolate solution ml