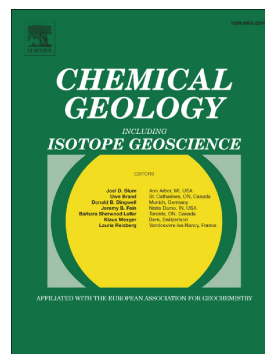


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Fluorine surface speciation in South Andean volcanic ashes

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Abstract

Fresh volcanic ash samples collected during the eruptions of the Hudson (1991), Chaitén (2008), Puyehue (2011), Calbuco (2015) and Copahue (2016) volcanoes were analyzed in order to identify the fluorine (F) bearing phases. XPS and HR-TEM was used to determine the solid speciation of F. In order to decrease the surface differential charging of samples, XPS data have been collected using an electron flood gun during spectral acquisition. Ash leaching at different pH conditions were also performed with the aim of understanding the factors that control the fluoride release to aqueous reservoirs. The results indicates that in the studied Patagonian ashes, F is concentrated onto the ash surface, likely in the form of F-Na and F-Ca salts but also within the glass lattice forming F-Si and F-Al bonds. Although the main F-source in the studied volcanic ashes is the aluminosilicate glass, this phase is stable at the neutral pH that dominates the aqueous reservoirs, thus the contribution to the pool of dissolved fluoride is minor.

Higher contributions are associated with soluble fluoride salts. In addition, the presence of coatings of F-Ca compounds inhibits the release of fluoride within the volcanic glass lattice, at least during the initial stages of the ash-water interaction.

Keywords: volcanic glass; geogenic fluoride; surface speciation; X-ray photoelectron spectroscopy; differential charging.

1. INTRODUCTION

One important environmental concern associated with volcanic eruptions is linked to the huge volumes of ashfall that may deliver hazardous elements over large distances from the source. At the place of deposition, a rapid dissolution of the water-soluble phases occurs, releasing a number of natural contaminants that may alter the quality of the impacted aqueous reservoirs (e.g., Oskarsson, 1980; Smithsonian Institution, 2000; Jones and Gislason, 2008; Ruggieri et al., 2010; Olsson et al., 2013; Bia et al., 2015). Most works attribute the rapid release of contaminants to the dissolution of mineral coatings precipitated onto the glass surfaces, while less attention is paid to the dissolution of the glassy fraction itself. At elevated pressures and water contents, hydrous melt structures from which volcanic glass crystalize, may resemble that of an aqueous fluid (e.g., Shen and Keppler, 1997). This disordered melt structure favors the incorporation of environmentally relevant trace elements (e.g., As and F) as impurities in the aluminosilicate glass (i.e., Stebbins et al., 2000; Stamboulis et al., 2005; Karpukhina et al., 2008; Brauer et al., 2009; Borisova et al., 2010; Dalou et al., 2015; Bia et al., 2017) and in consequence, the dissolution of glass shards may also contribute contaminants to aqueous reservoirs (e.g., Gislason and Oelkers, 2003; Bia et al., 2015).

A number of works indicate a rapid release of fluoride from volcanic ashes to the water due to the dissolution of F-coatings precipitated onto the glass surfaces likely CaF_2 , AlF_3 , $\text{Ca}_5(\text{PO}_4)_3\text{F}$, NaF , CaSiF_6 , etc. (e.g., Oskarsson, 1980; Cronin et al., 2003). In addition, the glassy fraction can also contribute F to the water (e.g., Gislason and Oelkers, 2003; Bia et al., 2015). It is well known that in aluminosilicate-glass, F is incorporated into the structure through two mechanisms: a) bonding between F and network-forming cations (Si, Al) and b) bonding between F and network-modifying cations (e.g. Na, K, Ca) (Kohn et al., 1991; Schaller et al., 1992; Stebbins and Zeng, 2000; Zeng and Stebbins, 2000; Stebbins et al., 2000; Kiczinski and Stebbins, 2002; Mysen et al., 2004; Stamboulis et al., 2005; Karpukhina et al., 2008; Brauer et al., 2009). Spectroscopy studies also suggest that in aluminosilicate-type structures, one or two non-bridging O atoms are replaced by F atom (Dalou et al., 2015).

Apart from the presence of F within the glassy fraction of volcanic ash, the condensation or sublimation of volcanic gases within the eruption plume may produce thin coatings of barely soluble F-salts onto ash particles (Delmelle et al., 2007). Due to the small size and irregular shape of these coatings, they cannot be characterized by conventional microscope techniques (e.g. Bagnato et al., 2013) and therefore their mineralogical composition has been traditionally inferred from molar ratios in ash leachates (e.g., Armienta et al., 2002; Edmonds et al., 2003; Witham et al., 2005). The mineral phases described by leaching experiments are water-soluble sulfate and halide salts mixed with F compounds (Delmelle et al., 2007). More recently, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy/energy dispersive X-ray spectroscopy (TEM/EDXS) techniques were used to determine the elemental composition of the coatings formed on the first nanometers of volcanic ashes surfaces (e.g., Delmelle et al, 2007; Gislason et al., 2011; Olsson et al., 2013; Bia et al.,

2015; Barone et al., 2016). Both techniques have become a valuable tool to study the surface properties and reactivity of a wide range of minerals, mainly oxides, sulfides and silicates. XPS provides information of the first few monolayers present at the mineral's surface (Nesbitt and Bancroft, 2014) and, is generally used to determine the oxidation state of near surface atoms, to characterize the sorption reactions onto mineral surfaces and to assess the impact of weathering at the mineral's surfaces (Hochella, 1988; Nesbitt and Bancroft, 2014). Concerning silicates minerals, the main difficulty in the analysis of the XPS data relies on the collection of a good-quality spectra, because most silicates (and oxides) are non-conductors, which produce charging and differential charging problems during data acquisition. This can be overcome by using strategies that compensate the charge effect (Nesbitt and Bancroft, 2014).

This study reports the F solid speciation of volcanic ashes collected after the eruptions of Hudson (1991), Chaitén (2008), Puyehue (2011), Calbuco (2015) and Copahue (2016) volcanoes. The analysis was performed using XPS in the grain-size fraction $<63 \mu\text{m}$ of all tephra samples and also in the glassy fraction of the last three samples. The identification of the F compounds in the near surface-region was performed by the deconvolution of the obtained F 1s spectra. During data acquisition, the compensation of charge effect was performed in order to avoid shifts and false peaks. Besides, the chemical composition of the ashes at greater depth near surface was determined by TEM-EDXS and SEM-EMPA analysis. Finally, leaching experiments under different pH conditions allowed identifying the factors that control the release of fluoride to aqueous reservoirs affected by ash deposition.

2. MATERIALS AND METHODS

2.1. Sampling

All samples used in this study correspond to ashes emitted in eruptions of Patagonian volcanoes that occurred in the last 30 years. The locations of the volcanoes and the corresponding site of sampling are shown in Figure 1. All samples were collected a few hours after the eruptions of the volcanoes Hudson (August 8th-15th 1991), Chaitén (May 2nd 2008), Puyehue (June 3rd-6th 2011), Calbuco (April 23rd 2015,) and Copahue (January 20th 2016). A detailed description of sampling are shown in the supplementary information file.

After collection, samples were air-dried and analyzed with a binocular magnifying glass in order to separate de glassy fraction. Then, samples were sieved through <63 μm mesh to separate the silty-clayed fraction, which represents the most frequent grain-size fraction in these samples.

FIGURE 1

2.2. Chemical and mineralogical characterization

The bulk chemical composition of the volcanic ashes was determined by ICP-OES (Spectro Ciros Vision). In addition, the chemical composition of the volcanic glasses was determined by Electron Micro-Probe Analysis (EMPA) at the LAMARX, laboratory, Universidad Nacional de Córdoba. High resolution-transmission electron microscopy (HR-TEM) observations and EDXS analysis were carried out at the Universidad de Chile. Details about data acquisition are shown in the supplementary information file.

The chemical and mineralogical characteristics of the ashes emitted during the eruptions of the Hudson, Chaitén and Puyehue volcanoes, have been described elsewhere (Bia et al., 2015). Observations using SEM/EDS showed that these samples mostly consist of abundant shards of glass and small grains of crystalline minerals. Although the X-ray diffractograms of the three ashes were typical of poorly crystalline materials, minerals such as quartz, plagioclase and cristobalite were identified in the Chaitén and Puyehue samples. In addition, Bia et al. (2015) report the chemical characterization of single grain minerals performed by SEM/EDS in the Hudson ashes where they identify Ti and Fe (hydr)oxide coatings associated with pyroxene and plagioclase, as well as frequent grains of ilmenite and subhedral to anhedral crystals of pyrite. Occasional halite, gypsum, illite and chromite were also identified. SEM/EDS analysis of the Chaitén ashes, reveal the presence of Fe and Mn oxides, ilmenite, olivine, and euhedral pyrite. Like Hudson, the glass surface shows abundant vesicles filled with fine particles. Acicular crystals of cristobalite are frequently observed in this sample. Minerals such as gypsum, Fe (hydr)oxides and cristobalite were identified by EDS mapping in the Puyehue ashes (Bia et al., 2015). Unlike these ashes, the XRD patterns of the Calbuco and Copahue ashes show more defined peaks, in agreement with the dominance of crystalline minerals (the corresponding XRD patterns are shown in the supplementary information file; Figure S12). The most abundant minerals identified by XRD in both samples were quartz, cristobalite, and plagioclase, while pyroxene was also identified in the Calbuco (2015) sample (Figure S12). In addition, minor and amorphous mineral phases such as ilmenite and Fe (hydr)oxides were identified by SEM-EDS. In Calbuco ashes very fine particles attached to the surface of the glass grains and filling the vesicles were frequently observed by SEM.

2.3. XPS measurements

The chemical composition of the near-surface region (2–10 nm) of the ash fraction <63 μm of all tephra samples was determined by XPS. In addition, XPS spectra of vitreous particles were also obtained in order to assess the speciation of F in different types of glassy fractions. The vitreous particles were separated from the bulk Puyehue, Calbuco and Copahue ashes by picking under a stereo zoom microscope. This could not be achieved with the Hudson and Chaitén samples due to their very fine grain-sized mode (Bia et al., 2015).

Details about XPS data analysis are in the supplementary information file.

2.3.1. *Difficulties in XPS data acquisition: charging effect in volcanic ashes.*

During the X-ray irradiation, all samples analyzed by XPS lose electrons. Conductive samples can compensate this lost almost immediately because of its ground connection (Nesbitt and Bancroft, 2014). However, grounding cannot neutralize non-conductive samples and therefore a charging effect is produced. In consequence, a modified spectrum is usually collected (see below). Many factors are responsible for the charging effect: lateral and vertical compositional heterogeneity of the sample, the mounting technique of the sample on the sample holder, crystallinity and size of particle sample, the performance of the instrument's charge neutralizer, etc. The two main effects of charging are: i) the kinetic energy of the photoelectron is decreased, and this is seen in the spectra as an increase of the binding energy, and ii) non-uniform charging caused by surface imperfections gives rise to peak broadenings, asymmetries, and in some case false peaks. To overcome this, it is necessary to replace the lost photoelectrons in order to provide a steady electrical environment and a stable spectrum. However, procedures are not always enough effective to compensate the

differential charge; when this is the case, it is critical to collect multiple spectra over time in order to monitor possible changes in the spectral shape. In addition, the measurement of a standard element (e.g.: O 1s, Si 2p) during data acquisition help to identify changes in the spectrum. Multiple spectra are also important to obtain the best linewidths on non-conductors, because the charge compensation may change slightly over time, resulting in peak broadening.

The studied volcanic ashes contain non-conductive minerals (i.e.: silicates, (hydr)oxides) and thus, they are prone to exhibit charging effects. To minimize these undesired effects, the sample was bombarded during data acquisition with low-energy electrons supplied by a flood gun, and three spectra of the same element, with no evidence of beam damage were collected. Besides, the spectrum of the O 1s was monitored from the beginning to the end of the measurements, in order to determine the extent of the charging effect. Oxygen was selected because of its abundance in the studied samples. The results shown in the supplementary information file suggest that the variations in the peaks position and intensity in the O 1s spectra were not relevant. In addition, the analysis of the Si 2p spectra of the bulk fraction of recent volcanic ashes and their corresponding vitreous fractions (see supplementary information file) shows that the charging effect was corrected in all samples except in the Calbuco and Puyehue glass samples. Even though the intensity of the XPS scans allowed identifying the signal of F 1s in these samples, the corresponding deconvolution analysis could not be achieved due to the observed changes in the spectrum shape.

2.4. Release experiments

Batch experiments were performed in order to determine the release of fluoride with time under variable pH conditions. About 1.0 g of dry ashes was suspended in 20 mL of Milli-Q water at pH 3.0, 6.5 and 10.0. The ash-to-water ratio was selected following the

recommendations of Armienta et al. (2002) and Witham et al. (2005) in order to avoid precipitation of salts due to oversaturation of the resulting leachates. The pH value of the suspensions was kept constant during the experiments by adding drops of either 0.1 M HNO₃ or NaOH solutions. After every 1.5, 24, 72, 168, 240 and 336 hours since the beginning of the experiments, the suspensions were centrifuged at 5000 rpm for 15 min and the supernatants were completely withdrawn. Then, 20 mL of Milli-Q water (at the same pH value) was added, and the procedure was repeated until reaching 336 h of ash-water interaction. The supernatants retrieved after each time step were filtered through a 0.45 µm cellulose membrane and stored for F determination. Details about fluoride determination are in the supplementary information file. The potential precipitation of secondary phases during the experiments was assessed on the basis of thermodynamics calculations using PHREEQC 3.5.0 (Parkhurst and Appelo, 2013). The results indicate that the solutions are all undersaturated not only in F-bearing salts, but also in other minerals identified at the volcanic ashes surfaces.

The F release rates were determined using the expression $Release\ rate = (CxQ) / m$ (Olsson et al., 2013); where C represents the released F concentration, Q refers to the ratio between the volume of solution and contact time and m represents the mass of the ash sample.

3. RESULTS AND DISCUSSION

3.1. Bulk and surface chemical composition of the ashes and vitreous particles

Table 1 shows the bulk chemical composition of the studied volcanic ashes and individual glass grains. According to the TAS classification (Le Maitre, 2002), Hudson (1991) ashes are trachy-andesitic in type, the Puyehue sample shows a trachy-dacitic

composition, Chaitén ashes are rhyolitic, Calbuco are basalt-andesitic and the Copahue ashes are of the basaltic trachy-andesitic type.

In all samples, the ratios between the concentrations in the bulk sample (A) and in the glass (G) of elements like Fe, Ca, Mg, and P are higher than 1.0, and indicate that all these elements are more concentrated in the bulk ash than in the glass grains (Table 1). The average value of F concentrations in the glassy fraction varies from $280 \pm 50 \mu\text{g g}^{-1}$ ($n = 31$) in the Chaitén and Calbuco glasses ($280 \pm 60 \mu\text{g g}^{-1}$; $n = 25$) to $480 \pm 90 \mu\text{g g}^{-1}$ ($n = 26$) in the Puyehue (2011) glass. Intermediate values were found in the Hudson glasses ($350 \pm 70 \mu\text{g g}^{-1}$; $n = 25$). A/G ratios determined in the Hudson and Puyehue samples were close to 1 indicating that F is not preferentially partitioned into the vitreous or crystalline phases in these samples (Table 1). The A/G ratio <1 in the Chaitén sample indicates that: i) F is not preferentially associated with the glass particles or ii) the presence of non F-bearing minerals in the crystalline fraction of the ashes produces the dilution of F concentrations in the bulk sample. On the contrary, the A/G values determined in the Calbuco sample are higher than 1, indicating that F is mostly associated with the crystalline fraction.

TABLE 1

Besides the chemical composition of the bulk ashes and their corresponding glassy fractions, the chemical composition (in atom %) of the top first nanometers of the bulk Hudson, Chaitén, Puyehue and Copahue ashes and the glassy fraction of the Calbuco and Copahue samples was also determined. Figure 2 shows the surface/bulk (S/B) ratios of some selected elements, as a measure of possible elemental surface enrichments or depletions.

FIGURE 2

The obtained S/B ratios indicate that F is enriched at the particle's surfaces, whatever the analyzed fraction. On the contrary, major elements such as Si, Al and Ca do not show marked variations, regarding their concentrations in the bulk ash or the particle's surface. Some major elements such as Na, K and Fe are depleted in the surface of most of the samples, while Mg is enriched in the Hudson, Chaitén and Puyehue ashes (Figure 2).

3.2. F speciation in fresh volcanic ashes and glass particles**3.2.1. F 1s XPS spectra**

Figure 3 shows the XPS spectra of the F 1s band obtained for the bulk fraction of the five volcanic ashes (a-e) while Figure 3f shows the surface F concentration. The corresponding binding energies (BE) assignments are shown in Table 2. Despite the fact that the intensity of the signal in Chaitén is high enough to confirm the presence of F, it is also too weak and noisy to perform the decomposition of the spectrum (Figure 3b). In the spectrum of the Calbuco sample, the charging effect could not be corrected (see Si 2p spectra in supplementary information file; Figure SI4c); nevertheless, the F 1s signal was high enough to discriminate a fake peak and to avoid interference in the decomposition of the spectrum (Figure 3d). Reference values used for peak identification (reported in the supplementary information file; Table SI7) suggest that the most abundant peaks in all samples at ~685 and ~686 eV may correspond to F-Al and F-Si compounds, respectively. In addition, the peaks at ~682-684 eV correspond to

F salts (i.e.: F-Na, F-K, F-Ca, F-Fe) while the signal at ~687 eV is assigned to F_x-Si bonds.

FIGURE 3

As mentioned above, the decomposition of the Chaitén spectrum could not be achieved due to its low intensity and noisy signal. However, the peak width of ~5 eV is too broad for only one contribution to the spectrum. This peak broadening can be the result of contributions from other individual signals, probably from F-salts compounds, with signals at ~683 eV.

Regarding the atom surface concentration (Figure 3f), Hudson, Chaitén and Puyehue samples show similar concentrations, while the highest contents of surficial F atoms were determined in the Calbuco and Copahue ashes.

TABLE 2

Figure 4 shows the XPS spectra of the F 1s band of the vitreous fraction of the Puyehue, Calbuco and Copahue ashes along with their corresponding surface F concentration (Figure 4d). The charging effects in the glass fraction of the Puyehue sample was not corrected (see Si 2p spectra in supplementary information file; Figure SI4c) but the signal of F 1s band is enough intense to confirm the presence of F (Figure 4a). Like in the analysed bulk samples, the peaks located at ~685 and ~686 eV are assigned to F-Al and F-Si bearing compounds, while the peaks at ~682-684 eV correspond to F-bearing salts. The signal at 688 eV identified in the Calbuco vitreous fraction could be attributed to F_x-Si species. As previously observed in the bulk

fractions, the concentration of surficial F in the vitreous fraction was the highest in the Copahue sample (Figure 4d).

FIGURE 4

3.2.2. TEM analysis

The presence of F-salts in the studied ash samples, inferred from the F-cation signals determined by the deconvolution of the XPS spectra, were confirmed through TEM-EDXS observations (Figure 5). The analysis performed on small particles attached onto the glass surface and on the bulk glass grains that showed signs of surface alteration, revealed the presence of a number of F-rich phases. In Figure 5a, the small crystals attached onto the glass surface in the Hudson sample (point 2), are enriched in F and Ca, thus suggesting the presence of F-Ca compounds. In the Chaitén sample, the attached aggregate (point 2; Figure 5b) is highly enriched in F, Fe, Na and Mg when compared with the aluminosilicate glass particle (point 1). Particles attached onto the glass grains of the Puyehue sample (point 2; Figure 5c) are enriched in F, Al, Fe, Na, Ca, K, Mg and As. In the Calbuco sample, the comparison was performed between two points in the attached aggregate (Figure 5d). The results indicate that the border of the aggregate's surface (point 2) shows lower Si contents than the bulk particle (point 1); in an opposite way Al, Fe, Na, Ca and F are enriched at the surface.

FIGURE 5

3.2.3. Fluoride released under different pH conditions

The trends of F release from the ashes in contact with solutions at pH 3.0, 6.5 and 10.0 were analysed in a period of 14 days (Figure 6). In all cases, the release involves

two stages: an initial stage, which occurs during the first 90 minutes, followed by a second stage that extends to the end of the experiments, after ~300 h of ash-solution reaction. Regardless the pH value, the amounts of fluoride released from the Hudson and Chaitén ashes during the first 90 minutes is about ~5 % of their respective bulk F contents. On the contrary, the fluoride released from the Copahue ash is significantly higher in the same time lapse, accounting for up to ~44% of the bulk F content at pH 10. Intermediate values were determined in the Puyehue and Calbuco experiments, where ~18 % of the bulk F content is released to the solution (data available in the supplementary information file, Table SI9a).

The first step, may involve the dissolution of relatively soluble F-bearing compounds derived from the dissolution of volcanic gases and aerosols sorbed/co-precipitate onto the ash surfaces during the eruption (Oskarsoon et al. 1980; Jones and Gislason, 2008; Bagnato et al., 2011; Olsson et al., 2013). The comparative analysis of the rates release at the initial stages of the experiments shows that a pseudo-equilibrium condition is reached faster in the Puyehue, Calbuco and Copahue samples than in the remaining samples. The rates of F release in these initial stages are reported in the supplementary information file (Table SI9b). The rate of F release from the Copahue ashes is $326 \mu\text{g g}^{-1}(\text{ash}) \text{ h}^{-1}$ at neutral pH, which is about 5-11 times higher than the initial rates determined for the Calbuco and Puyehue samples, and 60 to 100 times higher than the values determined in the Hudson and Chaitén samples. This behavior suggests the presence of soluble F-phases in Copahue ashes.

After 72 h of ash-water interaction, all kinetics curves become slightly flat (supplementary information file; figure SI9) which indicates that F is gradually released from more insoluble phases, probably the F-bearing glass. At this stage the rate of F release, is from 30 to 120 times slower than in the initial stage. The values vary from

3.3 $\mu\text{g g}^{-1}_{(\text{ash})} \text{h}^{-1}$ in the Copahue ashes to 0.05 $\mu\text{g g}^{-1}_{(\text{ash})} \text{h}^{-1}$ in Chaitén ashes at neutral pH. Intermediate values ($<1 \mu\text{g g}^{-1}_{(\text{ash})} \text{h}^{-1}$) were found in the Hudson, Puyehue and Calbuco ashes (data available in the supplementary information file, Table SI9b).

FIGURE 6

The release of F from the studied ashes is also a pH-dependent process. Figure 7 shows the variation of the fluoride concentrations with pH, after 1.5 h and 14 days of ash-solution interaction. Data obtained at 1.5 h were assigned to contributions from soluble F-phases, as the volcanic glass dissolution is expected to be minimal in the first hours of interaction. As seen in the figure, the behavior among the analyzed ashes was different. In the case of the Calbuco, Puyehue and Copahue ashes, a V-shape trend was observed with higher releases occurring at extreme pH conditions (highly acidic and alkaline pH).

During the glass dissolution process, it is expected that the release of F, Al and Si atoms may occur jointly with a higher release of these elements at extreme pH values. The solid curve shown in Figure 7f represents the concentration of Al released after the dissolution of basaltic glasses at 25°C, as predicted by the rate law suggested by Gislason and Oelkers, (2003). For the Calbuco, Puyehue and Copahue ashes, the Al concentration released after 14 days of reaction resemble the theoretical curve suggesting that the dissolution of the Al-silicate glass is taking place. The two remaining ash samples showed a different behavior. In the case of the Hudson and Chaitén samples, the highest F release occurs at acidic pH values and the lowest, at alkaline conditions. According to literature, F-minerals such as fluorapatite are more soluble at acidic pH (García and Borgnino, 2015) and thus, are expected to contribute F

to the leachates at this pH value. In addition, the release of F from the Chaitén sample at 1.5 h is clearly pH-independent suggesting that the dissolution of F salts compounds, like CaF_2 or NaF , has taken place (García and Borgnino, 2015). Therefore, these two F-phases likely dominate the release of fluoride during the early stages of the ash-water interaction.

FIGURE 7

Leachates of the Hudson, Chaitén and Puyehue ashes were also collected after three years of reaction (data shown in the supplementary information file). In such period of time, the concentration of fluoride released to the solution was similar or slightly higher than the values recorded after 14 days of reaction, revealing that the more available phases of F in the studied Patagonian ashes were almost completely released after two weeks of ash-water interaction.

3.3. F-bearing phases involved in the release of fluoride to the environment

In the studied Patagonian ashes the F-bearing phases have been identified by combining spectroscopic (XPS, EMPA, HR-TEM-EDX) and experimental (batch leaching experiments) techniques. The obtained data indicate that two main types of F-phases are present in the studied ashes: i) water-soluble F-salt coatings, that release F to water within the first hour of ash-water interaction, and ii) F-bearing aluminosilicate glass, that may release F in longer periods of ash-water interaction and specially when pH conditions are extreme.

A number of studies involving volcanic ashes worldwide, reported the rapid release of F when they are exposed to water, due to the dissolution of soluble F-minerals such

as CaSiF_6 as well as F-Na and F-Ca salts (Oskarsson, 1980; Cronin et al., 2003). In the Hudson sample, the presence of coatings of CaF_2 and/or fluorapatite was determined by XPS and HR-TEM/EDAXS measurements. In the Chaitén ashes, two types of F-salts were estimated using batch leaching experiments and identified by HR-TEM/EDAXS analysis. i) a pH independent and highly soluble salt, likely NaF or CaF_2 and ii) a F-phase more soluble at pH 3, likely fluorapatite. In the Puyehue, Calbuco and Copahue samples, NaF salts were confirmed by the deconvolution of the corresponding XPS spectra.

Once the more soluble F-salts have been removed, the release of F atoms from less soluble phases, such as the aluminosilicate glass, starts but this process may take hundred million years to be completed under the climatic conditions dominating the Patagonia and Pampean regions of South America (Bia et al., 2017). Typical peaks of F-Al and F-Si bondings in the XPS spectra of the Puyehue, Calbuco and Copahue ashes correspond to F atoms included within the aluminosilicate glass lattice, while the $\text{F}_x\text{-Si}$ species is the result of the glass alteration at highly acidic conditions in the eruption plume. Previous works have assigned this signal to four-coordinated species in aluminosilicate glass. For example, $\text{SiF}(\text{O}-)_3$ species were identified by RMN in fluoridated silica glass (Zeng and Stebbins, 2000), but some other possible species are SiF_4 , $\text{SiF}_3(\text{O}-)$, $\text{SiF}_2(\text{O}-)_2$, and $\text{SiF}(\text{O}-)_3$.

The presence of coatings of barely soluble F-Ca compounds in volcanic ashes may also inhibit the dissolution of the underlying glass, at least during the initial stages of the ash-water interaction. According to the literature (e.g., Tomassin and Touray, 1979; Berger et al., 1979; Guy and Schott, 1989; Gout et al., 1997; Crovisier et al., 2003; Oelkers et al., 2009; Declercq et al., 2013), the dissolution of natural aluminosilicate glasses occurs via a series of steps that involves a rapid release of alkaline elements near

the surface, followed by the hydrolysis of the glass network that produce the release of the network-forming elements. The result is the formation of a surface layer that passivates the glass surface, reducing the chemical interaction between the glass surface and the ions present in the solution (Piovesan et al., 2018), causing a drop down in the dissolution rate. In consequence, the type of secondary phases formed onto the glass surface depends on the composition of both, the glass itself and the solution in contact with the vitreous particles (Piovesan et al., 2018). Therefore, when volcanic ashes are in contact with acidic gases, a partial dissolution of glass occurs and fluoride is released along with alkaline elements. This process favors the precipitation of F-salts, which may rapidly dissolve in contact with water releasing F or may also inhibit further glass dissolution, when the solubility of the newly formed salt is lower.

The amount and rate of F released from volcanic ashes exposed to water is closely associated with the type of F-compounds present in the ashes and in turn, this has important environmental implications in regions affected by volcanic ash fall, like the southern South America (Stewart et al., 2006). In this region, the largest eruptions were recorded during the 20th century (i.e., Quizapu, 1932; Hudson, 1991) and produced heavy ashfall in regions as far as Rio Janeiro, Brazil (Quizapu eruption; González-Ferrán, 1995), the Malvinas Islands in the South Atlantic Ocean (Hudson eruption, 1991; Tilling, 2009) and Uruguay (Calbuco eruption, 2015; Van Eaton et al., 2016). Highly soluble F-phases present in volcanic ashes, are responsible for raising fluoride concentrations after ashfall in aquatic reservoirs and rainfall-fed water tanks (e.g., Stefánsson and Sigurjónsson, 1957; Collins, 1978; Cronin et al., 1998; Cronin et al., 2003). In a recent review, Flueck (2016) reported a rapid accumulation of fluoride in herbivores exposed to tephra from Puyehue and Calbuco eruptions. Surveys carried out after the eruption, revealed that wildlife exhibited pronounced clinical signs of fluorosis,

with levels of F in bone up to 10000 ppm of fluoride by 2014. Livestock including horses, cattle and sheep also had high levels of bone F and clinical fluorosis.

4. CONCLUSIONS

The volcanic ashes emitted after the eruptions of the Andean volcanoes Hudson (1991), Chaitén (2008), Puyehue (2011), Calbuco (2015) and Copahue (2016) contain elevated concentrations of F that can be released into the aqueous reservoirs affecting their use as drinking water sources, and causing adverse health effects for animals due to the exposure and dietary intake of ash-coated crops, pasture or soil.

Traditional X-ray photoelectron spectroscopy analysis of silicate minerals may lead to inaccurate elemental species identification due to charging effects. However, the use of an electron flood gun during spectral acquisition can help to decrease these charging effects and to obtain well resolved spectra than can be accurately fitted and quantified without resorting to constraints or assumptions. The decomposition of F 1s XPS spectra coupled with HR-TEM-EDX analysis, EMPA and batch leaching experiments allowed identifying the main F-bearing compounds present in recently emitted Patagonian ashes. The most soluble F-phases correspond to F-Na and F-Ca salts (likely fluorite and fluorapatite) precipitated as thin coatings onto the glass particles. Less available forms of F are represented by F atoms included as impurities within the glass lattice forming F-Si and F-Al bonds. The release of F from this phase is more significant under extreme pH conditions.

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References

- Armienta M.A., De la Cruz-Renya S., Morton O., Cruz O. and Cenicerros N. (2002) Chemical variation of tephra-fall deposit leachates for three eruptions from Popocatepetl volcano. *J. Volcanol. Geotherm. Res.* **113**, 61–80.
- Aradóttir E.S.P., Sigfússon B., Sonnenthal E.L., Björnsson G. and Jónsson H. (2013) Dynamics of basaltic glass dissolution — Capturing microscopic effects in continuum scale models. *Geochim. Cosmochim. Acta.* **121**, 311–327.
- Barone G., Mazzoleni P., Corsaro R.A., Costagliola P., Di Benedetto F., Ciliberto E., Gimeno D., Bongiorno C. and Spinella C. (2016). Nanoscale surface modification of Mt. Etna volcanic ashes. *Geochim. Cosmochim Acta.* **174**, 70–84.
- Bagnato E., Aiuppa A., Bertagnini C., Bonadonna C., Cioni R., Pistolesi M., Pedone M. and Hoskuldsson A. (2013) Scavenging of sulphur, halogens and trace metals by volcanic ash: The 2010 Eyjafjallajökull eruption. *Geochim. Cosmochim Acta.* **103**, 138–160.

- Berger G., Schott J. and Loubet M. (1987) Fundamental processes controlling the 1st stage of alteration of a basalt glass by seawater — an experimental study between 200 and 320 °C. *Chem. Geol.* **71**, 297–312.
- Bia G., Borgnino L., Gaiero D. and Garcia M.G. (2015) Arsenic-bearing phases in South Andean Volcanic ashes: Implications for As mobility in Aquatic environments. *Chem. Geol.* **26-35**, 393-394.
- Bia G., Garcia M.G. and Borgnino L. (2017) Changes in the As solid speciation during weathering of volcanic ashes: A XAS study on Patagonian ashes and Chacopampean loess. *Geochim. Cosmochim. Acta* **212**, 119-132.
- Borisova A.Y., Pokrovski G.S., Pichavant M., Freydier R. and Candaudap F. (2010) Arsenic enrichment in hydrous peraluminous melts: Insights from femtosecond laser ablation inductively coupled plasma-quadrupole mass spectrometry, and in situ X-ray absorption fine structure spectroscopy. *Am. Mineral.* **95**, 1095–1104.
- Brauer D.S., Karpukhina N., Law R.V. and Hill R.G. (2009) Structure of fluoride-containing bioactive glasses. *J. Mater. Chem.* **19**, 5629–5636.
- Collins C.M. (1978) Contamination of water supplies and water courses. Appendix 2 In: Healy, J., Lloyd, E.F., Rishworth, D.E., Wood, C.P., Glover, R.B., Dibble, R.R. (Eds.) The Eruption of Ruapehu, New Zealand, on 22 June 1969. *DSIR Bulletin*, 224.
- Cronin S.J., Hedley M.J., Neall V.E. and Smith G. (1998) Agronomic impact of tephra fallout from 1995 and 1996 Ruapehu volcano eruptions, New Zealand. *Environmental Geology* **34**, 21-30.
- Cronin S.J., Neall V.E., Lecointre J.A., Hedley M.J. and Loganathan P. (2003) Environmental hazards of fluoride in volcanic ash: a case study from Ruapehu volcano, New Zealand. *J. Volcanol. Geotherm. Res.* **121**, 271–291.

- Crovisier J.L., Advocat T. and Dussossoy J.L. (2003) Nature and role of natural alteration gels formed on the surface of ancient volcanic glasses (natural analogues of waste containment glasses). *J. Nucl. Mater.* **321**, 91–109.
- Dalou C. and Mysen B.O. (2015) The effect of H₂O on F and Cl solubility and solution mechanisms of in aluminosilicate melts at high pressure and high temperature. *American Mineralogist.* **100**, 633–643.
- Declercq J., Diedrich T., Perrot M., Gislason S.R. and Oelkers E.H. (2013) Experimental determination of rhyolitic glass dissolution rates at 40–200 °C and 2 < pH < 10.1. *Geochim. Cosmochim. Acta* **100**, 251–263.
- Delmelle P., Lambert M., Dufrene Y., Gerin P. and Oskarsson N. (2007) Gas/aerosol-ash interaction in volcanic plumes: new insights from surface analyses of fine ash particles. *Earth Planet. Sci. Lett.* **259**, 159-170.
- Edmonds M., Oppenheimer C., Pyle D.M. and Herd R.A. (2003) Rainwater and ash leachate analysis as proxies for plume chemistry at Soufrière Hills volcano, Montserrat. In: Oppenheimer, C., Pyle, D.M., Barclay, J. (Eds.), *Volcanic Degassing*. Geological Society, London.
- Farges F., Linnen R.L. and Brown Jr. G.E. (2006) Redox and speciation of tin in hydrous silicate glasses: A comparison with Nb, Ta, Mo, and W. *Canadian Mineralogist.* **44**, 795–810.
- Flueck W.T. (2016) The impact of recent volcanic ash depositions on herbivores in Patagonia: a review. *The Rangeland Journal.* **38**, 24-37.
- Garcia M.G. and Borgnino L. (2015) Fluoride in the context of the environment. In *Fluorine: Chemistry, Analysis, Function and Effects*. 3-21.
- Gislason S.R. and Oelkers E.H. (2003) The mechanism, rate and consequence of basaltic glass dissolution: II. An experimental study of the dissolution rates of basalts

- as a function of pH at temperatures from 6°C to 150°C. *Geochim. Cosmochim. Acta.* **67**, 3817–3832.
- Gislason S.R., Hassenkam T., Nedel S., Bovet N., Eiriksdottir E.S., Alfredsson H.A., Hem, C.P., Balogh Z.I., Dideriksen K., Oskarsson N., Sigfusson B., Larsen G. and Stipp S.L.S. (2011) Characterization of Eyjafjallajökull volcanic ash particles and a protocol for rapid risk assessment. *Proc. Nat. Acad. Sci. U.S.A.* **108**, 7307–7312.
- González-Ferrán O. (1995) Volcanes de Chile: Instituto Geográfico Militar, Santiago, Chile, (639 pp.).
- Gout R., Oelkers E.H., Schott J., Zwick A. (1997) The surface chemistry and structure of acid leached albite: new insights on the dissolution mechanism of the alkali feldspars. *Geochim. Cosmochim. Acta* **61**, 3013–3018.
- Guy C., Schott J. (1989) Multisite surface reaction versus transport control during the hydrolysis of a complex oxide. *Chem. Geol.* **78**, 181–204.
- Hochella MF Jr (1988) Auger electron and X-ray photoelectron spectroscopies. *Reviews in Mineral* **18**:573-637.
- Jones M.T. and Gislason S.R. (2008) Rapid releases of metal salts and nutrients following the deposition of volcanic ash into aqueous environments. *Geochim. Cosmochim. Acta.* **72**, 3661–3680.
- Karpukhina N., Law R.V. and Hill R.G. (2008) Solid state NMR study of calcium fluorosilicate glasses. *Adv. Mat. Res.* **39–40**, 25–30.
- Kiczinski T.J. and Stebbins J.F. (2002) Fluorine sites in calcium and barium oxyfluorides: F-19 NMR on crystalline model compounds and glasses. *J. Non-Cryst. Solids* **306**, 160–168.

- Kohn S.C., Dupree R., Mortuza M.G. and Henderson C.M.B. (1991) NMR evidence for five- and six-coordinated aluminum fluoride complexes in F-bearing aluminosilicate glasses. *Am. Mineral.* **76**, 309–312.
- Le Maitre R.W. (2002) *Igneous Rocks: A Classification and Glossary of Terms: Recommendations of International Union of Geological Sciences Subcommittee on the Systematics of Igneous Rocks*. Cambridge University Press.
- Mysen B.O., Cody G.D. and Smith A. (2004) Solubility mechanism of fluorine in peralkaline and meta-aluminous silicate glasses and in melts to magmatic temperatures. *Geochim. Cosmochim. Acta.* **68**, 2745–2769.
- Nesbitt H.W. and Bancroft G.M. (2014) High Resolution Core- and Valence-Level XPS Studies of the Properties (Structural, Chemical and Bonding) of Silicate Minerals and Glasses. *Mineralogy & Geochemistry.* **78**, 271-329.
- Oelkers, E.H., Golubev, S.V., Chairat, C., Pokrovsky, O.S., Schott, J., 2009. The surface chemistry of multi-oxide silicates. *Geochim. Cosmochim. Acta* **73**, 4617–4634.
- Olsson J., Stipp S.L.S., Dalby K.N. and Gislason S.R. (2013) Rapid release of metal salts and nutrients from the 2011 Grímsvötn, Iceland volcanic ash. *Geochim. Cosmochim. Acta.* **123**, 134–149.
- Oskarsson N. (1980) The interaction between volcanic gases and tephra: fluorine adhering to tephra of the 1970 Hekla eruption. *J. Volcanol. Geotherm. Res.* **8**, 251–266.
- Parkhurst D.L. and Appelo, C.A.J. (2013) Description of input and examples for PHREEQC version 3. A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey

- Techniques and Methods, book 6, chap. A43, 497 p., available only at <https://pubs.usgs.gov/tm/06/a43/>.
- Piovesan V., Bardez-Giboire I., Fournier M., Frugier P., Jollivet P., Montouillout V., Pellerin N. and Gin S. (2018) Chemical durability of peraluminous glasses for nuclear waste conditioning. *npj Mater. Degrad.* **2**, 7.
- Ruggieri F., Saavedra J., Fernandez-Turiel J.L., Gimeno D. and Garcia-Valles M., (2010) Environmental geochemistry of ancient volcanic ashes. *J. Hazard.Mater.* **183**, 353–365.
- Schaller T., Dingwell D.B., Keppler H., Knoller W., Merwin L. and Sebald A. (1992) Fluorine in silicate glasses: a multinuclear magnetic resonance study. *Geochim. Cosmochim. Acta.* **56**, 701–707.
- Shen A.H. and Keppler H. (1997) Direct observation of complete miscibility in the albite-H₂O system. *Nature.* **385**, 710–712.
- Smithsonian Institution, 2000. Copahue. Bulletin of the Global Volcanism Network (BGVN) 25 (6).
- Stamboulis A., Hill R.G. and Law R.V. (2005) Structural characterization of fluorine containing glasses by ¹⁹F, ²⁷Al, ²⁹Si and ³¹P MAS-NMR spectroscopy. *J. Non-Cryst. Solids.* **351**, 3289–3295.
- Stebbins J.F. and Zeng Q. (2000) Cation ordering at fluoride sites in silicate glasses: a high-resolution ¹⁹F NMR study. *J. Non-Cryst. Solids.* **262**, 1–5.
- Stebbins J.F., Kroeker S., Lee S.K. and Kiczanski T.J. (2000) Quantification of five- and six-coordinated aluminium ions in aluminosilicate and fluoride-containing glasses by high- field, high-resolution ²⁷Al NMR. *J. Non-Cryst. Solids.* **275**, 1–6.

- Stefánsson K. and Sigurjónsson J. (1957) Temporary increase in fluorine content of water following the eruption. In: Einarsson, T., Kjartansson, G., Thorarinsson, S. (Eds.) *The Eruption of Hekla 1947–48 III*, 3. Soc. Scientiarum Islandica, Reykjavik.
- Stewart C., Johnston D.M., Leonard G.S., Horwell C.J., Thordarson T. and Cronin S.J. (2006) Contamination of water supplies by volcanic ashfall: a literature review and simple impact modeling. *J. Volcanol. Geotherm. Res.* **158**, 296–306.
- Thomassin J.H., Touray J.C. (1979) Early stages of water-basaltic glass interaction — X-ray photo-electrons spectroscopy (XPS) and scanning electron-microscopy (SEM) investigations. *Bull. Miner.* **102**, 594–599.
- Tilling R.I. (2009) Volcanism and associated hazards: the Andean perspective. *Adv. Geosci.* **22**, 125–137.
- Van Eaton A.R., Amigo A., Bertin D., Mastin L.G., Giacosa R.E., Gonzalez G., Valderrama O., Fontijn K. and Behnke S.A. (2016) Volcanic lightning and plume behavior reveal evolving hazards during the April 2015 eruption of Calbuco volcano, Chile. *Geophys. Res. Lett.*, **43**.
- Witham C.S., Oppenheimer C. and Horwell C.J. (2005) Volcanic ash-leachates: A review and recommendations for sampling methods. *J. Volcanol. Geotherm. Res.* **141**, 299–326.
- Zeng Q. and Stebbins J.F. (2000) Fluoride sites in aluminosilicate glasses: high-resolution ^{19}F NMR results. *Am. Mineral.* **85**, 863–867.

FIGURE CAPTIONS

Figure 1. Location of sampling points and volcanoes that emitted the studied ashes. White circles: sampling site; black pentagons: location of the volcanoes. Map of the southern part of South American continent was modified from PIA03388 image.

Figure 2. Surface/bulk (S/B) ratios of the bulk volcanic ashes and vitreous particles. S/B values are shown in the supplementary information file Table SI6a and SI6b.

Figure 3. F 1s spectra of the studied volcanic ashes (a-e). Shirley background is shown as a solid curve at the base of the peaks in the spectra of the Puyehue (2011), Calbuco (2015) and Copahue (2016) volcanic ashes. The best fit curve is shown by a solid thick line; individual F 1s peaks are indicated with dashed lines. The solid curve in the F 1s spectra of Chaitén (2008) sample is only indicative of the trend of the signal. (f) Surface F concentrations expressed in atoms %.

Figure 4. F 1s spectra of the vitreous fractions of Puyehue (2011), Calbuco (2015) and Copahue (2016) ashes (a-c). A Shirley background is shown as a solid curve at the base of the peaks, and the best fit curve is shown by a solid thick line; individual F 1s peaks are indicated with dashed lines. The solid curve in F 1s spectra of the Puyehue (2011) glass sample is only indicative of the trend of the signal. (d) Surface F concentrations expressed in atoms %.

Figure 5. HR-TEM images and plots showing the ratios between the elemental concentrations determined in points 1 and 2 in the TEM images. Concentrations are reported in the supplementary information file Table SI8.

Figure 6. Fluoride released at pH 3 (triangles), 6.5 (circles), 10.0 (squares) during 336 h of reaction (a-e). (f) Fluoride concentrations released after 14 days and 3 years of exposure to Milli-Q water (pH 6.5). Concentrations are reported in the supplementary information file; Table SI9a. The curves drawn through the measured points are indicative only of the general trend followed by the samples.

Figure 7. Fluoride released after 1.5 h (dashed lines) and 14 days (solid lines) of reaction at pH 3.0, 6.5 and 10.0 from the bulk studied ashes (a-e). Concentrations are reported in the supplementary information file; Table SI9a. (f) Plot showing the log Al released as a function of pH in leachates obtained after 14 days of suspension. Solid thick line: theoretical dissolution of basaltic glass (Aradóttir et al., 2013); dashed lines: experimental results. Squares: Hudson (1991); circles: Chaitén (2008); triangles: Puyehue (2011); open circles: Calbuco (2015); open squares: Copahue (2016).

TABLES CAPTIONS

Table 1. Chemical composition of volcanic ashes (<63 μm) and volcanic glasses separated from the ashes. Bulk composition was determined by ICP/OES and ISE, while glass composition was measured with EMPA (reported values correspond to the average of more than 20 measurements). A/G corresponds to the ratio between the bulk concentration and the corresponding value in the glass. A/G values higher than 1.0 are in bold.

Table 2. XPS F 1s binding energy (eV) assignments for the studied ashes. The proportion of F-bearing phases are in percentage. BE values correspond to the maximum intensity of the fitted peak.

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Table 3. XPS F 1s binding energy (eV) assignments for the studied ashes. The proportion of F-bearing phases are indicated in terms of percentage. BE values correspond to the maximum intensity of the fitted peak.

<i>Samples</i>	<i>Designation</i>											
	F-salts				F-Al		F-Si		F _x -Si			
	BE	%	BE	%	BE	%	BE	%	BE	%		
<i>Volcanic ashes</i>												
Hudson (1991)					684.6	50.0			686.4	50.0		
Puyehue (2011)			683.8	26.0			685.7	42.1			687.9	31.9
Calbuco (2015)	682.5	10.3			684.2	31.2	685.8	36.2			687.3	22.3
Copahue (2016)			683.9	21.3			685.4	51.4	686.8	27.4		
<i>Vitreous particles</i>												
Calbuco (2015) glass			683.8	28.9			685.5	57.8			688.0	13.3
Copahue (2016) glass			683.9	21.3			685.5	54.4			687.1	24.2

HIGHLIGHTS

- Volcanic ashes from Patagonian volcanoes contain concentrations of F from 126 to 1500 $\mu\text{g g}^{-1}$.
- F is concentrated onto the volcanic ashes surface.
- F-Na and F-Ca salts are precipitated as thin coating onto the glass particle.
- F-Si and F-Al bonds correspond to F impurities within the glass structure.

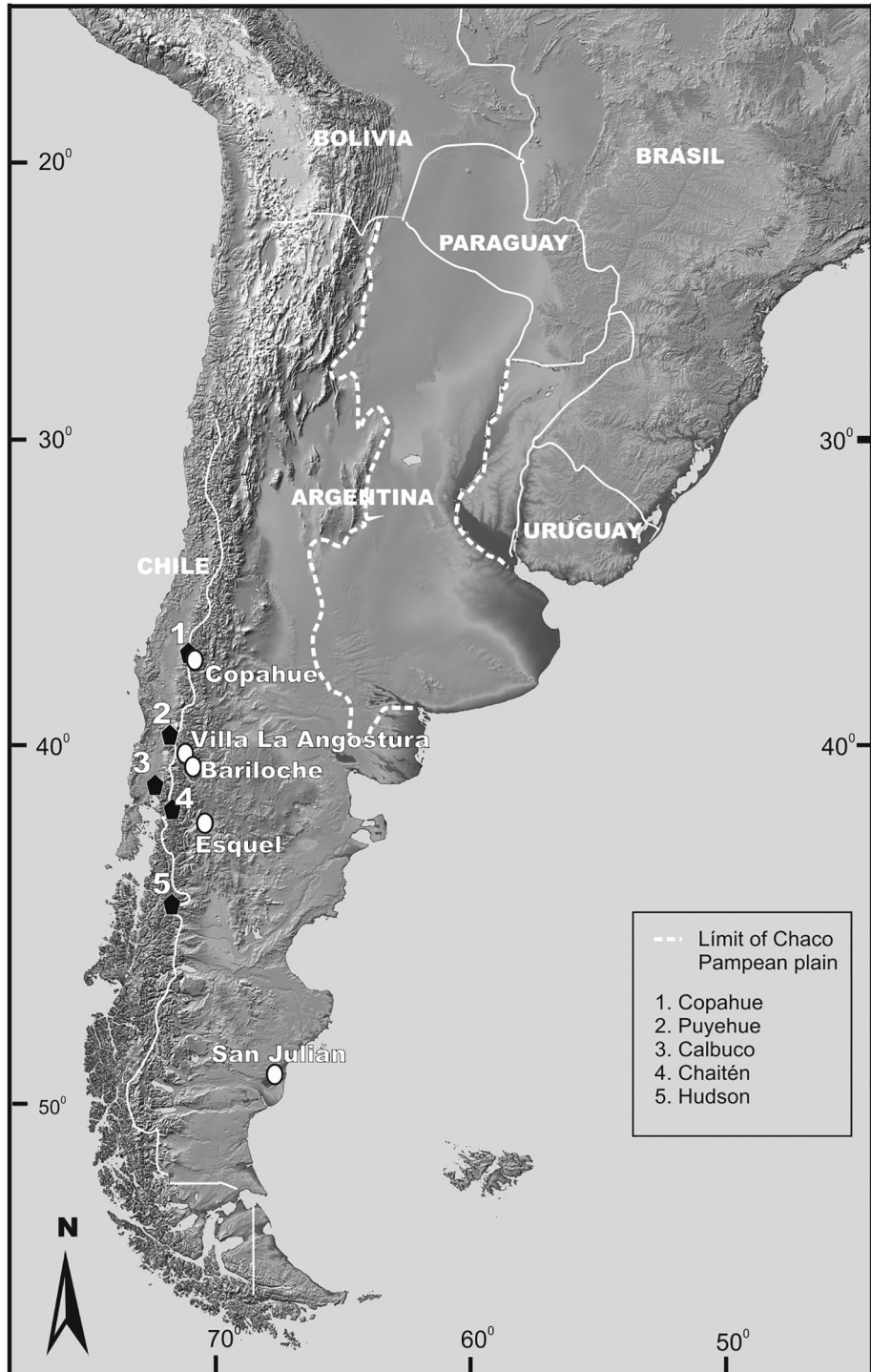


Figure 1

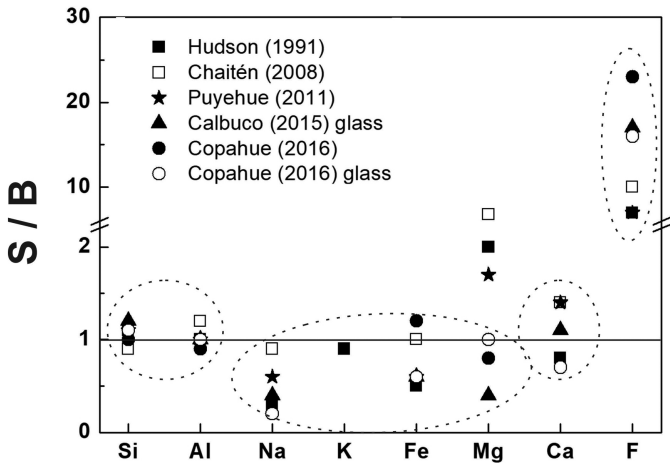


Figure 2

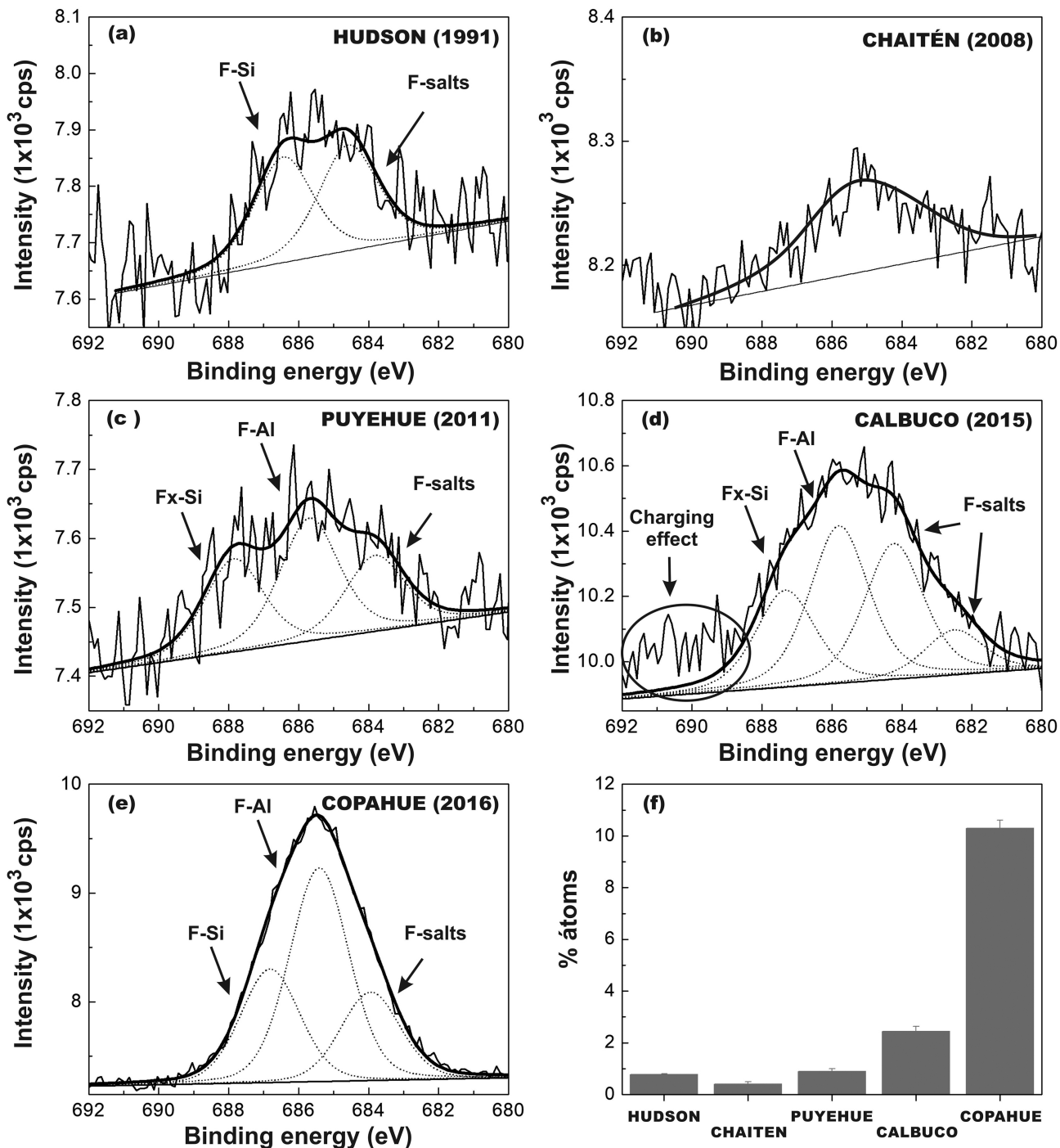


Figure 3

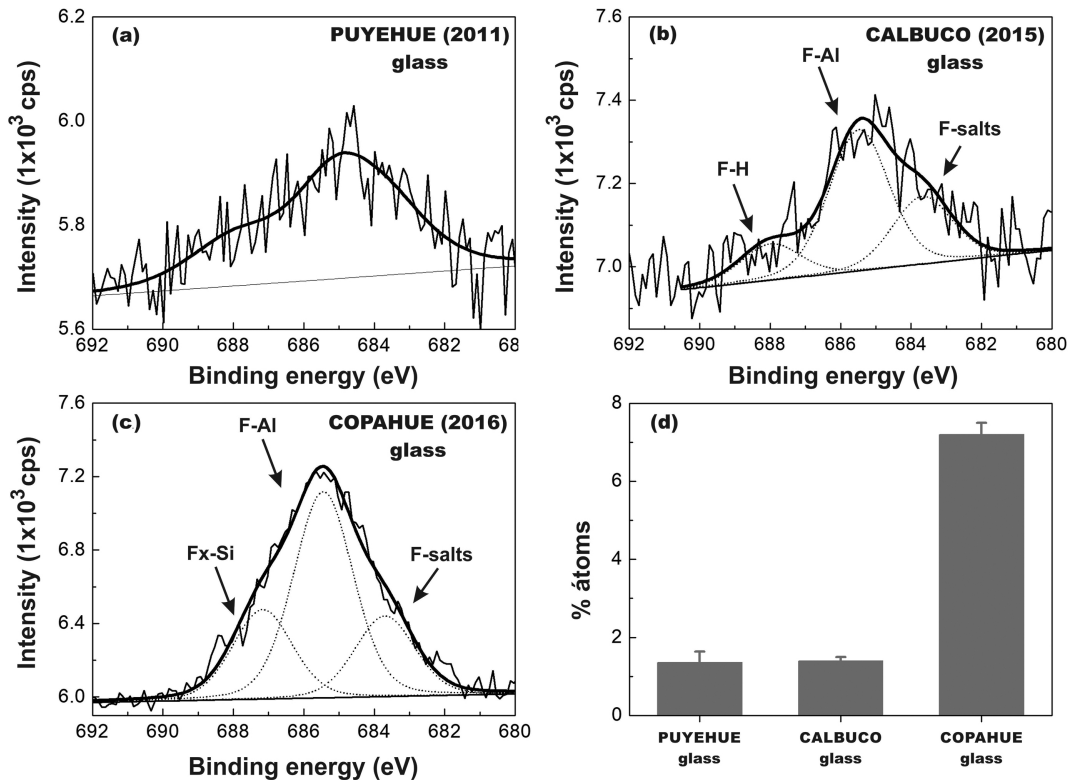


Figure 4

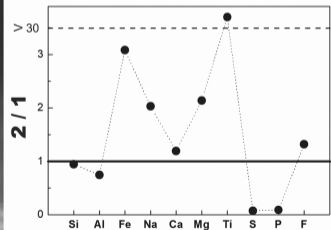
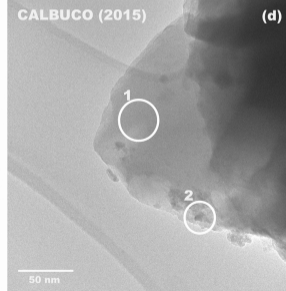
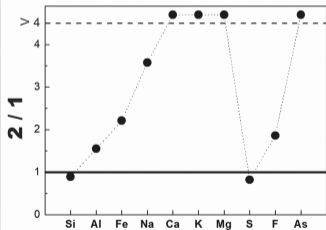
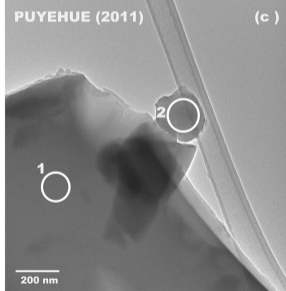
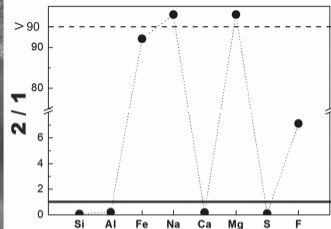
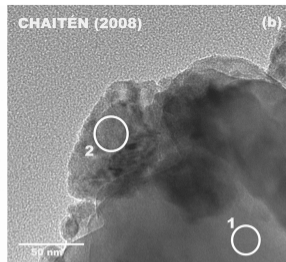
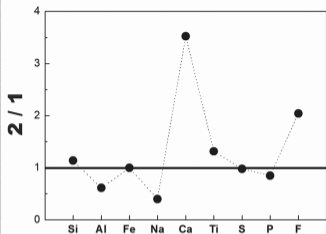
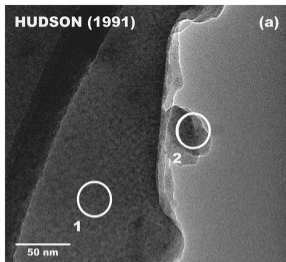


Figure 5

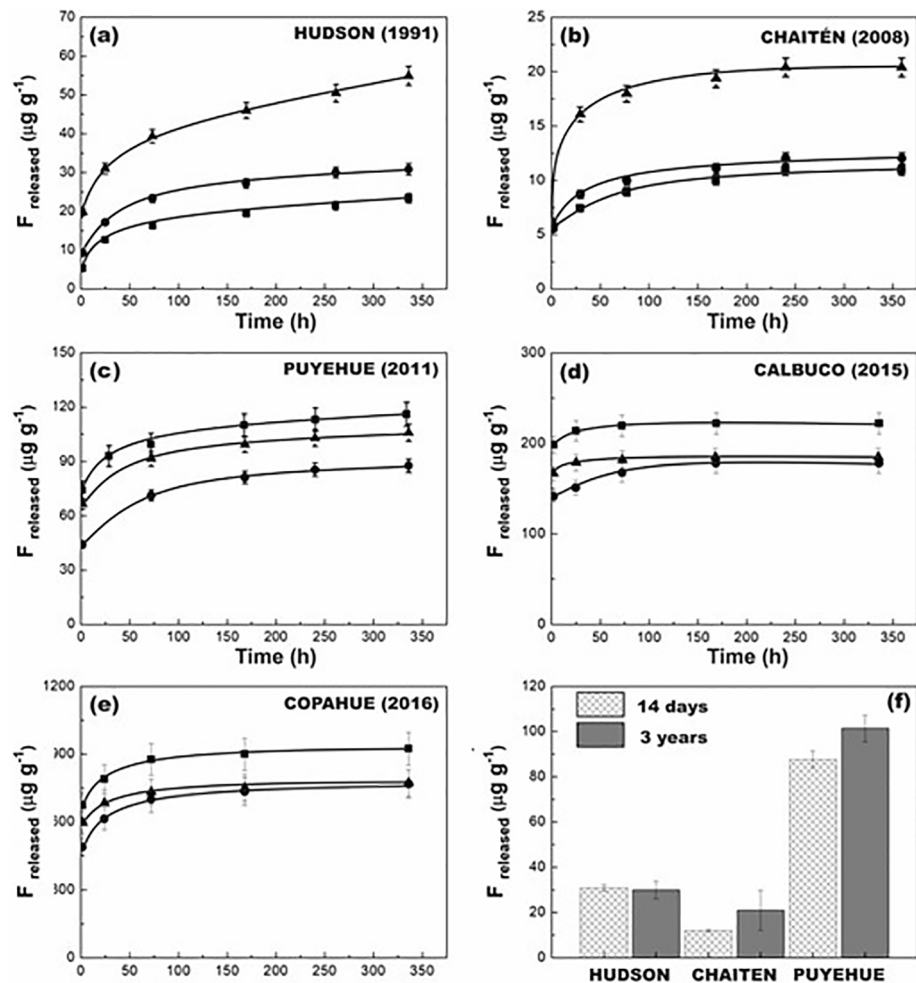


Figure 6

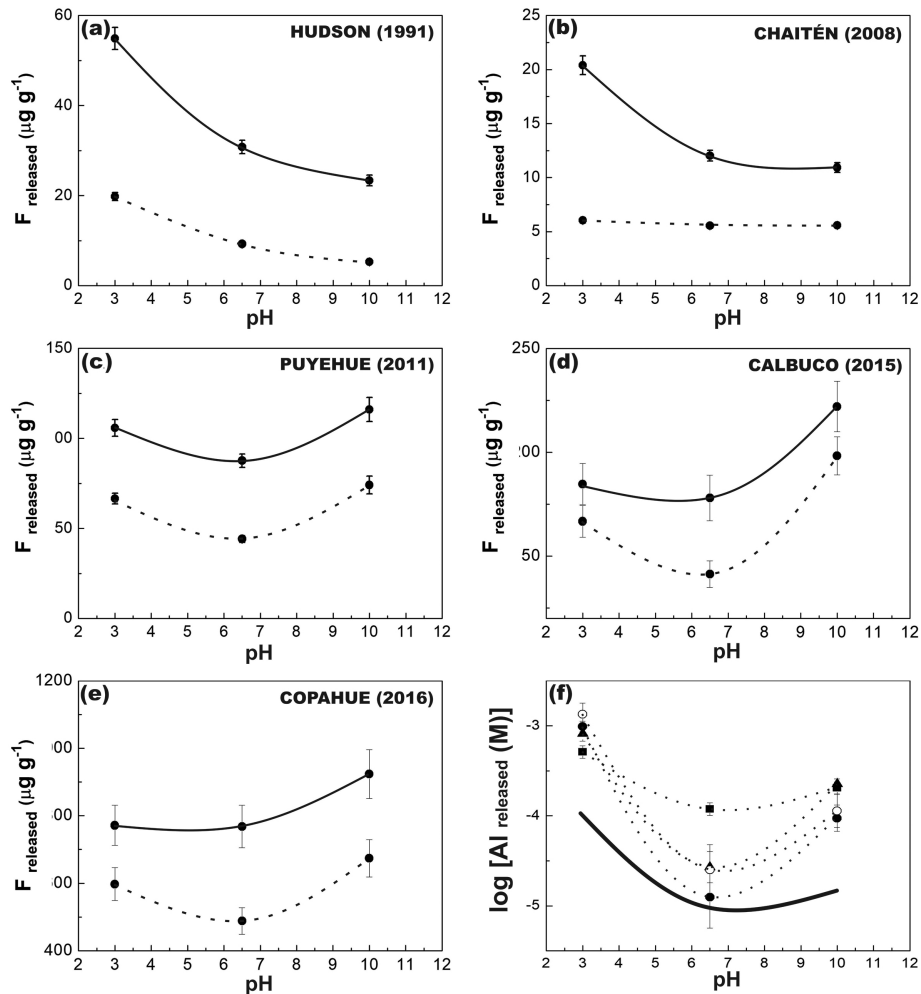


Figure 7