

1 **Environmental geochemistry of recent volcanic ashes from** 2 **Southern Andes**

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11 **Environmental context**

12 Explosive volcanic eruptions may cause significant environmental repercussions
13 affecting many cycles in the Earth system, particularly on the water cycle. The
14 potential contribution to the local geochemical fluxes through water of five historical
15 eruptions occurred along the 20th Century has been investigated in the Southern
16 Andes (Lonquimay 1988, Hudson 1991, Copahue 2000, Llaima 2008, Chaiten
17 2008). The major potential toxic trace element contents removed correspond to
18 arsenic, copper, fluoride, molybdenum, nickel, lead, and zinc in all cases.

19

20 **Abstract**

21 The potential contribution to the local geochemical balance of five historical eruptions
22 occurred along the 20th Century has been investigated in the Southern Volcanic Zone
23 (SVZ) of the Andean volcanic arc of South America (Lonquimay 1988, Hudson 1991,
24 Copahue 2000, Llaima 2008, Chaiten 2008). These ashes were characterized by SEM-
25 EDX and XRD, and their potential released geochemical fluxes were examined using
26 water and nitric acid batch leaching tests. Leachates were analyzed by ICP-OES, ICP-MS

27 and ISE. The major contents removed correspond to SO_4^{2-} and Cl^- . The potential toxic
28 trace element (PTTE) content was highly variable among the ash samples following this
29 order: Chaiten > Copahue > Hudson > Llaima > Lonquimay. The trace elements with
30 significant load in water batch leaching tests include $\text{Fe} > \text{F} > \text{B} > \text{P} > \text{Zn} > \text{As} > \text{Mn} > \text{Sr} >$
31 $\text{Ba} > \text{Ti} > \text{Cu} > \text{Ni} > \text{Li} > \text{Rb} > \text{Co} > \text{Cr} > \text{Cd} > \text{Sb}$. Some of these elements (As, Cu, F, Mo,
32 Ni, Pb, and Zn) are included in the drinking water guidelines due to their potential toxicity
33 and must be especially monitored in the environmental assessment of these ashfall
34 deposits.

35

36 *Keywords:* volcanic ash, trace elements, leaching, Chaiten, Copahue, Hudson, Llaima,
37 Lonquimay, Southern Volcanic Zone, Andes.

38

39 **1. Introduction**

40 Explosive volcanic eruptions are capable of causing significant environmental
41 repercussions affecting many cycles in the Earth system simultaneously.^[1] The
42 environmental impact could be at different geographic scales. For example, this
43 impact could induce climatic effects associated with the injection of sulphur
44 aerosols into the stratosphere in a truly global scale.^[2] Another consequences may
45 be the changes in the evapotranspirative properties at continental scale due to
46 ashfall emplacement^[3] and the input of key micro-nutrients, as iron, into the surface
47 ocean.^[4-7] More subtle chemical impacts may occur over much larger areas,
48 because fine volcanic ash can be widely dispersed by the prevailing atmospheric
49 motions, as in the case of the last eruption of Chaiten volcano^[8,9] or the recent
50 eruption of the Eyjafjallajokull volcano in Iceland (April-May 2010). Finally, the
51 surrounding areas to the volcano at regional scale may also receive the
52 environmental impacts dominated by the fallout of volcanic ash.^[10-12] One of the

53 most important environmental concerns of ashfall is related to water-soluble
54 constituents in volcanic ash. These constituents consist of macro- and micro-
55 nutrients suitable to fertilize continental and ocean ecosystems but also of trace
56 elements that may be toxic. The formation of water-soluble materials on ash is the
57 result of a complex interaction between particles and volatile compounds in the
58 volcanic plume. Volatile compounds of Cl, S, Na, Ca, K, Mg and F may condense
59 on ash particles during eruption and subsequent fallout.^[13] Acid dissolution of ash
60 and deposition of sulphate and halide salts onto ash may also contribute to
61 increase their contents.^[14] Interaction of pristine tephra with water dissolves soluble
62 accumulations on particle surfaces.^[1,12] Thus, initial release of soluble ash
63 compounds into the environment may cause short-term but potentially significant
64 changes on the regional geochemical balance. Although eruptions are short-lived,
65 ashfall deposits can remain in the local environment for years to decades, and in
66 case of hyper-arid conditions could be preserved during millions of years.^[15] In
67 addition, strong wind storms may resuspend the ash, causing environmental
68 effects similar to those of the original eruption.^[11] After the initial washing,
69 prolonged exposure of the ash to weathering may cause the slow release of
70 elements from the structure of constituent mineral phases. These releases may be
71 of equal or greater importance than the initial washing transporting potential toxic
72 trace elements (PTTEs) to the environment.^[16]

73 The goal of this study is to determine the potential contribution to the local
74 geochemical balance of volcanic ashes of five historical eruptions occurred along
75 the second half of the 20th Century in the Southern Volcanic Zone (SVZ) of the
76 Andean volcanic arc in southern South America (33-46 °S). With this aim, physical
77 and chemical characterization and batch leaching tests were carried out on ashes

78 from the eruption of the volcanoes Lonquimay (1988), Hudson (1991), Copahue
79 (2000), Llaima (2008) and Chaiten (2008). These eruptions are paradigmatic cases
80 of eruptions foreseeable in one of the most volcanically active regions on the Earth.
81 Although there are several works on these eruptions, few have focused on
82 environmental geochemical aspects of the ashes. This work, for the first time,
83 provides a new and broader perspective of the geochemical hazards associated
84 with the volcanic ashes in the southern Andes.

85

86

87 **2. Studied volcanoes**

88 Pyroclastic materials considered in this work come from volcanoes of the
89 Andean SVZ, which form a continuous volcanic arc segment 1400 km long (Figure
90 1). The samples considered derive from five eruptions covering a wide
91 compositional range in terms of magma silica content.

92 The northernmost Copahue volcano (37.85 °S 71.17 °W, 2997 m a.s.l.) is
93 the major active stratovolcano in the central part of the SVZ, located in the border
94 between Chile and Argentina. Its eruptive episode from July to October 2000 is the
95 largest eruption known from this volcano. Frequent explosions caused basaltic
96 andesite ashfall around the village of Caviahue. Acid rain and small-volume mud-
97 flows were other volcanic hazards observed at this time.^[17]

98 The Lonquimay volcano in Chile (38.37 °S 71.58 °W, 2865 m a.s.l.) is
99 located 50 km south of the Copahue volcano. The Lonquimay sample comes from
100 the 1988 eruption; a small eruption of the “Navidad” cone, which resulted in the
101 death of several thousands of animals. It was the first strombolian type eruption in
102 the last 100 years, active during 13 months and characterized by the production of

103 0.12 km³ of basaltic andesite tephra distributed over ~500 km².^[18,19]

104 The Llaima volcano (38.69 °S 71.73 °W, 3125 m a.s.l.) is one of the most
105 active volcanoes in the Andes, with more than 49 reported episodes of activity
106 since 1640. It began a new strombolian eruption episode on January 2008.^[20]

107 The most recent ash sample comes from the 2008 Plinian eruption of the
108 Chaiten volcano (42.83 °S 72.64 °W, 1122 m a.s.l.). It is a small elliptical (3x4 km
109 in diameter) post-glacial caldera, 10 km northeast of Chaiten town in the Gulf of
110 Corcovado, in southern Chile. The 2008 eruption was the largest explosive
111 eruption globally since Hudson, Chile, in 1991, and was the first explosive rhyolitic
112 eruption since Novarupta, Alaska, in 1912.^[8,21]

113 Finally, the southernmost eruption studied in the SVZ is from the Hudson
114 volcano or Cerro Hudson (45.90 °S, 72.47 °W, 1905 m a.s.l.). The August 1991
115 eruption of Hudson volcano was developed in two phases. Phase 1 (P1, August 8)
116 produced both lava flows and a phreatomagmatic tephra fall (0.2 km³, bulk
117 volume). The paroxysmal phase P2 was Plinian and lasted four days (August 12-
118 15). The tephra was basaltic in phase P1 and trachyandesitic in phase P2. The
119 second phase produced a much great damage than the first in agriculture and
120 cattle sheep. The large 1991 Plinian eruption of Hudson was one of the largest
121 explosive eruptions of the 20th century.^[22] involving 4.3 km³ (bulk volume) of tephra
122 fall deposits covering more than 150,000 km² in Chile and Argentina.^[23,24]

123

124 **3. Materials and methods**

125 **3.1 Sampling**

126 Table 1A shows sampling location, distance from volcano, eruption date,
127 collection date and pristinity of studied ashes. Eruptions are ordered according to

128 their N-S position along the SVZ. Samples were collected by a plastic shovel in
129 order to avoid any possible contamination. Fieldwork was conducted directly during
130 the volcanic eruptions in the case of Copahue, Chaiten and Hudson eruption. The
131 thickness of the ash deposit sampled was variable ranging from few centimeters
132 (Copahue, Chaiten and Hudson) to several decimeters (Lonquimay and Llaima).
133 The materials were sampled on the ground, except for Chaiten ash, which was
134 sampled on a plastic surface. The Hudson volcanic ash was collected in the first
135 phase of 1991 eruption. In the case of Llaima eruption, the pyroclastic deposit (not
136 affected by rainwater action) was collected three days after the onset of the
137 eruption. The <2 mm fraction of lapilli was employed in this last case, due to the
138 lack of actual ash samples of this eruption, obtaining a more comparable material
139 to the rest. Different amount of sample (between 100-1000 g) were placed in
140 polyethylene bags and brought to the laboratory. Samples were dried at 40 °C in
141 an oven and stored in polyethylene containers until preparation in the laboratory.

142

143

144 **3.2 SEM-EDX and XRD analysis**

145 Ash samples were mounted on carbon stubs and coated with carbon prior to be
146 studied in a FEI Quanta 200 ESEM FEG scanning electron microscope (SEM)
147 equipped with an energy dispersive X-ray (EDX) system for semi-quantitative
148 chemical analysis (minimum spot size, 5 µm; working distance, 10 mm;
149 accelerating voltage, 20 kV). Samples were carefully examined by SEM at different
150 magnifications for morphological features, and analyzed by EDX to know the
151 chemical composition of glass shards and other mineral phases.

152 The mineralogical characterization was made by X-ray diffraction (XRD)

153 analysis. Samples were powdered in an agate mortar and the diffractograms were
154 obtained using a Bruker D-5005 instrument (Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$, at 40
155 kV and 40 mA), collecting data between 4 to 60° of 2θ , with a scan step of 0.05°
156 and a step duration of 3 s. Diffractogram evaluation was carried out using the
157 DIFFRAC software.

158

159 **3.3 Bulk chemical analysis**

160 Concentrations of major elements in volcanic ashes were determined by
161 inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 3100
162 X, Perkin Elmer), and trace elements by inductively coupled plasma mass
163 spectrometry (ICP-MS, Elan 6000, Perkin Elmer). Whole-rock analysis by ICPs
164 was performed on a split (0.1 g) of each sample. It was digested with HNO₃:
165 HClO₄:HF (2.5:2.5:5 ml, v/v), doubly evaporated to incipient dryness with addition
166 of HNO₃, and finally volume was made up to 100 ml with 1 % (v/v) HNO₃. Loss or
167 gain on ignition (LOI-GOI) was determined on 1 g sample at 1,000 °C. The
168 precision and accuracy of analytical determinations were monitored using
169 reference materials of the Geological Survey of Japan (rhyolite JR-3 and basalt JB-
170 3).^[25,26]

171

172 **3.4 Batch leaching tests**

173 Leaching experiments were performed on unground ashes. Several leaching
174 tests can be used to simulate the geochemical release of constituents from ash.^[27]
175 Among such type of experiments, the one-stage leaching procedure is the most
176 used.^[15,27] In the present study, two batch leaching tests were performed using
177 deionized water and nitric acid as leachants.^[28] The former leachant is less

178 aggressive and its slightly acid pH allows a rapid screening of the potentially
179 hazardous elements that can be leached from the ashes. Nitric acid extraction is
180 useful for the assessment of the maximum load of PTTEs environmentally
181 available.^[29,30] Concentrated HNO₃ has been selected because it produces
182 extreme conditions and maintains, at the same time, the compatibility of the
183 leachate with the input solution for chemical analysis by ICP-OES and ICP-MS
184 (direct determination after dilution). In addition, it is essential to consider the acid
185 leaching because there are environments where this situation occurs. There are
186 very acidic waters in the studied region. We can find examples very well studied in
187 the Copahue Volcano area.^[31] The pH of water of Caviahue Lake ranges between
188 2.1 and 2.7; pH of Agrio River is lower than 3 before this lake. The most hyperacid
189 conditions are observed in the Copahue hot springs where there are values of pH
190 as low as 0.2.

191 For water batch leaching tests, 0.1 g of ash was mixed with 5 ml Milli Q Plus
192 deionized water type (18.2 MΩ cm⁻¹) in 14x100 mm polypropylene test tubes. After
193 12 h of stirring at 20 rpm at room temperature, the water leachate pH was
194 monitored, the leached solutions were filtered through cellulose membranes
195 (Whatmann, 0.45 μm pore size, 142 mm diameter) and the volume was made up to
196 100 ml in 1% (v/v) HNO₃. Following this methodological approach, new batch
197 leaching tests were performed using 1 ml of analytical grade HNO₃ (65 %) and 0.1
198 g of sample. In these batch leaching tests, deionised water was added to the
199 resulting leached solution to facilitate the filtering. The final solution had a volume
200 of 100 ml with 1% (v/v) HNO₃.

201 In addition to the elements analyzed in the whole-rock analysis, Cl, S, B, Br,
202 and Hg concentrations were analyzed by ICP-MS in the batch samples. Given the

203 physico-chemical characteristics of the samples studied, the Cl, Br, and S
204 concentrations were expressed as Cl^- , Br^- , and SO_4^{2-} , respectively. The methods to
205 determine major and trace elements using ICP-MS analysis were described
206 previously.^[32-34] Furthermore, only in water batches the fluoride concentration was
207 determined using an ion selective electrode (ISE) for fluoride (Orion, Thermo
208 Scientific), and concentrations of HCO_3^- were modelled with the Geochemical
209 Workbench (GWB 8.0.2) software.^[35]

210

211 **3.5 Data presentation**

212 Tables 1A and 1B show the sampling information, the mineralogical
213 composition, and the bulk geochemistry (major and trace elements) of the studied
214 samples. Data collected in Table 2 show the enrichment factors (EF) of ash bulk
215 composition respect to the crustal average contents.^[36] Tables 3 and 4 present the
216 concentrations of those elements released in water and nitric acid batch leaching
217 tests. Tables 5 and 6 display the relative mass leached factors (RML) for water and
218 nitric acid batches, respectively. The RML is defined as the fraction, expressed as
219 %, of leached element (element/solid by weight) obtained from the batch leaching
220 tests (i.e., water batch test and nitric acid batch tests) over the total element
221 concentration (element/solid by weight).^[27,37] Although Se, Ag, Te, Pt, and Au were
222 analyzed, they could not be studied because their concentrations were below or
223 very close to the respective detection limits. RMLs were not determined for Cl,
224 SO_4^{2-} , B, F, Br, and Hg because these elements were not analyzed in bulk ashes.

225 Once determined the RMLs for each element and for each leaching method,
226 the elements were grouped according to their mobility expressed by their RML.
227 High mobility was assumed for elements showing RML >5%, moderate mobility for

228 elements with RML between 0.5 and 5%, and low mobility for those elements
229 having RML <0.5%. The low mobility group shows a low potential hazard for the
230 environment.^[37]

231

232 **4. Results and discussion**

233 **4.1 Ash characterization**

234 The characterization based on SEM and XRD analysis showed that glass is
235 the main constituent of all types of ash, though there are minor amounts of
236 anorthite, andesine, quartz and diopside as well (Table 1A). XRD pattern of
237 Chaiten ash also indicates the presence of cristobalite. This feature agrees with the
238 findings of other works.^[38,39] The presence of cristobalite is suggested to be
239 associated with the reduction of amorphous silica by carbon monoxide to its
240 reactive suboxide SiO during explosive eruptions, which is later oxidized to form
241 one-dimensional crystalline silica nanostructures.^[39] An alternative mechanism for
242 cristobalite formation is the breakage of small spherulites in the ancient dome
243 during the initial explosions.^[38]

244 General SEM images of studied volcanic ashes are reported in Figure 2.
245 The differences in mineral contents and morphological features, mainly the grain-
246 size distribution, allowed us to classify the samples into three broad groups of
247 ashes: (1) Poorly vesicular equant blocky fragments (5-200 μm) accompanied of
248 fine-grained particles ($\sim 1 \mu\text{m}$) characterize the Copahue and Hudson ashes; rare
249 Y-shard, platelike, curved and angular shards (wall vesicles breakage remains)
250 occur also in both samples; Hudson ash is relatively crystal poor and the blocky
251 glass particle morphology is very similar to ash from the 2001 basaltic eruption of
252 Mt. Etna.^[40,42] (2) Vesicular and fluidal particles with very irregular shape were

253 depicted, mainly, in Lonquimay and Llaima samples, in which, for both, little
254 amount of fine-grained particles coexist with very large particles (50-200 μm). (3)
255 Finally, vesicular spongy clasts and equant blocky glass particles (5-200 μm)
256 coexist with abundant $<1 \mu\text{m}$ particles in Chaiten sample, reflecting the distance to
257 the source (106 km) and the importance of the first Plinian phase of 2008 eruption.

258 [38]

259 These three groups fingerprint three different volcanic styles. The high
260 content of glass in Group 1 indicates a very explosive magma, practically without
261 crystalline phases, probably due to the fast ascent of the magma to the surface,
262 whereas ashes of the Group 2 show the typical characteristics of explosive
263 eruptions where the magma interacts with water.^[43] Finally, the cristobalite-bearing
264 ash of Group 3 indicates a very explosive eruption, probably related to an ongoing
265 lava dome.^[38]

266 The Total Alkali Silica (TAS) diagram for the classification of volcanic rocks
267 ^[44] allows to order the studied ashes from more basaltic to more rhyolitic
268 compositions: Llaima > Hudson > Copahue > Lonquimay > Chaiten (Table 1A).
269 The major element compositions obtained from this study are similar to those
270 reported by previous authors.^[17,19,21,45] No previous published data were found for
271 the Llaima ash erupted in 2008.

272 When the compositions of the ash samples are compared with the crustal
273 average contents^[36] (Table 2), the elements exhibiting higher enrichment factors,
274 ordered according to the decreasing values for the most recent Chaiten ash,
275 include As > Cs > Sb > Bi > Th > U > Pb > Cd > Zn > Sr (Table 2). These results
276 evidence that beyond the differences on major element chemistry, the ash samples
277 present the same EFs patterns. This feature is due to similar reactions occurs in

278 the volcanic eruptive plumes either by adsorption of volcanic salt aerosols on ash
279 and/or acid dissolution of ash and deposition of sulphate and halide salts onto
280 ash.^[14] Pioneering studies of chemical species in volcanic emissions provide that
281 geochemically very rare PTTEs are so abundant in the eruptive plumes that they
282 may be present in high concentrations in volcanic ash, being this pathway a very
283 important natural input to the environment.^[45-47] Hudson ash is a singular case
284 because its EFs evidenced a more enriched trend for rare earth elements (REE)
285 than for PTTEs. As reported by previously published data, its eruption products
286 (including tephra) were relatively rich in TiO₂, Na₂O, and incompatible trace
287 elements, including REE, compared with samples of similar silica content derived
288 from other volcanoes in the Andean SVZ.^[24,41]

289

290 **4.2 Water batch leaching tests**

291 The environmental geochemical hazards of ashfall depend on the short-term
292 water leaching of materials adsorbed and/or deposited onto the ash particle
293 surfaces and the long-term implications related to glass weathering. The
294 dissolution of volcanic glass in natural conditions occurs at rates several orders of
295 magnitude lower than in ash-leachate dissolution according to several
296 experimental works.^[1,48-50] These works found that the dissolution of glasses and
297 other compounds could occur even with shorter shaking times than the 12 h
298 considered here, therefore, these results could be taken as typical of an early
299 stage of weathering. The data in Table 3 indicate that the interaction between
300 volcanic ash and deionised water caused the increase of pH from slightly acid (pH
301 ~ 5 of deionised water) to weakly alkaline. Reactions of minerals with water and
302 their thermodynamic fundamentals highlighted as pH changes are very common

303 when mineral phases are contacted with water.^[51] Volcanic ash consists mainly of
304 glass but silicate compounds of Ca, Mg, and Na are also present.^[52,53] According to
305 the studies on surface chemistry of multi-oxide silicates, the reactions at the
306 mineral–water interface pass through three stages: (1) virtually instantaneous
307 exchange of an alkaline ion by H^+ (or as (H_3O^+)), i.e., with increase of pH; (2)
308 generation and fast growth of a residual layer poor in that alkaline and rich in Si
309 and/or Al (thicker at higher acidity); and (3) interaction of feldspar-solution through
310 the residual layer (process necessarily slower, at pH lower than in previous steps).
311 The first stage involves a reversible reaction where H^+ forms the feldspar $HAISi_3O_8$
312 when Na^+ is released. At the end of the second stage, a layer of this compound is
313 developed by incongruent dissolution. Similar results were obtained with a
314 potassium-rich feldspar.^[54] If there is enough time, the third stage, the slow one,
315 controls the process of aqueous dissolution (weathering). This is the process that
316 must have taken place on the batches studied here.

317 In a first approach, the studied elements may be grouped according to their
318 mobility expressed by their RML (Table 5):

319 (1) High mobile elements (RML > 5 %): Ni, Zn, As, Mo, and Cd.

320 (2) Moderate mobile elements (RML between 0.5 and 5%): Ca, Mg, Na, Li, Cu, Pb,
321 and P.

322 (3) Low mobile elements (RML < 0.5 %): K, Si, Be, Al, Ti, V, Cr, Fe, Mn, Co, Ga,
323 Ge, Rb, Sr, Y, Zr, Nb, Sn, Sb, Cs, Ba, Ta, W, Tl, Bi, Th, U, and REE.

324 This classification is a generalization. In a more detailed observation of
325 results, some elements appear in more than one class depending of the
326 considered ash, here they are included in the most common group. For example,
327 As and Cd present high mobility in Chaiten, Hudson and Copahue ashes but

328 moderate mobility in Llaima and Lonquimay samples.

329 The elements with preferential enrichment on ash compared to its bulk
330 composition are sulphur (as sulphate), chlorine, and fluorine.^[55] Generally, up to
331 10-20% of HCl and 30-40% of SO₄ can be scavenged by ash in the eruptive
332 column.^[1,56,58] Independently of the magma silica content, sulphates and chlorides
333 are the major compounds observed in Chaiten, Hudson and Copahue ash water
334 leaching tests, with particular emphasis for the latter sample (Table 3). Negligible
335 values of these compounds reported for Lonquimay ash water leachate confirm its
336 no pristine character, while in Llaima water leachate the low content of sulphate
337 compounds onto particle surfaces could explain this trend.

338 Concentrations of F⁻ vary considerably among the samples. The F⁻ release
339 from the Hudson ash is far greater than for any other sample. Early ash analysis
340 revealed high levels of fluoride after the 1991 eruption.^[59,60] Comparing to the other
341 samples, F⁻ concentration in Hudson ash leachate (4386 µg l⁻¹) is over 20 times
342 more than in the Chaiten ash and nearly 200 times more than in the Lonquimay
343 ash (Table 3). Llaima water leachate has also a notable fluoride concentration (610
344 µg l⁻¹).

345 In general, the most immobile major elements considered in the weathering
346 processes are Al and Fe (solubility product, K_s, of their hydroxides are extremely
347 low, 10⁻³³ and 10⁻³⁹, respectively).^[61,62] This is not observed in the studied samples,
348 in which the molar ratio Si/Al in rock is lower than in aqueous leachate only for
349 Lonquimay sample. For the other ashes this ratio is reversed and Si/Al is higher in
350 rock than in water (Table 1A and 3). This implies that Al dissolves more readily
351 than Si, especially, for Chaiten and Copahue ash samples. Furthermore, some
352 relatively high values for Fe and Mn were also observed in concentrations with

353 orders of magnitude of tens to hundreds of $\mu\text{g l}^{-1}$ (Table 3). The explanation of
354 these anomalies could be related to the stable complexes formed by these rock-
355 forming elements, which may be dissolved in these conditions. These results
356 confirm that deposition of airborne ash from volcanic eruptions is a way to inject
357 significant amounts of bio-available Fe into both continental and ocean waters.^[5,6]

358 The presence of silicate compounds of Ca, Mg, and Na in volcanic ash is a
359 feature well known.^[50] These compounds seem to be susceptible to weathering
360 only in Chaiten and Copahue ash samples, as their moderate mobility indicates.
361 Alkaline and alkaline-linked elements with higher ionic radius (Rb, Cs, and Sr)
362 seem also weakly mobilized (Table 5).

363 The trace elements with higher mobility were Ni, Zn, As, Mo, and Cd.
364 Remarkable high mobility was reported for As and Mo in Hudson water leachate
365 (22.2 and 72.8 RML %), As and Bi in Chaiten water leachate (21.1 and 43.2 RML
366 %), and, finally, Ni in Lonquimay water leachate (35.7 RML %).

367 The case of P is singular, with moderate mobility in Hudson and Llaima
368 samples. This element typically concentrates in a single mineral –apatite- in silicic
369 igneous rocks, although it appears also within the network of alkali aluminium
370 silicates. The presence of apatite in Hudson ash is well documented by
371 mineralogical and petrographic observations.^[63]

372 Some of the elements released in water leachates from ashes are macro- and
373 micronutrients, evidencing the fertilizing potential of the ashes. However, many others
374 are potentially toxic trace elements (PTTE) even at very low concentrations. Some of
375 the latter elements (As, Cu, F, Mo, Ni, Pb, and Zn) are included in the drinking water
376 guidelines^[64-66] due to their potential toxicity and must be especially monitored in
377 the environmental assessment of these ashfall deposits.

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379

380 **4.3 Comparison between water and nitric acid batch leaching**
381 **tests**

382 Comparing water and nitric acid batch results, deionised water is an
383 extractant without buffering capacity that leaches primarily the easily soluble salts
384 adsorbed on ash particle surface, while the acid leach continues this process, as
385 evidenced by the similar suite of predominant elements in solution. This feature is
386 commonly reported in ash leachates.^[15,16,67]

387 Once determined the RMLs for each element in the nitric acid batches, they
388 were grouped according to their mobility in:

389 (1) High mobile elements (RML > 5 %): Mg, Co, Ni, Cu, Zn, As, Mo, Cd, and Pb.

390 (2) Moderate mobile elements (RML between 0.5 and 5 %): Ca, Na, K, Li, Be, Al P,
391 Ti, V, Cr, Fe, Ga, Rb, Sr, Y, Sn, Ba, Hf, Tl, Bi, U, and REE.

392 (3) Low mobile elements (RML < 0.5 %): Si, Mn, Ge, Zr, Nb, Sb, Cs, Ta, W, and
393 Th.

394 As in the case of water leaching tests, this grouping is a generalization. An
395 extreme case is the Llaima acid leachate, where As > Ni > Zn show high mobility,
396 and the other elements classified as high mobile only reach moderate mobility.

397 A special case is Si. It is well established that the solubility of amorphous
398 silica, the most abundant constituent of volcanic ash, is higher than for crystalline
399 silica (quartz).^[68,69] The different forms of amorphous silica have the same
400 fundamental structure (highly polymerized chains of SiO₄) with a slight decreasing
401 solubility at pH in the acidic range. These considerations suggest that higher Si
402 content would be expected in water leachate than in nitric acid leachate.

403 Natural amorphous silica glass in volcanic ash ranges from low silica
404 content (basaltic glass, 45–55 wt% of SiO₂, m/m) to high silica content (rhyolite
405 glass, >69 wt% of SiO₂, m/m). This variation influences the glass solubility, making
406 it difficult to predict a general chemical weathering behaviour for volcanic glass.
407 Nevertheless, the higher Si content in water leachate of Chaiten rhyolitic glass
408 seems to support a major dissolution capacity for natural glass with higher SiO₂
409 content (Table 3).

410 In order to compare the Si concentrations in Table 3 (water) with those
411 reported in Table 4 (nitric acid) it is necessary to multiply the concentration in the
412 last table by 5 (0.1 g of ash were used in both cases but with 5 ml of water in the
413 first batch and 1 ml of nitric acid in the second). This comparison (expressed as
414 Si_n/Si_w in Table 4) shows that the Si concentration extracted with water (Si_w) is
415 larger than with HNO₃ (Si_n) only for the rhyolitic Chaiten ash, being Si_n > Si_w in the
416 basaltic glasses. This apparent contradiction may be justified by experimental
417 studies on dissolution rates of natural glasses as a function of their composition at
418 different pH.^[49,70] The lifetime of 1 mm radius glass spheres at 25 °C and pH of 4,
419 in chemical conditions far from equilibrium, is increased from 500 to 4500 yr when
420 composition changes from basaltic to rhyolitic. Therefore, the chemical weathering
421 of basaltic glass, far from equilibrium in acidic solutions, is faster than for rhyolite,
422 reaching similar dissolution rates as other silicate minerals normally found in ash of
423 low silica composition.^[70] These studies conclude that Si-poor glasses exhibit
424 similar dissolution rates as crystalline phases, explaining their higher solubility in
425 acidic conditions. Among the studied samples, higher Si content was verified for
426 the most basaltic sample of Llaima eruption, being three times larger the Si
427 concentration extracted with HNO₃ than with water.

428 The lack of sulphate compounds in Lonquimay and Llaima particle surfaces
429 according to their water leachates, is confirmed in nitric leachates. There is a clear
430 higher sulphate content in nitric than in water leachates only for Chaiten and
431 Copahue ash samples (Table 3 and 4). Although there are no available analytical
432 results on sulphide ion, but on total sulphur expressed as sulphate, its presence is
433 not excluded in these samples. Acid leaching dissolves all existing S compounds
434 better than water leaching. However, such figures suggest that nitric acid, a strong
435 oxidizer, is also oxidizing sulphur compounds of lower valence, including sulphides.
436 Given the experimental procedure (different dilution in aqueous and nitric batches),
437 the ratio between sulphur in a nitric leachate (S_n) and sulphur in an aqueous
438 leachate (S_w) has been calculated (Table 4). This ratio (S_n/S_w) suggests presence
439 as S^{2-} principally in Chaiten and Copahue ash samples, feature probably related to
440 the high volatile contents of these high silica eruptions.

441 Again the case of P is paradigmatic, with high mobility in Chaiten and
442 Hudson nitric acid leachates (Table 6). As mentioned above, P usually occurs as
443 apatite, Furthermore, in most natural systems, apatite usually contains fluorine
444 instead of the hydroxyl groups forming fluorapatite although it can be also found in
445 some silicates as in the feldspar network.^[71] Though fluorapatite ($K_s = 10^{-60.6}$) is less
446 soluble than hydroxylapatite ($K_s = 10^{-58.3}$), its solubility increases when pH
447 decreases.^[72,73] The behaviour of apatite in the weathering of igneous rocks has
448 been studied in detail by electron microscopy.^[74] Weathering mobilizes early not
449 only P of the original rock, but also REE and Y. Furthermore, dissolution
450 experiments at 25 °C of natural apatite and fluorapatite show an increase of REE
451 release with decreasing pH.^[71] These observations could explain the REE-enriched
452 trend depicted in Hudson nitric acid leachate. In feldspar network, P displays an

453 affinity for alkalis and Al, not for Si, in water saturated rhyolitic melts.^[75] The
454 accumulation of P in alkali feldspar increases with the excess of Al, expressed by
455 the alumina saturation index A/CNK. This feature is in agreement with the
456 peraluminous composition of Chaiten ash, with a A/CNK index of 1.08 (Table 1A).

457 Although with small variations, the high mobility of PTTEs such as Ni, As, V,
458 Mo, Zn, Cu and Pb in nitric acid leachate is coherent with the observed in water
459 batch leaching tests confirming that they are dominantly combined with halogens
460 and sulphate as metal salts adsorbed on particle surfaces.^[1,14,76,77]

461

462

463 **5. Conclusions**

464 The combination of SEM-EDX examination with XRD analysis and batch
465 leaching tests clearly highlight the main environmental concerns related to the
466 volcanic ashes. These concerns are related to the presence of fine grain size
467 particulate matter and to the chemical hazard once they interact with water. Among
468 the studied samples. SEM images show the higher hazard is posed by the high
469 content of the finest size fraction (<4 μm aerodynamic diameter) of Copahue and
470 Chaiten ashes. In the last sample, its potential injury is increased due to the
471 presence of nanofibers of cristobalite. The environmental hazard posed by fine ash
472 particles continues after the end of the eruption because windstorms resuspend
473 the ash, causing harmful effects similar to those occurring during the eruption.

474 The interaction ash-water may represent a significant input of key micro-
475 nutrients, as iron, into both continental and ocean waters, but it could cause an
476 important environmental stress due to the pH increase and the potential toxicity of
477 ash leachates. The major compounds released during the first interaction between

478 pristine ashes and water are SO_4^{2-} , Cl^- , and F^- , although with important differences
479 in concentration levels among the studied ashes.

480 The trace elements with significant load in water batch leaching tests,
481 ordered from higher to lower concentrations, are $\text{Fe} > \text{F} > \text{B} > \text{P} > \text{Zn} > \text{As} > \text{Mn} >$
482 $\text{Sr} > \text{Ba} > \text{Ti} > \text{Cu} > \text{Ni} > \text{Li} > \text{Rb} > \text{Co} > \text{Cr} > \text{Cd} > \text{Sb}$ (Table 3). Although the trace
483 element content is highly variable among the ash samples, a general observation
484 indicates the following order, from higher to lower content: Chaiten > Copahue >
485 Hudson > Llaima > Lonquimay. The latter sample is explained by the loss of
486 elements during the exposition of the ashfall deposit to the geological external
487 agents. The relatively higher elemental fluxes of Chaiten and Copahue ash water
488 leachates are partly due to the high content of fine particles observed in these
489 samples

490 From the point of view of drinking water quality, some of the elements
491 detected in the leachates (As, Cu, F, Mo, Ni, Pb, and Zn) are included in the drinking
492 water guidelines due to their potential toxicity and must be especially monitored in
493 the environmental assessment of these ashfall deposits. Any quantitative inference
494 of these results on the quality of surface water affected by ashfall must be carefully
495 taken into account because of the water leaching data in Table 3 are based upon
496 the experimental water/ash ratio of 5:1 (v/m). This ratio could be different in natural
497 conditions in function of the ashfall deposit volume and the precipitation or the
498 receiving water volume.

499

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- 717
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Figure captions

Figure 1. Location map of the studied volcanoes.

Figure 2. SEM images of recent volcanic ashes from Southern Andes. Explanation in the text.

Tables

Table 1A. General features of the studied volcanic ashes: collection date, location, coordinates of sampling sites, distance from volcano, mineral composition (***, common; **, frequent; *, scarce; (*), rare, nd, not detected), bulk geochemistry (major oxides as %, m/m) and LOI, Loss On Ignition.

	COPAHUE	LONQUIMAY	LLAIMA	CHAITEN	HUDSON
Longitude	71°09'51.23"W	71°33'12.69"W	71°37'30.69"W	71°20'45.56"W	72°41'2.19"W
Latitude	37°51'16.93"S	38°22'18.75"S	38°41'57.39"S	42°54'29.94"S	45°24'11.70"S
Eruption date	1st Sep 2000	25th Dec 1988	1st Jan 2008	3rd May 2008	8th April 1991
Collection date	1st Sep 2000	21st Jan 2009	3rd Jan 2008	3rd May 2008	8th April 1991
Distance from volcano	0.73 km	0.20 km	9 km	106 km	60 km
Pristine	yes	no	yes	yes	yes
Classification	Basaltic trachy-andesite	Basaltic trachy-andesite	Basalt	Rhyolite	Trachy-basalt
Glass	***	***	***	***	***
Anorthite	**	**	**	nd	**
Andesine	nd	nd	nd	**	nd
Quartz	nd	nd	nd	**	nd
Cristobalite	nd	nd	nd	**	nd
Diopside	nd	nd	nd	nd	(*)
SiO ₂	52.07	53.45	47.53	72.06	47.60
Al ₂ O ₃	17.54	16.82	18.50	14.66	16.35
Fe ₂ O ₃	8.28	9.96	10.18	1.88	11.48
MnO	1.40	2.32	1.71	0.07	1.96
MgO	4.39	2.49	6.93	0.60	4.37
CaO	7.09	5.64	9.65	1.99	8.23
Na ₂ O	3.60	4.88	2.93	4.18	4.08
K ₂ O	1.86	0.98	0.56	2.89	1.27
TiO ₂	1.25	1.57	1.03	0.20	2.19
P ₂ O ₅	0.28	0.37	0.18	0.08	0.74
LOI-GOI	1.15	-0.02	-0.56	1.65	-0.31
Total	98.91	98.47	98.64	100.26	97.95
Si/Al molar	2.52	2.70	2.18	4.17	2.47
A/CNK	0.84	0.87	0.81	1.08	0.71

Table 1B. Concentration ($\mu\text{g g}^{-1}$) of trace elements of bulk volcanic ashes.

	COPAHUE	LONQUIMAY	LLAIMA	CHAITEN	HUDSON
Li	11.71	12.83	6.96	41.06	7.59
Be	1.37	1.04	0.67	1.62	1.14
B	8.99	8.21	16.01	28.02	6.36
Sc	11.91	15.37	16.24	1.95	17.59
V	188.9	75.0	237.5	13.8	313.0
Cr	89.7	13.6	83.8	19.0	31.9
Mn	1082	1795	1324	563	1520
Co	24.27	13.06	36.76	2.57	26.34
Ni	29.17	1.30	54.98	4.31	8.28
Cu	52.63	41.05	108.70	8.45	53.67
Zn	102.6	152.8	107.2	51.2	141.1
Ga	18.8	21.0	17.8	14.1	19.7
Ge	0.91	1.15	0.88	1.07	1.10
As	7.60	8.27	4.65	38.41	0.92
Rb	53.8	18.6	10.8	98.8	30.0
Sr	505	472	472	167	535
Y	23.2	30.4	17.3	11.2	30.8
Zr	204.0	112.5	72.2	93.2	177.7
Nb	6.97	2.57	1.97	7.17	8.12
Mo	1.05	0.06	-0.19	1.02	0.03
Cd	0.41	0.33	0.20	0.25	0.42
Sn	2.45	1.92	1.18	2.41	2.25
Sb	0.40	0.51	0.25	1.51	0.06
Cs	2.97	1.99	1.02	6.42	0.91
Ba	408	319	177	617	376
La	23.5	13.3	7.4	24.4	24.7
Ce	51.3	32.0	17.4	46.5	56.8
Pr	6.58	4.67	2.47	4.97	7.71
Nd	26.8	21.7	11.3	16.5	33.7
Sm	5.43	5.40	2.89	2.83	7.29
Eu	1.44	1.93	1.02	0.66	2.39
Gd	5.61	5.91	3.20	2.98	7.60
Tb	0.89	1.05	0.57	0.43	1.20
Dy	5.05	6.28	3.46	2.38	6.89
Ho	0.93	1.24	0.69	0.43	1.26
Er	2.75	3.58	2.06	1.37	3.68
Tm	0.39	0.52	0.30	0.20	0.50
Yb	2.51	3.40	1.96	1.44	3.17
Lu	0.38	0.52	0.31	0.23	0.49
Hf	5.48	3.38	2.31	3.18	4.46
Ta	0.51	0.22	0.81	0.68	0.66
Tl	0.65	0.16	0.08	0.64	0.32
Pb	14.26	13.51	6.73	22.38	7.52
Bi	0.33	0.07	0.03	0.30	0.06
Th	9.34	2.97	1.27	13.03	3.33
U	2.32	0.88	0.41	3.26	0.76

Table 2. Enrichment factors (EFs) of volcanic ashes with respect to the crustal average contents.^[36]

	COPAHUE	LONQUIMAY	LLAIMA	CHAITEN	HUDSON
Li	0.90	0.99	0.54	3.16	0.58
Be	0.91	0.69	0.45	1.08	0.76
Sc	0.40	0.51	0.54	0.06	0.59
V	0.82	0.33	1.03	0.06	1.36
Cr	0.48	0.07	0.45	0.10	0.17
Mn	0.77	1.28	0.95	0.40	1.09
Co	0.84	0.45	1.27	0.09	0.91
Ni	0.28	0.01	0.52	0.04	0.08
Cu	0.70	0.55	1.45	0.11	0.72
Zn	1.28	1.91	1.34	0.64	1.76
Ga	1.05	1.17	0.99	0.78	1.10
Ge	0.57	0.72	0.55	0.67	0.68
As	7.60	8.27	4.65	38.41	0.92
Rb	1.68	0.58	0.34	3.09	0.94
Sr	1.94	1.81	1.82	0.64	2.06
Y	1.16	1.52	0.87	0.56	1.54
Zr	2.04	1.12	0.72	0.93	1.78
Nb	0.63	0.23	0.18	0.65	0.74
Mo	1.05	0.06	< 0.01	1.02	0.03
Cd	4.19	3.39	2.09	2.54	4.32
Sn	0.98	0.77	0.47	0.96	0.90
Sb	2.01	2.54	1.27	7.53	0.28
Cs	2.97	1.99	1.02	6.42	0.91
Ba	1.63	1.28	0.71	2.47	1.50
La	1.47	0.83	0.46	1.53	1.54
Ce	1.56	0.97	0.53	1.41	1.72
Pr	1.69	1.20	0.63	1.28	1.98
Nd	1.67	1.36	0.71	1.03	2.10
Sm	1.55	1.54	0.82	0.81	2.08
Eu	1.31	1.76	0.92	0.60	2.17
Gd	1.70	1.79	0.97	0.90	2.30
Tb	1.48	1.76	0.95	0.71	2.01
Dy	1.37	1.70	0.94	0.64	1.86
Ho	1.19	1.59	0.89	0.56	1.61
Er	1.25	1.63	0.93	0.62	1.67
Tm	1.22	1.63	0.94	0.62	1.58
Yb	1.14	1.55	0.89	0.66	1.44
Lu	1.27	1.74	1.03	0.76	1.62
Hf	1.83	1.13	0.77	1.06	1.49
Ta	0.51	0.22	0.81	0.68	0.66
Tl	1.80	0.46	0.21	1.79	0.89
Pb	1.78	1.69	0.84	2.80	0.94
Bi	5.50	1.16	0.47	5.05	1.05
Th	2.67	0.85	0.36	3.72	0.95
U	2.55	0.97	0.45	3.59	0.84

Table 3. Raw water batch geochemistry (0.1 g ash in 5 ml water). Concentrations as mg l⁻¹.

Element	COPAHUE	LONQUIMAY	LLAIMA	CHAITEN	HUDSON
Ca	10.02	3.43	2.63	4.68	4.63
Mg	12.24	< 0.01	< 0.01	0.78	0.85
Na	6.43	0.08	0.44	3.79	6.70
K	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Si	0.83	1.06	1.28	3.44	1.41
Cl	9.63	2.51	5.29	5.99	9.09
SO₄	68.97	< 0.01	< 0.01	4.59	6.28
HCO₃	4.85	6.39	0.12	11.90	12.42
pH	7.83	7.89	7.22	8.04	7.65
Si/Al molar	0.53	3.17	1.45	2.33	1.16

Table 3 (continuation). Raw water batch geochemistry (0.1 g ash in 5 ml water): trace elements. Concentrations expressed as $\mu\text{g l}^{-1}$.

Element	COPAHUE	LONQUIMAY	LLAIMA	CHAITEN	HUDSON
Li	3.98	0.42	0.99	7.05	1.20
Be	0.08	0.16	< 0.01	0.06	0.31
B	119.80	60.15	27.42	154.44	80.30
F	419.7	22.3	610.5	220.0	4386.4
Al	1488	322	846	1414	1165
P	90.0	4.0	226.0	4.0	1358.0
Ti	8.89	49.73	23.22	19.57	75.21
V	1.84	< 0.01	2.11	5.98	4.81
Cr	3.55	2.57	2.36	2.25	0.41
Fe	1725	316	293	1401	745
Mn	240.39	17.60	7.94	61.03	59.15
Co	12.62	0.18	0.25	0.46	0.56
Ni	26.36	10.13	10.61	11.29	9.94
Cu	24.56	3.54	12.84	19.42	5.63
Zn	217.7	58.3	102.5	93.7	82.0
Ga	0.20	0.11	0.13	0.66	0.18
Ge	0.06	0.06	< 0.01	< 0.01	0.15
As	7.21	5.84	0.84	186.49	5.39
Br	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Rb	3.09	0.43	< 0.01	4.79	1.30
Sr	48.42	7.14	12.00	9.62	16.37
Y	0.31	0.23	0.02	0.53	0.44
Zr	< 0.01	< 0.01	< 0.01	< 0.01	1.95
Nb	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Mo	0.34	0.53	1.94	3.13	0.51
Cd	0.76	0.01	0.07	0.32	0.32
Sn	0.42	0.15	1.19	1.11	0.24
Sb	0.16	< 0.01	< 0.01	< 0.01	0.03
Cs	0.04	0.02	0.01	0.66	0.02
Ba	16.87	2.68	1.94	11.35	6.72
La	1.44	0.16	0.13	0.80	0.42
Ce	2.20	1.53	0.17	1.49	0.92
Pr	0.20	< 0.01	< 0.01	0.19	0.09
Nd	0.84	0.16	0.06	0.63	0.50
Sm	0.12	0.02	0.01	0.10	0.06
Eu	0.00	< 0.01	< 0.01	0.01	< 0.01
Gd	0.13	0.05	< 0.01	0.14	0.11
Tb	< 0.01	< 0.01	< 0.01	0.00	< 0.01
Dy	0.03	< 0.01	0.01	0.09	0.06
Ho	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Er	0.00	< 0.01	< 0.01	0.03	0.00
Tm	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Yb	< 0.01	< 0.01	< 0.01	0.00	0.01
Lu	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Hf	0.12	< 0.01	3.78	2.98	1.04
Ta	0.03	< 0.01	0.49	0.46	0.03
W	0.10	0.12	0.03	0.21	0.09
Tl	0.00	< 0.01	< 0.01	< 0.01	0.23
Pb	3.03	0.86	1.00	2.54	2.08
Bi	0.07	< 0.01	< 0.01	3.00	< 0.01
Th	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
U	< 0.01	< 0.01	0.06	0.09	< 0.01

Table 4. Raw nitric acid batch geochemistry (0.1 g ash in 1 ml HNO₃). Concentrations expressed as mg l⁻¹. Si_n/Si_w ratio, Si in nitric batch to Si in water batch. S_n/S_w ratio, S in nitric batch to S in water batch.

Element	COPAHUE	LONQUIMAY	LLAIMA	CHAITEN	HUDSON
Ca	90.3	40.7	104.1	225.0	117.6
Mg	301.9	88.5	201.9	113.5	204.1
Na	40.53	5.78	15.69	32.03	35.66
K	25.42	0.67	2.22	20.26	7.19
Si	9.23	10.37	16.42	3.76	7.22
Cl	10.41	<0.01	<0.01	<0.01	8.56
SO₄	586.37	<0.01	<0.01	159.79	16.81
HCO₃	1927	982	2280	1924	2383
Si_n/Si_w	2.23	1.95	2.57	0.22	1.02
S_n/S_w	1.70	<0.01	<0.01	6.96	0.54

Table 4 (continuation). Raw nitric acid batch geochemistry (0.1 g ash in 1 ml HNO₃): trace elements. Concentrations expressed as µg l⁻¹.

Element	COPAHUE	LONQUIMAY	LLAIMA	CHAITEN	HUDSON
Li	51.5	36.1	23.1	181.3	58.4
Be	1.99	1.47	1.59	7.24	0.57
B	1033	551	609	695	740
Al	77751	30915	91370	126501	22791
P	5330	3700	450	10050	16130
Ti	1324	6020	2168	1475	8748
V	236.7	34.5	152.1	449.1	362.1
Cr	77.45	<0.01	97.91	237.41	46.66
Fe	477294	215645	184825	271852	371134
Mn	6317	5809	3283	9350	7131
Co	347.8	79.3	176.6	113.0	206.9
Ni	621.1	96.5	536.4	249.9	183.7
Cu	1632	588	533	329	1669
Zn	1375	1455	718	2397	3326
Ga	21.40	8.77	16.19	65.39	10.83
Ge	0.99	0.17	0.28	0.39	0.93
As	306.9	43.7	63.8	2500.7	20.6
Br	<0.01	<0.01	<0.01	19.72	<0.01
Rb	39.93	5.17	1.74	157.47	20.53
Sr	879	154	541	368	310
Y	51.4	45.7	11.4	94.2	99.7
Zr	32.8	50.6	15.5	18.7	186.2
Nb	<0.01	<0.01	<0.01	<0.01	2.56
Mo	20.3	12.5	14.0	32.6	14.9
Cd	4.67	2.06	0.59	9.37	7.91
Sn	9.45	2.94	1.23	7.67	13.05
Sb	<0.01	<0.01	<0.01	<0.01	<0.01
Cs	1.30	1.15	0.49	38.47	1.35
Ba	1091	384	139	564	288
La	73.9	19.0	6.0	63.4	81.1
Ce	163.8	46.0	13.0	145.0	185.7
Pr	21.06	6.24	1.62	18.87	24.81
Nd	89.20	29.07	7.76	81.01	104.28
Sm	16.98	7.81	1.56	18.25	22.18
Eu	2.59	2.10	0.53	3.41	4.94
Gd	16.47	7.60	1.68	18.89	22.94
Tb	2.02	1.16	0.10	2.74	3.13
Dy	11.54	7.69	1.75	16.38	18.67
Ho	1.49	1.29	0.07	2.78	3.05
Er	5.22	4.66	0.94	8.31	9.46
Tm	0.36	0.38	<0.01	0.92	1.11
Yb	3.98	3.88	0.81	7.25	8.49
Lu	0.47	0.44	<0.01	0.88	0.96
Hf	11.68	4.00	4.19	4.91	32.19
Ta	<0.01	0.06	<0.01	<0.01	0.30
W	<0.01	<0.01	<0.01	<0.01	<0.01
Tl	3.47	0.13	0.67	0.58	11.23
Pb	135.4	41.5	16.9	146.7	197.5
Bi	9.37	0.21	<0.01	14.78	<0.01
Th	6.34	<0.01	<0.01	4.66	6.51
U	2.76	1.60	0.84	4.34	2.35

Table 5. Relative mass leached factors or RMLs (%) in water batches.

Element	COPAHUE	LONQUIMAY	LLAIMA	CHAITEN	HUDSON
Ca	9.56	3.88	1.46	1.43	3.09
Mg	2.24	<0.01	<0.01	0.95	0.13
Na	1.16	0.01	0.09	0.53	0.87
K	<0.01	<0.01	<0.01	<0.01	<0.01
Si	0.02	0.02	0.02	0.04	0.02
Li	1.64	0.15	0.61	0.75	0.62
Be	0.36	1.12	<0.01	0.16	0.89
Al	0.08	0.02	0.04	0.08	0.05
P	0.36	0.01	1.25	0.05	1.66
Ti	0.01	0.02	0.02	0.07	0.02
V	0.05	<0.01	0.04	1.89	0.06
Cr	0.19	0.86	0.12	0.52	0.05
Fe	0.14	0.02	0.02	0.46	0.04
Mn	0.11	<0.01	<0.01	0.47	0.02
Co	2.51	0.06	0.03	0.78	0.08
Ni	4.37	35.66	0.84	11.41	4.71
Cu	2.26	0.39	0.51	10.00	0.41
Zn	10.26	1.74	4.14	7.97	2.28
Ga	0.05	0.02	0.03	0.21	0.04
Ge	0.33	0.24	<0.01	<0.01	0.54
As	4.59	3.22	0.78	21.15	22.91
Rb	0.28	0.11	<0.01	0.21	0.17
Sr	0.46	0.07	0.11	0.25	0.12
Y	0.07	0.03	0.00	0.21	0.06
Zr	<0.01	<0.01	<0.01	<0.01	0.04
Nb	<0.01	<0.01	<0.01	<0.01	<0.01
Mo	1.58	40.30	<0.01	13.35	72.77
Cd	8.95	0.11	1.53	5.67	3.00
Sn	0.83	0.37	4.39	2.01	0.42
Sb	1.97	<0.01	<0.01	<0.01	1.98
Cs	0.07	0.05	0.03	0.45	0.09
Ba	0.20	0.04	0.05	0.08	0.07
La	0.30	0.06	0.07	0.14	0.07
Ce	0.21	0.22	0.04	0.14	0.06
Pr	0.15	0.00	0.00	0.16	0.05
Nd	0.15	0.03	0.02	0.17	0.06
Sm	0.10	0.02	0.01	0.16	0.03
Eu	<0.01	<0.01	<0.01	0.09	<0.01
Gd	0.11	0.04	0.01	0.21	0.05
Tb	<0.01	<0.01	<0.01	<0.01	<0.01
Dy	0.03	<0.01	0.01	0.17	0.03
Ho	<0.01	<0.01	<0.01	<0.01	<0.01
Er	<0.01	<0.01	<0.01	0.09	<0.01
Tm	<0.01	<0.01	<0.01	<0.01	<0.01
Yb	<0.01	<0.01	<0.01	<0.01	0.01
Lu	<0.01	<0.01	<0.01	<0.01	<0.01
Hf	0.11	<0.01	7.11	4.08	0.92
Ta	0.25	<0.01	2.65	2.94	0.19
W	<0.01	<0.01	<0.01	0.10	<0.01
Tl	<0.01	<0.01	-1.80	<0.01	2.88
Pb	1.03	0.29	0.65	0.49	1.08
Bi	1.03	<0.01	<0.01	43.16	<0.01
Th	<0.01	<0.01	<0.01	<0.01	<0.01
U	<0.01	<0.01	0.59	0.11	<0.01

Table 6. Relative mass leached factors or RMLs (%) in nitric acid batches (nd, not determined).

Element	COPAHUE	LONQUIMAY	LLAIMA	CHAITEN	HUDSON
Ca	1.59	0.81	1.43	15.11	1.94
Mg	10.18	4.72	4.57	30.11	7.53
Na	1.35	0.13	0.68	0.99	1.14
K	1.47	0.07	0.45	0.81	0.66
Si	0.03	0.03	0.07	0.01	0.03
Li	3.93	2.26	3.14	4.22	7.48
Be	1.30	1.14	2.25	4.27	0.48
Al	0.75	0.28	0.88	1.56	0.26
P	3.90	1.82	0.54	29.31	4.88
Ti	0.16	0.51	0.33	1.18	0.65
V	1.12	0.37	0.61	31.13	1.12
Cr	0.77	-1.06	1.11	11.97	1.42
Fe	7.36	2.48	2.46	19.78	4.49
Mn	0.52	0.26	0.23	15.89	0.46
Co	12.79	4.87	4.54	42.05	7.63
Ni	19.01	59.67	9.23	55.47	21.55
Cu	27.69	11.49	4.64	37.26	30.23
Zn	11.96	7.64	6.34	44.79	22.90
Ga	1.02	0.34	0.86	4.44	0.53
Ge	0.97	0.12	0.30	0.35	0.82
As	36.03	4.24	12.98	62.30	21.68
Rb	0.66	0.22	0.15	1.53	0.67
Sr	1.55	0.26	1.08	2.11	0.56
Y	1.98	1.21	0.62	8.03	3.14
Zr	0.14	0.36	0.20	0.19	1.02
Nb	<0.01	<0.01	<0.01	<0.01	0.31
Mo	17.23	nd	<0.01	30.53	nd
Cd	10.16	4.98	2.73	36.00	18.14
Sn	3.45	1.23	0.99	3.04	5.64
Sb	<0.01	<0.01	<0.01	<0.01	<0.01
Cs	0.39	0.46	0.45	5.73	1.44
Ba	2.39	0.97	0.75	0.87	0.74
La	2.81	1.14	0.77	2.49	3.19
Ce	2.85	1.16	0.71	2.99	3.18
Pr	2.86	1.07	0.62	3.63	3.13
Nd	2.98	1.07	0.65	4.70	3.01
Sm	2.79	1.16	0.51	6.18	2.96
Eu	1.61	0.87	0.49	4.93	2.01
Gd	2.62	1.03	0.50	6.07	2.93
Tb	2.03	0.88	0.17	6.17	2.53
Dy	2.04	0.98	0.48	6.58	2.63
Ho	1.43	0.84	0.10	6.12	2.36
Er	1.70	1.05	0.43	5.79	2.50
Tm	0.83	0.58	<0.01	4.45	2.14
Yb	1.42	0.91	0.39	4.81	2.60
Lu	1.11	0.68	<0.01	3.70	1.92
Hf	1.90	0.95	1.72	1.48	7.01
Ta	<0.01	0.22	<0.01	<0.01	0.44
W	1.95	1.19	2.00	<0.01	1.50
Tl	4.77	0.63	8.23	0.86	34.23
Pb	8.48	2.47	2.37	6.27	25.54
Bi	25.36	2.43	<0.01	46.72	<0.01
Th	0.61	<0.01	<0.01	0.34	1.90
U	1.06	1.45	1.93	1.27	3.00

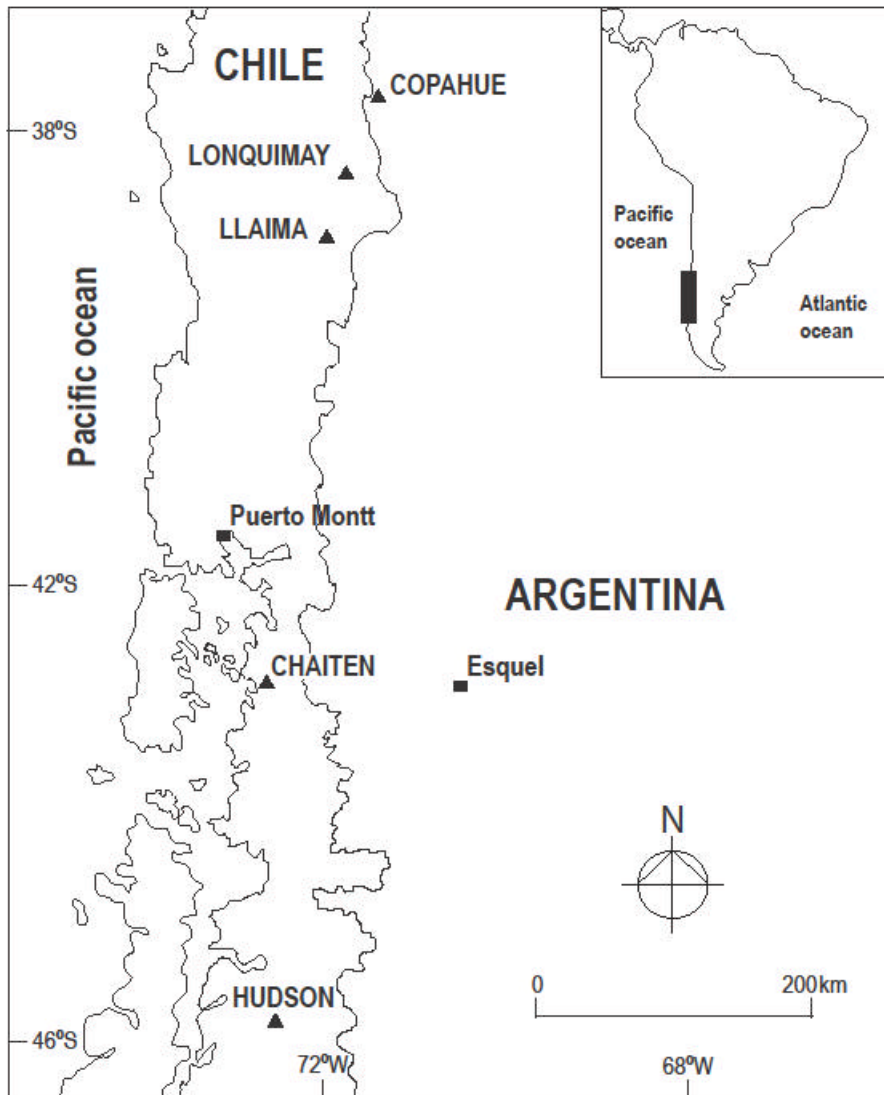


Figure 1

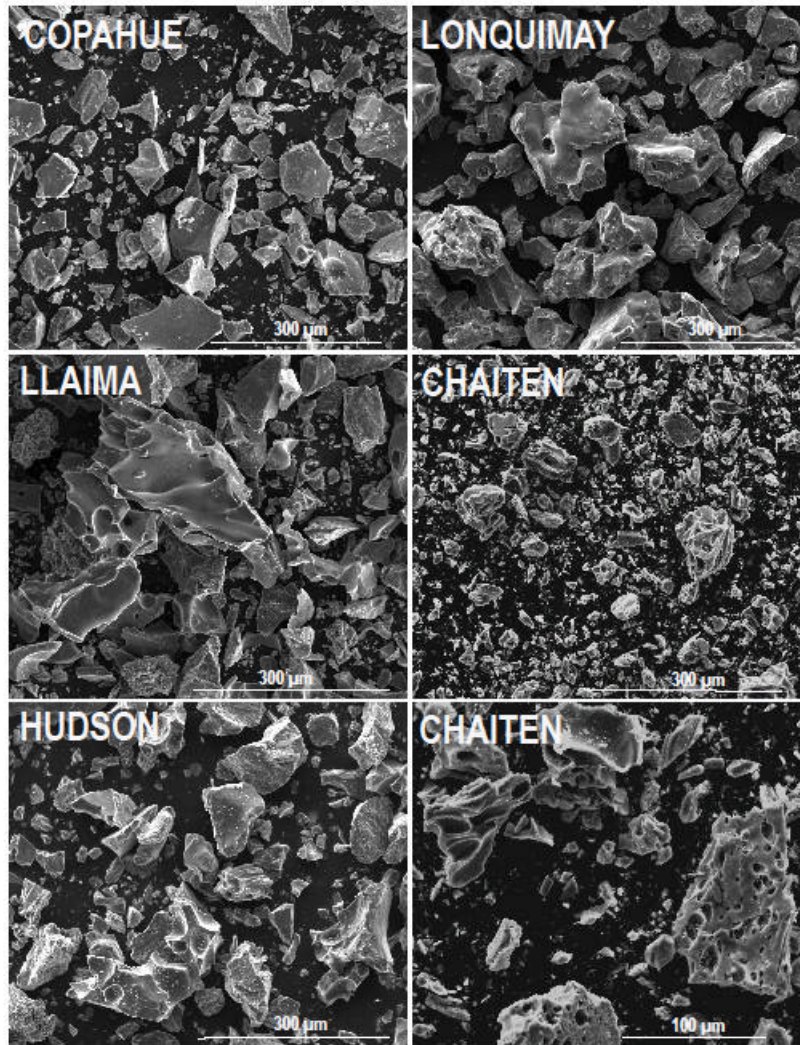


Figure 2