

1 Insights into the behaviour of S, F, and Cl at Santiaguito Volcano,
2 Guatemala, from apatite and glass

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12 **ABSTRACT**

13 The mineral apatite can incorporate all of the major magmatic volatile species
14 into its structure. Where melt inclusions are not available, magmatic apatite may
15 therefore represent an opportunity to quantify volatile concentrations in the pre-
16 eruptive melt. We analysed apatites and matrix glasses from andesites and
17 dacites erupted from Santiaguito Volcano, Guatemala, between the 1920s and
18 2002. X-ray mapping shows complex zoning of sulphur in the apatite grains, but
19 typically with sulphur-rich cores and sulphur-poor rims. Apatite
20 microphenocrysts are enriched in F and depleted in Cl relative to inclusions.
21 Matrix glasses are dacite to rhyolite and contain low F but up to 2400 ppm Cl.
22 Overall, the data are consistent with progressive depletion of Cl in the most
23 evolved melts due to crystallisation and degassing. In the absence of pristine
24 melt inclusions, we used apatite, together with published partitioning data, to
25 reconstruct the likely volatile contents of the pre-eruptive melt, and hence
26 estimate long-term average gas emissions of SO₂, HF and HCl for the ongoing
27 eruption. The data indicate time-averaged SO₂ emissions of up to 157
28 tonnes/day, HCl of 74-1382 tonnes/day and up to 196 tonnes/day HF. Apatite
29 may provide a useful measure of long-term volatile emissions at volcanoes
30 where direct emissions measurements are unavailable, or for comparison with
31 intermittent gas sampling methods. However, significant uncertainty remains
32 regarding volatile distribution coefficients for apatite, and their variations with
33 temperature and pressure.

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36 **Keywords:** Santiaguito; apatite; pre-eruptive volatile concentrations; gas
37 emissions; degassing; petrologic method

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39

40 **1. INTRODUCTION**

41 The exsolution of dissolved magmatic volatiles into bubbles during magma
42 ascent and eruption is one of the most important processes affecting the physical
43 properties of any volcanic system. Whereas H₂O and CO₂ are the most important
44 volatiles by volume, S, F and Cl can have significant environmental consequences
45 on a local to global scale, with relevance to atmospheric chemistry, human health,
46 and ecology (e.g. Robock, 2000; Allen et al., 2000; Martin et al., 2009).
47 Constraining the fluxes of these volatiles is an important means to assess the
48 current and past impact of volcanic activity on the Earth's surface environment.
49 In the absence of direct measurements of gas emissions, the volatile contents of
50 melt inclusions, trapped in phenocrysts and isolated at depth, are routinely used
51 to infer pre-eruptive melt volatile concentrations (e.g. Edmonds et al., 2001;
52 Wallace, 2005; Humphreys et al, 2008, Bouvier et al., 2008). Comparison of these
53 pre-eruptive volatile concentrations with those preserved in the matrix glass
54 gives a petrologic estimate of volatiles degassed during volcanic eruptions
55 (Devine et al., 1984; Thordarson et al., 1996).

56

57 However, in some magmas, melt inclusions may only be present in phases that
58 are liable to leakage or degassing, or they may be present but too small for
59 analysis, or have undergone devitrification or significant post-entrapment
60 modification. In such cases, an alternative method for assessment of pre-eruptive
61 volatile contents is required. Here we explore and evaluate the potential use of
62 apatite in place of melt inclusions, to infer pre-eruptive concentrations of S, F and
63 Cl in the magmatic liquid at Santiaguito volcano, Guatemala, commenting on the
64 advantages and limitations of the method. This work builds on previous studies,
65 for example at Huaynaputina, Peru (Dietterich and de Silva 2010) and Irazú
66 volcano, Costa Rica (Boyce and Hervig 2009). We use the data to infer pre-

67 eruptive volatile concentrations in magmas erupted from Santiaguito volcano,
68 and hence estimate the time-averaged gas emissions of this long-lived, but poorly
69 monitored, volcanic dome complex.

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72 **2. GEOLOGICAL BACKGROUND AND PETROLOGY**

73 Activity at the silicic lava dome complex of Santiaguito, Guatemala, began in 1922
74 and continues at the time of writing (2015). The dome sits on the shoulder of the
75 much older Santa María volcanic edifice, which in 1902 was the site of a major
76 bimodal explosive eruption, dominated by dacite pumice. Activity at the
77 Santiaguito edifice is characterized by extrusion of lava domes and flows, with
78 regular explosive release of gas and ash (Rose, 1972; Rose, 1987; Bluth and Rose,
79 2004; Escobar Wolf et al., 2010), and substantial passive degassing between
80 explosions (Holland et al., 2011). Persistent cloud cover, challenging terrain, and
81 the explosive nature of the volcanic activity have limited the measurement of
82 volatile emissions using satellite- or ground-based remote sensing methods or
83 direct techniques (Santa María Volcano Observatory written records; Rodriguez
84 et al., 2004; Holland et al., 2011). However, previous work indicates that the
85 effusive eruption of Santiaguito should result in significant halogen output in the
86 volcanic plume as a result of open-system degassing (Villemant et al., 2003;
87 Balcone-Boissard et al., 2010).

88

89 **2.1 PETROLOGY OF SANTA-MARÍA - SANTIAGUITO**

90 The chemical and petrological features of the Santa María - Santiaguito magmas
91 have previously been described (Rose 1972; Rose 1987; Jicha et al., 2010; Singer
92 et al., 2011; Scott et al., 2012; 2013; Singer et al., 2014), and we summarize the
93 main points below. The Santa María magmas are typically basaltic andesite, but
94 span a wide range of compositions from 51 wt% to 69 wt% SiO₂ (e.g. Rose 1987).
95 The earliest magmas erupted from Santiaguito itself were similar in composition
96 to the 1902 pumice from Santa María (Rose et al., 1972; Singer et al., 2011).
97 Santiaguito eruptive products are typically porphyritic andesites to dacites (62-
98 66 wt% SiO₂) with ~20-30 vol% plagioclase phenocrysts and ~5 vol%
99 orthopyroxene + Fe-Ti oxides + augite ± olivine ± amphibole. The plagioclase

100 phenocrysts commonly display one or more resorption surfaces with clear,
101 euhedral rims; in many of the more recent samples the majority of the
102 plagioclase crystals show severe resorption textures and a network of large,
103 irregular, devitrified melt inclusions in the core. Accessory minerals include
104 apatite, cristobalite, and pyrrhotite, the latter as inclusions in titanomagnetite
105 phenocrysts. The groundmass consists of matrix glass, euhedral plagioclase, and
106 equant to feathery microlites of orthopyroxene and titanomagnetite.

107

108 Glomerocrysts of plagioclase ± orthopyroxene ± olivine are common and contain
109 large pools of interstitial glass (figure 1). These glomerocrysts preserve
110 asymmetry at plagioclase-plagioclase-melt boundaries (figure 1d), due to the
111 development of curved plagioclase-melt interfaces, rather than simple
112 impingement textures with planar crystal surfaces. This suggests changes in the
113 differential growth rates between different plagioclase crystallographic axes.
114 These textures are similar to those observed in slowly cooling gabbroic
115 cumulates (Holness et al., 2012) and, by analogy, suggests very slow growth. We
116 therefore infer that these glomerocrysts may represent fragments of disrupted
117 mush that would have gone on to form solid plutonic rocks at depth. Matrix and
118 glomerocryst glass compositions range from ~66 to ~76 wt% SiO₂ and are
119 similar to the compositions of melt inclusions (64.5 - 73.5 wt% SiO₂, Singer et al.,
120 2014).

121

122 Thermobarometry based on amphibole phenocryst compositions suggests
123 magma crystallisation temperatures of ~940 to 980°C (±22°C) at moderately
124 oxidising conditions in the region of NNO+0.5 to NNO+2 (Scott et al., 2012;
125 Singer et al. 2014), and this agrees with observed maximum surface eruption
126 temperatures (850-950 °C, Sahetapy-Engel et al., 2004). Fe-Ti oxide
127 compositions from the 1902 eruption give temperatures of 860-885 °C for the
128 dacite and 925-1040 °C for the andesite (Singer et al., 2014). Petrological and
129 geochemical studies of Santiaguito show that the lavas have become more mafic
130 with time since the eruption recommenced in 1922 (Escobar Wolf et al., 2010;
131 Scott et al., 2013).

132

133 Apatite is present in all samples as microphenocrysts and/or as inclusions within
134 phenocryst phases (typically clinopyroxene), indicating early apatite saturation
135 in the melt (figure 2). Some crystals are fully included within the host mineral
136 while others are partly open to the matrix (figure 2), permitting variable degrees
137 of equilibration with the host melt. The common occurrence of apatites included
138 in pyroxene may be related to synneusis. The inclusions are equant and thus
139 clearly distinct from the acicular quench crystals commonly observed in
140 plagioclase phenocrysts elsewhere (e.g. Wyllie et al., 1962; Bacon, 1986), which
141 are thought to form as a result of growth from a melt boundary layer at the
142 crystal-melt interface. Apatite microphenocrysts are texturally similar to those
143 present as inclusions; their timing of crystallisation relative to the inclusions is
144 unclear but we assume that the microphenocrysts were at least open to
145 significant equilibration with the host melt. The apatites are relatively large, up
146 to 150 μm in length, which is typically significantly larger than groundmass
147 plagioclase, orthopyroxene and titanomagnetite microlites.

148

149 2.2 MAGMA SUPPLY AND FRACTIONATION

150 There is clear evidence of open-system processes at Santa-María – Santiaguito,
151 with a large range of magma compositions erupted, from basaltic andesite to
152 dacite. The deep supply of magma is dominated by hybrid basaltic andesites,
153 fractionating amphibole in the deep crust and assimilating crustal material to
154 form more silicic compositions (Singer et al., 2011; Singer et al., 2014; Jicha et al.,
155 2010). The shallow magmatic system is thought to comprise an elongate,
156 perhaps chemically stratified magma storage region (Rose 1972; Scott et al.,
157 2013), in which magmas decompress, degas and crystallise. There is clear
158 evidence for mixing of more mafic magmas with the dacites (Singer et al., 2011;
159 2014) including reversely zoned plagioclase and the presence of mafic enclaves,
160 as well as plutonic material.

161

162 2.3 SAMPLES STUDIED

163 Our dataset comes from analysis of 24 samples from Santiaguito, representing
164 many of the dome and flow units of the complex, and dating from the 1920s to
165 2002, as reported in Scott et al., (2012, supplementary table A) and in Scott

166 (2012). We consider in detail the glass dataset of Scott et al. (2013,
167 supplementary table D) together with some new glass analyses and a large
168 dataset of apatite compositions.

169

170

171 **3. ANALYTICAL METHODS**

172

173 Mineral analyses were obtained by electron probe microanalysis on a four-
174 spectrometer JEOL JXA-8600 electron microprobe in the Research Laboratory for
175 Archaeology and the History of Art, University of Oxford. For apatite, long
176 exposure to the electron beam results in sample damage in the form of volatile
177 migration; this effect is strongly anisotropic and is most significant for halogen
178 analyses conducted parallel to the c-axis of the crystal (e.g. Stormer et al., 1993;
179 Goldoff et al., 2012; Stock et al., 2015). Selection of analytical beam conditions is
180 a trade-off between the accuracy of halogen concentrations (needing a lower
181 accelerating voltage and beam current to minimise electron beam-induced
182 migration) and the precision of heavy and minor element analyses (e.g. Fe, Mn,
183 requiring at least 15kV accelerating voltage and higher beam currents, Stock et
184 al., 2015). For most analyses, we used relatively short (30s) peak count times for
185 all elements, a 15 kV accelerating voltage and a 15 nA defocused (5 μ m) beam,
186 with F, Cl and P analysed first. We found no discernible difference between
187 analyses of grains with different crystallographic orientations, within the
188 uncertainty of our analyses and the variance of the crystal population. We also
189 analysed a subset of analyses using a 10 nA, 5 μ m electron beam and these were
190 consistent with the lower-F compositions of those analysed at 15 nA, albeit with
191 slightly larger analytical uncertainties (see table 1). For these analyses, 120s
192 peak counting times were used for F, Cl and S. Analyses with totals <95 wt%
193 were excluded, as were those that did not give good stoichiometric formulae.
194 Wilberforce and Durango apatite, oriented both parallel and perpendicular to the
195 electron beam, were used as secondary standards to check the accuracy of the
196 analyses. These did show slightly higher F contents for crystals oriented with the
197 c-axis parallel to the electron beam, as demonstrated previously (e.g. Stormer et
198 al. 1993). The sulphur peak position was checked prior to analysis and S was

199 calibrated using BaSO₄. Analytical precision was typically better than 0.2 wt% for
200 F, 0.13 wt% for Cl and ~500 ppm for S, and is given in table 1.

201

202 We also performed element mapping on eighteen apatites from five different
203 samples, including microphenocrysts and inclusions in pyroxene, using a JEOL
204 JXA-8800 electron microprobe at the University of Oxford with a 15 kV, 15 nA
205 electron beam. These crystals did not subsequently undergo quantitative
206 analysis. Mapping used WDS for S, Cl, and F, and simultaneous EDS for all other
207 elements (Al, Ca, Fe, K, Na, P, Si, Ti). Resulting images were 256 by 256 pixels,
208 with a count time of ~45 microseconds per pixel.

209

210 For glasses, we used the existing matrix glass dataset of Scott et al. (2013) (see
211 table 2). We also analysed a small set of interstitial glasses from the
212 glomerocrysts, using a 15 kV, 6 nA defocused (10 µm) beam, with alkalis
213 analysed first to avoid electron-beam damage (e.g. Devine et al., 1995;
214 Humphreys et al., 2006a). Peak counting times were 90s for F and S, 60s for Cl,
215 80s for Mg, 12s for Na and 30s for all other elements. The sulphur peak position
216 was checked prior to analysis and calibrated using BaSO₄.

217

218

219 **4. RESULTS**

220

221 **4.1 APATITE COMPOSITIONS**

222 Apatites from Santiaguito are typically fluorapatite with ~0.6 to 1.5 wt% Cl
223 (table 1). Minor elements include ~0.2-1.2 wt% FeO, 0.1-0.35 wt% MgO, 0.1-0.5
224 wt% MnO, up to ~0.7 wt% SiO₂, and up to ~4000 ppm sulphur. There are no
225 significant compositional differences between apatites in andesitic samples and
226 those in the dacites, or between different phases of the eruption. The volatile
227 contents of the Santiaguito apatites are similar to those of some other
228 subduction-related systems for which data are available (Figure 3). Apatite
229 sulphur contents are similar in all textural associations. Those fully included in
230 their host phenocrysts contain on average 1656 ppm S (1 σ 687 ppm; n=52),
231 while those that are open to the matrix contain 1367 ppm S (1σ 602 ppm, n=42)

232 and microphenocrysts contain 1396 ppm S (1σ 804 ppm; $n=41$; Table 1). In
233 other words, the mean S concentrations from the population of apatites in each
234 textural category are separated by less than one standard deviation. However,
235 the data suggest that there are detectable differences in halogen concentrations
236 for apatite in different textural situations (Table 1; see also supplementary
237 figure), with the mean values of each apatite category separated by more than 1
238 standard deviation. Microphenocrysts record higher mean fluorine contents
239 (1.98 wt% F, 1σ 0.45 wt%) and lower mean chlorine (1.00 wt% Cl, 1σ 0.11 wt%)
240 than inclusions within phenocrysts (1.50 wt% F, 1σ 0.46 wt% and 1.19 wt% Cl,
241 1σ 0.15 wt%). Median concentrations are slightly lower for the
242 microphenocrysts and inclusions (Table 1), reflecting a spread of a minority of
243 data points to high F contents. Inclusions that are partially open to the matrix
244 tend to record slightly higher mean F (2.25 wt%, 1σ 0.54 wt%) but similar mean
245 Cl (1.01 wt%, 1σ 0.18 wt%) to the microphenocrysts. The rims of individual
246 microphenocrysts systematically record lower Cl and higher F than the cores. We
247 estimated OH contents for apatite using stoichiometry and assuming a fully
248 occupied Z site (e.g. Piccoli and Candela, 2002); average calculated OH contents
249 are 0.82 pfu for the apatite inclusions, compared with 0.46 pfu for inclusions
250 open to the matrix and 0.60 pfu for the microphenocrysts (see Table 1). However,
251 propagated OH uncertainties are very high and the assumption of complete
252 stoichiometry may be unrealistic, particularly if significant C is present (e.g.
253 Suetsugu et al. 2000).

254

255 Element mapping of individual crystals confirms that S, F, and Cl zoning is
256 common even in very small apatites, but demonstrates that the form of the
257 zoning may be quite variable. Apatites containing melt inclusions, or those
258 entrapped adjacent to melt inclusions in the host phenocryst, commonly have
259 patches enriched in F and Cl adjacent to the melt; S contents tend to be
260 unaffected (Figure 4a). Included apatites may contain sulphur-rich cores but
261 typically do not show significant zoning of halogens. Inclusions open to the
262 matrix also typically contain sulphur-rich cores and may show enrichment in
263 fluorine towards the matrix, but with no equivalent systematic pattern in Cl
264 contents (Figure 4). Microphenocrysts may have sulphur-rich cores, and typically

265 show F-rich rims (Figure 4). Some grains show more complex sulphur zoning
266 (Figure 4).

267

268 4.2 MATRIX GLASS COMPOSITIONS

269 The glass analyses presented include matrix glass, glass embayments at the
270 margins of phenocrysts and glass trapped within glomerocrysts. The
271 supplementary data from Scott et al. (2013) are given together with the new data
272 in Table 2. Matrix glasses show a continuous range from 66-80 wt% SiO₂ and
273 follow systematic major element variations. All the glasses show decreasing CaO,
274 Na₂O and Al₂O₃ and increasing K₂O with increasing SiO₂. The MgO, CaO, FeO and
275 TiO₂ contents of the matrix glasses decrease systematically with increasing bulk
276 rock SiO₂ content, and the least evolved matrix glasses become more Si-rich
277 (figure 5). The glasses plot along a systematic trend in the haplogranite ternary,
278 and this has been interpreted as reflecting decompression crystallisation (Scott
279 et al., 2012, fig. 11).

280

281 Glasses from most individual samples show a clear increase of K₂O and TiO₂ with
282 increasing SiO₂, with glasses from the most evolved bulk rocks falling to lower
283 concentrations at > 75 wt% SiO₂, but the overall picture is scattered (figure 5). A
284 similar overall pattern is seen for FeO although the degree of scatter is higher
285 and the downturn to lower FeO contents occurs at lower SiO₂. FeO does not
286 correlate with K₂O or Al₂O₃, but correlates well with MgO (figure 5). The matrix
287 glass compositions generally compare well with those of plagioclase-hosted melt
288 inclusions from the 1902 dacite pumice and basaltic andesite scoria (Singer et al.,
289 2014; figure 5). The glomerocryst interstitial glasses are similar to the matrix
290 glass, but with slightly lower CaO, slightly higher K₂O and TiO₂, and markedly
291 higher FeO (figure 5).

292

293 Analytical totals are high in all the glasses analysed (table 2), which suggests low
294 dissolved H₂O concentrations. The matrix glasses contain up to 2400 ppm Cl, but
295 the majority have much lower concentrations (average 835 ppm, 1 σ 352 ppm,
296 Table 2; figure 6). Overall, variations of Cl with SiO₂ show a similar pattern to
297 TiO₂, with concentrations increasing with fractionation and then dropping

298 towards lower Cl contents in the most evolved glasses (figure 6). F
299 concentrations were consistently below detection limits (~ 0.35 wt% F). Only a
300 few glasses had sulphur contents above detection limit (~ 135 ppm S); these
301 contained 0.05 to 0.13 wt% SO_3 (200 to 520 ppm S). The interstitial glasses from
302 the glomerocrysts typically contain higher Cl concentrations (1780 ± 440 ppm Cl,
303 figure 6) but similar sulphur concentrations to the matrix glasses.

304

305 These data are more or less consistent with previously reported glass
306 compositions in samples erupted from Santa María–Santiaguito, with the
307 exception of apparently low H_2O contents in our samples, inferred from the lack
308 of significantly low analytical totals. Villemant et al. (2003) reported bulk
309 groundmass compositions for dome rocks with 0.07-0.93 wt% H_2O and 114-676
310 ppm Cl, whereas the bulk groundmass of Plinian fall deposits contained typically
311 1-1.5 wt% H_2O and 780-950 ppm Cl. Volatile contents of matrix glass in clasts
312 from the 1902 Plinian eruption were 0.55-2.4 wt% H_2O (estimated by difference)
313 and 937-1397 ppm Cl (Villemant et al., 2003). Balcone-Boissard et al. (2010)
314 reported similar halogen contents, also for melt inclusions from Plinian clasts
315 from the 1902-1929 eruptions (100-300 ppm F, 700-1600 ppm Cl), but with
316 much higher H_2O contents (estimated at 5-7 wt% H_2O). Singer et al. (2014)
317 analysed H_2O in plagioclase-hosted melt inclusions from the 1902 dacite pumice
318 by secondary ion mass spectrometry and recorded concentrations up to 6.85 wt%
319 H_2O .

320

321

322 5. DISCUSSION

323 5.1 INTERPRETATION OF GLASS COMPOSITIONAL VARIATIONS

324 Taken together, the matrix glass compositions exhibit chemical trends that
325 indicate progressive fractionation driven by decompression and degassing; this
326 is consistent with the progressive decrease in H_2O content seen in plagioclase-
327 hosted melt inclusions (Singer et al., 2014). The increase in MgO, FeO, TiO_2 and
328 K_2O with SiO_2 in individual samples suggests that fractionation is dominated by
329 plagioclase \pm pyroxene, consistent with the observed modal abundance of ~ 75 -
330 80% plagioclase within the phenocryst assemblage (Scott et al., 2013). The most

331 silica-rich glasses can only have formed at very low pressures, and the wide
332 range of normative SiO₂ contents seen in the whole dataset is consistent with
333 crystallisation of hydrous magma over a wide pressure range (Blundy &
334 Cashman 2001). The presence of amphibole phenocrysts in some of the more
335 evolved rocks indicates crystallisation at ~150 MPa or more (assuming H₂O
336 saturation; e.g. Browne and Gardner 2006). Phase equilibria experiments
337 (Andrews 2014) suggest that the Santa Maria 1902 dacite was stored at
338 pressures similar to 150-170 MPa (if H₂O-saturated) at 850 °C prior to eruption.
339 Face-value application of the thermobarometer proposed by Ridolfi et al. (2010)
340 indicates crystallisation depths >12 km (Scott et al., 2013), and there is also
341 geochemical evidence of substantial fractionation of amphibole from the magma,
342 seen as a decrease in Dy/Yb with increasing SiO₂ and La/Lu in the whole-rock
343 dataset of Scott et al. (2013). Although pressures predicted by the Ridolfi et al.
344 (2010) barometer are likely to be over-estimated (Andrews 2014; Erdmann et al.
345 2014), these data together indicate polybaric crystallisation in the Santa Maria –
346 Santiaguito system. The interpretation of decompression crystallisation is
347 supported by the well-developed groundmass and amphibole breakdown
348 textures (Scott et al., 2012); the high H₂O contents of melt inclusions (Singer et al.,
349 2014) and successful phase equilibria experiments (Andrews, 2014); and
350 positive correlations between FeO, TiO₂ and MgO, and CaO and Al₂O₃ in the
351 glasses, suggesting crystallisation of pyroxene, Fe-Ti oxides and plagioclase.

352

353 The high FeO and TiO₂ contents of the glomerocryst glass embayments may
354 support the interpretation that some of the erupted crystal load is derived from
355 disaggregated plutonic material that represents the fractionation products of the
356 magma, perhaps prior to saturation of Fe-Ti oxides. The glomerocryst and matrix
357 glasses have very low H₂O contents compared with melt inclusion compositions
358 reported in previous studies (c.f. Balcone Boissard et al. 2010). We interpret this
359 as variable diffusional loss of H₂O during magma ascent, degassing and
360 crystallisation. However, the glomerocryst glasses retain high Cl and F
361 concentrations, probably due to much slower (minimal) diffusion of halogens
362 from these crystal clots during ascent. Overall, the glomerocryst glass

363 compositions suggest that they represent partially re-equilibrated fragments of
364 early-formed crystal mush.

365

366 5.2 BEHAVIOUR OF THE HALOGENS

367 With SiO₂ or K₂O as an index of differentiation, Cl contents of the glasses increase
368 during fractionation from ~0.03 wt% to >0.15 wt% Cl, then decrease after ~75
369 wt% SiO₂. This indicates incompatible behaviour of Cl until the later stages of
370 crystallisation, when it undergoes exsolution into a fluid phase, consistent with
371 the conclusions of Villemant et al. (2003) based on correlation between H₂O and
372 Cl contents of glass. Fluorine concentrations of the glasses were below detection
373 limits. However, we can use the volatile contents of apatite to give more
374 information on the evolution of volatiles during magma ascent and
375 crystallisation.

376

377 The F/Cl ratio of apatite is dependent on the ratio of halogen fugacities, $f_{\text{HF}}/f_{\text{HCl}}$,
378 as well as temperature and pressure (Piccoli & Candela 1994). Therefore, in the
379 absence of additional information, the cause of the observed compositional
380 change is difficult to determine without ambiguity. The observation of higher F
381 and lower Cl contents in the apatite microphenocrysts relative to inclusions
382 could be produced by decreasing temperature, or by increasing pressure (Piccoli
383 and Candela, 2002; Doherty et al. 2014). Recent work also indicates that Cl
384 partitioning between apatite and melt in the presence of a fluid phase is
385 dependent primarily on melt halogen (Cl) concentration, with a subsidiary
386 dependence on pressure (Cl concentrations in apatite increasing with decreasing
387 pressure; Doherty et al. 2014; Webster et al. 2009). We cannot rule out that
388 decreasing temperature during crystallisation played a role in the changing
389 apatite compositions. However, a number of factors suggest that the changing
390 apatite chemistry is related to compositional variations in the coexisting melt
391 and/or fluid. Firstly, the correlation between H₂O and Cl in glasses (Villemant et
392 al., 2003), indicates that the magma reached fluid saturation and exsolution
393 resulted in decreasing Cl concentrations in the melt. Loss of Cl from the melt by
394 exsolution of a fluid phase, together with incompatible, non-volatile behaviour of
395 F (i.e. F does not migrate into the free fluid phase but increases in concentration

396 in the melt) would be consistent with increasing $f_{\text{HF}}/f_{\text{HCl}}$ during crystallisation
397 and degassing. This would require loss of Cl to occur between crystallisation of
398 the pyroxene or plagioclase phenocrysts (that host the apatite inclusions) and
399 crystallisation of the apatite microphenocrysts.

400

401 The Cl depletion of microphenocryst rims relative to microphenocryst cores
402 could also reflect primary variations in melt composition during apatite
403 crystallisation, or re-equilibration of the microphenocrysts with the partially
404 degassed matrix melt. The variability in halogen contents of apatites open to the
405 matrix, and the small-scale zoning observed when inclusions are trapped
406 adjacent to glass, indicates relatively rapid halogen diffusion in apatite. However,
407 Cl zoning in the microphenocrysts is typically more diffuse than that seen in the
408 partially enclosed crystals, and occurs on similar scales in all crystallographic
409 orientations, whereas halogen diffusivities are strongly anisotropic (Brenan et al.,
410 1993). This suggests that the microphenocrysts do in fact record primary growth
411 zoning and not partial re-equilibration.

412

413 5.3 BEHAVIOUR OF SULPHUR

414 The population of apatite analyses records a wide spread of sulphur
415 concentrations and there is no statistically significant difference in S content
416 between microphenocrysts and inclusions. However, the X-ray mapping shows
417 that apatite microphenocryst cores are enriched in sulphur relative to the rims,
418 with minor but detectable fluctuations between core and rim in some grains (see
419 figure 4). Although early-formed sulphide inclusions are occasionally found in
420 the cores of magnetite and pyroxene phenocrysts, no sulphides are found in the
421 groundmass and this is consistent with the relatively high measured oxygen
422 fugacity of $+1 < \Delta \text{NNO} < +2$ (Andrews 2014; Singer et al. 2014). This suggests that
423 sulphur is not compatible in any late-crystallising phase in these magmas, and
424 therefore that the decrease in sulphur contents in apatite rims must indicate
425 either a decrease in sulphur concentration in the melt resulting from degassing,
426 or a decrease in the partition coefficient $D_{\text{S}^{\text{ap-m}}}$ due to a change in conditions in
427 the magma. The S partition coefficient for apatite depends on oxygen fugacity
428 (Peng et al., 1997), melt sulphur content and temperature (Parat and Holtz, 2004;

429 2005). At Santiaguito, we have no evidence for strong changes in magma oxygen
 430 fugacity, which is relatively high (estimates range from NNO+0.5 to NNO+2, Scott
 431 et al., 2012; Andrews 2014; Singer et al., 2014). Temperature variations may
 432 have been important during magma fractionation and ascent, given that
 433 temperature estimates for the dacites are 860-885 °C but 925-1040 °C for the
 434 basaltic andesite (Singer et al., 2014). However, D_S^{ap-m} increases with decreasing
 435 temperature (Parat and Holtz, 2004, see later), so cooling during fractionation
 436 would have the effect of increasing the S content of apatite in equilibrium with
 437 the melt, resulting in reverse zoning instead of the observed normal zoning. We
 438 therefore conclude that for the most part, the volatile contents of apatite at
 439 Santiaguito are related to changes in melt volatile concentration and degassing.

440

441 5.4 QUANTIFICATION OF PRE-ERUPTIVE VOLATILE CONTENTS

442 We used published apatite-melt partition coefficients to estimate pre-eruptive
 443 melt volatile concentrations from the analysed apatite compositions. Apatite
 444 inclusions in the phenocryst phases are essentially protected from the external
 445 melt environment and should therefore retain a reliable record of their original
 446 volatile contents, as long as they are not in contact with any melt pockets (see
 447 above; figure 4). To determine the volatile concentrations in the melt prior to
 448 ascent and degassing, we take representative compositions of apatite inclusions
 449 and the cores of microphenocrysts (table 3). Volatile concentrations in the melt
 450 after decompression and immediately prior to extrusion are derived from matrix
 451 glass compositions.

452

453 5.4.1 Sulphur

454 We estimated D_S^{ap-m} by first calculating the apatite saturation temperature (i.e.,
 455 the temperature at which apatite appears on the liquidus), following Piccoli and
 456 Candela (1994) and Dietterich and De Silva (2010):

$$457 \quad AST (K) = \frac{(26400 \cdot C_{SiO_2}^{AST} - 4800)}{12.4 \cdot C_{SiO_2}^{AST} - \ln\left(\frac{C_{P_2O_5}^{AST}}{1 - \frac{X}{100}}\right) - 3.97} \quad [1]$$

458 where AST is the apatite saturation temperature; $C_{SiO_2}^{AST}$ and $C_{P_2O_5}^{AST}$ are the
 459 weight fractions of SiO₂ and P₂O₅ in the melt at the point of apatite saturation,

460 and X is the fractional crystallinity of the magma at the point of apatite saturation.
 461 In the Santiaguito magmas there are abundant apatite inclusions in phenocryst
 462 phases including plagioclase, pyroxene and Fe-Ti oxides, which suggests that
 463 apatite saturation occurred relatively early. This is also supported by the lack of
 464 significant P_2O_5 enrichment in the bulk rock compositions (generally < 0.25 wt%
 465 P_2O_5 , see Scott et al., 2013). We therefore assume that $C^{AST}_{SiO_2}$ and $C^{AST}_{P_2O_5}$ are
 466 equivalent to representative bulk rock compositions ($\sim 62-65$ wt% SiO_2 and $0.21-$
 467 0.23 wt% P_2O_5 , Scott et al., 2013). We also infer from the abundance of apatites
 468 included in phenocrysts that X may be rather low, and must certainly be less than
 469 ~ 0.3 (the proportion of phenocrysts observed in the samples on eruption, Scott
 470 et al. 2012; 2013). This range of parameter values gives a range of calculated AST
 471 = $897-987$ °C (with ‘preferred’ values in the range $897-963$ °C, based on the
 472 observation of abundant apatite inclusions within phenocrysts including both
 473 plagioclase and pyroxene, leading to the assumption that a reasonable upper
 474 limit for the magma crystallinity at apatite saturation is $X=0.15$, i.e., half of that
 475 on eruption). These estimates are at the upper end of (or slightly higher than)
 476 temperature estimates for the more evolved magmas (e.g. amphibole-plagioclase
 477 geothermometry, $840-950$ °C, Scott et al., 2012; two-oxide temperatures, $860-$
 478 885 °C, Singer et al., 2014; Andrews 2014), and at the lower end of temperature
 479 estimates for the basaltic andesite ($925-1040$ °C, pyroxene and two-oxide
 480 thermometry, Singer et al., 2014).

481

482 We then used the empirical relationship obtained by Peng et al. (1997) for the El
 483 Chichón trachyandesite to determine a partition coefficient for sulphur:

$$484 \quad \ln D = \frac{21130}{AST (K)} - 16.2 \quad [2]$$

485 which gives $D_{S^{ap-m}}$ of $2.4-6.4$ for the ‘preferred’ apatite saturation temperatures
 486 ($897-963$ °C). These experimental data were acquired at more oxidising
 487 conditions (equivalent to the $MnO-Mn_3O_4$ to MH buffers) than the Santiaguito
 488 magma, and at more appropriate fO_2 conditions $D_{S^{ap-m}}$ would be slightly reduced,
 489 by perhaps a factor of 2 (Peng et al. 1997). In contrast, the strong increase of $D_{S^{ap-}}$
 490 m with decreasing temperature (Peng et al. 1997) means that cooling during
 491 fractionation would result in increasing S contents of apatite in equilibrium with
 492 a melt of constant composition, resulting in reverse zoning.

493

494 Using $D_{S^{ap-m}}$ of 2.45-6.4, combined with our measured compositions of apatite
495 inclusions (1656 ± 687 ppm) predicts melt sulphur concentrations in the range
496 151-957 ppm S. Apatite microphenocryst cores (1396 ppm \pm 804) give melt
497 concentrations of 92-899 ppm S. In comparison, measured matrix glass
498 concentrations were generally low, < 360 ppm S (table 2). This suggests that the
499 apatite compositions are a reasonable reflection of coexisting melt sulphur
500 compositions, at least if temperatures are in the lower part of our range (leading
501 to higher partition coefficients). Many of the apatites show systematic zoning,
502 commonly with sulphur-poor rims. It seems unlikely that this is a result of
503 changing temperature during crystallisation, as this would require significant
504 heating (to 940-1100 °C) to crystallise apatite with the lowest observed rim S
505 concentrations (~ 400 ppm) without any change in melt concentration. It is
506 possible that interaction with mafic magma at depth in the volcanic system could
507 cause such a heating effect; however it seems more likely that the apatites may
508 record syn-eruptive sulphur loss related to degassing.

509

510 5.4.2 Fluorine and Chlorine

511 To determine Cl and F concentrations in the melt we used empirical partition
512 coefficients determined for hydrous silicic melts (65-71 wt% SiO₂) in equilibrium
513 with melt and a fluid phase at 200 MPa, 900-924 °C and NNO to NNO+2.1
514 (Webster et al., 2009). These parameters are a good match for the estimated
515 magma storage conditions at Santiaguito, although true ternary F-Cl-OH
516 exchange coefficients would be more strictly appropriate than apparent partition
517 coefficients. The data of Webster et al. (2009) show that $X_{F^{ap}}$ increases with
518 increasing F and decreasing Cl concentration in the melt; X_F/X_{Cl} (ap) increases
519 linearly with X_F/X_{Cl} (m), with X_F/X_{Cl} (ap) ranging from 0.26 to 14.9 (Webster et
520 al., 2009). Their experiments were run at higher Cl contents than the Santiaguito
521 glass, so we only used data from the less Cl-rich experiments that resulted in
522 apatite with ≤ 2 wt% Cl. These give values of apparent $D_{F^{ap-m}}$ (calculated as $D =$
523 F_{ap}/F_m) from 12.7-37. For the same experiments, equivalent values of $D_{Cl^{ap-m}}$
524 range from 1.0-3.5.

525

526 Using mid-range values for apparent partition coefficients $D_{F^{ap-m}}$ ($D=25$) and
527 $D_{Cl^{ap-m}}$ ($D=2.25$), the apatite microphenocryst compositions indicate melt halogen
528 concentrations in the range 0.06-0.11 wt% F and 0.38-0.53 wt% Cl; apatite
529 inclusions give melt halogen concentrations of 0.04-0.08 wt% F and 0.46-0.60 wt%
530 Cl. Given the full variation in the partitioning data, the possible range of melt
531 concentrations is large, more like 0.04-0.17 wt% F and 0.29-1.19 wt% Cl (table
532 3). This range is consistent with the low measured glass F compositions (lower
533 than the detection limit for at ~ 0.35 wt% F) and suggests that there has not been
534 significant degassing of F during magma ascent and crystallisation. In contrast,
535 melt inclusions have 700-1600 ppm Cl (Balcone-Boissard et al. 2010), which is
536 substantially lower than the concentrations predicted from our apatite
537 compositions; our matrix glasses analyses show even lower Cl contents (Table 2).
538 This result is similar to that of previous studies (e.g. Boyce and Hervig 2009;
539 Webster et al., 2009), which also found anomalously high apatite-based
540 estimates for pre-eruptive melt Cl (but not F) concentrations when compared to
541 melt inclusions.

542

543 It has been suggested previously that a discrepancy between melt inclusion Cl
544 contents and those calculated from apatite could be due to exsolution of a low-
545 density aqueous vapour from a higher density single-phase fluid coexisting with
546 the magma during ascent (Webster et al. 2009). Subsequent segregation of the
547 low density vapour would result in increasing salinity of the remaining saline
548 fluid and re-equilibration of apatite to more Cl-rich compositions (Webster et al.,
549 2009). There is no direct evidence of the presence of a high density saline fluid at
550 Santiaguito, although the melt Cl contents predicted from apatite may be
551 approaching the concentration at which a dense fluid could become stable
552 (Signorelli and Carroll 2001; Webster 2004). However, the process described by
553 Webster et al. (2009) should result in partial equilibration of the larger apatite
554 grains to leave Cl-rich rims, whereas Cl-poor rims are observed. It is unlikely that
555 the discrepancy between predicted and observed melt Cl concentrations is the
556 result of apatite growing at volatile-undersaturated conditions, because previous
557 melt inclusion studies demonstrate Cl-H₂O loss during magma ascent (Villemant
558 et al., 2003; Singer et al., 2014). We can also rule out early crystallisation in a

559 higher temperature, less fractionated melt, as this would result in a lower D_{Cl}^{ap-m}
560 (Webster et al. 2009) and hence higher melt Cl contents for a given apatite
561 composition. This leaves the most obvious explanation for the low Cl contents of
562 the matrix glasses that the matrix has substantially degassed, resulting in loss of
563 Cl into the vapour phase during ascent. This is supported by the covariation of Cl
564 and H₂O in melt inclusions and residual matrix glasses of Plinian clasts
565 (Villemant et al., 2003).

566

567

568 5.5 THE 'PETROLOGIC METHOD' USING APATITE

569 The pre-eruptive dissolved volatile concentrations predicted from apatite can be
570 used to estimate the flux of SO₂, HF, and HCl from Santiaguito, in the same way
571 that the 'petrological method' is commonly used with melt inclusions (e.g.
572 Thordarson et al., 1996; Wallace 2005; Dietterich and de Silva 2010). First, the
573 amount of volatiles degassed is constrained using the difference between
574 apatite-based estimates of pre-eruptive melt volatile concentrations (0.29-1.19
575 wt% Cl, 0.03-0.17 wt% F, 218-676 ppm S, table 3) and matrix glass volatile
576 concentrations. We use the upper estimates of matrix glass concentrations (0.03
577 wt% F from Balcone-Boissard et al., 2010; 0.11 wt% Cl and 358 ppm S, tables 2
578 and 3) in order to obtain a minimum estimate of the extent of degassing. The
579 total volume of magma erupted at Santiaguito since 1922 is 1.1–2 km³ (Harris et
580 al., 2003; Ebmeier et al., 2012; Scott et al., 2013); using a typical dacite magma
581 density of 2500 kg m⁻³ gives a total erupted mass of 2.75×10^{12} to 5×10^{12} kg.
582 Assuming a mean phenocryst content of ~30% (Scott et al., 2012), this equates
583 to $1.9 - 3.5 \times 10^{12}$ kg melt. Thus the total mass of volatiles emitted since 1922 is
584 up to 2.8×10^9 kg S, $2.4 \times 10^9 - 4.5 \times 10^{10}$ kg Cl and up to 6.3×10^9 kg F (table 3).

585

586 This suggests time-averaged SO₂ emissions of up to 157 tonnes/ day (table 3),
587 which is similar to previous estimates based on sporadic field measurements
588 (between 20 and 960 tonnes/day, see table 4, Andres et al. 1993; Rodriguez et al.,
589 2004; Holland et al., 2011). The same method suggests time-averaged estimates
590 of 74-1380 tonnes/day HCl and up to 196 tonnes/day HF (table 3). These results
591 give gas species ratios of HF/SO₂ ~ 1.25, and HCl/SO₂ ~ 0.5 to 8.8. Because the

592 melt Cl concentrations calculated from apatite are rather high compared with
593 melt inclusions (see earlier), we consider that the lower HCl flux values are
594 probably more reliable. There are no published field-based estimates of
595 Santiaguito's halogen emissions, so we are unable to compare this with
596 independent constraints on HCl flux from the volcano. It is not trivial to compare
597 long-term petrological estimates with spot measurements of gas emissions at
598 any individual volcano, primarily because gas fluxes may be highly variable in
599 time, depending on the level of volcanic activity. For example, the HCl flux (and
600 consequently the HCl/SO₂ ratio) at arc volcanoes is typically related to direct
601 magma extrusion and falls to very low levels during periods of non-extrusion (e.g.
602 Edmonds et al. 2001). Spot field measurements for SO₂ at Santiaguito are highly
603 variable in time and also appear to depend on whether there is active extrusion
604 at the lava dome (Rodriguez et al., 2004; Holland et al., 2011).

605

606 A well-monitored volcanic system that also shows long-term dome-building
607 activity is Soufrière Hills Volcano, Montserrat. Cl is degassed from the andesite
608 magma during extrusion but sulphur is mostly supplied by deeper degassing of
609 unerupted mafic magma (e.g. Edmonds et al., 2001; Edmonds et al., 2010).
610 Soufrière Hills Volcano has emitted approximately $4.0 \pm 0.6 \times 10^9$ kg sulphur
611 during the course of the prolonged 1995-2011 dome-forming eruption, including
612 both SO₂ and H₂S (Edmonds et al., 2014). Similarly to Santiaguito, SO₂ emission
613 rates have been highly variable during the eruption (e.g. 42 to >1900 tonnes/day
614 during 1996-1997, Young et al. 1998), with long-term time-averaged SO₂
615 emission rates ~600 tonnes/day SO₂ (Christopher et al. 2010; Edmonds et al.
616 2014), approximately twice the upper estimate for the SO₂ flux emitted at
617 Santiaguito (see table 4). At Soufrière Hills Volcano, the HCl/SO₂ ratio is <0.3
618 during pauses, >1 (up to ~10) during active extrusion (Christopher et al., 2010;
619 Edmonds et al., 2014), with HCl emission rates of >400 tonnes/day during dome-
620 building and <80 tonnes/day during pauses in extrusion (Edmonds et al., 2002).
621 The inferred HCl flux at Santiaguito is therefore in line with that observed during
622 dome growth at Soufrière Hills. However, the HCl/SO₂ ratios at Santiaguito
623 extend to higher values than Soufrière Hills Volcano. One explanation for this is
624 the apparently substantially lower SO₂ fluxes at Santiaguito. This may reflect

625 differences in the details of the deep plumbing system (a substantial proportion
626 of the SO₂ supply at Soufrière Hills is contributed by unerupted mafic magma,
627 whereas the long-term petrologic estimates for Santiaguito consider only
628 sulphur degassed from the magma that is erupted; alternatively mafic magma
629 supply rates at Santiaguito may differ from those at Soufrière Hills). The
630 mismatch between apatite and melt inclusion Cl contents is another source of
631 uncertainty here.

632

633

634 5.6 APATITE: ITS POTENTIAL FOR TRACKING VOLCANIC DEGASSING

635 There is considerable potential for using apatite to infer magmatic volatile
636 contents and time-averaged gas emissions for S, F, and Cl, as an alternative to
637 melt inclusion-based methods (e.g. Huaynaputina, Peru, Dietterich and de Silva
638 2010). This may prove particularly useful when direct emissions measurements
639 are unavailable, for historic and prehistoric eruptions, and for comparison with
640 intermittent gas sampling methods, which are typically highly variable in time.
641 However, there still remain significant problems associated with using apatite to
642 infer magmatic volatile concentrations, not least in estimating the point at which
643 apatite started to crystallise. One of the most significant problems is uncertainty
644 over the presence and composition of any fluid(s) coexisting with the melt,
645 coupled with a lack of constraints on the ultimate fate of a brine phase, if present.
646 This uncertainty still exists for melt inclusion studies, but for apatite the problem
647 is trickier because of the strong dependence of apatite halogen contents on fluid
648 composition (Webster et al., 2009). More focus is required on demonstrating
649 possible fluid immiscibility, including documenting the presence of multiple fluid
650 bubbles in melt inclusions, as well as the composition of fluid inclusions. Melt
651 inclusions are useful to constrain whether there has been volatile saturation in
652 the melt.

653

654 Additional problems arise when there is also substantial variability in the
655 compositions of apatite. Apatite inclusions and microphenocrysts presented here
656 show considerable compositional variability, with 1 relative standard deviation
657 ~12-15% for Cl, 25-30% for F and 40-50% for S. For the most part this

658 variability appears to be real, although improved precision (e.g. by use of ion
659 microprobe techniques) would be helpful, as would direct analysis of OH for
660 accurate determination of Cl/OH and F/OH ratios. Significant variability between
661 grains means that it is difficult to demonstrate that apatites represent
662 equilibrium compositions, as well as to determine which values are truly
663 representative of pre-eruptive magmatic conditions, and at what conditions. Syn-
664 eruptive diffusive equilibration of microphenocrysts with degassed matrix glass
665 can, in principle, be distinguished from crystallisation effects by considering the
666 lengthscale and anisotropy of compositional gradients. Accurate and precise
667 knowledge of magmatic conditions (fO_2 , pressure and temperature) is required
668 for sensible choice of partition coefficients, and thermodynamic calculations may
669 help in this regard. Finally, application of apatite as a tracer of magmatic volatiles
670 would be enhanced by knowledge of partitioning characteristics of all the
671 volatiles (including OH and C), as well as direct determination of these elements
672 in both apatite and melt.

673

674

675 **7. CONCLUSIONS**

676 The eruption of Santiaguito volcano, Guatemala, is highly active and amongst the
677 longest-lived of its kind in the world. However, due to its location, climate and
678 the surrounding terrain there are few constraints on gas emissions from this
679 volcano. Apatite in Santiaguito lavas retains evidence of volatile zoning,
680 recording loss of sulphur and chlorine between early entrapment of inclusions
681 and crystallisation of microphenocryst rims. This is likely related to degassing of
682 Cl and S from the magma together with aqueous vapour. Pre-eruptive melt
683 volatile concentrations were determined from the apatite compositions using
684 published partition coefficients. These were used, together with matrix glass
685 compositions, to derive time-averaged estimates of SO_2 , HF, and HCl fluxes from
686 Santiaguito. These results indicate time-averaged fluxes of up to 157 tonnes/day
687 SO_2 , up to 196 tonnes/day HF, and 74-1380 tonnes/day HCl. Estimated ratios are
688 HF/ SO_2 ~1.25, and HCl/ SO_2 0.5-8.8. These fluxes are in line with estimates from
689 other arc volcanoes; however the uncertainties are large and additional work is
690 needed to constrain volatile exchange coefficients between apatite and melt \pm

691 fluid(s), including in volatile-undersaturated systems, as well as direct analysis of
692 OH in both apatite and melt.

693

694

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706

707

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935

936 **FIGURE CAPTIONS**

937

938 Figure 1.

939 Photomicrographs of typical dome rocks from Santiaguito Volcano. (a)
940 Porphyritic texture with abundant plagioclase phenocrysts (pl), pyroxene (px)
941 and vesicles (v). (b) Typical groundmass texture with abundant euhedral
942 microlites of plagioclase, pyroxenes and oxides. (c) Matrix glass (arrowed) can be
943 found as small patches and embayments near the margins of glomerocrysts. (d)
944 Cumulate-type grain boundary textures are found in some plagioclase
945 glomerocrysts. This is manifest as marked asymmetry of plagioclase-plagioclase
946 junctions, resulting in small filaments of feldspar (arrowed; expected grain
947 boundary marked with dashed line) joining adjacent grains of the glomerocryst.
948 This is similar to that observed in gabbros (Holness et al. 2012) and suggests
949 very slow cooling. Dark blebs are partially devitrified melt inclusions. Scale bar is
950 1 mm in all images except d (100 μm).

951

952 Figure 2.

953 Back-scattered electron SEM images showing typical occurrences of apatite in
954 dome rocks from Santiaguito Volcano, both as abundant inclusions within
955 pyroxene (px) phenocrysts or crystal clots of pyroxene with oxides (ox), and as
956 microphenocrysts in the matrix. Some of the inclusions are open to the matrix (a).
957 In (a) many of the apatite inclusions themselves contain tiny melt inclusions that
958 appear as dark dots.

959

960 Figure 3.
961 Ternary diagrams showing (a) S, F, Cl and (b) F, Cl, OH volatile compositions of
962 apatite inclusions (squares) and microphenocrysts (circles) from Santiaguito,
963 expressed as ions per formula unit, with sulphur contents $\times 10$ for ease of
964 comparison. Also shown are fields for other subduction-related systems:
965 Shiveluch Volcano, Kamchatka (Humphreys et al., 2006), Huaynaputina, Peru
966 (Dietterich and de Silva, 2010), Monte Vulture, Italy (Liu and Comodi, 1993) and
967 Yerington batholith (Streck and Dilles, 1998). 'Other arc volcanoes' (black field)
968 are as reported in Webster et al., (2009), and comprise Krakatau, Indonesia;
969 Pinatubo, Philippines; Mt St Helens, Washington; Santorini, Greece; Lascar, Chile;
970 and Bishop Tuff, California. Insets highlight in grey the sections shown in the
971 main figures.

972
973 Figure 4.
974 Back-scattered electron SEM images and X-ray maps showing volatile element
975 zoning in apatite inclusions and microphenocrysts from Santiaguito Volcano. (a)
976 SG-09-33-1, three inclusions in pyroxene host. Small filaments of melt are
977 trapped at the lower margin of the inclusion, clearly visible in the K map. Re-
978 equilibration of Cl^{ap} with the melt is apparent. The inclusion also has a sulphur-
979 rich core. (b) SG-09-33-7, single inclusion within pyroxene host. There is no
980 small-scale re-equilibration as in (a) despite the presence of a small melt pocket,
981 but still clear S-enrichment in the core of the inclusion. (c) SG-09-36-11,
982 microphenocryst with melt embayment. Both F and Cl show clear core-rim
983 zoning, with higher volatile contents at the rim. There is also short lengthscale,
984 high-amplitude zoning in Cl at the rim of the melt embayment. The
985 microphenocryst shows slight S enrichment in the core.

986
987 Figure 5.
988 Glass compositions from Santiaguito Volcano (open squares, matrix glasses from
989 Scott et al. 2013; filled squares, glomerocryst glass from this study) together with
990 published plagioclase-hosted melt inclusion data from the basaltic andesite (dark
991 filled circles) and pumice (light filled circles) of Santa María, 1902 (Singer et al.
992 2014). Black triangles and underlying grey arrow in (b) and (c) illustrate

993 relatively clear trends seen for individual samples (here, SG-09-03, see table 2).
994 (a) CaO shows a clear decrease with increasing SiO₂. (b) K₂O contents increase
995 with increasing SiO₂ but the most evolved samples (with ~75 wt% SiO₂) have
996 lower concentrations. (c) TiO₂ shows the same pattern as K₂O but more
997 exaggerated. (d) Good correlation between Fe and Mg contents. (e) and (f). TiO₂
998 and CaO concentrations decrease with increasing bulk rock SiO₂ content.

999

1000 Figure 6.

1001 Cl contents of matrix glasses (open squares) and glomerocryst glasses (filled
1002 squares) from Santiaguito Volcano plotted against the SiO₂ content of the host
1003 bulk rocks. Cl concentrations follow a similar pattern to K₂O and TiO₂ (see figure
1004 5), increasing and then decreasing after ~75 wt% SiO₂. Error bars shows ±1
1005 sigma analytical uncertainty on the analyses; horizontal line represents the
1006 detection limit (~300 ppm Cl). Two grey ovals represent the range in
1007 composition of matrix glasses and melt inclusions from the 1902 Plinian
1008 eruption (dark grey) and later dome rocks (light grey) as measured by electron
1009 microprobe (Villemant et al. 2003; Balcone-Boissard et al., 2010).

1010

1011 Supplementary figure

1012 Histograms showing the distribution of apatite F, Cl and S compositions,
1013 separated into different textural categories (inclusions in phenocrysts, inclusions
1014 that are open to re-equilibration with the matrix glass, and microphenocrysts).
1015 Vertical axis is *n*, number of observations, in all cases.

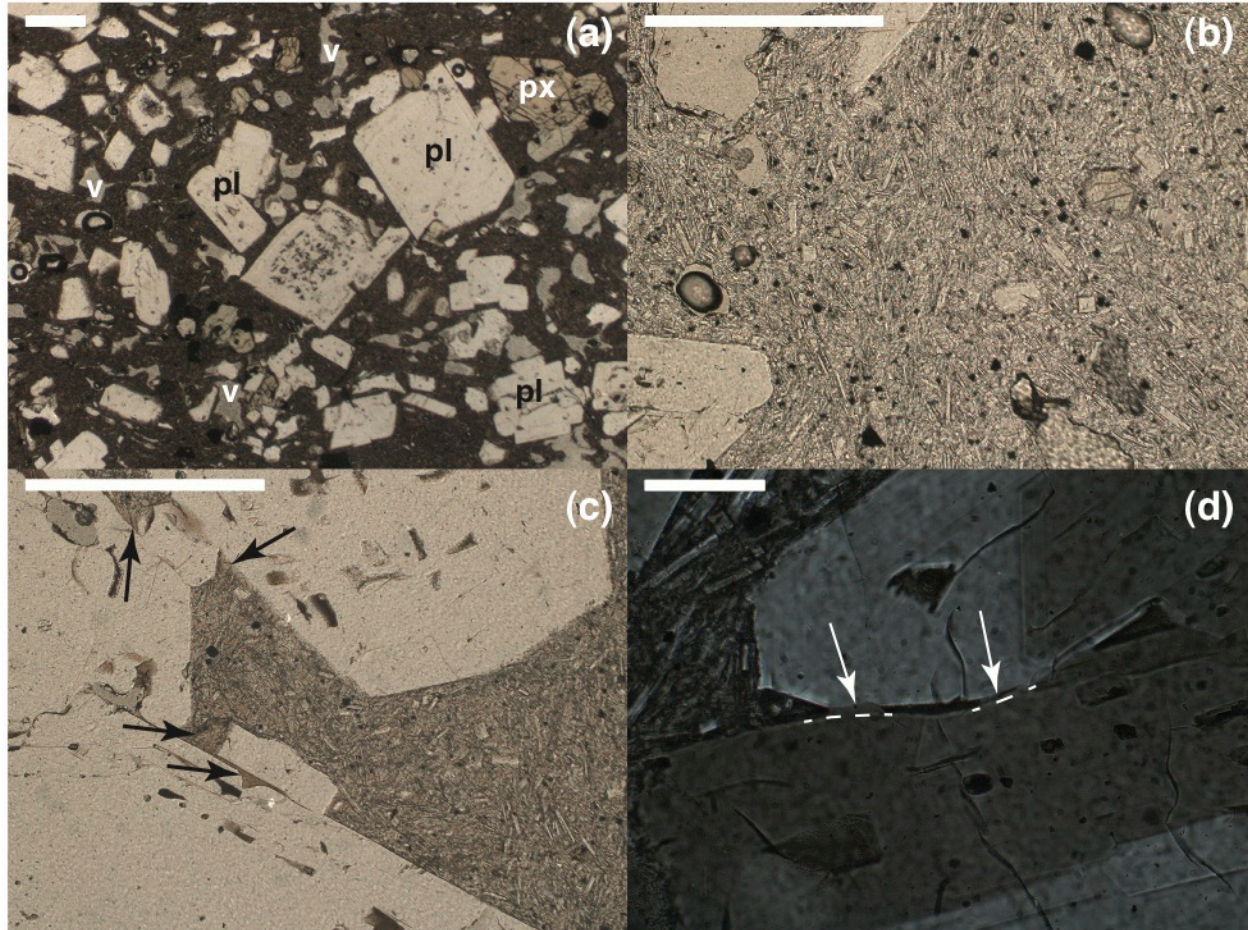


Figure 1

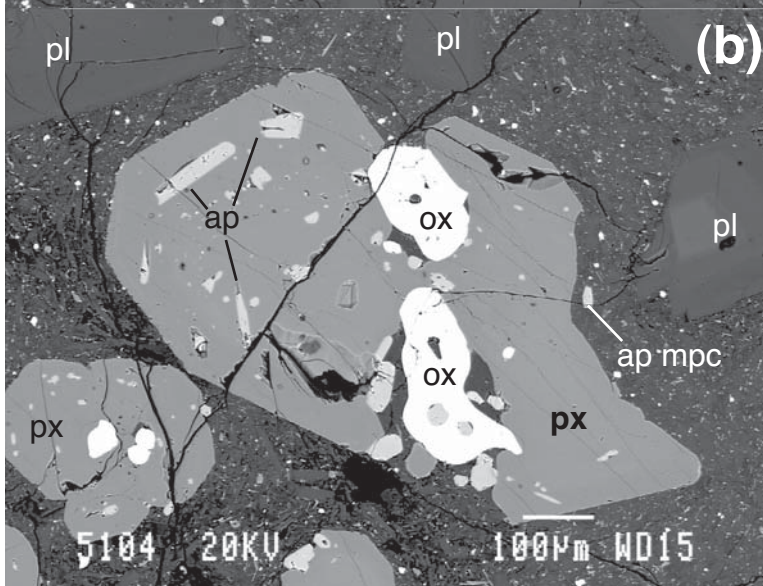
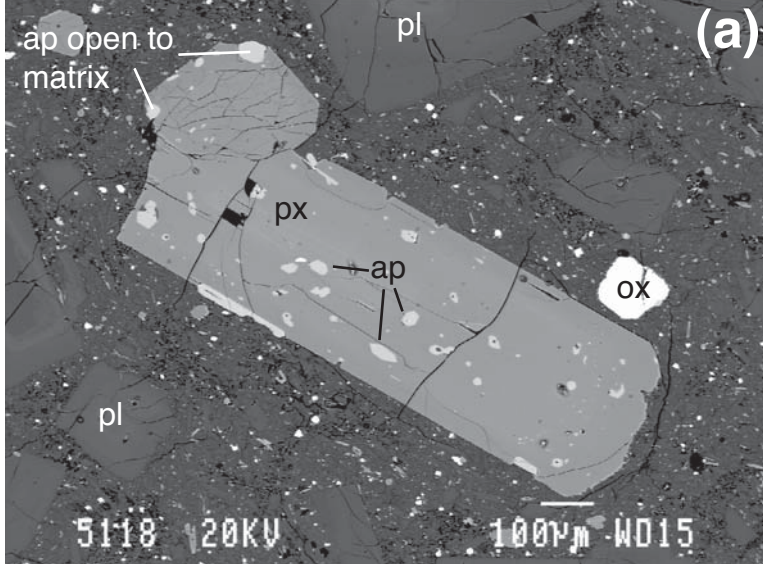


Figure 2

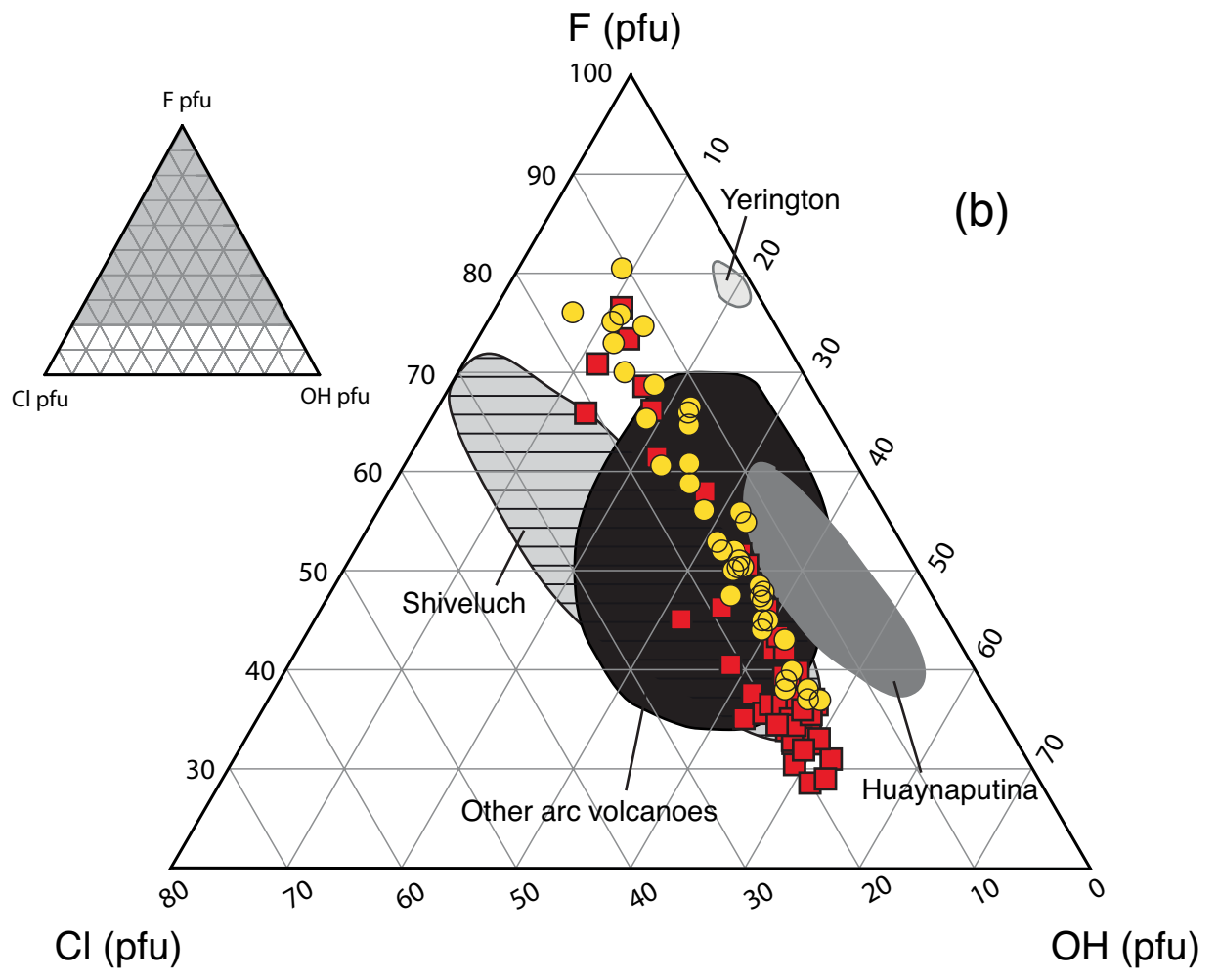
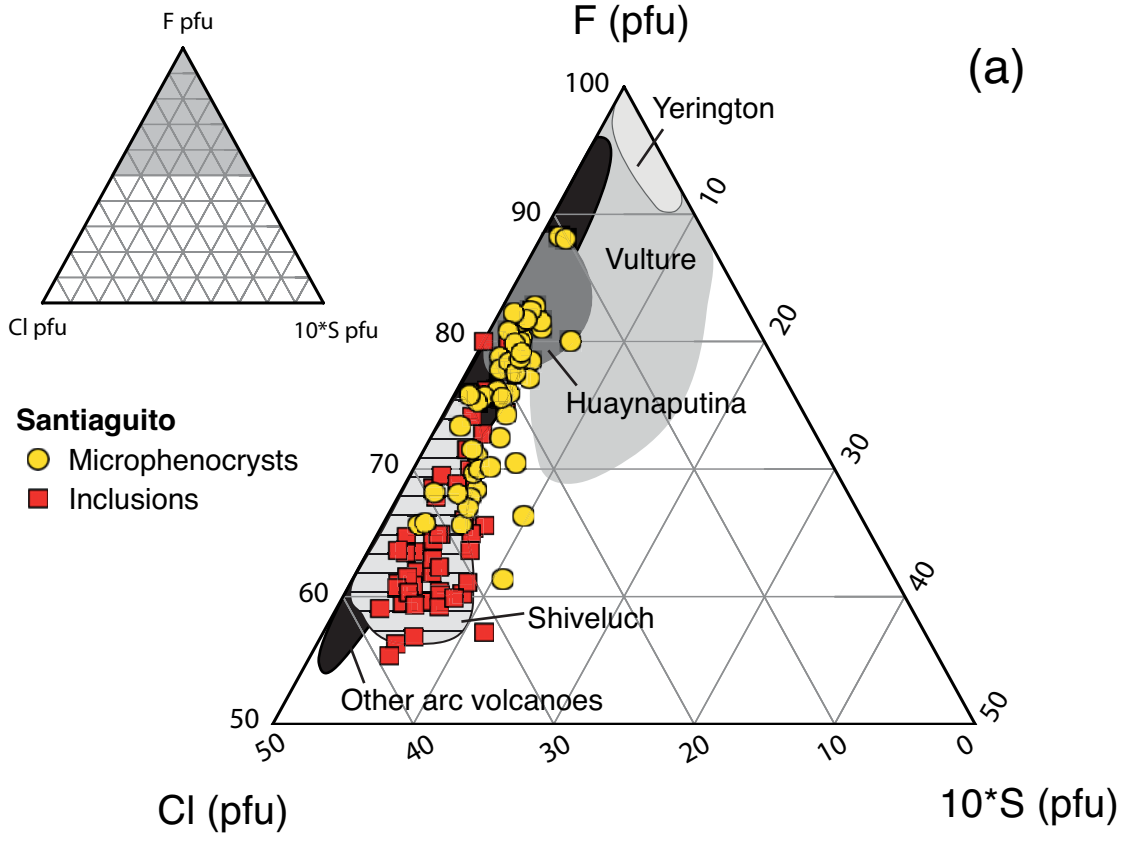


Figure 3

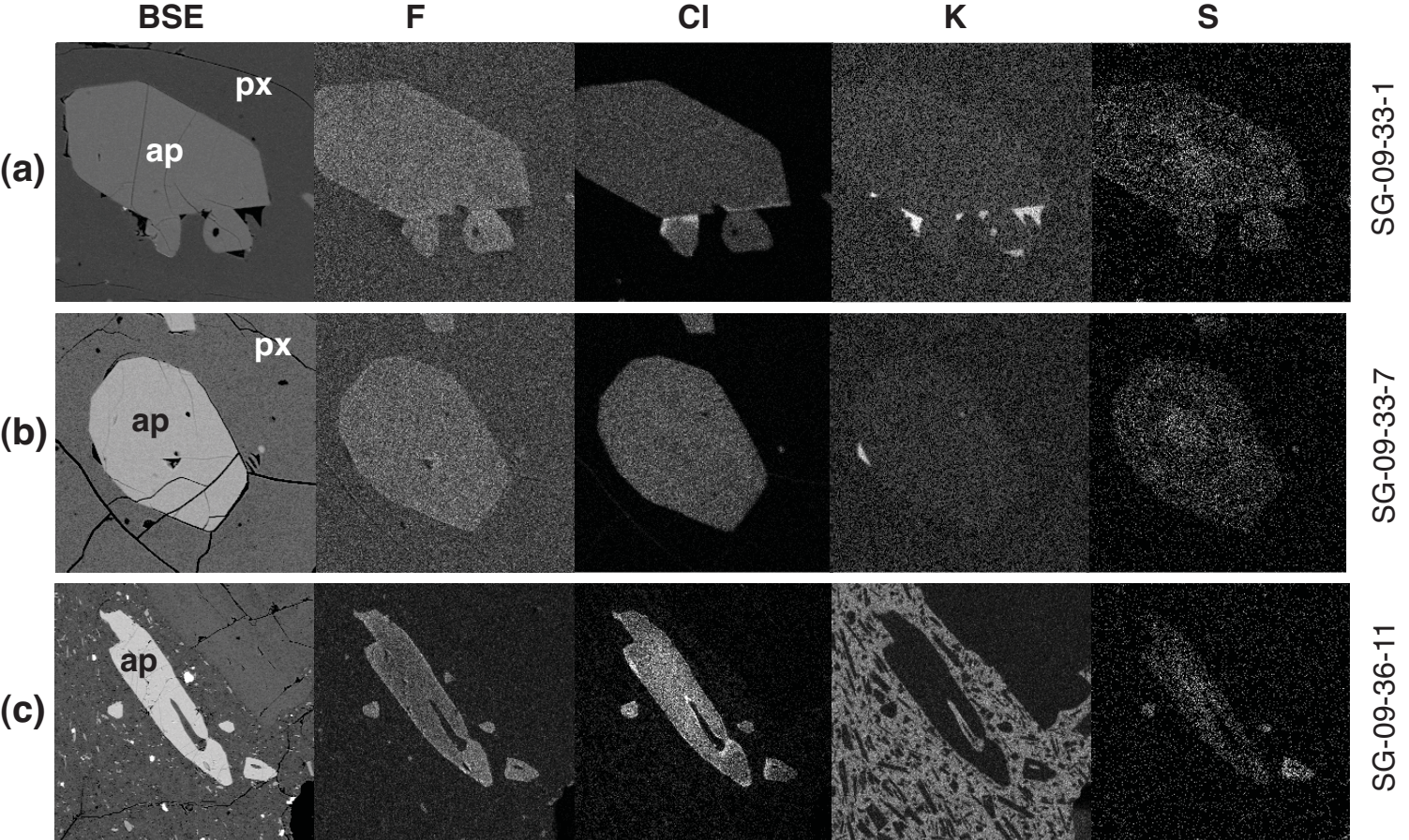


Figure 4

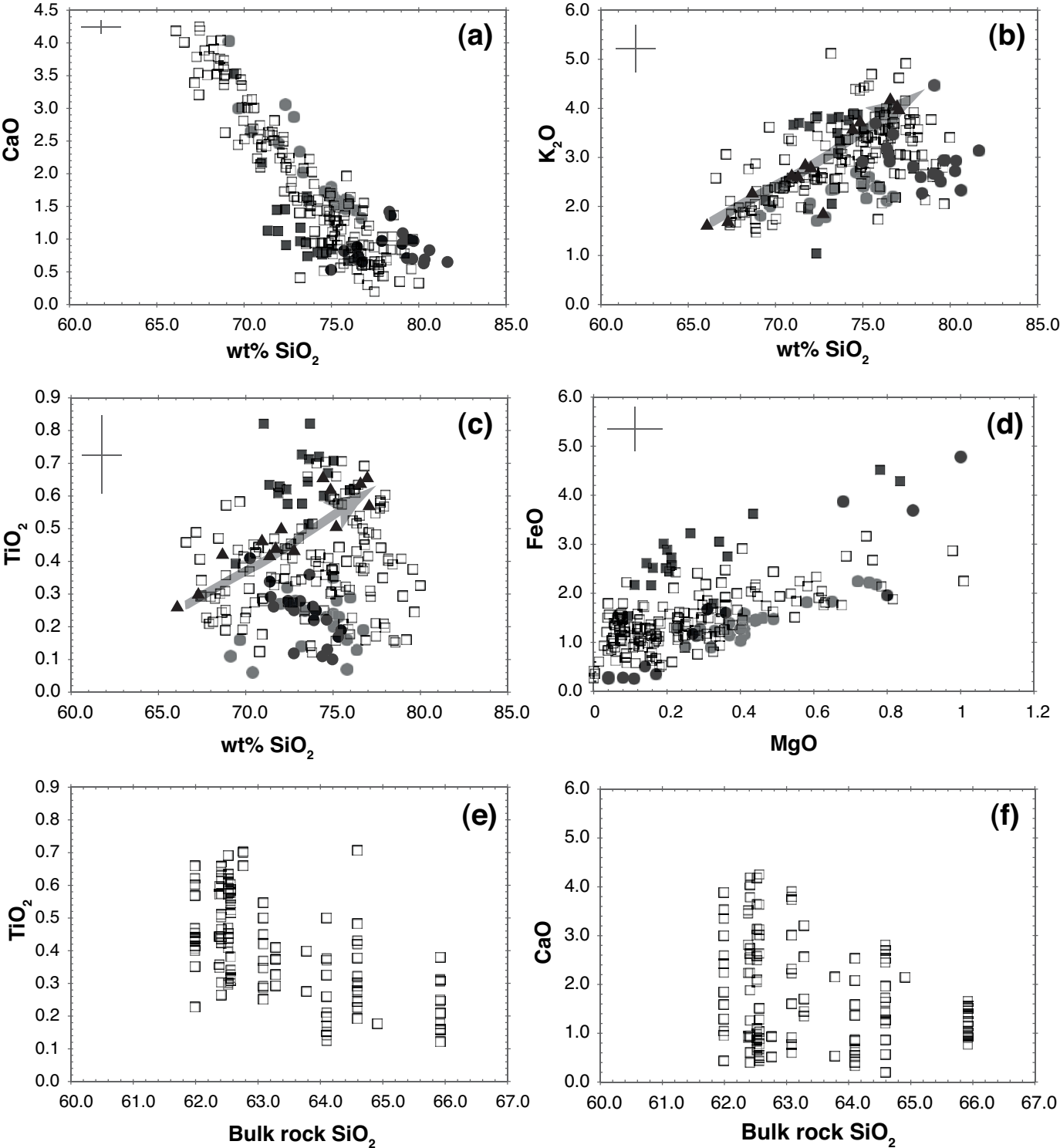


Figure 5

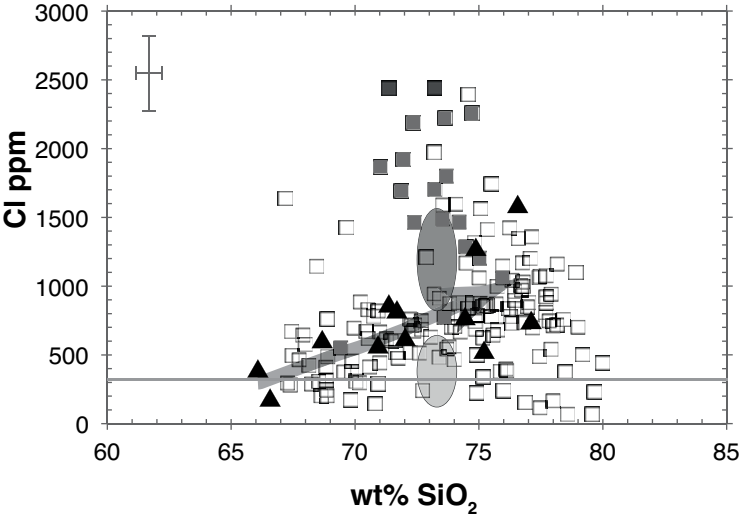


Figure 6

TABLE 1.

Electron microprobe analyses of apatite. Analyses were taken in the centre of each 20 grain section unless otherwise specified.

Point identifier	Sample number	Analytical setup	Unit	Vent	Sample type	SiO ₂	FeO	MnO	MgO	CaO	P ₂ O ₅	SO ₃	F	Cl	Total	O = F,Cl	S ppm	stdev F (wt%)	stdev Cl (wt%)	
12	SG-09-32	Inclusion	15Na, 30s on peak	Rmb	Monje	Dome	0.17	0.70	0.13	54.32	40.97	0.40	1.38	1.40	99.47	0.90	1592	0.16	0.14	
23	SG-09-32	Inclusion	15Na, 30s on peak	Rmb	Monje	Dome	0.14	0.61	0.20	53.52	41.11	0.22	1.88	1.00	98.68	1.02	899	0.19	0.12	
32	SG-09-32	Inclusion	15Na, 30s on peak	Rmb	Monje	Dome	0.24	0.56	0.21	52.52	40.61	0.22	1.55	1.02	98.66	0.79	2154	0.16	0.12	
65	2006-69	Inclusion	15Na, 30s on peak	-	Caliente	Bomb	0.13	0.45	0.24	53.67	39.50	0.44	1.19	1.17	96.80	0.77	1752	0.15	0.13	
70	2006-69	Inclusion	15Na, 30s on peak	-	Caliente	Bomb	0.20	0.74	0.23	53.86	40.99	0.33	2.52	1.01	99.87	1.29	1327	0.22	0.12	
81	2006-69	Inclusion	15Na, 30s on peak	-	Caliente	Bomb	0.16	0.75	0.25	53.32	39.57	0.45	1.08	1.36	96.94	0.76	1808	0.14	0.14	
83	2006-69	Inclusion	15Na, 30s on peak	-	Caliente	Bomb	0.10	0.57	0.22	53.74	39.83	0.34	1.45	1.40	97.67	0.93	1366	0.16	0.14	
84	2006-69	Inclusion	15Na, 30s on peak	-	Caliente	Bomb	0.09	0.47	0.24	54.14	39.33	0.22	1.31	1.06	96.85	0.79	887	0.16	0.12	
100	SG-09-24	Inclusion	15Na, 30s on peak	-	Caliente	Collapse	0.18	0.66	0.22	53.02	40.84	0.53	1.22	1.31	97.98	0.81	2133	0.15	0.13	
102	SG-09-24	Inclusion	15Na, 30s on peak	-	Caliente	Collapse	0.13	0.89	0.24	53.36	40.96	0.29	2.41	1.44	99.72	1.34	1165	0.21	0.14	
103	SG-09-24	Inclusion	15Na, 30s on peak	-	Caliente	Collapse	0.18	0.49	0.21	53.32	39.36	0.37	1.16	1.32	97.57	0.79	1483	0.15	0.13	
104	SG-09-24	Inclusion	15Na, 30s on peak	-	Caliente	Collapse	0.11	0.42	0.14	53.64	39.93	0.23	1.61	1.54	97.63	1.03	902	0.17	0.15	
108	SG-09-24	Inclusion	15Na, 30s on peak	-	Caliente	Collapse	0.29	0.21	0.20	53.61	40.32	0.53	2.59	1.18	98.93	1.36	2122	0.22	0.13	
109	SG-09-01	Inclusion	15Na, 30s on peak	RcM1	Caliente	Flow	0.20	0.87	0.23	53.34	39.83	0.18	1.34	1.07	97.50	0.81	1774	0.16	0.12	
114	SG-09-01	Inclusion	15Na, 30s on peak	RcM1	Caliente	Flow	0.24	0.94	0.15	52.99	39.32	0.45	1.82	0.96	98.01	0.98	1811	0.19	0.11	
117	SG-09-01	Inclusion	15Na, 30s on peak	RcM1	Caliente	Flow	0.23	0.74	0.19	0.26	53.63	39.10	0.44	1.50	1.09	97.19	0.88	1775	0.17	0.12
119	SG-09-01	Inclusion	15Na, 30s on peak	RcM1	Caliente	Flow	0.25	1.04	0.24	0.28	53.27	39.54	0.42	1.42	1.02	97.49	0.83	1685	0.17	0.12
136	SG-09-01	Inclusion	15Na, 30s on peak	RcM1	Caliente	Flow	0.15	0.94	0.54	0.33	53.16	39.20	0.30	1.26	1.37	97.05	0.84	1183	0.16	0.13
145	SG-09-07	Inclusion	15Na, 30s on peak	RcM3	Caliente	Flow	0.33	0.45	0.19	0.30	54.00	39.30	0.66	1.41	1.09	97.72	0.84	2645	0.16	0.12
168	SG-09-07	Inclusion	15Na, 30s on peak	RcM3	Caliente	Flow	0.28	0.31	0.18	0.25	54.93	38.97	0.30	2.64	0.92	98.78	1.32	2203	0.22	0.11
232	SG-09-04	Inclusion	15Na, 30s on peak	RcL	Caliente	Flow	0.35	0.82	0.13	0.31	54.01	39.27	0.37	1.50	1.04	97.79	0.87	1463	0.17	0.12
34172_a1_2	SG-09-05	Inclusion	10 nA, 120s on peak	RcL	Caliente	Flow	0.18	0.55	0.24	0.16	52.93	40.26	0.55	1.17	1.19	97.23	0.76	2188	0.21	0.17
34172_a1_3	SG-09-05	Inclusion (rim)	10 nA, 120s on peak	RcL	Caliente	Flow	0.13	0.84	0.21	0.19	52.82	41.09	0.35	1.27	1.15	98.06	0.80	2290	0.22	0.16
34172_a1_4	SG-09-05	Inclusion	10 nA, 120s on peak	RcL	Caliente	Flow	0.32	0.18	0.38	0.22	52.84	39.07	0.44	1.04	0.99	97.74	0.74	1874	0.20	0.18
34172_a1_5	SG-09-05	Inclusion	10 nA, 120s on peak	RcL	Caliente	Flow	0.38	0.88	0.28	0.23	53.11	40.49	0.72	1.22	1.19	98.60	0.78	2868	0.21	0.17
34172_a1_7	SG-09-05	Inclusion	10 nA, 120s on peak	RcL	Caliente	Flow	0.28	0.95	0.19	0.18	52.59	40.93	0.54	1.12	1.15	97.92	0.73	2153	0.20	0.16
34172_a1_9	SG-09-05	Inclusion	10 nA, 120s on peak	RcL	Caliente	Flow	0.19	0.49	0.19	0.23	54.03	40.13	0.20	1.32	0.98	97.85	0.78	4053	0.21	0.17
34172_a3_3	SG-09-05	Inclusion	10 nA, 120s on peak	RcL	Caliente	Flow	0.21	0.87	0.20	0.16	53.80	41.42	0.28	1.59	1.05	99.58	0.91	1140	0.24	0.16
34172_a3_7	SG-09-05	Inclusion	10 nA, 120s on peak	RcL	Caliente	Flow	0.35	0.80	0.17	0.17	52.93	40.85	0.72	1.25	1.17	98.33	0.79	2880	0.22	0.16
34172_a3_1	SG-09-05	Inclusion	10 nA, 120s on peak	RcL	Caliente	Flow	0.28	0.39	0.18	0.14	52.86	39.97	0.50	1.40	1.12	96.85	0.84	2012	0.23	0.16
113	1121-67	Inclusion	15Na, 30s on peak	Rb	Brujo	Dome	0.23	0.69	0.20	53.06	39.66	0.62	1.30	1.24	97.41	0.83	2473	0.15	0.13	
134	1121-67	Inclusion	15Na, 30s on peak	Rb	Brujo	Dome	0.22	0.60	0.26	53.23	38.49	0.37	1.17	1.24	95.58	0.77	1475	0.15	0.13	
137	1121-67	Inclusion	15Na, 30s on peak	Rb	Brujo	Dome	0.27	0.78	0.22	53.32	40.57	0.74	1.33	1.33	98.55	0.86	2975	0.16	0.14	
138	1121-67	Inclusion	15Na, 30s on peak	Rb	Brujo	Dome	0.10	0.64	0.23	54.20	40.84	0.31	1.20	1.26	97.89	0.79	1251	0.15	0.13	
139	1121-67	Inclusion	15Na, 30s on peak	Rb	Brujo	Dome	0.22	0.62	0.20	53.06	39.34	0.43	1.30	1.24	97.41	0.83	1704	0.16	0.13	
140	1121-67	Inclusion	15Na, 30s on peak	Rb	Brujo	Dome	0.21	0.73	0.23	54.25	39.75	0.64	1.33	1.14	98.27	0.82	2558	0.16	0.13	
144	1121-67	Inclusion	15Na, 30s on peak	Rb	Brujo	Dome	0.22	0.64	0.21	53.49	40.80	0.46	1.20	1.15	98.16	0.76	1856	0.15	0.13	
147	1121-67	Inclusion	15Na, 30s on peak	Rb	Brujo	Dome	0.10	0.75	0.14	54.10	40.77	0.34	1.14	1.03	98.74	0.81	1559	0.15	0.14	
148	1121-67	Inclusion	15Na, 30s on peak	Rb	Brujo	Dome	0.16	0.92	0.27	53.42	41.09	0.23	1.05	1.25	98.39	0.72	911	0.14	0.13	
129	550-67	Inclusion	15Na, 30s on peak	RbC	Brujo	Flow	0.14	0.72	0.20	0.26	54.65	39.29	0.15	2.77	0.84	99.02	1.36	604	0.22	0.10
8	SG-09-30	Inclusion	15Na, 30s on peak	RbC	Brujo	Flow	0.11	0.76	0.34	0.25	54.05	40.46	0.23	1.26	1.26	98.72	0.82	912	0.16	0.13
9	SG-09-30	Inclusion	15Na, 30s on peak	RbC	Brujo	Flow	0.09	0.74	0.16	0.23	54.79	39.68	0.17	1.24	0.77	99.19	0.80	1678	0.16	0.13
12	SG-09-30	Inclusion	15Na, 30s on peak	RbC	Brujo	Flow	0.23	0.86	0.42	0.23	53.84	40.12	0.39	1.24	1.35	98.69	0.83	1567	0.16	0.13
35	SG-09-30	Inclusion	15Na, 30s on peak	RbC	Brujo	Flow	0.21	0.79	0.11	0.21	54.30	39.68	0.35	2.10	0.97	98.71	1.10	1392	0.20	0.11
41	SG-09-30	Inclusion	15Na, 30s on peak	RbC	Brujo	Flow	0.23	0.77	0.22	0.24	53.97	40.91	0.38	1.29	1.13	99.13	0.80	1514	0.16	0.12
42	SG-09-30	Inclusion	15Na, 30s on peak	RbC	Brujo	Flow	0.19	0.81	0.19	0.23	53.86	39.81	0.26	1.24	0.91	98.51	0.81	1612	0.16	0.12
167	SG-09-38	Inclusion	15Na, 30s on peak	ReA	Mitad	Flow	0.33	0.74	0.17	0.24	53.88	40.36	0.41	2.25	1.13	99.54	1.21	1637	0.20	0.12
80	2003-69	Inclusion	15Na, 30s on peak	Re	Mitad	Dome	0.10	0.57	0.22	0.26	54.35	39.70	0.22	2.39	1.02	98.83	1.24	882	0.21	0.12
6	2002-69	Inclusion	15Na, 30s on peak	Re	Mitad	Dome	0.25	0.81	0.22	0.22	53.57	39.92	0.44	1.14	1.26	97.61	0.76	1750	0.15	0.13
21	SG-09-36	Inclusion	15Na, 30s on peak	ReA	Mitad	Flow	0.15	0.73	0.22	0.22	53.84	39.92	0.44	1.64	0.99	97.05	0.91	1346	0.18	0.11
							Mean	0.21	0.71	0.23	0.23	53.59	40.19	0.41	1.50	1.19		1656		
							stdev	0.10	0.19	0.10	0.04	0.54	0.75	0.17	0.46	0.15		687		
							Median	0.21	0.74	0.20	0.23	53.60	40.29	0.38	1.31	1.18		1541		

Point identifier	Sample number	Unit	Vent	Type	SiO ₂	FeO	MnO	MgO	CaO	P ₂ O ₅	SO ₃	F	Cl	Total	O = F,Cl	S ppm	stdev F (wt%)	stdev Cl (wt%)		
58	2006-69	Open to matrix	15Na, 30s on peak	-	Caliente	Bomb	0.16	0.54	0.20	53.55	39.93	0.28	2.08	0.83	98.11	1.06	1135	0.20	0.11	
64	2006-69	Open to matrix	15Na, 30s on peak	-	Caliente	Bomb	0.22	0.71	0.25	53.90	40.42	0.47	1.44	1.44	98.44	0.84	1875	0.16	0.12	
66	2006-69	Open to matrix	15Na, 30s on peak	-	Caliente	Bomb	0.24	0.93	0.25	0.19	53.73	39.92	0.35	2.61	1.07	98.84	1.34	1383	0.22	0.12
68	2006-69	Open to matrix	15Na, 30s on peak	-	Caliente	Bomb	0.19	0.68	0.19	0.19	53.83	39.92	0.35	2.61	1.07	98.84	1.34	1383	0.22	0.12
69	2006-69	Open to matrix	15Na, 30s on peak	-	Caliente	Bomb	0.10	0.60	0.26	54.24	38.75	0.20	2.14	0.98	97.28	1.12	813	0.20	0.12	
71	2006-69	Open to matrix	15Na, 30s on peak	-	Caliente	Bomb	0.26	0.82	0.16	0.26	54.39	39.65	0.55	1.44	1.31	99.21	0.83	2021	0.17	0.12
74	2006-69	Open to matrix	15Na, 30s on peak	-	Caliente	Bomb	0.09	0.32	0.25	54.39	41.07	0.12	1.70	0.96	98.89	0.93	465	0.18	0.11	
95	2006-69	Open to matrix	15Na, 30s on peak	-	Caliente	Bomb	0.28	0.68	0.26	54.48	41.23	0.32	2.23	0.92	100.39	1.15	1269	0.20	0.11	
89	SG-09-24	Open to matrix	15Na, 30s on peak	-	Caliente	Collapse	0.33	0.56	0.16	0.16	52.06	36.64	0.26	2.46	0.92	93.38	1.24	1022	0.21	0.11
124	SG-09-01	Open to matrix	15Na, 30s on peak	-	Caliente	Collapse	0.17	0.24	0.15	0.24	54.00	40.73	0.24	0.92	0.94	97.33	0.39	932		

stdev S (ppm)	Si	Fe	Ca	Mg	Mn	S	P	F	Cl	OH*
544	0.03	0.10	10.07	0.03		0.05	6.00	0.75	0.41	0.834
408	0.02	0.09	9.95	0.05		0.03	6.04	1.03	0.29	0.673
646	0.04	0.08	10.02	0.06		0.07	6.01	0.73	0.31	0.962
569	0.02	0.07	10.24	0.06		0.06	5.96	0.67	0.35	0.975
495	0.03	0.11	9.91	0.06		0.04	5.96	1.37	0.29	0.337
577	0.03	0.11	10.17	0.07		0.06	5.96	0.61	0.41	0.984
363	0.02	0.08	9.97	0.06		0.02	6.10	0.74	0.31	0.949
404	0.02	0.07	10.36	0.06		0.03	5.94	0.74	0.32	0.939
627	0.03	0.10	9.93	0.06		0.07	6.04	0.68	0.39	0.937
464	0.02	0.13	9.85	0.06		0.04	5.97	1.32	0.42	0.263
523	0.03	0.07	10.08	0.06		0.05	6.03	0.65	0.39	0.956
408	0.02	0.06	10.16	0.04		0.03	5.97	0.90	0.46	0.636
626	0.05	0.03	9.95	0.05		0.07	5.91	1.42	0.35	0.234
502	0.03	0.13	10.10	0.06		0.05	5.96	0.81	0.42	0.770
677	0.05	0.12	10.00	0.06		0.08	5.96	0.70	0.45	0.845
413	0.02	0.06	10.01	0.06		0.03	6.03	0.93	0.38	0.699
553	0.04	0.14	10.17	0.08	0.02	0.06	5.87	1.01	0.29	0.698
547	0.04	0.11	10.22	0.07	0.03	0.06	5.89	0.99	0.33	0.828
533	0.04	0.15	10.11	0.07	0.04	0.06	5.93	0.80	0.31	0.897
445	0.03	0.14	10.19	0.09	0.08	0.04	5.91	0.71	0.41	0.874
665	0.06	0.07	10.21	0.08	0.03	0.09	5.87	0.79	0.33	0.887
447	0.05	0.05	10.32	0.07	0.03	0.04	5.78	1.47	0.27	0.263
490	0.06	0.12	10.23	0.08	0.02	0.05	5.88	0.84	0.31	0.848
708	0.03	0.08	10.01	0.04	0.04	0.07	6.02	0.65	0.36	0.989
555	0.02	0.12	9.89	0.05	0.03	0.05	6.08	0.70	0.34	0.956
638	0.06	0.17	9.76	0.06	0.06	0.06	6.07	0.57	0.40	1.025
811	0.07	0.14	9.91	0.06	0.04	0.09	5.97	0.67	0.35	0.975
703	0.05	0.14	9.85	0.05	0.03	0.07	6.06	0.62	0.34	1.041
953	0.12	0.14	9.85	0.05	0.03	0.13	5.91	0.66	0.36	0.975
512	0.04	0.13	9.93	0.04	0.03	0.04	6.04	0.87	0.31	0.826
812	0.06	0.12	9.86	0.04	0.01	0.09	6.02	0.69	0.34	0.966
678	0.05	0.06	10.03	0.04	0.03	0.07	5.99	0.79	0.34	0.877
676	0.04	0.10	10.15	0.06		0.08	5.93	0.67	0.38	0.951
521	0.04	0.09	10.33	0.07		0.05	5.90	0.67	0.38	0.948
742	0.05	0.11	9.94	0.06		0.10	5.98	0.73	0.39	0.879
481	0.02	0.09	10.11	0.06		0.04	6.02	0.66	0.37	0.964
561	0.04	0.09	10.02	0.05		0.06	6.02	0.73	0.37	0.902
687	0.04	0.11	10.20	0.06		0.08	5.91	0.74	0.34	0.922
586	0.04	0.09	10.01	0.05		0.06	6.03	0.66	0.34	0.998
463	0.02	0.11	10.11	0.06		0.04	6.02	0.66	0.39	0.958
410	0.03	0.13	9.99	0.07		0.03	6.07	0.58	0.37	1.051
312	0.02	0.11	10.25	0.07	0.03	0.02	5.82	1.53	0.25	0.219
396	0.02	0.11	10.13	0.07	0.05	0.03	5.99	0.70	0.37	0.928
242	0.02	0.11	10.05	0.06	0.05	0.02	6.04	0.69	0.37	0.946
519	0.04	0.13	10.10	0.06	0.06	0.05	5.95	0.69	0.40	0.913
488	0.04	0.12	10.18	0.05	0.02	0.05	5.88	1.16	0.29	0.550
509	0.04	0.11	10.03	0.06	0.03	0.05	6.01	0.71	0.33	0.961
498	0.03	0.12	10.18	0.07	0.03	0.05	5.95	0.72	0.34	0.942
513	0.06	0.11	9.98	0.06	0.03	0.05	5.91	1.23	0.34	0.432
387	0.02	0.08	10.18	0.07	0.03	0.03	5.88	1.32	0.30	0.375
572	0.04	0.12	10.14	0.06	0.00	0.06	5.97	0.64	0.38	0.986
473	0.03	0.11	10.30	0.06	0.03	0.05	5.88	0.92	0.30	0.776

stdev S (ppm)	Si	Fe	Ca	Mg	Mn	S	P	F	Cl	OH*
458	0.03	0.08	10.16	0.06		0.04	5.93	1.16	0.25	0.597
589	0.04	0.10	10.08	0.06		0.06	5.97	0.79	0.31	0.899
433	0.04	0.13	9.92	0.05		0.03	5.93	1.38	0.41	0.215
506	0.03	0.10	10.05	0.05		0.05	5.89	1.44	0.32	0.247
387	0.02	0.09	10.36	0.07		0.03	5.85	1.20	0.30	0.498
635	0.04	0.09	10.02	0.05		0.07	5.87	1.34	0.30	0.362
293	0.01	0.05	10.12	0.06		0.02	6.04	0.94	0.28	0.782
484	0.05	0.10	9.97	0.07		0.04	5.96	1.21	0.27	0.527
433	0.06	0.09	10.36	0.04		0.04	5.76	1.45	0.29	0.263
417	0.03	0.18	9.92	0.06		0.03	5.91	1.52	0.27	0.215
566	0.03	0.10	10.10	0.06		0.06	5.93	1.11	0.29	0.599
449	0.03	0.05	9.94	0.06		0.03	6.02	1.26	0.23	0.515
598	0.04	0.11	10.05	0.05		0.06	6.00	0.74	0.32	0.938
500	0.07	0.09	9.95	0.05		0.04	5.87	1.54	0.39	0.607
576	0.05	0.12	9.97	0.06		0.06	6.02	0.77	0.31	0.928
600	0.04	0.16	9.92	0.06		0.06	5.90	1.42	0.27	0.307
594	0.04	0.10	9.99	0.06		0.06	5.97	1.03	0.29	0.681
642	0.05	0.11	10.04	0.05		0.07	5.90	1.20	0.28	0.519
381	0.02	0.07	10.13	0.06		0.03	6.05	0.66	0.32	1.013
533	0.04	0.08	9.97	0.06		0.05	5.90	1.46	0.35	0.191
392	0.04	0.09	10.20	0.09		0.03	5.84	1.23	0.42	0.254
476	0.08	0.10	10.10	0.08	0.03	0.05	5.82	1.38	0.30	0.318
550	0.05	0.12	10.08	0.06	0.04	0.06	5.80	1.54	0.28	0.177
360	0.03	0.10	10.11	0.06	0.03	0.02	5.84	1.70	0.20	0.104
455	0.04	0.12	9.80	0.05	0.04	0.04	5.93	1.70	0.26	0.039
425	0.03	0.07	10.28	0.06	0.03	0.03	5.78	1.67	0.19	0.139
471	0.06	0.17	10.10	0.06	0.04	0.04	5.76	1.65	0.31	0.041
784	0.08	0.10	10.17	0.06	0.03	0.12	5.69	1.54	0.26	0.200
340	0.02	0.09	10.23	0.09	0.04	0.02	6.01	1.48	0.45	0.067
527	0.03	0.11	10.07	0.09	0.04	0.05	5.82	1.43	0.39	0.178
432	0.06	0.13	10.23	0.09	0.02	0.04	5.79	1.36	0.27	0.368
572	0.04	0.10	10.15	0.07	0.02	0.06	5.94	0.84	0.29	0.772
512	0.04	0.11	10.21	0.06	0.02	0.05	5.86	1.14	0.28	0.584
249	0.01	0.08	10.40	0.06	0.02	0.01	5.79	1.54	0.22	0.240
281	0.02	0.18	10.24	0.07	0.03	0.02	5.87	1.19	0.24	0.574
514	0.04	0.15	10.24	0.06	0.02	0.05	5.80	1.29	0.30	0.408
501	0.04	0.10	10.31	0.07	0.03	0.05	5.87	0.89	0.31	0.800
365	0.03	0.09	10.05	0.07	0.02	0.03	5.88	1.53	0.34	0.138
528	0.02	0.08	10.25	0.07	0.02	0.06	5.90	0.89	0.33	0.776
377	0.03	0.09	10.36	0.07	0.02	0.03	5.87	1.01	0.30	0.691
536	0.04	0.09	10.04	0.08	0.02	0.06	5.97	0.86	0.31	0.830
396	0.02	0.06	10.38	0.06	0.03	0.03	5.92	0.71	0.34	0.953

stdev S (ppm)	Si	Fe	Ca	Mg	Mn	S	P	F	Cl	OH*
450	0.02	0.07	10.07	0.06		0.04	5.96	1.22	0.29	0.496
368	0.02	0.09	9.94	0.06		0.02	5.97	1.46	0.30	0.241
442	0.03	0.09	10.06	0.06		0.03	5.94	1.29	0.25	0.453
491	0.03	0.07	9.96	0.06		0.04	5.95	1.49	0.23	0.275
550	0.03	0.06	10.05	0.05		0.05	5.99	1.01	0.31	0.686
503	0.08	0.10	10.19	0.06		0.05	5.90	0.96	0.29	0.756
520	0.04	0.07	10.08	0.05		0.05	5.97	1.02	0.30	0.678
197	0.06	0.07	10.17	0.05		0.01	5.98	0.88	0.33	0.788
434	0.04	0.10	10.26	0.05		0.03	5.90	0.95	0.35	0.700
434	0.02	0.06	10.27	0.07	0.02	0.04	5.84	1.37	0.27	0.353
408	0.03	0.09	10.36	0.06	0.03	0.03	5.77	1.52	0.26	0.224
293	0.02	0.09	10.15	0.06	0.03	0.02	5.92	1.32	0.24	0.441
277	0.01	0.05	9.99	0.06	0.02	0.01	5.95	1.52	0.34	0.138
380	0.02	0.04	10.35	0.06	0.03	0.03	5.84	1.31	0.32	0.375
394	0.03	0.09	10.28	0.06	0.03	0.03	5.79	1.61	0.21	0.180
526	0.03	0.05	10.16	0.06	0.01	0.05	5.85	1.40	0.31	0.289
542	0.04	0.07	10.39	0.06	0.02	0.06	5.77	1.33	0.23	0.440
565	0.04	0.09	10.33	0.06	0.02	0.06	5.79	1.18	0.31	0.517
473	0.03	0.04	10.26	0.05	0.02	0.04	5.87	1.21	0.34	0.447
352	0.02	0.06	10.29	0.07	0.02	0.02	5.92	1.01	0.30	0.694
587	0.04	0.09	10.22	0.07	0.02	0.07	5.86	1.04	0.30	0.662
423	0.03	0.09	10.28	0.07	0.02	0.04	5.91	1.04	0.30	0.753
417	0.06	0.08	10.49	0.07	0.02	0.04	5.69	1.50	0.28	0.

Point identifier	Sample number	Vent	Bulk rock													stdev Cl			Reference	
			SiO ₂ wt%	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Cl	Total	wt%	S ppm		Cl ppm
1	SG-09-01	Caliente	61.99	76.23	0.62	10.76	2.87		0.98	0.95	3.51	3.86	0.31	bd	0.142	100.24	0.074	1424	Matrix glass	Scott et al. (2013) supplementary data
2	SG-09-01	Caliente	61.99	69.87	0.42	17.48	1.29		0.23	3.35	5.76	2.10	0.05	bd	0.046	100.59	0.042	455	Matrix glass	Scott et al. (2013) supplementary data
3	SG-09-01	Caliente	61.99	67.74	0.23	18.06	1.76		0.63	3.89	5.93	1.67	0.09	bd	0.046	100.04	0.042	464	Matrix glass	Scott et al. (2013) supplementary data
5	SG-09-01	Caliente	61.99	73.04	0.47	13.00	2.14		0.78	1.59	4.80	2.97	0.16	bd	0.063	99.02	0.049	629	Matrix glass	Scott et al. (2013) supplementary data
6	SG-09-01	Caliente	61.99	72.59	0.45	15.44	1.03		0.08	2.24	5.46	2.60	0.06	bd	0.051	100.00	0.045	514	Matrix glass	Scott et al. (2013) supplementary data
7	SG-09-01	Caliente	61.99	70.53	0.43	16.46	1.14		0.24	3.00	5.41	2.42	0.12	bd	0.062	99.81	0.049	619	Matrix glass	Scott et al. (2013) supplementary data
10	SG-09-01	Caliente	61.99	67.38	0.41	17.82	2.03		0.43	3.54	5.98	1.62	0.09	bd	bd	99.30			Matrix glass	Scott et al. (2013) supplementary data
11	SG-09-01	Caliente	61.99	69.54	0.44	16.68	2.18		0.44	3.53	5.32	2.34	0.20	bd	bd	100.67			Matrix glass	Scott et al. (2013) supplementary data
13	SG-09-01	Caliente	61.99	74.00	0.40	14.06	1.51		0.29	1.84	4.92	2.95	0.18	bd	0.047	100.21	0.042	465	Matrix glass	Scott et al. (2013) supplementary data
14	SG-09-01	Caliente	61.99	71.46	0.35	16.27	0.96		0.11	2.60	5.85	1.98	0.04	bd	0.060	99.69	0.048	601	Matrix glass	Scott et al. (2013) supplementary data
15	SG-09-01	Caliente	61.99	74.87	0.60	12.09	2.68		0.76	1.29	4.39	3.32	0.20	bd	0.069	100.27	0.052	687	Matrix glass	Scott et al. (2013) supplementary data
16	SG-09-01	Caliente	61.99	75.17	0.66	12.30	2.44		0.49	1.05	4.49	3.39	0.13	bd	0.085	100.22	0.057	852	Matrix glass	Scott et al. (2013) supplementary data
17	SG-09-01	Caliente	61.99	71.26	0.44	15.34	1.99		0.39	2.42	5.13	2.62	0.16	bd	0.062	99.82	0.049	618	Matrix glass	Scott et al. (2013) supplementary data
18	SG-09-01	Caliente	61.99	77.91	0.57	11.58	1.38		0.18	0.43	4.05	3.92	0.08	bd	0.094	100.19	0.060	941	Matrix glass	Scott et al. (2013) supplementary data
19	SG-09-07	Caliente	62.38	70.75	0.44	14.37	1.94		0.45	2.24	5.14	3.38	0.31	bd	0.078	99.09	0.055	781	Matrix glass	Scott et al. (2013) supplementary data
21	SG-09-07	Caliente	62.38	68.87	0.57	16.70	2.23		0.09	3.52	6.15	1.47	0.09	bd	bd	99.69			Matrix glass	Scott et al. (2013) supplementary data
23	SG-09-07	Caliente	62.38	75.34	0.44	13.04	1.28		0.12	0.91	4.42	4.46	0.09	bd	0.141	100.25	0.074	1411	Matrix glass	Scott et al. (2013) supplementary data
25	SG-09-07	Caliente	62.38	68.86	0.36	16.39	2.00		0.54	3.46	5.18	2.87	0.32	bd	0.076	100.04	0.054	761	Matrix glass	Scott et al. (2013) supplementary data
26	SG-09-07	Caliente	62.38	74.82	0.60	11.47	2.25		0.56	0.94	3.81	4.36	0.17	bd	0.132	99.11	0.071	1316	Matrix glass	Scott et al. (2013) supplementary data
27	SG-09-07	Caliente	62.38	71.73	0.35	15.73	1.35		0.38	2.81	5.36	2.46	0.28	bd	0.047	100.49	0.043	474	Matrix glass	Scott et al. (2013) supplementary data
51	SG-09-05	Caliente	62.52	68.53	0.30	17.99	1.37		0.25	3.65	6.01	1.99	0.15	bd	bd	100.25			Matrix glass	Scott et al. (2013) supplementary data
52	SG-09-05	Caliente	62.52	72.37	0.44	14.96	1.76		0.30	2.10	5.72	2.54	0.08	bd	0.067	100.34	0.051	673	Matrix glass	Scott et al. (2013) supplementary data
53	SG-09-05	Caliente	62.52	76.78	0.69	11.49	2.22		0.35	0.65	4.19	3.61	0.13	bd	0.103	100.21	0.063	1030	Matrix glass	Scott et al. (2013) supplementary data
54	SG-09-05	Caliente	62.52	76.43	0.63	12.11	2.18		0.31	0.86	4.48	3.59	0.10	bd	0.096	100.79	0.061	962	Matrix glass	Scott et al. (2013) supplementary data
58	SG-09-05	Caliente	62.52	70.59	0.42	15.85	1.90		0.61	3.01	5.15	2.49	0.17	bd	0.041	100.25	0.040	412	Matrix glass	Scott et al. (2013) supplementary data
59	SG-09-05	Caliente	62.52	75.50	0.57	11.77	2.34		0.61	0.98	4.21	3.45	0.26	bd	0.078	99.77	0.055	779	Matrix glass	Scott et al. (2013) supplementary data
60	SG-09-05	Caliente	62.52	70.44	0.45	16.62	1.62		0.23	3.14	5.59	2.37	0.10	bd	0.067	100.63	0.051	671	Matrix glass	Scott et al. (2013) supplementary data
61	SG-09-05	Caliente	62.52	76.18	0.62	12.63	1.80		0.08	0.86	4.70	3.36	0.10	bd	0.084	100.42	0.057	836	Matrix glass	Scott et al. (2013) supplementary data
62	SG-09-05	Caliente	62.52	76.28	0.61	12.33	1.47		0.08	0.72	4.67	3.54	0.13	bd	0.078	99.90	0.055	780	Matrix glass	Scott et al. (2013) supplementary data
63	SG-09-05	Caliente	62.52	72.24	0.44	15.80	1.32		0.12	2.50	5.73	2.56	0.11	bd	0.052	100.85	0.045	518	Matrix glass	Scott et al. (2013) supplementary data
64	SG-09-05	Caliente	62.52	71.64	0.47	15.27	1.59		0.27	2.58	5.55	2.59	0.19	bd	0.052	100.19	0.045	518	Matrix glass	Scott et al. (2013) supplementary data
66	SG-09-05	Caliente	62.52	75.05	0.59	12.86	1.56		0.07	1.11	4.56	3.43	0.07	bd	0.088	99.39	0.058	875	Matrix glass	Scott et al. (2013) supplementary data
67	SG-09-05	Caliente	62.52	72.67	0.41	15.04	1.45		0.06	2.05	5.40	2.68	0.05	bd	0.075	99.88	0.054	749	Matrix glass	Scott et al. (2013) supplementary data
69	SG-09-05	Caliente	62.52	67.46	0.30	18.40	1.21		0.09	4.19	5.87	1.85	0.10	bd	0.050	99.51	0.044	496	Matrix glass	Scott et al. (2013) supplementary data
70	SG-09-04	Caliente	62.56	71.62	0.33	16.35	1.22		0.08	2.63	5.76	2.32	0.11	bd	0.060	100.49	0.048	604	Matrix glass	Scott et al. (2013) supplementary data
71	SG-09-04	Caliente	62.56	76.34	0.52	12.66	1.86		0.31	1.03	4.47	3.18	0.11	bd	0.073	100.54	0.053	731	Matrix glass	Scott et al. (2013) supplementary data
72	SG-09-04	Caliente	62.56	73.82	0.52	13.57	1.60		0.25	1.51	4.87	3.07	0.20	bd	0.087	99.49	0.058	873	Matrix glass	Scott et al. (2013) supplementary data
73	SG-09-04	Caliente	62.56	77.71	0.59	11.88	1.79		0.04	0.50	4.30	3.78	0.06	bd	0.108	100.75	0.064	1075	Matrix glass	Scott et al. (2013) supplementary data
75	SG-09-04	Caliente	62.56	77.69	0.58	11.81	1.76		0.13	0.55	4.27	3.77	0.14	0.076	0.092	100.87	0.060	304	Matrix glass	Scott et al. (2013) supplementary data
76	SG-09-04	Caliente	62.56	68.82	0.31	17.85	1.27		0.13	3.63	5.93	2.05	0.07	bd	0.041	100.10	0.040	411	Matrix glass	Scott et al. (2013) supplementary data
77	SG-09-04	Caliente	62.56	67.44	0.34	18.45	1.41		0.26	4.25	5.78	1.68	0.26	bd	0.067	99.94	0.051	670	Matrix glass	Scott et al. (2013) supplementary data
78	SG-09-04	Caliente	62.56	69.85	0.38	16.98	1.33		0.25	3.01	6.01	2.12	0.07	bd	bd	100.01			Matrix glass	Scott et al. (2013) supplementary data
79	SG-09-04	Caliente	62.56	76.12	0.53	12.69	1.48		0.07	0.89	4.63	3.58	0.10	bd	bd	100.09			Matrix glass	Scott et al. (2013) supplementary data
80	SG-09-04	Caliente	62.56	70.18	0.32	16.99	1.43		0.18	3.12	5.90	2.08	0.11	bd	bd	100.30			Matrix glass	Scott et al. (2013) supplementary data
81	SG-09-04	Caliente	62.56	76.52	0.54	12.64	1.57		0.04	0.78	4.63	3.54	0.10	bd	0.084	100.45	0.057	837	Matrix glass	Scott et al. (2013) supplementary data
82	SG-09-04	Caliente	62.56	75.28	0.58	13.15	1.51		0.06	1.28	4.51	3.41	0.15	bd	0.086	100.01	0.057	856	Matrix glass	Scott et al. (2013) supplementary data
83	SG-09-04	Caliente	62.56	77.69	0.56	12.10	1.59		0.08	0.54	4.38	3.69	0.10	bd	0.081	100.82	0.056	808	Matrix glass	Scott et al. (2013) supplementary data
84	SG-09-04	Caliente	62.56	77.99	0.60	11.91	1.39		0.06	0.43	4.31	3.77	0.13	bd	0.071	100.67	0.052	711	Matrix glass	Scott et al. (2013) supplementary data
88	SG-09-03	Caliente	62.41	72.02	0.50	15.07	1.37		0.16	2.24	5.16	2.81	0.13	bd	0.063	99.51	0.049	631	Matrix glass	Scott et al. (2013) supplementary data
89	SG-09-03	Caliente	62.41	74.39	0.66	11.86	2.76		0.69	0.95	4.04	3.59	0.17	bd	0.077	99.18	0.054	773	Matrix glass	Scott et al. (2013) supplementary data
90	SG-09-03	Caliente	62.41	70.90	0.47	15.97	0.92		0.12	2.74	5.40	2.64	0.09	bd	0.057	99.31	0.047	573	Matrix glass	Scott et al. (2013) supplementary data
91	SG-09-03	Caliente	62.41	72.73	0.44	13.90	2.05		0.62	1.88	5.41	1.88	0.12	bd	bd	99.02			Matrix glass	Scott et al. (2013) supplementary data
92	SG-09-03	Caliente	62.41	74.84	0.62	12.18	1.74		0.36	0.95	4.18	3.75	0.21	bd	0.129	98.96	0.070	1290	Matrix glass	Scott et al. (2013) supplementary data
93	SG-09-03	Caliente	62.41	66.08	0.27	18.09	2.25		1.01	4.19	5.76	1.64	0.22	bd	0.040	99.53	0.039	400	Matrix glass	Scott et al. (2013) supplementary data
94	SG-09-03	Caliente	62.41	67.27	0.30	18.67	1.24		0.28	3.79	6.07	1.71	0.12	bd	bd	99.45			Matrix glass	Scott et al. (2013) supplementary data
95	SG-09-03	Caliente	62.41	76.57	0.64	11.15	1.73		0.19	0.39	3.77	4.21	0.11	bd	0.160	98.92	0.078	1597	Matrix glass	Scott et al. (2013) supplementary data
97	SG-09-03	Caliente	62.41	75.18	0.51	13.76	0.90		0.06	1.26	4.88	3.43	0.10	bd	0.054	100.13	0.045	536	Matrix glass	Scott et al. (2013) supplementary data
98	SG-09-03	Caliente	62.41	71.69	0.44	15.85	1.17		0.17	2.51	5.10	2.87	0.08	bd	0.082	99.96	0.056	820	Matrix glass	Scott et al. (2013) supplementary data
99	SG-09-03	Caliente	62.41	77.08	0.57	12.05	1.10		0.11	0.62	4.33	4.01	0.11	bd	0.075	100.06	0.053	746	Matrix glass	Scott et al. (2013) supplementary data

100	SG-09-03	Caliente	62.41	76.96	0.66	11.48	2.10	0.22	0.61	3.83	4.07	0.27	bd	0.085	100.29	0.057	849	Matrix glass	Scott et al. (2013) supplementary data	
102	SG-09-03	Caliente	62.41	71.37	0.42	16.08	1.19	0.12	2.64	5.41	2.59	0.05	bd	0.087	99.95	0.057	867	Matrix glass	Scott et al. (2013) supplementary data	
103	SG-09-03	Caliente	62.41	68.67	0.42	16.96	2.12	0.44	4.04	5.04	2.30	0.10	bd	0.062	100.16	0.048	617	Matrix glass	Scott et al. (2013) supplementary data	
2	SG-09-09	Lahar	62.76	74.05	0.70	11.50	3.16	0.74	0.94	4.25	3.66	0.20	bd	0.160	99.38	0.076	1595	Matrix glass	Scott et al. (2013) supplementary data	
7	SG-09-09	Lahar	62.76	74.56	0.70	11.98	2.43	0.22	0.52	4.39	4.40	0.05	0.078	0.239	99.57	0.087	314	2393	Matrix glass	Scott et al. (2013) supplementary data
8	SG-09-09	Lahar	62.76	73.54	0.66	12.38	2.42	0.28	0.93	5.69	2.57	0.08	bd	0.159	98.69	0.071	1589	Matrix glass	Scott et al. (2013) supplementary data	
11	1234-67	-	-	67.89	0.21	17.83	1.15	0.25	3.51	5.67	1.98	0.06	bd	0.064	98.61	0.045	644	Matrix glass	Scott et al. (2013) supplementary data	
12	1234-67	-	-	78.16	0.41	11.68	1.12	0.18	0.68	4.13	3.57	0.11	bd	0.116	100.15	0.061	1160	Matrix glass	Scott et al. (2013) supplementary data	
13	1234-67	-	-	73.89	0.23	15.15	1.18	0.31	2.03	5.41	2.39	0.14	bd	0.070	100.80	0.047	701	Matrix glass	Scott et al. (2013) supplementary data	
14	1234-67	-	-	68.84	0.19	18.61	1.14	0.28	3.36	6.74	1.56	0.06	bd	0.067	100.77			Matrix glass	Scott et al. (2013) supplementary data	
15	1234-67	-	-	72.69	0.27	14.77	1.26	0.36	1.78	5.20	2.57	0.05	bd	0.069	99.01	0.048	686	Matrix glass	Scott et al. (2013) supplementary data	
16	1234-67	-	-	75.75	0.40	13.39	1.47	0.13	1.36	4.60	3.09	0.13	bd	0.068	100.39	0.051	681	Matrix glass	Scott et al. (2013) supplementary data	
35	SG-09-06	Caliente	63.08	68.84	0.25	18.17	1.47	0.29	3.73	6.13	1.74	0.07	bd	0.106	100.69			Matrix glass	Scott et al. (2013) supplementary data	
37	SG-09-06	Caliente	63.08	77.43	0.55	11.38	1.51	0.23	0.60	4.06	4.16	0.19	bd	0.106	100.21	0.064	1062	Matrix glass	Scott et al. (2013) supplementary data	
38	SG-09-06	Caliente	63.08	76.81	0.45	12.26	1.62	0.35	0.92	4.26	3.70	0.14	bd	0.073	100.57	0.053	734	Matrix glass	Scott et al. (2013) supplementary data	
39	SG-09-06	Caliente	63.08	73.74	0.42	13.98	1.67	0.39	2.23	4.79	3.18	0.15	bd	0.077	100.62	0.055	771	Matrix glass	Scott et al. (2013) supplementary data	
40	SG-09-06	Caliente	63.08	76.69	0.50	12.08	1.72	0.14	0.77	4.29	3.69	0.16	bd	0.100	100.15	0.062	1003	Matrix glass	Scott et al. (2013) supplementary data	
41	SG-09-06	Caliente	63.08	68.24	0.29	17.61	1.21	0.34	3.91	5.81	1.87	0.11	bd	0.067	99.38			Matrix glass	Scott et al. (2013) supplementary data	
42	SG-09-06	Caliente	63.08	72.20	0.35	14.67	2.14	0.58	2.32	5.36	2.71	0.20	bd	0.076	100.60	0.054	760	Matrix glass	Scott et al. (2013) supplementary data	
44	SG-09-06	Caliente	63.08	74.24	0.42	14.05	1.03	0.18	1.60	4.96	2.91	0.07	bd	0.067	99.52	0.051	666	Matrix glass	Scott et al. (2013) supplementary data	
45	SG-09-06	Caliente	63.08	70.21	0.37	16.31	1.81	0.63	3.01	5.46	2.37	0.16	bd	0.089	100.42	0.058	885	Matrix glass	Scott et al. (2013) supplementary data	
49	SG-09-06	Caliente	63.08	67.98	0.29	18.35	1.50	0.31	3.80	6.07	1.82	0.15	bd	0.058	100.33	0.047	577	Matrix glass	Scott et al. (2013) supplementary data	
18	SG-09-38	Mitad	63.28	75.15	0.33	13.65	1.52	0.08	1.35	5.09	3.12	0.02	bd	0.062	100.35	0.049	622	Matrix glass	Scott et al. (2013) supplementary data	
19	SG-09-38	Mitad	63.28	67.40	0.29	17.90	1.21	0.03	3.21	6.23	2.11	0.06	bd	0.028	98.48	0.033	281	Matrix glass	Scott et al. (2013) supplementary data	
21	SG-09-38	Mitad	63.28	74.94	0.37	14.10	1.30	0.22	1.70	5.01	2.86	0.12	bd	0.079	100.71	0.055	788	Matrix glass	Scott et al. (2013) supplementary data	
22	SG-09-38	Mitad	63.28	72.26	0.38	15.24	1.49	0.23	2.56	5.04	2.62	0.25	bd	0.076	100.13	0.054	757	Matrix glass	Scott et al. (2013) supplementary data	
23	SG-09-38	Mitad	63.28	74.73	0.41	13.55	1.70	0.32	1.45	4.60	3.05	0.08	bd	0.088	99.97	0.058	875	Matrix glass	Scott et al. (2013) supplementary data	
24	SG-09-23	Caliente	64.91	70.93	0.18	16.62	1.09	0.32	2.15	6.11	2.59	0.09	bd	0.029	100.09	0.034	291	Matrix glass	Scott et al. (2013) supplementary data	
29	SG-09-29	Brujo	63.78	72.40	0.28	15.67	1.03	0.05	2.15	4.73	3.44	0.07	bd	0.072	99.88	0.053	717	Matrix glass	Scott et al. (2013) supplementary data	
33	SG-09-29	Brujo	63.78	76.44	0.40	12.14	0.83	0.04	0.53	4.44	3.25	0.09	bd	0.090	98.25	0.059	896	Matrix glass	Scott et al. (2013) supplementary data	
1	SG-09-32	Monje	64.1	78.57	0.15	12.47	0.27	0.00	1.37	4.67	2.13	0.05	bd	0.044	99.68			Matrix glass	Scott et al. (2013) supplementary data	
2	SG-09-32	Monje	64.1	79.99	0.33	10.77	0.89	0.25	0.33	3.51	3.41	0.04	bd	0.044	99.55	0.042	441	Matrix glass	Scott et al. (2013) supplementary data	
4	SG-09-32	Monje	64.1	77.44	0.21	11.67	0.58	0.09	0.87	4.09	3.05	0.08	bd	0.049	98.13	0.044	488	Matrix glass	Scott et al. (2013) supplementary data	
5	SG-09-32	Monje	64.1	73.19	0.50	14.07	1.34	0.23	0.41	3.75	5.12	0.04	bd	0.197	98.85	0.087	1974	Matrix glass	Scott et al. (2013) supplementary data	
6	SG-09-32	Monje	64.1	76.71	0.37	12.46	0.93	0.03	0.62	4.01	3.91	0.02	bd	0.097	99.15	0.061	971	Matrix glass	Scott et al. (2013) supplementary data	
8	SG-09-32	Monje	64.1	73.40	0.26	15.21	1.05	0.23	2.09	5.45	2.56	0.03	bd	0.091	100.36	0.059	912	Matrix glass	Scott et al. (2013) supplementary data	
9	SG-09-32	Monje	64.1	70.79	0.12	16.88	0.60	0.01	2.53	6.13	2.51	0.02	bd	0.062	99.62			Matrix glass	Scott et al. (2013) supplementary data	
13	SG-09-32	Monje	64.1	77.45	0.17	12.93	0.36	0.00	0.66	4.88	3.56	0.03	bd	0.104	100.04			Matrix glass	Scott et al. (2013) supplementary data	
14	SG-09-32	Monje	64.1	79.57	0.38	10.71	1.25	0.07	0.54	3.66	2.79	0.06	bd	0.054	99.03			Matrix glass	Scott et al. (2013) supplementary data	
16	SG-09-32	Monje	64.1	73.70	0.14	14.47	0.69	0.09	1.58	5.47	2.76	0.08	bd	0.054	99.05	0.046	543	Matrix glass	Scott et al. (2013) supplementary data	
17	SG-09-32	Monje	64.1	77.98	0.20	12.10	0.41	0.00	0.85	4.68	3.03	0.04	bd	0.074	99.30			Matrix glass	Scott et al. (2013) supplementary data	
18	SG-09-34	Monje	64.59	75.50	0.71	11.36	2.91	0.40	0.57	3.54	4.69	0.11	bd	0.174	99.97	0.082	1744	Matrix glass	Scott et al. (2013) supplementary data	
19	SG-09-34	Monje	64.59	70.99	0.28	17.00	0.90	0.11	2.45	6.03	2.39	0.07	bd	0.067	100.29	0.051	667	Matrix glass	Scott et al. (2013) supplementary data	
20	SG-09-34	Monje	64.59	75.73	0.32	13.76	1.06	0.12	1.28	4.75	3.31	0.10	bd	0.100	100.54	0.062	998	Matrix glass	Scott et al. (2013) supplementary data	
22	SG-09-34	Monje	64.59	70.52	0.27	16.72	1.13	0.17	2.69	5.39	2.96	0.08	bd	0.083	100.01	0.057	829	Matrix glass	Scott et al. (2013) supplementary data	
23	SG-09-34	Monje	64.59	74.85	0.30	13.57	1.84	0.55	1.42	5.06	2.80	0.05	bd	0.074	100.52	0.054	744	Matrix glass	Scott et al. (2013) supplementary data	
24	SG-09-34	Monje	64.59	69.96	0.23	17.41	1.07	0.17	2.81	6.15	2.39	0.07	0.082	0.069	100.41	0.052	327	694	Matrix glass	Scott et al. (2013) supplementary data
25	SG-09-34	Monje	64.59	76.33	0.43	11.81	1.63	0.49	0.87	4.17	4.00	0.19	bd	0.104	100.02	0.063	1042	Matrix glass	Scott et al. (2013) supplementary data	
26	SG-09-34	Monje	64.59	76.09	0.23	13.35	0.67	0.17	1.64	5.08	2.07	0.12	bd	0.040	99.46	0.039	398	Matrix glass	Scott et al. (2013) supplementary data	
28	SG-09-34	Monje	64.59	77.46	0.48	10.66	1.58	0.12	0.20	3.44	4.92	0.09	bd	0.107	99.06	0.064	1071	Matrix glass	Scott et al. (2013) supplementary data	
31	SG-09-34	Monje	64.59	76.79	0.38	12.48	1.12	0.33	1.44	4.17	2.68	0.33	bd	0.100	99.81	0.062	998	Matrix glass	Scott et al. (2013) supplementary data	
32	SG-09-34	Monje	64.59	70.03	0.25	16.98	0.78	0.16	2.53	6.05	1.75	0.08	bd	0.067	98.60			Matrix glass	Scott et al. (2013) supplementary data	
33	SG-09-34	Monje	64.59	75.86	0.19	14.07	0.63	0.06	1.96	5.26	1.74	0.05	bd	0.067	99.83			Matrix glass	Scott et al. (2013) supplementary data	
34	SG-09-34	Monje	64.59	72.29	0.42	14.28	1.94	0.51	1.73	4.46	3.80	0.18	bd	0.071	99.67	0.052	714	Matrix glass	Scott et al. (2013) supplementary data	
35	2006-69	Caliente	-	78.41	0.39	11.87	1.27	0.15	0.84	4.38	3.06	0.05	bd	0.076	100.49	0.054	757	Matrix glass	Scott et al. (2013) supplementary data	
36	2006-69	Caliente	-	68.63	0.24	18.19	0.99	0.15	3.76	5.87	1.92	0.05	bd	0.048	99.79			Matrix glass	Scott et al. (2013) supplementary data	
37	2006-69	Caliente	-	73.38	0.22	14.25	1.51	0.55	1.63	5.73	2.37	0.04	bd	0.042	100.75	0.040	484	Matrix glass	Scott et al. (2013) supplementary data	
38	2006-69	Caliente	-	68.13	0.21	19.42	0.86	0.05	4.03	6.07	1.89	0.06	bd	0.117	99.34	0.067	1169	Matrix glass	Scott et al. (2013) supplementary data	
39	2006-69	Caliente	-	76.76	0.47	11.19	1.96	0.29	0.60	3.70	3.99	0.27	bd	0.088	100.14	0.058	880	Matrix glass	Scott et al. (2013) supplementary data	
41	2006-69	Caliente	-	77.00	0.42	12.76	1.04	0.07	1.13	4.52	3.05	0.06	bd	0.084	99.57	0.057	837	Matrix glass	Scott et al. (2013) supplementary data	
42	2006-69	Caliente	-	74.56	0.36	13.57	1.48	0.08	1.29	4.51	3.57	0.07	bd	0.044	99.88	0.041	442	Matrix glass	Scott et al. (2013) supplementary data	
43	2006-69	Caliente	-	70.99	0.29	16.34	1.33	0.07	2.40	5.75	2.57	0.09	bd					Matrix glass	Scott et al. (2013) supplementary data	

45	2006-69	Caliente	-	75.01	0.35	12.90	1.28	0.08	0.99	4.66	3.32	0.07	bd	0.106	98.77	0.064	1060	Matrix glass	Scott et al. (2013) supplementary data		
46	2006-69	Caliente	-	74.91	0.38	13.57	1.07	0.07	1.36	5.19	2.80	0.05	bd	0.050	99.45	0.044	501	Matrix glass	Scott et al. (2013) supplementary data		
47	2006-69	Caliente	-	69.82	0.19	17.39	1.11	0.23	3.44	5.74	1.62	0.11	bd		99.65			Matrix glass	Scott et al. (2013) supplementary data		
48	2006-69	Caliente	-	78.91	0.41	10.71	1.57	0.07	0.35	3.70	3.77	0.05	bd		99.54			Matrix glass	Scott et al. (2013) supplementary data		
49	2006-69	Caliente	-	77.73	0.44	11.70	1.32	0.10	0.61	4.44	3.40	0.07	bd	0.088	99.90	0.058	877	Matrix glass	Scott et al. (2013) supplementary data		
51	SG-09-24	Caliente	65.92	73.79	0.12	13.70	0.93	0.34	1.39	4.87	2.89	0.07	bd	0.056	98.18	0.046	558	Matrix glass	Scott et al. (2013) supplementary data		
53	SG-09-24	Caliente	65.92	77.12	0.31	11.08	1.76	0.68	0.91	3.82	3.07	0.16	0.082	0.136	99.13	0.072	327	1358	Matrix glass	Scott et al. (2013) supplementary data	
54	SG-09-24	Caliente	65.92	77.91	0.21	12.30	0.63	0.16	1.04	4.46	2.79	0.00	bd	0.054	99.54	0.046	541	Matrix glass	Scott et al. (2013) supplementary data		
55	SG-09-24	Caliente	65.92	75.95	0.31	12.28	0.99	0.16	0.77	4.07	3.57	0.05	bd	0.115	98.27	0.066	1146	Matrix glass	Scott et al. (2013) supplementary data		
56	SG-09-24	Caliente	65.92	76.86	0.16	13.31	0.54	0.19	1.56	5.11	2.18	0.05	bd		99.96			Matrix glass	Scott et al. (2013) supplementary data		
57	SG-09-24	Caliente	65.92	75.97	0.18	13.34	0.76	0.28	1.54	5.09	2.40	0.11	bd		99.67			Matrix glass	Scott et al. (2013) supplementary data		
58	SG-09-24	Caliente	65.92	79.65	0.25	11.27	0.58	0.11	1.00	4.44	2.05	0.07	bd		99.42			Matrix glass	Scott et al. (2013) supplementary data		
59	SG-09-24	Caliente	65.92	79.18	0.16	11.51	0.69	0.09	0.78	3.95	2.87	0.08	bd	0.050	99.35	0.044	502	Matrix glass	Scott et al. (2013) supplementary data		
60	SG-09-24	Caliente	65.92	75.56	0.21	13.04	0.71	0.15	1.15	4.68	2.99	0.08	bd	0.065	98.64	0.050	645	Matrix glass	Scott et al. (2013) supplementary data		
61	SG-09-24	Caliente	65.92	78.46	0.16	12.25	0.60	0.21	1.04	4.73	2.84	0.08	bd		100.39			Matrix glass	Scott et al. (2013) supplementary data		
62	SG-09-24	Caliente	65.92	74.90	0.31	14.25	0.81	0.33	1.66	5.10	2.47	0.11	bd		99.93			Matrix glass	Scott et al. (2013) supplementary data		
63	SG-09-24	Caliente	65.92	76.59	0.38	12.62	1.14	0.16	1.24	4.36	3.40	0.07	bd	0.135	100.09	0.072	1345	Matrix glass	Scott et al. (2013) supplementary data		
66	SG-09-24	Caliente	65.92	75.15	0.16	13.98	0.50	0.18	1.51	5.11	2.69	0.06	bd		99.34			Matrix glass	Scott et al. (2013) supplementary data		
67	SG-09-24	Caliente	65.92	74.48	0.25	13.19	1.45	0.41	0.94	4.43	3.90	0.02	bd	0.117	99.16	0.067	1168	Matrix glass	Scott et al. (2013) supplementary data		
69	1000-67	Mitad	65.74	67.17	0.49	17.95	1.25	0.07	3.39	5.34	3.06	0.12	bd	0.164	99.00	0.079	1638	Matrix glass	Scott et al. (2013) supplementary data		
74	1000-67	Mitad	65.74	68.45	0.47	17.55	1.35	0.06	3.53	5.28	2.76	0.14	bd	0.114	99.71	0.066	1144	Matrix glass	Scott et al. (2013) supplementary data		
83	1000-67	Mitad	65.74	66.57	0.46	18.61	1.15	0.08	4.01	5.64	2.58	0.14	bd	0.018	99.26	0.026	181	Matrix glass	Scott et al. (2013) supplementary data		
84	1000-67	Mitad	65.74	69.65	0.58	16.58	1.50	0.04	2.44	5.47	3.62	0.21	bd	0.143	100.23	0.074	1427	Matrix glass	Scott et al. (2013) supplementary data		
85	1121-67	Brujo	-	75.69	0.61	11.50	2.48	0.36	0.62	4.23	3.83	0.17	bd	0.087	99.57	0.058	870	Matrix glass	Scott et al. (2013) supplementary data		
86	1121-67	Brujo	-	74.16	0.38	14.32	1.25	0.15	1.44	5.15	3.37	0.12	bd	0.088	100.43	0.058	879	Matrix glass	Scott et al. (2013) supplementary data		
88	1121-67	Brujo	-	75.35	0.31	12.34	1.88	0.82	1.21	4.51	2.87	0.25	bd	0.086	99.62	0.057	860	Matrix glass	Scott et al. (2013) supplementary data		
89	1121-67	Brujo	-	77.83	0.35	11.20	1.09	0.05	0.66	3.85	3.33	0.06	bd	0.075	98.50	0.053	747	Matrix glass	Scott et al. (2013) supplementary data		
90	1121-67	Brujo	-	74.02	0.34	13.41	1.47	0.34	1.12	4.87	3.36	0.12	bd	0.071	99.13	0.052	707	Matrix glass	Scott et al. (2013) supplementary data		
92	1121-67	Brujo	-	68.90	0.22	18.22	0.77	0.09	2.63	6.84	2.31	0.05	bd	0.049	100.09	0.043	486	Matrix glass	Scott et al. (2013) supplementary data		
93	1121-67	Brujo	-	70.93	0.29	15.25	1.75	0.47	2.09	4.97	3.33	0.11	0.089	0.082	99.37	0.056	358	819	Matrix glass	Scott et al. (2013) supplementary data	
94	1121-67	Brujo	-	75.06	0.38	12.06	1.92	0.36	0.77	3.92	4.43	0.25	bd	0.156	99.31	0.077	1563	Matrix glass	Scott et al. (2013) supplementary data		
95	1121-67	Brujo	-	77.06	0.49	11.44	1.58	0.21	0.30	3.76	4.62	0.03	bd	0.120	99.60	0.068	1202	Matrix glass	Scott et al. (2013) supplementary data		
97	1121-67	Brujo	-	78.14	0.40	11.63	1.31	0.09	0.71	4.11	3.41	0.07	bd	0.072	99.95	0.052	718	Matrix glass	Scott et al. (2013) supplementary data		
98	1121-67	Brujo	-	73.18	0.35	14.61	0.98	0.05	1.41	5.23	3.60	0.01	bd	0.094	99.52	0.060	943	Matrix glass	Scott et al. (2013) supplementary data		
99	1121-67	Brujo	-	78.99	0.29	10.87	0.91	0.13	0.83	4.02	2.60	0.07	bd	0.070	98.79	0.052	700	Matrix glass	Scott et al. (2013) supplementary data		
100	1121-67	Brujo	-	72.85	0.34	14.74	1.30	0.14	1.65	4.84	3.24	0.06	bd	0.121	99.28	0.068	1210	Matrix glass	Scott et al. (2013) supplementary data		
34172_m5_1	SG-09-05	Caliente	63.08	73.59	0.51	14.66	1.53	0.05	0.99	1.65	5.27	3.08	0.15	bd	100.60			Matrix glass	New data (this study)		
34172_m7_2	SG-09-05	Caliente	63.08	74.47	0.60	13.53	2.16	0.01	0.16	0.77	4.66	3.88	0.16	bd	0.129	100.53	0.076	1285	Glomerocryst glass	New data (this study)	
34172_m4_2	SG-09-05	Caliente	63.08	74.71	0.67	12.91	2.45	0.08	0.21	0.80	4.64	3.87	0.20	bd	0.226	100.75	0.101	2257	Glomerocryst glass	New data (this study)	
34172_m7_1	SG-09-05	Caliente	63.08	74.20	0.72	13.29	2.52	0.07	0.16	0.80	4.87	3.76	0.19	bd	0.147	100.73	0.081	1465	Glomerocryst glass	New data (this study)	
34172_m6_1	SG-09-05	Caliente	63.08	73.62	0.71	13.45	2.62	0.05	0.14	0.74	4.79	3.82	0.21	bd	0.222	100.37	0.100	2222	Glomerocryst glass	New data (this study)	
34172_mg3_3	SG-09-05	Caliente	63.08	73.22	0.58	13.30	2.72	0.13	0.21	1.17	6.23	2.05	0.18	bd	0.170	99.98	0.088	1703	Glomerocryst glass	New data (this study)	
34172_m6_3	SG-09-05	Caliente	63.08	75.03	0.71	12.16	2.75	0.16	0.37	0.84	4.32	3.59	0.20	bd	0.120	100.24	0.074	1203	Glomerocryst glass	New data (this study)	
34172_mg4_1	SG-09-05	Caliente	63.08	71.87	0.61	14.80	2.89	0.16	0.20	1.45	6.41	1.95	0.19	bd	0.169	100.69	0.088	1693	Glomerocryst glass	New data (this study)	
34172_m6_2	SG-09-05	Caliente	63.08	73.21	0.73	13.22	3.01	0.04	0.19	0.97	4.69	3.79	0.22	bd	0.244	100.32	0.105	2439	Glomerocryst glass	New data (this study)	
34172_mg1_1	SG-09-05	Caliente	63.08	72.34	0.62	13.69	3.22	0.10	0.26	1.46	6.96	1.04	0.23	bd	0.219	100.14	0.100	2188	Glomerocryst glass	New data (this study)	
34172_m3_4	SG-09-05	Caliente	63.08	73.69	0.82	11.12	4.29	0.18	0.83	1.59	4.24	3.33	0.28	0.068	0.180	100.61	0.090	274	1800	Glomerocryst glass	New data (this study)
34172_m3_3	SG-09-05	Caliente	63.08	71.02	0.82	12.30	4.52	0.03	0.78	2.17	4.57	3.66	0.26	bd	0.187	100.32	0.092	1866	Glomerocryst glass	New data (this study)	
34183_mg1_3	SG-09-16	Caliente	-	69.42	0.39	17.20	1.79	0.07	0.33	3.53	5.37	2.13	0.14	bd		100.37			Glomerocryst glass	New data (this study)	
34183_mg1_2	SG-09-16	Caliente	-	75.96	0.62	12.25	2.17	0.05	0.11	0.67	4.58	3.92	0.11	bd	0.106	100.54	0.069	1059	Glomerocryst glass	New data (this study)	
34183_mg4_1	SG-09-16	Caliente	-	72.40	0.58	14.11	2.51	0.08	0.20	0.91	5.39	3.84	0.18	bd	0.146	100.33	0.081	1463	Glomerocryst glass	New data (this study)	
34183_mg3_2	SG-09-16	Caliente	-	73.54	0.64	12.63	2.57	0.05	0.21	0.95	4.68	3.50	0.19	bd	0.149	99.13	0.082	1488	Glomerocryst glass	New data (this study)	
34183_mg4_2	SG-09-16	Caliente	-	71.94	0.63	13.77	3.05	0.16	0.34	1.12	5.02	3.63	0.21	0.048	0.192	100.12	0.093	191	1921	Glomerocryst glass	New data (this study)
34183_mg4_3	SG-09-16	Caliente	-	71.36	0.63	13.67	3.62	0.16	0.43	1.13	5.04	3.70	0.19	bd	0.244	100.18	0.105	2438	Glomerocryst glass	New data (this study)	

Table 3. Details of "petrologic method" calculations using apatite and matrix glass compositions

	F wt%		Cl wt%		S, ppm	
	Avg	± 1 σ	Avg	± 1 σ	Avg	± 1 σ
Apatite (microphenocrysts)	1.98	0.45	1	0.11	1396	804
Apatite (inclusions)	1.5	0.46	1.19	0.15	1656	687
<i>Melt, from apatite microphenocrysts[€]:</i>						
Calculated melt (using low D [€])	0.166	0.043	1.02	0.17	570	302
Calculated melt (mid-range D)	0.085	0.022	0.453	0.076		
Calculated melt (using high D)	0.057	0.015	0.291	0.049	218	125
<i>Melt, from apatite inclusions[€]:</i>						
Calculated melt (using low D)	0.118	0.036	1.19	0.15	676	263
Calculated melt (mid-range D)	0.06	0.018	0.529	0.067		
Calculated melt (using high D)	0.041	0.012	0.34	0.043	259	109
Matrix glass (*§¶)	0.03		0.083	0.033	135-358	§
Mass degassed, as wt% of melt	min	0	0.126		0	
	max	0.179	1.290		804	
Mass melt erupted since 1922, kg	1.9 × 10 ¹² to 3.5 × 10 ¹² (see text for details)					
Mass F, Cl, S degassed, kg	min		2.4E+09			
	max	6.3E+09	4.5E+10		2.81E+09	
Avg tonnes/day (from 1922-2014)	min		74	HCl		
	max	196	1382	HCl	157	SO ₂

€ For D values see text

* Balcone-Boissard et al. (2010) matrix glass concentrations used for F

§ Most glasses have sulphur bd so use detection limit (135 ppm) as lower limit here. Upper limit is maximum detected concentration (see Table 2)

¶ Average detected matrix glass concentrations used for Cl, Table 2

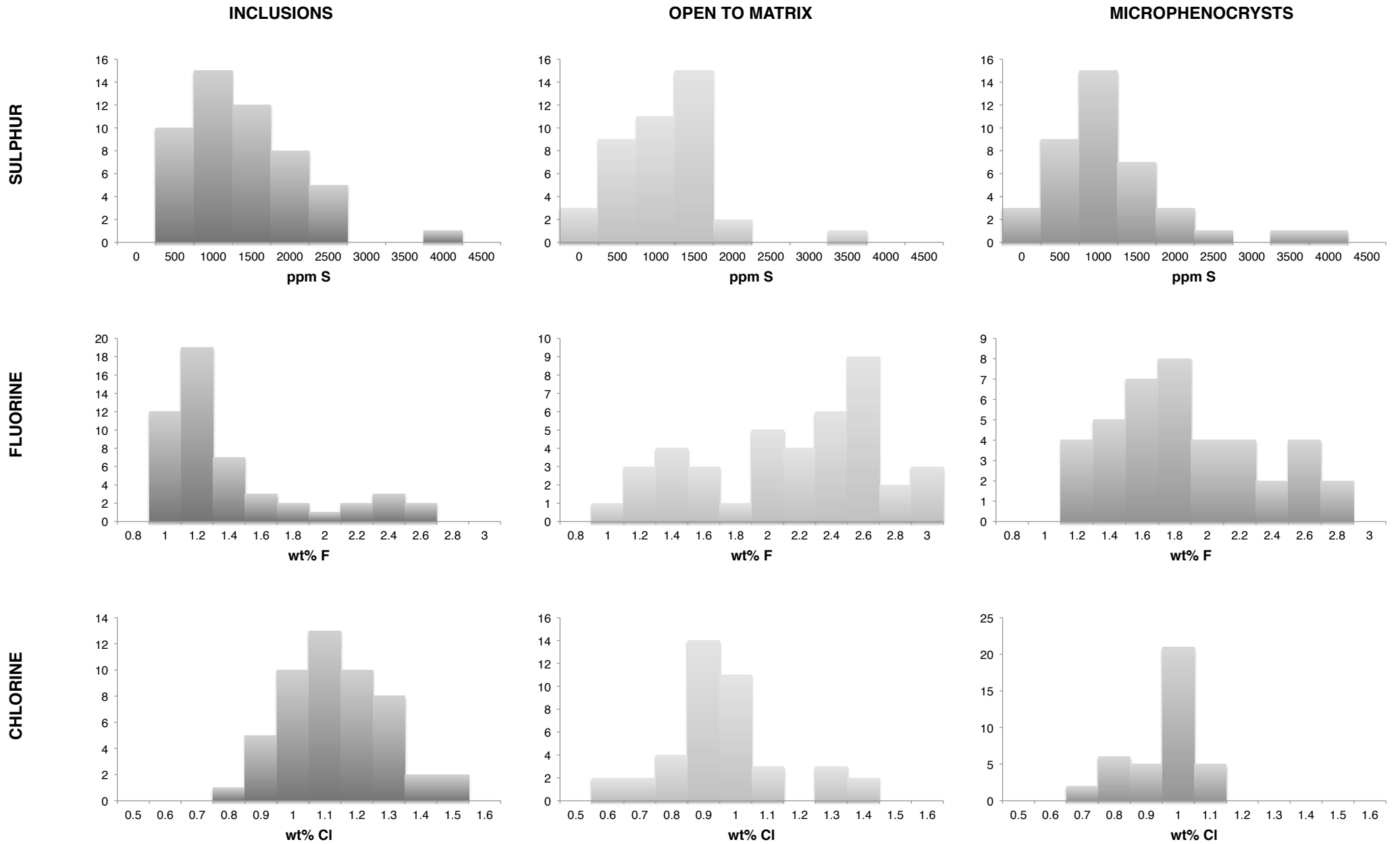
Table 4. Estimated volatile flux from Santiaguito, based on apatite analyses (this study), with directly measured flux from other volcanoes for comparison.

Halogen/ SO₂ ratios for Santiaguito were calculated from the petrological data as described in the text.

For Mount St Helens, reported flux data were used to calculate halogen/ SO₂ ratios.

§ SO₂ fluxes show short-term variations from 30 - 154 tonnes/day within individual cycles of explosion and repose.

			SO₂ (tonnes/day)	HF / SO₂ (by mass)	HF (tonnes/day)	HCl / SO₂ (by mass)	HCl (tonnes/day)	References
Santiaguito, Guatemala	This study – petrologic method using apatite and matrix glass		Up to 145	1.3	Up to 196	0.51 to 9.5	74 to 1382	
Santiaguito, Guatemala	Persistent degassing, average rates	July 1976 to February 1991	30-210	-	-	-	-	Andres et al., 1993
	Periods of eruption, average rates	July 1976 to February 1980	60-960	-	-	-	-	Andres et al., 1993
Santiaguito, Guatemala	Persistent degassing (period of higher lava extrusion rate)	May 2001 to August 2002	20 - 190	-	-	-	-	Rodriguez et al., 2004
Santiaguito, Guatemala (§)	Daily average across complete explosion-repose cycles	January 2008 - February 2009	55-85	-	-	-	-	Holland et al., 2011
Fuego, Guatemala	Persistent degassing	May 2001 to August 2002	280 - 340		-	-	-	Rodriguez et al., 2004
Pacaya, Guatemala	Persistent degassing	March 1999 to September 2002	350 - 2380		-	-	-	Rodriguez et al., 2004
Tacana, Guatemala	Persistent degassing	November 1999	30		-	-	-	Rodriguez et al., 2004
Popocatepetel, Mexico	Dome-building			0.015-0.019		0.11-0.13		Love et al., 1998
Lascar, Chile	Dome-building			0.16		0.35		Mather et al., 2004
Mount St Helens, Washington, USA	Dome-building	October 2004 to November 2005	14 to 240	0.008 to 0.14		2 0.06 to 1.0		14 Gerlach et al., 2008; Edmonds et al., 2008
Soufrière Hills, Montserrat	Dome-building	April 1996 to June 1997	42 to 1933	0.007	39	0.3 to 12.6	>400 to 6000	Young et al., 1998; Allen et al., 2000; Edmonds et al., 2001; Edmonds et al., 2002
Sakurajima, Japan	Dome-building			0.009-0.015		0.14-0.33		Mori and Notsu, 2003



Supplementary figure