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1 **Uptake of gaseous thallium, tellurium and vanadium into anhydrous**  
2 **alum, Lascar volcano fumaroles, Chile**  
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31 Abstract

32

33 Formation of secondary sulphate minerals during the reaction between volcanic gases  
34 and rocks modulates the composition and flux of gaseous emanations. We report on the  
35 sub-surface formation of anhydrous alum ( $M^I M^{III} (X^{VI}O_4)_2$  with  $M^I = NH_4^+, Na^+, K^+$ ;  $M^{III} =$   
36  $Al^{3+}, Fe^{3+}$  and  $X^{VI} = S^{6+}$ ) in the 330°C fumaroles of the Lascar volcano (Chile). The alum  
37 occurs as a few millimetres thick crust that grew internally by two-way diffusion of  
38 reaction gases and diffusive influx of rock cations within the crust. The average growth  
39 rate is estimated at ca. 0.3  $\mu\text{m}/\text{day}$ , based on the 19-year-long activity of the degassing  
40 fracture hosting the crust. The growth rate is controlled by the slow migration of the  
41 rock cations and decreases towards crust rim.

42 The crust selectively concentrates Tl, V and Te (thousands of  $\mu\text{g}/\text{g}$ ) and to a lesser extent  
43 Mo (hundreds of  $\mu\text{g}/\text{g}$ ). The uptake of gaseous Tl, V and Mo is not due to saturation of  
44 the gas with Tl, V and Mo compounds but to the possibility for the elements to enter the  
45 crystal structure of alum:  $Tl^+, V^{3+}$  and  $Mo^{6+}$  might substitute for the  $M^I, M^{III}$  and  $X^{VI}$  ions,  
46 respectively. The process of Te uptake remains uncertain, but must be related to the  
47 incorporation of Tl and V with which Te tightly correlates.

48 Thallium, V and Te concentrations increase by a factor  $> 20$  from core to rim, where they  
49 reach 8760, 8508, and 1687  $\mu\text{g}/\text{g}$  respectively. This trend correlates with the decrease  
50 of crust growth rate. This indicates that the low rate of rock cations supply to the outer  
51 edge of the crust favours the substitution of Tl, V and Te in the crystal network. Such  
52 surface enrichment does not occur for Mo, because Mo competes with S, another  
53 element from the gas. This suggests that the surface of mature alum crust has a high  
54 adsorption capacity for those gaseous metals able to compensate for the lack of rock-  
55 derived cations.

56 Based on the composition of gases escaping from the fracture hosting the crust, it is  
57 estimated that the partition coefficients of Tl ( $3.3 \times 10^7$ ), V ( $1.1 \times 10^7$ ) and Te ( $0.6 \times 10^7$ )  
58 between crust surface and gases are two to four orders of magnitude higher than for  
59 other volatile metals and metalloids. It follows that gases equilibrating with anhydrous  
60 alums lose between 77 and 95% of their initial Tl content, but less than 1% of Pb. Given  
61 the Tl emission rate of Lascar volcano (5 g/day), between 17 and 104 g of toxic Tl would  
62 deposit every day if all Lascar gases were to equilibrate with anhydrous alums.

63

## 64 1. INTRODUCTION

65

66 Sub-aerial degassing of high-temperature magmas directly releases large amount of  
67 sulfur, metals and metalloids to the atmosphere (e.g., Allard et al., 2000; Moune et al.,  
68 2010; Mather et al, 2012; Zelenski et al., 2013; Gauthier et al., 2016). Conversely, gases  
69 continuously emanating from the crustal magma reservoirs feeding stratovolcanoes  
70 have a more complex history, and only a fraction escapes from the ground. The other  
71 fraction is trapped within the volcanic edifices, due to the dissolution of magmatic gases  
72 into groundwater (Doukas and Gerlach, 1995) and/or hydrothermal system (Symonds  
73 et al., 1992), formation of secondary sulphate minerals during gas-rock reactions  
74 (Zimbelman et al., 2005), condensation of sulpho-salt melts during gas expansion in  
75 fractures (Henley and Berger, 2013) and precipitation of gas sublimates at fumaroles  
76 vents as gas cools and mixes with air (Bunsen 1851; Stoiber and Rose, 1974). The extent  
77 of element uptake in the ground has implications for volcano monitoring (Symonds et  
78 al., 2001; Le Guern et al., 1993), and also controls the global versus local environmental  
79 impact of magmatic gases, especially regarding toxic heavy metals.

80 Several studies have collected gas sublimates and condensates at the mouth of  
81 fumaroles to document the condensation sequence of elements (e.g., Bernard and Le  
82 Guern, 1986; Symonds et al., 1987; Taran et al., 2001). In agreement with  
83 thermochemical data, they showed that semi-volatile elements (Cd, Pb, Bi, Cu, Zn)  
84 condense over a wide temperature range, from 800 to less than 400°C, depending on gas  
85 composition and oxidation state (e.g., Symonds et al., 1987; Le Guern et al., 1993;  
86 Churakov et al., 2000). Fewer studies noted that fumarolic incrustations are also  
87 enriched in some volatile metals (e.g. Cu, Tl) that are not saturated in the gas phase  
88 (Naughton et al., 1976; Kodosky and Keskinen; 1990; Okrugin et al. 2017). They  
89 suggested that gaseous elements partition into, or adsorb on the alteration minerals  
90 coating degassing conduits. There is growing evidence that underground gas-rock  
91 reactions significantly influence the chemistry of volcanic gases ultimately released in  
92 the atmosphere (Henley and Berger, 2013; Henley and Seward, 2018; King et al., 2018;  
93 Palm et al., 2018). For instance, Henley et al. (2012) emphasized the fractionation of  
94 chalcophile elements (As-Sb-Bi-Sn-Pb-Tl) during sub-surface precipitation of sulpho-  
95 salts and suggested that over 90% of As might be trapped underground.

96 This study focuses on the partitioning of gaseous elements into secondary sulphates,  
97 which commonly form when acid gases interact with basaltic or more evolved rocks rich  
98 in aluminium and alkalis (Getahun et al., 1996; Africano and Bernard, 2000; Zimbelman  
99 et al., 2005). The range of secondary sulphate minerals is wide due to the numerous  
100 possibilities of combining rock-derived cations ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Al^{3+}$ ,  $Fe^{3+}$ ) with gas-  
101 derived ions ( $NH_4^+$ ,  $SO_4^{2-}$ ). In addition, trace ions with valence ranging from +1 to +6  
102 might substitute for major cations, further increasing mineral variety (Lipson et al.,  
103 1935; Giester, 1994; Balic Zunic et al. 1994; Dutrizac and Jambor, 2000). For instance,  
104 more than one hundred of sulphate minerals occur in the fumarolic incrustations of  
105 Tolbachik volcano, Kamchatka (Mindat.org database, 2019).

106 The geochemical study of gas-rock interaction meets with the difficulty of accessing the  
107 active areas of stratovolcanoes and collecting underground samples. To circumvent this  
108 difficulty, Henley et al. (2012) studied paleo-fumarole conduits, now exposed at the  
109 surface by tectonics. Here, we use a sub-surface fumarole crust showing growth layers  
110 to reconstruct the temporal evolution of the gas-rock reaction within a degassing  
111 fracture of the Lascar volcano (Chile). This evolution is studied by measuring in situ  
112 major-trace element concentrations and oxygen isotopes along core-rim profiles. The  
113 bulk Pb and Sr isotopic composition of the crust is also measured to constrain the origin  
114 of the crust. The composition of the outermost layer of the crust is compared to the  
115 composition of gases emanating from the same fracture (Menard et al., 2014), in order  
116 to assess the partition coefficients of elements between gas and crust. A major result of  
117 this study is the recognition of selective incorporation of gaseous Tl, V and possibly Te in  
118 the crystal structure of the sulphate. This effect potentially depletes volcanic emanations  
119 in these elements and contributes to concentrate them within the edifice.

120

## 121 2. BRIEF OVERVIEW OF LASCAR VOLCANO

122

123 Lascar ( $23^{\circ}22'S$ ,  $67^{\circ}44'W$ , 5590m) is one of the most active stratovolcanoes of the  
124 Central Volcanic Zone (CVZ) of the Andes (Fig. 1a) (Stern, 2004). The volcano rests on a  
125 pre-Cenozoic basement, made of Devonian to early Carboniferous sandstones (Lila  
126 formation), Permian granites and volcanic rocks (Cas formation), Permo-Trias volcanic  
127 products (Peine strata and Cerro Negro Strata) (Gardeweg et al., 1998, 2011). The  
128 volcano is composed of two cones, the westernmost crater of the eastern edifice being

129 the current focus of activity (Fig. 1b). The volcano has produced about 30 to 40 km<sup>3</sup> of  
130 magma during its 220 ka history. Since the nineteenth century Lascar produced ca. 30  
131 eruptions andesitic-to-dacitic in composition (Gardeweg et al., 1998, 2011).  
132 Petrochemical modelling indicates the occurrence of large magmatic reservoir at 6 km  
133 depth, which is mobilized during dacitic eruptions, and several shallower reservoirs  
134 sampled by smaller but more frequent mafic eruptions (Matthews et al., 1999). Between  
135 the 1984 reactivation and the last major eruption in 1993, Lascar showed a cyclic  
136 activity including sequences of dome growth, degassing pulse, dome subsidence, and  
137 explosive events (Matthews et al., 1997). The 1993 eruption (VEI 4) produced a 25 km-  
138 high sub-plinian ash column whose collapse generated pyroclastic flows up to 8.5 km  
139 NW from the summit. The eruption deposited 10<sup>9</sup> tons of tephra, coated by gypsum  
140 likely recycled from tertiary sediments (Risacher and Alonso, 2001). Since 1993, Lascar  
141 alternated passive degassing and vulcanian eruptions, and produced its last eruption in  
142 October 2015.

143 A major feature of Lascar volcano is the high fumarolic activity that feeds a persistent  
144 gas plume. Sampling of the active crater fumaroles between 2002 and 2006 revealed  
145 temperatures in the range of 30-385°C and the contribution of magmatic gases,  
146 hydrothermal fluids, and meteoric water to volcanic emanations (Tassi et al., 2009). The  
147 hottest fumaroles (250-385°C) occurred within a narrow area to the northeast of the  
148 active crater. Menard et al. (2014) sampled the gas plume between 2009 and 2012, and  
149 estimated that the volcano releases 150-940 t/d SO<sub>2</sub>, 170-210 t/d HCl, and up to 100 t/d  
150 HF. They also identified little volatile (i.e., Co, V, Sc, REE, Y, HFSE, Th, U, alkali-earth and  
151 alkaline metals), moderately volatile (Cu, Cr, W, In, Mo, Sn, Pb), and highly volatile (Cd,  
152 Zn, B, Tl, Sb, Bi, Se, As, Te) groups of trace elements.

153

### 154 3. FUMAROLE CRUST SAMPLE

155

156 A fumarole crust was sampled in November 2012 in the arcuate fracture located along  
157 an older crater wall east of the active crater, at an elevation of 5375 m (Fig. 1b). This  
158 fracture opened following the 1993 eruption (Matthews et al., 1997). Gases emanating  
159 from the fracture were also sampled in 2012 through filter packs ca. 2m from the  
160 fracture (Fig. 2a) and analysed by Menard et al. (2014). The gases have a low SO<sub>2</sub>/HCl  
161 molar ratio (0.21) compared to plume aerosols (average of 1.7) and fumaroles from the

162 active crater (average of 3.0) (Menard et al., 2014, Tassi et al., 2009). Such low SO<sub>2</sub>/HCl  
163 ratio is indicative of extensive gas–water–rock interactions. The temperature of the  
164 bottom of the fracture where the crust formed, measured by thermal camera, was 330°C  
165 (Fig. 2b). This temperature is unexpectedly elevated given the distance from the active  
166 crater (ca. 500 m) and the hydrothermal signature of the gases.

167 The studied crust was attached to the lower surface of a lava block that obstructed the  
168 fracture (Fig. 2cd). It was collected ca. 30 cm underground. The crust was initially fully  
169 green, but some parts became blue a few minutes after sampling as the crust  
170 equilibrated with air. Crust colours faded during the first year that followed sampling.  
171 The crust coats the rock over ca. 100 cm<sup>2</sup> and is a few mm thick (Fig. 2d). It includes  
172 several outgrowths, more or less cracked and hollow (Fig. 2e). Inspection of different  
173 cross sections under a binocular microscope revealed that they formed via concentric  
174 addition of growth layers. A globular outgrowth, ca. 8 mm in diameter and filled with  
175 crust material was selected for this study (Fig. 2f).

176

## 177 4. METHODS

178

179 All analyses were done at Laboratoire Magmas et Volcans (LMV), Clermont-Ferrand,  
180 except Secondary Ion Mass Spectrometry (SIMS) measurements which were carried out  
181 at CRPG, Nancy.

182

### 183 4.1. Electron Microscopy

184

185 The selected crust chip was embedded in resin, polished on SiC discs using ethanol to  
186 preserve water-soluble phases. An area of 2.0×1.5 mm showing well-formed growth  
187 layers was selected for chemical analysis (Fig. 2f). All analyses, with the exception of  
188 oxygen isotopic composition, were performed on this reference area (referred to as side  
189 A). This area was first surveyed by Scanning Electron Microscopy (SEM, JSM 5910LV)  
190 operating in Backscattered Electron (BSE) imaging mode. Detected elements (S, O, Al, Fe,  
191 Mg, Na, Ca and K) were mapped by Energy Dispersive Spectroscopy (EDS). Quantitative  
192 analyses of major elements, with the exception of O, were subsequently performed by  
193 Electron Probe Microanalysis (EPMA, Cameca SX 100) along two core-rim profiles,  
194 referred to as A1 and A2 (location shown in Table S1), with a 15-kV accelerating voltage,

195 10-nA beam current, and 30 $\mu$ m spot size. Relative in-run errors ( $2\sigma$ ) are typically 4%  
196 for Al and S, 12% for Fe, Mg and Na, 20% for K and 30% for Ca.

197

#### 198 4.2. Laser ablation inductively coupled plasma mass spectrometry

199

200 Concentrations of minor and trace elements (Li, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr,  
201 Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Te, Cs, Ba, Hf, Ta, Tl, Pb, Bi, Th, U and Rare Earth Elements)  
202 were measured on the EPMA spots by laser ablation inductively coupled plasma mass  
203 spectrometry (LA-ICPMS) using an excimer 193nm Resonetics M-50E laser system and  
204 an Agilent 7500cs quadrupole ICPMS. Measurements were done with a dwell time of 25  
205 ms, spot size of 27  $\mu$ m, laser repetition rate of 3 Hz, He and N<sub>2</sub> flow rates of 575 and 2  
206 ml/min, respectively. Backgrounds were measured for 30s before each ablation. Oxide  
207 production as measured by ThO/Th on the NIST 610 standard glass was 0.9%.  
208 Aluminium content was used for internal normalization, with reference to EPMA data.  
209 The NIST 610 was measured several times at the beginning of the session and then  
210 every 25 spots. As no significant drift occurred, the average of the NIST 610  
211 measurements were used for signal calibration, using the GeoRem database values  
212 (Jochum et al., 2005). Relative error on the NIST 610 is less than 1% for each measured  
213 trace elements. The GLITTER software was used for the trace-element data reduction.  
214 Detection limit was <1ppm for all elements except Se, which was measured by wet  
215 chemistry (cf. 4.5).

216

#### 217 4.3 Raman spectroscopy

218

219 Raman spectroscopy was used to characterize crust mineralogy. Raman spectra were  
220 collected using an InVia confocal Raman micro-spectrometer manufactured by  
221 Renishaw and equipped with a 532 nm diode laser, a CCD detector, an edge filter, a  
222 motorized XYZ stage and a Leica DM 2500M optical microscope. Laser power on the  
223 sample was reduced to  $\sim$  1 mW and slit aperture was set to 65  $\mu$ m. A 50 $\times$  microscope  
224 objective and a 2400 l/mm grating were used. Spectral resolution was better than 1  
225  $\text{cm}^{-1}$ . Daily calibration of the spectrometer was performed based on a Si 520.5  $\text{cm}^{-1}$   
226 peak. The spectra were recorded in the 60-1320 and 2920-3740  $\text{cm}^{-1}$  wavenumber  
227 ranges using Wire 4.2 software.

228

#### 229 4.4. Secondary Ion Mass Spectrometry

230

231 Following Raman analysis, the surface of the sample became crackled. A 1 mm-thick  
232 slice was sawed to perform oxygen isotope analysis by SIMS on the opposite side of the  
233 slice (referred to as side B). The use of a thin slice also limits degassing of the epoxy  
234 resin and of the hydrated sulphate sample within the mass spectrometer. Oxygen  
235 isotopes ( $\delta^{18}\text{O}$ ) measurements were carried out with a SIMS 1270. The slice was coated  
236 with three 4nm-thick layers of gold to assure a good electrical conduction of the porous  
237 sample. The same protocol has been applied to standard samples. Oxygen isotope  
238 compositions were measured along 3 core-to-rim profiles in the same area as major-  
239 trace element analysis. Profile B1 and B3 were perpendicular, and profile B2 was in  
240 between profile 1 and 3 (locations reported in Table S2). The spot size was 15  $\mu\text{m}$  and  
241 the distance between spots was 40 $\mu\text{m}$  in the first and the second profile, and 56.6  $\mu\text{m}$  for  
242 the third profile.

243 The SIMS was set in multi-collection mode with  $^{16}\text{O}$ ,  $^{17}\text{O}$  and  $^{18}\text{O}$  isotopes counted in L2,  
244 H1 and axial faraday cups, respectively. The field aperture and MRP were set at 2000  
245 and 6000, respectively. We applied a 30 $\mu\text{m}$  raster during the 120 s pre-sputtering, and a  
246 25 $\mu\text{m}$  raster during data acquisition. The total analytical time for one measurement was  
247 6 min. The calcite CCcigA reference material with  $\delta^{18}\text{O} = 18.94\text{‰} \pm 0.14(2\sigma)$  (Pfister et  
248 al., 2018) was first repeatedly analysed in order to assure the SIMS measurements  
249 stability. Instrumental mass bias and drift were corrected by measuring at the beginning  
250 and at the end of each profile the composition of a sulphate standard with homogeneous  
251 and known isotopic composition (CRPG internal standard  $\text{BaSO}_4$  from Maïza, with  $\delta^{18}\text{O}$   
252 of 14.45‰). The in-run error was on average 0.25‰ ( $2\sigma$ ).

253

#### 254 4.5. N, H, S and Se bulk analysis

255

256 Bulk concentrations of N, H, S and Se were measured on finely crushed surface  
257 scrapings. Nitrogen, H and S were analysed using a Flash 2000 CHNS-O elemental  
258 analyser from Thermo Fisher Scientific. Circa 1 mg of powder and a similar amount of  
259  $\text{V}_2\text{O}_5$  were precisely weighted in a tin capsule using a microbalance, and introduced into  
260 the 950°C high-temperature reactor. The combustion gases ( $\text{N}_2$ ,  $\text{H}_2\text{O}$  and  $\text{SO}_2$ ) were

261 separated in the coupled chromatography column and quantified by thermal  
262 conductivity. Cystine ( $C_6H_{12}NO_4S_2$ ) was used for calibration. Selenium was measured by  
263 ICPMS after sample dissolution in 6M HCl, evaporation and dilution in 0.5M  $HNO_3$ .

264

#### 265 4.6 Pb and Sr isotope bulk analysis

266

267 Four crust chips were powdered in an agate mortar. Circa 50 mg of sample were  
268 dissolved and Pb and Sr were extracted using anion exchange resin (AG1-X8) and Sr  
269 chelating resin (Sr Spec), respectively, following the methods described in Vlastelic et al.  
270 (2013). The isotopic compositions were measured on a Neptune Plus MC-ICPMS (Pb)  
271 and on a Triton TIMS (Sr). Instrumental mass bias correction is detailed in Table S3.

272

## 273 5. RESULTS

274

### 275 5.1. Crust mineralogy

276

277 Electron microscopy survey of the crust section shows a finely crystallized sulphate of  
278 Al, Fe, Na, Mg, K and Ca. Electron microprobe analyses performed along the two core-rim  
279 profiles A1 and A2 give between 19.5 and 23 wt% S, between 5.4 and 9.3 wt% Al, and  
280 between 0.5 and 4.2 wt% Fe (Table S1). Sodium ranges from 0.6 to 3.9 wt%, Mg from 0.7  
281 to 3 wt% and K from 0.2 to 1.6 wt%. Calcium is generally less than 1 wt%, but frequent  
282 spikes (up to 8.5 wt%) occur due to the presence of anhydrite nuggets. Aluminium  
283 negatively correlates with Fe and Mg, whereas K negatively correlates with Na. Atomic  
284 abundances follow the relation:  $S/(Al+Fe)=0.16(Ca+Mg)+1.9$ , which is consistent with  
285 the occurrence of a double sulphate of Al and Fe.

286 Raman spectra (Fig. 3) show the characteristic vibration bands of (1) anhydrous alums,  
287 with major occurrence of  $(NH_4)Al(SO_4)_2$  (godovikovite bands at 318, 483, 610 and 653,  
288 1076, 1287, 3148, 3208, 3331  $cm^{-1}$ ), and minor occurrence of  $(NH_4)Fe(SO_4)_2$  (sabeite  
289 main band at 1033  $cm^{-1}$ ) and  $(NH_4)_2Mg_2(SO_4)_3$  (efremovite main band at 1049  $cm^{-1}$ )  
290 (Kosek et al., 2018); (2) hydrated sulphates including  $MgSO_4 \cdot 6H_2O$  (exahydrate bands at  
291  $460 \pm 5$ , 610, 983-984, 1080 and 3435  $cm^{-1}$ ), mirabilite ( $Na_2SO_4 \cdot 10H_2O$ ) and/or hydrated  
292 alums (band at 990/991  $cm^{-1}$ ); and (3)  $CaSO_4$  (anhydrite bands at 416, 499, 609, 627,  
293 675, 1017 and 1129  $cm^{-1}$ ) (Frezzotti et al., 2012). The average K/Al atomic ratio of



294 0.10±0.05 (1 $\sigma$ ) is consistent with minor occurrence of K in godovikovite (Shimobayashi  
295 et al., 2011). Bulk volatile element analysis in the surface scrapings yields 1.37-1.51 wt%  
296 N, 3.19-3.32 wt% H and 18.10-19.15 wt% S, which indicates relatively low proportion of  
297 godovikovite (<25 wt%) and high proportion of hydrated phases in the outer layer of  
298 the crust. Inspection of the unpolished surface of the crust by electron microscopy  
299 (Supplementary material S4) reveals the occurrence of 5-10  $\mu$ m Te-rich crystals  
300 embedded within fine-grained Na<sub>2</sub>SO<sub>4</sub>. Once corrected for background Na, S and O  
301 (assuming all Na signal is from background Na<sub>2</sub>SO<sub>4</sub>) the composition of these crystals  
302 turns out to be TeO<sub>2</sub> with minor amount of S. Other surface minerals are anhydrite,  
303 quartz, Ba sulphate, and a Tl-rich Al sulphate whose composition cannot be precisely  
304 determined due to its very small size (ca. 1  $\mu$ m).

305

## 306 5.2. Crust layering and compositional zonation

307

308 The SEM image of the crust section shows at least 11 concentric growth layers (U1-U11)  
309 whose thickness (500-30  $\mu$ m) generally decreases towards crust rim (Fig. 4a). The  
310 growth layers do not have the same thickness in all directions indicating an anisotropic  
311 growth. Element mapping (Fig. 4b-d) shows that Al tends to increase towards the layer  
312 boundaries, the boundaries themselves being enriched in Fe. Anhydrite occurs as  
313 particles, whose number increases towards crust rim as their size decreases. Generally  
314 major elements do not show core-rim trends beyond a slight decrease of S and K, and  
315 increase of Na in the external shells (U1 to U3). The sum of the measured major  
316 elements, plus O, N and H calculated taking into account anhydrous minerals only  
317 (godovikovite, sabieite, efremovite and anhydrite) decreases from 90 to 80 wt.% from  
318 core to rim (Table S1). This indicates an increase of water content and/or porosity  
319 towards crust rim. The first possibility is supported by the 40% increase of the EDS  
320 oxygen signal from core to rim, and the elevated H content (>3 wt%) in the surface  
321 scrapings. It is not known whether the outer shell of the crust was initially hydrated, or  
322 hydrated between sampling (2012) and analysis (2014).

323 In situ trace element concentrations are reported in Table S1. Many trace elements  
324 commonly transported by magmatic gases (Pb, Bi, Zn, Cu, Cd, Sn, Rb) occur in the crust  
325 in concentrations that are similar to or lower than those of Lascar lavas, and do not  
326 show core-rim trends (Fig. 5). Tellurium, thallium and molybdenum stand out, with

327 concentrations between  $4 \cdot 10^2$  and  $10^7$  times those of lavas (Fig. 5). Selenium, arsenic  
328 and vanadium show second order enrichments (between 22 and 37) principally at crust  
329 rim. Vanadium together with Tl and Te show a marked zonation across the crust, with  
330 concentrations increasing from 297, 210 and 71 ppm in crust core to 8508, 8760 and  
331 1687 ppm at crust rim, respectively (Fig. 6a). This increase is the most pronounced near  
332 the rim of the crust, between U6 and U1, with a local high in layers U3-U4 (1897 ppm V,  
333 2622 ppm Tl and 944 ppm Te). Molybdenum does not show such zonation, but slightly  
334 higher concentrations in the middle of the crust (600-924 ppm) compared to core and  
335 rim (205-710 ppm). Despite their large ranges of variation, Tl, V and Te are little  
336 fractionated from each other, with  $Tl/V=1.4 \pm 1.1(2\sigma)$ ,  $Tl/Te=3.6 \pm 2.7(2\sigma)$  and  
337  $V/Te=2.9 \pm 2.4(2\sigma)$  (Fig. 6b).

338

### 339 5.3. Oxygen isotope profiles

340

341 In situ  $\delta^{18}O$  values measured along the three profiles of side B are reported in Table S2.  
342  $\delta^{18}O$  compositions calibrated with the  $BaSO_4$  standard from Maïza show similar ranges  
343 of variation along B1 (-1.2 to +8.2‰), B2 (-1.6 to +5.4‰) and B3 (-2.2 to +6.4‰)  
344 profiles. These variations are clearly outside the errors of individual measurements,  
345 which do not exceed 0.4‰.  $\delta^{18}O$  does not show systematic core-rim trend but high-  
346 frequency fluctuations (Fig. 7). Depending on the profile,  $\delta^{18}O$  display between 12 and  
347 20 oscillations that are not obviously linked to the growth layers. Profile B2 tends to  
348 show a smooth evolution of  $\delta^{18}O$  between +2.5 and 5.4‰, on which superimpose low  
349  $\delta^{18}O$  spikes. The average  $\delta^{18}O$  of the three profiles ( $+3.5 \pm 1.8(\sigma)$ ,  $n=165$ ) is identical to  
350 the composition of Lascar gas condensates ( $+3.5 \pm 1.2(\sigma)$   $n=2$ ) (Tassi et al., 2009). Thus,  
351 despite the small-scale heterogeneity of  $^{18}O/^{16}O$  within the crust, no net isotopic  
352 fractionation occurs between vapour and the bulk sulphate crust.

353

### 354 5.4. Bulk Pb and Sr isotope composition

355

356 The bulk Pb and Sr isotope compositions of the four crust chips are reported in Table S3.  
357 The variations of  $^{206}Pb/^{204}Pb$  (18.803-18.821),  $^{207}Pb/^{204}Pb$  (15.648-15.661),  $^{208}Pb/^{204}Pb$   
358 (38.783-38.830), and  $^{87}Sr/^{86}Sr$  (0.706329-0.706482) are small and identical, within  
359 error, to the composition of lavas from the 1993 eruption ( $^{206}Pb/^{204}Pb=18.817-18.819$ ;

360  $^{207}\text{Pb}/^{204}\text{Pb}=15.654-15.657$ ;  $^{208}\text{Pb}/^{204}\text{Pb}=38.795-38.803$ ;  $^{87}\text{Sr}/^{86}\text{Sr}=0.706337-0.706438$ )  
361 (Rosner et al. 2003).

362

## 363 6. DISCUSSION

364

365 This study investigates a time series of metal variations in a zoned sulphate crust that  
366 grew on a lava block continuously exposed to fumarole gas flux from Lascar volcano.  
367 The following discussion will focus on crust formation processes and time-scale, the  
368 extent of element extraction from the lava block relative to the gas flux, and the  
369 extensive uptake of V, Tl and Te from the gas phase.

370

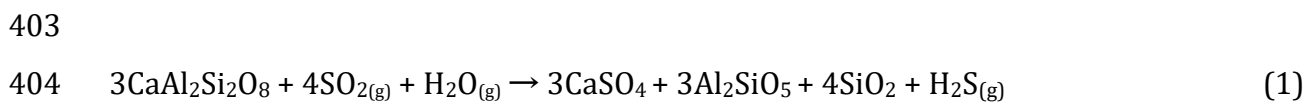
### 371 6.1. Crust formation processes

372

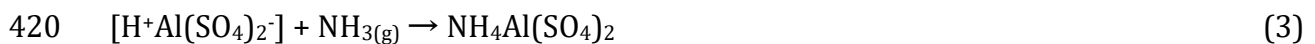
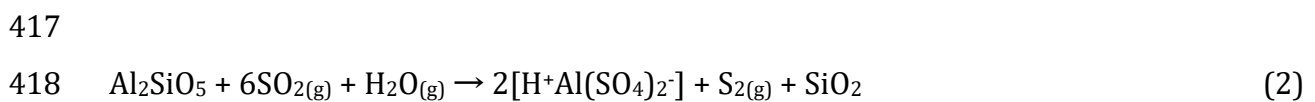
373 Anhydrous alums frequently occur at the degassing vents of burning coal-dumps (BCDs)  
374 (see review by Kosek et al., 2018). There, godovikovite commonly forms stalactite or  
375 thick crusts in subsurface cavities. Anhydrous alums are less common in volcanic  
376 fumaroles: godovikovite has been described in the Phlegrean fields and La Fossa crater  
377 on the island of Vulcano (Mindat.org database, 2019), while its hydrated form  
378 (Tschermigite) has been found in the thermal fields of Southern Kamchatka Peninsula  
379 (Zhitova et al., 2019), East African rift (Lowenstern et al., 1999) and possibly Merapi  
380 volcano, Indonesia (Kavalieris, 1994). Steklite,  $\text{KAl}(\text{SO}_4)_2$ , the K-analogue of  
381 godovikovite, has been identified in the fumarole deposits of Tolbachik volcano,  
382 Kamchatka (Murashko et al., 2013). Godovikovite is stable between 210 and 390°C  
383 (Zhitova et al., 2019), in agreement with the temperature (330°C) of the Lascar  
384 degassing fracture where the studied crust was sampled. Godovikovite hydrates into an  
385 amorphous phase below 200°C, and into tschermigite below 60°C. Conversely, it loses  
386 ammonium above 380°C to form millosevichite (Zhitova et al., 2019). The occurrence of  
387 godovikovite throughout the crust indicates that the temperature has remained  
388 relatively stable during crust formation history. The suspected hydration of the outer  
389 shell of the sulphate crust is likely a post-formation process, as observed in a BCDs crust  
390 (Parafiniuk and Kruszewski, 2009).

391 Symonds et al. (1992) estimated that even under highly oxidizing conditions ( $f\text{O}_2$  of  $10^{-5}$ ), sulphuric acid and its hygroscopic forms are undersaturated above 202 °C in a gas

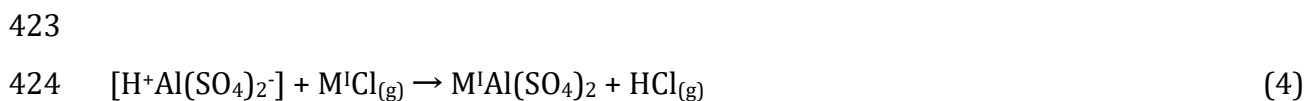
393 with less than 0.01% moles S, i.e. more than 10 times the S content of Lascar gases  
 394 (Tassi et al., 2009). Thus, the Lascar crust must have formed by the interaction between  
 395 gases and silicate rocks. This happens either through the reaction between  $\text{SO}_{3(\text{g})}$  and  
 396 silicate without change in S oxidation state, or through the disproportionation of  $\text{SO}_{2(\text{g})}$   
 397 to  $\text{SO}_4^{2-}$  that bonds with rock derived cations, and reduced S released as  $\text{S}_{2(\text{g})}$  or  $\text{H}_2\text{S}_{(\text{g})}$   
 398 (Henley et al., 2015; Renggli et al., 2018). Because this reaction requires diffusion of  
 399 elements towards the gas-rock interface, sulphates of Ca, Na and to a lesser extent Mg  
 400 preferentially form, while sulphates of less mobile networkforming cations (Al, Fe) are  
 401 rarely observed in experiments (Renggli et al., 2018; King et al., 2018). For instance,  
 402 anhydrite might form through chemisorption of  $\text{SO}_{2(\text{g})}$  on anorthite (Henley et al., 2015):



406 Johnson and Burnett (1993) nevertheless reported the formation of a mixture K-Na  
 407 anhydrous alum and thenardite following one week reaction at 850°C between  
 408 crystalline albite ( $\text{NaAlSi}_3\text{O}_8$ ) and a gas mixture with  $\text{SO}_2/\text{O}_2=1$  obtained by thermal  
 409 decomposition of  $\text{K}_2\text{S}_2\text{O}_8$ . This experiment demonstrates that, in oxidizing conditions,  
 410 gas-derived (K and S) and silicate-derived (Na and Al) elements combine to form  
 411 anhydrous alum. The layered structure of anhydrous alums, which results from stacking  
 412 thin layers of  $\text{Al}(\text{SO}_4)_2^-$  and layers of large cations ( $\text{K}^+$ ,  $\text{NH}_4^+$ ) (West et al., 2008;  
 413 Murashko et al., 2013; Zhitova et al., 2019), suggests a two step formation process. One  
 414 possibility is that the anion layer first forms by chemisorption of  $\text{SO}_{2(\text{g})}$  on residual  
 415 silicate but is weakly bonded to  $\text{H}^+$ , allowing the sorption of larger species from the gas  
 416 subsequently:



422 and generally, for any monovalent cation  $\text{M}^I$  transported as chloride in the gas,



426 The formation of godovikovite requires a sustained supply of gaseous  $\text{NH}_3$ . Nitrogen  
427 may originate from the devolatilization of sediments subducted into magmas source  
428 (Snyder et al., 2003) and/or unusually elevated nitrate concentration in Atacama  
429 terrains due to the hyperarid climate (Ericksen G., 1983).

430 After the initial stage of gas-rock interaction, growth of a sulphate crust requires  
431 transport of elements through the sulphate. Different growth textures will form  
432 depending on whether rock cations migrate towards the sulphate-gas interface, or gas-  
433 derived elements migrate towards the sulphate-silicate interface, or rock and gas  
434 elements both migrate within the sulphate. Renggli et al. (2018) studied the formation of  
435 anhydrite coating during short (24-72H) high-temperature (700-800°C) reaction  
436 between  $\text{SO}_{2(g)}$  and Fe-free glass. They observed that the thickest coatings (ca. 200  $\mu\text{m}$ )  
437 tend to detach from the glass surface and to wrinkle and buckle, which they ascribed to  
438 stress accumulation within the coating due to internal sulphate growth. They suggested  
439 that the empty space between the buckled coating and silicate substrate might fill with  
440 sulphate material in case of longer durations. The outgrowths of the Lascar crust very  
441 likely form via a similar process (Fig. 8ab), although the aluminous composition and  
442 thickness of the sulphate crust indicate that the extent of reaction is much higher. In  
443 particular, the prolonged gas-rock reaction results in the formation of growth layers.  
444 The layers are ascribed to a decreasing growth rate towards crust surface due to the  
445 slow diffusion of rock-cations within the altered rock and the sulphate. Element  
446 migration occurs through evolving vacancies, defects and grain boundaries, and is much  
447 less efficient for Al than for Ca, Na, Mg and other divalent cations (Henley et al., 2015;  
448 Palm et al., 2018). As the crust grows, the progressive exhaustion of cations in the  
449 reacted rock also requires cations to diffuse over longer distances. The thin layers at  
450 crust outer edge are consistent with a slow growth due to a low rate of rock cations  
451 supply. As shown on Figure 8c, the structure of the crust is consistent with a model  
452 where all layers grow simultaneously, but at decreasing rate towards the rim.

453 In the internal growth model, the small-scale  $^{18}\text{O}/^{16}\text{O}$  variations across the crust have no  
454 temporal significance. They result from the stacking of the temporal O isotope signal of  
455 the gas. The substantial isotope variations nevertheless require the input of sources  
456 with different compositions, such as meteoric water with  $\delta^{18}\text{O}$  of -19‰ at Lascar  
457 summit (Tassi et al., 2009) and magma-derived water with  $\delta^{18}\text{O}$  between +6 and +12‰  
458 (Giggenbach et al., 1992; Taran et al., 1989). Part of the  $^{18}\text{O}/^{16}\text{O}$  variations can also result

459 from equilibrium isotopic fractionation between the different sulphate minerals that are  
460 finely distributed within the crust.

461 Two observations suggest that the crust started to grow ca. 19 years before being  
462 sampled in 2012: (1) The fracture hosting the crust opened following the 1993 eruption  
463 (Matthews et al., 1997). (2) Lead and Sr isotope compositions indicate that the crust is  
464 genetically linked to the 1993 eruption, either through degassing of un-erupted magmas,  
465 or acid alteration of the rock on which the crust grew. The 2-3 mm thickness of the crust  
466 then requires an average growth rate of 0.3 - 0.4  $\mu\text{m}/\text{day}$ . By comparison, the growth  
467 rates of sulphates formed in 850°C experiments are between less than 1 $\mu\text{m}/\text{day}$  for  
468 natural basalts and 2-7 $\mu\text{m}/\text{day}$  for glass (Johnson and Burnett, 1993).

469

## 470 6.2. Selective uptake of Tl, Te and V

471

472 The concentrations of Tl and Te are very elevated in the sulphate crust, but they are not  
473 unusual for fumarole deposits that commonly host Tl and Te gas sublimates. For  
474 instance, Tl and Te concentrations in excess of 2000 and 70 ppm, respectively, have  
475 been reported for Merapi (Indonesia), El Misti (Peru) and Vulcano (Italy) fumarole  
476 deposits (Kavalieris, 1994; Birnie and Hall, 1974; Fulignati and Sbrana, 1998). However,  
477 Tl and Te generally condense together with other metals of comparable volatility, such  
478 as Pb, Bi, Cd, Cu or Zn, which is not the case for the Lascar crust. Consequently ratios  
479 such as Tl/Pb (125-4558) and Te/Pb (28-2023) are orders of magnitude higher in the  
480 Lascar crust than in worldwide fumarolic gases, condensates and solid deposits, where  
481 they rarely exceed 3 and 10, respectively (Fig. 9). Only condensates from the fumaroles  
482 of the Avacha volcano (Kamchatka Peninsula, Russia), which are abnormally enriched in  
483 Tl (Okrugin et al., 2017), have Tl/Pb (up to 73) and Te/Pb (up to 36) ratios close to the  
484 Lascar crust values. On the other hand, Tl and Te concentrate in the crust together with  
485 V, which generally behaves as a non-volatile element in volcanic gases (Symonds et al.,  
486 1987; Mather et al., 2012), except in highly oxidizing conditions (Hughes and Stoiber,  
487 1985; Taran et al., 2001).

488 Generally, the trace element chemistry of the crust appears unrelated to the chemistry of  
489 Lascar gases, which are enriched in As, Se, Bi, B, Zn, Pb, Sn, Mo, In, in addition to Te and  
490 Tl, and depleted in V and other refractory lithophile elements (Menard et al., 2014). This  
491 strongly suggests that the Tl, Te and V enrichments in the crust are not inherited from

492 the gas phase—in the sense that similar Tl-Te-V enrichments relative to other metals do  
 493 not occur in gases—, but result from crust formation process. Both the gas phase and the  
 494 host rock can supply Tl, Te and V to the crust. Although a dominant contribution from  
 495 the gas phase is expected given the extreme enrichment of these elements in the crust,  
 496 especially regarding Te that occurs at the ppb level in rocks, a contribution from rock  
 497 cannot be ruled out. This possibility is taken into account in the calculation of the  
 498 distribution coefficient of elements between crust and vapours ( $D_{\text{Crust/Gas}}$ ):

$$499 \quad D_{\text{Crust/Gas}} = [X]_{\text{Cc}}/[X]_{\text{Gas}} \quad (5)$$

$$501 \quad \text{with } [X]_{\text{Cc}} = [X]_{\text{C}} - [Zr]_{\text{C}} \cdot [X]_{\text{R}}/[Zr]_{\text{R}}$$

$$502 \quad \text{and } [X]_{\text{Gas}} = \{X\}_{\text{Gas}}/\{\text{SO}_2\}_{\text{Gas}} \cdot [\text{SO}_2]_{\text{Gas}}$$

503  
 504 where  $[X]_{\text{Cc}}$  is the element concentration in the crust corrected for inputs from the rock,  
 505 assuming all Zr originate from the altered rock. Zirconium is used because high-field  
 506 strength elements are generally strongly depleted in magmatic gases.  $[X]_{\text{C}}$  and  $[X]_{\text{R}}$  are  
 507 the measured concentrations in the crust outer layer (U1) and in 1993 lavas (Menard et  
 508 al., 2014), respectively.  $[X]_{\text{Gas}}$  is the mass fraction of elements in gases.  $\{X\}_{\text{Gas}}$  and  $\{\text{SO}_2\}_{\text{Gas}}$   
 509 are the volume-normalized masses of trace metal and  $\text{SO}_2$  in the gas escaping from the  
 510 fracture hosting the crust, respectively (sample Las 18 from Menard et al., 2014) (Fig  
 511 2a).  $[\text{SO}_2]_{\text{Gas}}$  is the mass fraction of  $\text{SO}_2$  estimated at 10% based on the composition of  
 512 gases emanating from the active crater fractures with similar temperatures (285-385°C)  
 513 (Tassi et al., 2009). The mass fraction of element originating from the gas phase  
 514 ( $[X]_{\text{Cc}}/[X]_{\text{C}}$ ) is estimated at < 30% for U and Hf, 50% for Pb and Rb, 66-82% for Co, Cu,  
 515 Ni, Cr, Nb and Cs, 90-98% for Li, Zn, Bi, Cd and Sb, and >99% for As, Se, V, Mo, Tl, Te and  
 516 S.  $[X]_{\text{Cc}}/[X]_{\text{C}}$  is plotted against  $D_{\text{Crust/Gas}}$  on Figure 10 for elements with  $[X]_{\text{Cc}} > 0$ . The  
 517 generally high to very high values of  $D_{\text{Crust/Gas}}$  reflect the very low content of trace metals  
 518 in gases, in the range of  $10^{-2}$  -  $10^1$  ppb.  $D_{\text{Crust/Gas}}$  is ca. 4 for S, in the range of  $1 - 5 \times 10^3$  for  
 519 Se, As and Sb,  $10^4 - 10^5$  for Pb, U, Zn, Hf, Cu, Rb, and  $1-4 \times 10^5$  for Cs, Mo, Cr, Ni, Co, Cd, Li  
 520 and Nb. Tellurium, vanadium and thallium stand out, with  $D_{\text{Crust/Gas}}$  between  $6 \times 10^6$  and  
 521  $3.3 \times 10^7$ . This order clearly does not reflect the volatility sequence of elements, but the  
 522 ability of elements to enter the surface of the crust. For most elements  $D_{\text{Crust/Gas}}$  does not

525 markedly change if the inner layer (U11) composition is used in the calculation.  
526 However, for Tl, V and Te  $D_{\text{Crust}/\text{Gas}}$  decreases proportionally to the rim/core ratio (>20),  
527 and remains distinctly elevated only for Tl ( $1 \times 10^6$ ).

528 The enrichment of Tl and Te in the crust relative to the gas is comparable to that existing  
529 between Fe-Mn crust and seawater, in the range of  $10^7 - 5 \times 10^8$  (Hein et al., 2003). The  
530 enrichment of V is higher in the fumarole crust than in seawater Fe-Mn crust ( $2 \times 10^5$ ).  
531 The enrichment of Tl, Te and other metals in marine Fe-Mn crust has been ascribed to  
532 oxidative sorption on, or structural incorporation in Mn oxides and Fe oxy-hydroxide  
533 (Hein et al., 2003, Peacock and Moon, 2012; Kashiwabara et al., 2014). Unlike marine  
534 crusts that concentrate 30+ elements by 6 orders of magnitude or more, the enrichment  
535 of Tl, Te and V in the fumarole crust is very selective and requires a very specific  
536 enrichment process.

537

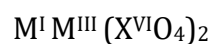
### 538 6.3. Isomorphic substitution of Tl and V

539

540 Within the crust, Tl and V bearing phases are not detected at the highest resolution of  
541 scanning electron microscopy, indicating that Tl and V are in solid solution in the  
542 sulphate, or occur in the form of nanoparticles. The former possibility is strongly  
543 supported by the layered structure of alums that facilitates element substitution.  
544 Anhydrous alums are a series of more than 30 double sulphates sharing the general  
545 formula (Giester, 1994; West et al., 2008; Kosek et al., 2018):

546

547



548

549 where  $M^I$  is an univalent species ( $K^+$ ,  $Na^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $Ag^+$ ,  $Tl^+$ ,  $NH_4^+$ ),  $M^{III}$  is a trivalent metal  
550 ( $Al^{3+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $V^{3+}$ ,  $Sc^{3+}$ ,  $Mn^{3+}$ ,  $Ga^{3+}$ ,  $Rh^{3+}$ ,  $In^{3+}$ ,  $Tl^{3+}$ ),  $X^{VI}$  is an hexavalent element ( $S^{6+}$ ,  
551  $Se^{6+}$ ,  $Cr^{6+}$ ,  $Mo^{6+}$ ,  $W^{6+}$ ). The structure of anhydrous alums consists of parallel sheets of  
552  $M^{III}O_6$  octahedra and  $X^{VI}O_4$  tetrahedra, separated by large 12-fold coordinated  $M^I$  ions  
553 (West et al., 2008; Murashko et a., 2013; Zhitova et a.l., 2019). Isomorphic substitutions  
554 play an important role in alum composition and can be predicted from the ionic radii of  
555 elements (Shannon, 1976). Previous studies showed that univalent Tl ( $r=1.70\text{\AA}$ ) and  
556 trivalent V ( $r=0.64\text{\AA}$ ) tend to substitute for  $K^+$  ( $r=1.64\text{\AA}$ ) and  $Al^{3+}$  ( $r=0.535\text{\AA}$ )  
557 respectively (see synthesis by Giester, 1994). In godovikovite,  $Tl^+$  might substitute for



558  $\text{NH}_4^+$  ( $r=1.67\text{\AA}$  for 12-fold coordination) (Sidey, 2016). The Tl-rich sulphate crystal lying  
559 on crust surface (Supplementary material S4) provides evidence for Tl incorporation  
560 into the crystal structure of alum. At magmatic temperature and oxygen fugacity, Tl and  
561 V dominantly occur in the gas phase as +1 ( $\text{TlCl}$  or  $\text{Tl}_2\text{Cl}_2$ ) and +3 ions ( $\text{VF}_3$  or  $\text{VOCl}$ ),  
562 respectively (Hughes and Stoiber, 1985; Churakov et al., 2000). The enrichment of Tl  
563 and V in the Lascar crust is thus consistent with incorporation of gas derived  $\text{Tl}^+$  and  $\text{V}^{3+}$   
564 in the  $\text{M}^{\text{I}}$  and  $\text{M}^{\text{III}}$  sites, respectively, without change in valence state. Coupled  
565 incorporation of Tl and V might be energetically favourable since  $\text{TlV}(\text{SO}_4)_2$  is a stable  
566 compound (Perret et al., 1972). This may result from  $\text{Tl}^+$  and  $\text{V}^{3+}$  being both slightly  
567 larger than the ions they replace, limiting the distortion of the crystal network that may  
568 arise from individual substitution. Trivalent Tl, although generally of minor occurrence,  
569 can also probably significantly enter the  $\text{M}^{\text{III}}$  site as it does in potassium jarosite  
570 (Dutrizac et al., 2005).

571

#### 572 6.4 Structural incorporation versus adsorption of Te

573

574 Unlike Tl and V, tellurium is not reported to enter the crystal structure of anhydrous  
575 alum, alum or alunite. This reflects the fact that  $\text{Te}^+$  and  $\text{Te}^{3+}$  are unstable and  $\text{Te}^{6+}$  (0.43  
576  $\text{\AA}$ ), unlike  $\text{Se}^{6+}$ , is too large to substitute for four-fold coordinated  $\text{S}^{6+}$  (0.12  $\text{\AA}$ ) in  $\text{SO}_4^{2-}$   
577 (Shannon, 1976). Moreover, as discussed later for Mo (section 6.6.), Te concentration  
578 would not show a drastic increase towards crust rim if it were to substitute for sulphur.  
579 Tellurium is expected to be dominantly transported as  $\text{Te}_{2(\text{g})}$  (Grundler et al., 2013) in  
580 Lascar eccentric degassing system where redox conditions are governed by the  $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$   
581 buffer of the rocks (Tassi et al. 2009, Giggenbach, 1987). Two processes of  $\text{Te}_{2(\text{g})}$   
582 incorporation into the crust are envisioned. (a) The fact that Te correlates with Tl and V  
583 suggests that Te is incorporated by coupled substitution. For instance,  $\text{Te}_{2(\text{g})}$  could enter  
584 the  $\text{M}^{\text{I}}$  site via coupled substitution with trivalent Tl, in which two large  $\text{Te}^0$  atoms (2.06  
585  $\text{\AA}$  radius) and one small atom of  $\text{Tl}^{3+}$  ( $< 1 \text{\AA}$  radius) substitute for three  $\text{M}^{\text{I}}$  atoms (ca. 1.7  
586  $\text{\AA}$  radius). If this substitution controls the Te and  $\text{Tl}^{3+}$  budget of the crust, the atomic  
587 abundance of Te must be twice that of  $\text{Tl}^{3+}$ . The average measured  $(\text{Tl}^+ + \text{Tl}^{3+})/\text{Te}$  ratio  
588 of 2.2 then requires a somewhat realistic  $\text{Tl}^+/\text{Tl}^{3+}$  atomic ratio of 3.3. (b) The occurrence  
589 of  $\text{TeO}_2$  crystals on crust surface suggests that gaseous Te is adsorbed at the surface of  
590 anhydrous alum. Tellurium adsorption processes have been mainly described in

591 seawater and soils, where  $\text{Te}^{\text{IV}}$  and  $\text{Te}^{\text{VI}}$  species adsorb at the surface of  $\text{Fe}^{\text{(III)}}$  hydroxides  
592 and illite via the formation of inner-sphere complexes (Hein et al., 2003, Kashiwabara et  
593 al., 2014; Qin et al., 2017). Adsorption of gaseous Te at the surface of mordenite zeolite  
594 has also been reported (Kodaira and Ikeda, 2014). This reaction occurs via sorption of  
595 nano- chains of Te atoms on dipoles formed by  $\text{AlO}_2^-$  and  $\text{Na}^+$  in mordenite crystalline  
596 structure. The layers of  $\text{Al}(\text{SO}_4)_2^-$  and cations in anhydrous alums could represent  
597 reactive sites allowing Te sorption as for mordenite, but the occurrence of  $\text{Te}^{\text{IV}}$  on crust  
598 surface requires that tellurium oxidizes in a second step. The scenarios (a) and (b) are  
599 certainly not incompatible, because the adsorption process is the precursor to the  
600 chemisorption reaction, during which elements are incorporated in the crustal structure  
601 of sulphate (King et al., 2018).

602

#### 603 6.5. Growth rate control on Tl-V-Te zonation

604

605 The concentrations of Tl, V and Te increase by a factor  $>20$  from the core to the outer  
606 edge of the sulphate crust. This trend correlates with a decrease of the thickness of the  
607 growth layers, pointing out a control of growth rate on Tl, V and Te content (Fig. 11).  
608 Such growth rate control on metal abundance has been described in marine Fe-Mn  
609 crusts (e.g., Hein et al., 2003) where metal-rich hydrogenic phases are diluted by metal-  
610 poor detrital phases. The growth rate of the sulphate crust is controlled by the slow  
611 diffusion of rock cations by comparison to gas species. Rock cation supply is critical for  
612 the outermost layer of the mature crust because rock cations have to diffuse over long  
613 distances in the sulphate but also in the thick rock layer already depleted in cations  
614 (Fig. 8c). A straightforward consequence of the low rate of cation supply to the  
615 outermost layer of the crust is to favour the substitution of gas derived Tl, V and Te in  
616 the crystal structure of alum. The extremely elevated Tl-Te-V concentrations at crust rim  
617 thus first result from the lack of cations with which they compete for the  $\text{M}^{\text{I}}$  and  $\text{M}^{\text{III}}$  sites  
618 of anhydrous alum. In addition, as discussed for Te, it is possible that elements are  
619 adsorbed to some degree at the surface of the crust.

620

#### 621 6.6. The molybdenum issue

622

623 Molybdenum stands out from Tl, V and Te because its elevated concentration in the  
624 crust (205-924 ppm) reflects a high concentration in the gas (32 ng/m<sup>3</sup>) (Menard et al.,  
625 2014), and not an anomalously high crust/gas ratio (Fig. 10). The high Mo concentration  
626 of the gas might be related to its enrichment in HCl, which promotes Mo volatility in the  
627 form of MoO<sub>2</sub>Cl<sub>2</sub> (Rempel et al., 2008). In addition, Mo does not show a comparable  
628 zonation as Tl-V-Te across the crust, but tends to correlate with S. This highlights a  
629 fundamental difference in the process by which Tl-Te-V and Mo are incorporated into  
630 the crust. In the absence of Mo mineral, Mo must also enter the crystal network of  
631 anhydrous alum. Unlike Te, Mo possibly enters the X<sup>VI</sup> site (Giester, 1994) although Mo<sup>6+</sup>  
632 (r=0.41 Å) is barely smaller than Te<sup>6+</sup> (r=0.43 Å) in tetrahedral coordination (Shannon,  
633 1976). Molybdenum essentially competes with S for this site. Because both Mo and S  
634 entirely originate from the gas phase (Fig. 10), the Mo content of the crust first depends  
635 on the Mo/S ratio of the gas, which has seemingly little varied during crust formation  
636 history (Mo/S=27±12×10<sup>-4</sup>). Thus, the major difference between Tl-V-Te and Mo is that  
637 the formers compete with rock-derived cations, whose rate of supply decreases towards  
638 crust rim, whereas the second competes with another element of the gas.

639

#### 640 6.7. Implications for trace element degassing

641

642 Figure 9 shows that the aerosols collected within the Lascar plume have four orders of  
643 magnitude lower Tl/Pb and Te/Pb compared to the fumarole crust, but remarkably  
644 similar Tl/Te ratio (1.5±0.6 (2σ) versus 3.6±2.7(2σ)). Likewise, aerosols and crust also  
645 have similar Tl/V ratio (0.54±0.42 (2σ) and 1.4±1.1(2σ), respectively). At Lascar, the  
646 small fractionation between Tl, Te and V contrasts with the large fractionation existing  
647 between Tl-Te-V and other volatile elements. This supports the idea that the  
648 underground partitioning of Tl, Te and V into anhydrous alums, such as godovikovite,  
649 significantly influences the abundance of these three elements in the gas plume. In the  
650 following, we evaluate quantitatively the effect of preferential incorporation of Tl over  
651 Pb into anhydrous alums on the Tl/Pb ratio. The trace element content of a gas  
652 equilibrating with a rock follows the general law of fluid/rock interaction:

653

$$654 [X]_G^f = \frac{[X]_R^i + N[X]_G^i}{N + D \frac{X}{S/G}} \quad (6)$$

655

656 where  $[X]_G^f$  and  $[X]_G^i$  are the initial and final concentrations of element X in gas,  $[X]_R^i$  is  
657 the initial concentration of X in rock,  $D_{S/G}^X$  is the partition coefficient between solid and  
658 gas, and N is the gas/rock mass ratio. In the case of extensive gas-rock interaction,  
659  $[X]_R^i \ll N[X]_G^i$ , and thus:

660

$$661 \left[ \frac{Tl}{Pb} \right]_G^f = \frac{N + D_{S/G}^{Pb}}{N + D_{S/G}^{Tl}} \times \left[ \frac{Tl}{Pb} \right]_G^i \quad (7)$$

662

663 Using distribution coefficients between crust surface and gas ( $D_{S/G}^{Tl}=3.3 \times 10^7$  and  
664  $D_{S/G}^{Pb}=1.1 \times 10^4$ ) calculated as described in section 6.2, a gas/rock mass ratio between  
665  $1.6 \times 10^6$  and  $1.0 \times 10^7$  is needed to decrease Tl/Pb from 1-5 in the initial gas (Johnson and  
666 Canil, 2011) to 0.23 in average Lascar aerosols (Menard et al., 2014). The sulphate crust  
667 formed by the interaction between gas and rock uptakes between 77 and 95% of the  
668 initial Tl content of the gases, but less than 1% of Pb. The fraction of Tl trapped in the  
669 ground translates into a daily deposition rate between 17 and 104 g, based on Lascar  
670 average Tl emission rate of 5 g/day (recalculated from Tl/SO<sub>2</sub> mass ratio of 10<sup>-8</sup> in the  
671 gas plume and mean SO<sub>2</sub> flux of 500t/day from Menard et al. (2014) who erroneously  
672 calculated metal emission rates). The estimated fraction of Tl trapped underground  
673 should be considered as an upper bound, because it is likely that gases do not fully  
674 equilibrate with sulphates, and anhydrous alums might not form everywhere in the  
675 degassing network. For instance, 3 out of the 11 fumaroles sampled by Tassi et al.  
676 (2009) within Lascar active crater have temperature within the stability field of  
677 godovikovite.

678 Godovikovite has been discovered in burning coal-dumps in 1988, thus after the main  
679 surveys of fumarolic incrustations (Stoiber and Rose, 1974; Naughton et al., 1976;  
680 Oskarsson, 1981). This raises the possibility that godovikovite is more frequent than  
681 described in early reports. In support of this idea, godovikovite and isostructural steklite  
682 have been recently found in the fumarolic fields of Tolbachik, Mutnovsky and  
683 Avachinsky volcanoes, Kamchatka (Murashko et al., 2013 and M. Zelenski, personal  
684 communication). Generally, trapping of Tl in the ground is probably a widespread  
685 phenomenon due to the frequent occurrence of K-Na sulphates. For instance, Okrugin et  
686 al. (2017) noted that the altered rocks of Vulcano contain more than three orders of

687 magnitude more Tl (up to 280 ppm) than the fumarolic fluids (14–82 ppb Tl) (Cheynet  
688 et al. 2000; Boyce et al. 2007; Fulignati and Sbrana 1998). We hypothesize that Tl might  
689 substitute for K in alunite and for Na in natroalunite, which are common alteration  
690 phases at Vulcano (Boyce et al. 2007). Selective uptake of gaseous elements by  
691 isomorphic substitution in fumarolic minerals is not limited to Tl, Te and V. At Kilauea  
692 volcano, K and Cu might substitute for Na into thenardite (Naughton et al., 1976). At  
693 Mount St. Augustine, Alaska, Cr and V might substitute for Fe in fumarole incrustations  
694 (Kodosky and Keskinen; 1990). In high-sulphidation epithermal deposits,  $\text{Ag}^+\text{-As}^{3+}$ , and  
695 possibly  $\text{Au}^{3+}\text{-Cu}^+$  ion pairs substitute for  $\text{Fe}^{2+}$  into pyrite (Chouinard et al., 2005; Scher  
696 et al., 2013).

697 Selective entrapment of some gaseous elements into alteration minerals has significant  
698 consequences: (1) As modelled above, they can modify extensively key trace element  
699 ratios, such as Tl/Pb. At global scale, the Tl/Pb ratio of volcanic aerosols shows two  
700 order of magnitude variations (0.03 to 3.3), with no systematic difference between arc  
701 and hotspots volcanoes (Baker et al., 2009; Edmonds et al., 2018). Our results on the  
702 Lascar volcano suggest that Tl entrapment in alteration sulphates might explain part of  
703 the Tl/Pb variations in volcanic emanations, in addition to gas source heterogeneity  
704 (Okrugin et al., 2017), diffusive fractionation of Pb and Tl at the melt-gas interface  
705 (Johnson and Canil, 2011), and chemical evolution of gas during cooling (Churakov et al.,  
706 2000). (2) Substitution reactions potentially deplete volcanic emanations in some  
707 elements, which lead to underestimate the volatility of these latter. For instance V is the  
708 second most depleted element in the Lascar plume (Menard et al., 2014) although there  
709 is evidence from the studied crust that V is significantly transported by subsurface  
710 gases. (3) Highly toxic elements such as Tl are immobilized within volcanic edifices  
711 instead of being released in the atmosphere, in the same manner as heavy metals are  
712 retained by alunite group minerals in polluted sites (Kolitsch and Pring, 2001;  
713 Figueiredo and da Silva, 2011). Thallium pollution of soils around Lascar volcano is an  
714 example of such local impact (Queirolo et al., 2009).

715

## 716 7) Conclusions

717

718 This study of the fine-scale chemical and isotopic zonation of an underground fumarolic  
719 crust from the Lascar volcano reached the following conclusions:

- 720 (1) Magmatic-hydrothermal gases from the Lascar volcano, 330°C in temperature,  
721 precipitate anhydrous alums underground as they react with rocks. The studied  
722 specimen occurs as a few millimetres thick crust that grew internally by poly-  
723 diffusion reactions within the sulphate. The growth rate is on average  
724 0.3 µm/day, but decreases towards crust rim due to the slow diffusive influx of  
725 rock cations.
- 726 (2) The crust selectively uptakes gaseous Tl, V and Te and, to a lesser extent Mo.  
727 This uptake results from the incorporation of the elements into the crystal  
728 structure of alum: Tl<sup>+</sup>, V<sup>3+</sup> and Mo<sup>6+</sup> substitute for K<sup>+</sup>, Al<sup>3+</sup> and S<sup>6+</sup> into the M<sup>I</sup>, M<sup>III</sup>  
729 and X<sup>VI</sup> sites of alum, respectively. The process of Te uptake remains uncertain,  
730 but must be tightly related to Tl-V incorporation.
- 731 (3) The extent of Tl, V and Te uptake is the highest at the outer edge of the crust,  
732 where the low rate of rock cations supply favours the substitution process. Such  
733 surface enrichment does not occur for Mo, because Mo competes with S, which is  
734 continuously supplied from the gas. Thus, the extreme enrichment of Tl, V and  
735 Te at the surface of the mature alum crust first reflects their ability to substitute  
736 for rock-derived cations and to compensate for their lack.
- 737 (4) Gases equilibrating with anhydrous alums lose a large amount of Tl, V and Te,  
738 but insignificant amount of other volatile trace elements (Pb, Cu, Zn, Bi, Sb, As,  
739 Se). This dramatically fractionates key trace elements ratios in volcanic  
740 emanations, such as Pb/Tl, or Se/Te. This also decreases the amount of Tl, V and  
741 Te released in the atmosphere. Immobilization of toxic Tl within the Lascar  
742 volcano contributes to the local Tl soil-pollution.
- 743 (5) Sub-surface gas-rock interaction within stratovolcanoes acts as a filter stripping  
744 some elements from the gas phase. A better understanding of the mechanism  
745 and extent of incorporation of metals and metalloids in the wide range of  
746 fumarole alteration minerals is needed to evaluate quantitatively the impact of  
747 underground gas-rock interaction on the degassing fluxes of volcanoes.

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**Supplementary material**

- Table S1 : In situ major and trace element concentrations
- Table S2 : In situ oxygen isotope composition
- Table S3 : Bulk Pb and Sr isotope compositions
- Supplementary material S4: Electron microscopy survey of crust surface

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768 Figure captions

769

770 Figure 1

771 Location maps. (a) Schematic map of northern Chile showing the location of the Lascar  
772 volcano. (b) Schematic map of Lascar craters showing the degassing fracture (star)  
773 where the fumarolic crust was sampled in November 2012 (modified from Menard et al.,  
774 2014).

775

776 Figure 2

777 Sampling site and crust sample. (a) Thermal image showing the location of gas sampling  
778 (filter packs) ca. 2m from the degassing hole. (b) Thermal image of the degassing hole  
779 where the crust was sampled in November 2012. (c) Photo of the degassing hole. Arrow  
780 indicates the lava block under which the crust was sampled. (d) Drawing of the crust  
781 and the host rock, respecting size proportions. (e) Photo of crust surface showing  
782 several outgrowths, more or less cracked and hollow. (f) Polished section of the studied  
783 outgrowth showing growth layers and the area selected for in-situ chemical analyses.

784

785 Figure 3

786 Raman spectra of the three major phases. (a) 100-1300  $\text{cm}^{-1}$  range. (b) 2900-3700  $\text{cm}^{-1}$   
787 range. Characteristic vibration bands of  $(\text{NH}_4)\text{Al}(\text{SO}_4)_2$  (godovikovite),  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$   
788 (exahydrate),  $\text{CaSO}_4$  (anhydrite) and hydrated alums (990/991  $\text{cm}^{-1}$ ) are indicated.

789

790 Figure 4

791 SEM image of the studied crust section. (a) Concentric growth layers and spot locations  
792 of EPMA and ICPMS analyses are highlighted. (b-d) Mapping of Al, Fe and Ca.

793

794 Figure 5

795 Lava-normalized trace element concentrations. Normalized concentrations are shown  
796 for crust core (average of unit 11) and crust rim (average of unit 1). Because Se was not  
797 measured by LA-ICPMS, the bulk Se concentration in crust surface scrapings ( $2.4 \pm 1.2$   
798 ppm) is used. Concentrations of the 1993 lava used for normalization are from Menard  
799 et al. (2014). Elements are sorted from left to right according to their increasing



800 enrichment in crust core. Propagated error on lava-normalized trace element  
801 concentrations is within symbol size.

802

803 Figure 6

804 Chemical variations across the crust. (a) Thallium, vanadium and tellurium  
805 concentrations plotted against distance to crust rim. Data are from profile A1. Profile A2  
806 (not plotted) shows the same variations. Error on trace element concentrations is within  
807 symbol size. (b) Tl/V, Tl/Te and V/Te concentration ratios plotted against distance to  
808 crust rim.

809

810 Figure 7

811 Core-rim  $\delta^{18}\text{O}$  profiles. The three profiles (B1, B2 and B3) are normalized to the length  
812 of the A1 profile. The average in-run error (0.25‰,  $2\sigma$ ) is indicated. The grey band  
813 indicates the  $\delta^{18}\text{O}$  of Lascar fumaroles condensates (Tassi et al., 2009). Compositions of  
814 local meteoric water (Tassi et al., 2009) and andesitic water (Giggenbach, 1992; Taran et  
815 al., 1989) are indicated.

816

817 Figure 8

818 Schematic drawing of the processes leading to the formation of a thick alum crust. (a) A  
819 sulphate layer grows via diffusive influx of rock cations and two-way diffusion of  
820 reaction gases within the sulphate. Gaseous  $\text{NH}_3$  and trace metals (Tl, V and Te) are  
821 incorporated into the crust following Eqs. 2-4. (b) Internal sulphate growth results in  
822 stress accumulation within the coating ( $\sigma$ ). The thickening sulphate layer detaches from  
823 the rock surface, wrinkles and buckles. The layer also starts to split into two layers due  
824 to higher growth rate near the sulphate-rock interface. (c) As the sulphate crust grows,  
825 the exhaustion of cations in the reacted rock requires cations to migrate over longer  
826 distances. The growth rate decreases towards crust surface due to the low rate of rock  
827 cations supply. This results in the formation of thinner growth layers at the outer edge  
828 of the crust. The lack of rock cations also favours the substitution of Tl, V and probably  
829 Te into the crystal structure of alum, yielding the extreme enrichment observed at crust  
830 rim. (a-c) Grey scale indicates the depletion of major cations in the silicate, white colour  
831 corresponding to  $\text{SiO}_2$ . (a) and (b) are modified from Renggli et al., (2018).

832

833 Figure 9

834 Te/Pb versus Tl/Pb plot comparing the signature of Lascar crust and aerosols to those  
835 of worldwide volcanic aerosols, fumarole condensates and solid deposits. Propagated  
836 error on trace element ratios is within symbol size (Lascar data). Lascar aerosol data are  
837 from Menard et al. (2014). Other data are from Kavalieris (1994), Moune et al. (2010),  
838 Zelenski et al. (2013, 2014), Chaplygin et al. (2016), Taran et al. (1995), Zelenski and  
839 Bortnikova (2005), Okrugin et al. (2017), Fulignati and Sbrana (1998), Boyce et al.  
840 (2007), Gauthier et al. (2016) and Mather et al. (2012).

841

842 Figure 10

843 Crust/gas distribution coefficient plotted against element fraction originating from the  
844 gas. Distribution coefficients are calculated by normalizing the concentration of  
845 elements in the outer shell of the Lascar crust (U1 layer) to their abundance in the gas  
846 escaping from the fracture hosting the crust. Crust concentrations are corrected for rock  
847 inputs, as explained in text.

848

849 Figure 11

850 Correlation between  $1/\text{Tl}$  and growth layer thickness, a proxy for crust growth rate.  
851 Median values are plotted for each unit. Error bars on x and y axis indicate upper and  
852 lower bounds for each layer.

853

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