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Reassessment of the sulfur and halogen emissions from the Millennium Eruption of Changbaishan (Paektu) volcano

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Abstract

The 946 CE 'Millennium Eruption' of Changbaishan (aka Paektu) volcano ranks among the largest volcanic events of the Common Era. Its fallout represents a widespread precisely-dated marker horizon yet little is known of its environmental impacts. Here, we revisit petrologic constraints on the pre-eruptive conditions of the dominant rhyolitic magma in order to estimate the eruption's volatile budget. We show that silicic reservoirs may lose more than half of their volatile complements prior to eruption and estimate that the Millennium Eruption emitted just 2–7 Tg of sulfur and 5–10 Tg of chlorine to the atmosphere, depending on the accepted eruption magnitude. These values are lower than previous petrologic estimates but consistent with ice core glaciochemistry and tree-ring-based climate reconstructions. We further suggest that any reawakening of Changbaishan / Paektu should be heralded by enhanced CO₂ emissions if driven by basalt intrusion, or by H₂-H₂O-rich and halogen-poor gases if resulting from evolution of a silicic reservoir. Our findings emphasise the importance of robust assessments of pre-eruptive conditions, especially in respect of temperature, when applying petrologic arguments to evaluate outgassing from silicic volcanism.

1. Introduction

Changbaishan / Paektu volcano (hereafter CPV) is renowned for the so-called Millennium Eruption, dated to late 946 CE (likely on or around 2nd November of that year; Oppenheimer et al., 2017). It is one of the few 1st millennium CE eruptions confidently identified in Greenland ice cores (Sun *et al.*, 2014), providing independent means to estimate volatile yields, and enabling synchronisation of cryospheric, marine and terrestrial archives and proxies (e.g., tree-ring based paleoclimate reconstructions) with a precisely-dated event. With an estimated volume of (dense) magma of 24 km³ (i.e., DRE, corresponding to a magnitude of 6.8; Horn and Schmincke, 2000), it also ranks as one of the largest eruptions in history (Oppenheimer, 2011). Both rhyolite and trachyte magmas were erupted, the former

35 dispersed widely via a Plinian eruption column (22 km³ DRE), the latter dispersed and
36 emplaced via pyroclastic density currents and associated co-ignimbrite plumes (2 km³ DRE). A
37 re-evaluation of the isopach record has suggested downsizing these magnitude estimates by
38 a factor of two (Yang et al., 2021) highlighting the uncertainty in volume calculations but not
39 diminishing the importance of understanding the eruption's potential environmental, climatic
40 and societal impacts from local to hemispheric scales (e.g., Horn and Schmincke, 2000; Xu et
41 al., 2013).

42 Prior studies of CPV include treatments of stratigraphy (e.g., Wei et al., 2013; Pan et al., 2020;
43 Yang et al., 2022; Zhao et al., 2020); geochemistry of Millennium Eruption deposits (e.g., Zou
44 et al., 2010, 2014); geophysical signals associated with the last unrest episode (e.g., Xu et al.,
45 2012; Wei et al., 2013); and imaging of the deep structure (e.g., Kyong-Song et al., 2016;
46 Hammond et al., 2020). The volatile budget for the Millennium Eruption was first estimated
47 using the 'petrological method' (Horn and Schmincke, 2000), suggesting yields of Cl and F to
48 the atmosphere each exceeding 40 Tg (1 Tg=10¹²g) and a minimum of 2 Tg of S (i.e., 4 Tg of
49 SO₂). While the role of excess gas in the reservoir (Scaillet et al., 2003) was neglected in these
50 estimates, such a modest syn-eruptive S degassing is not uncommon for silicic eruptions
51 (Westrich and Gerlach, 1991).

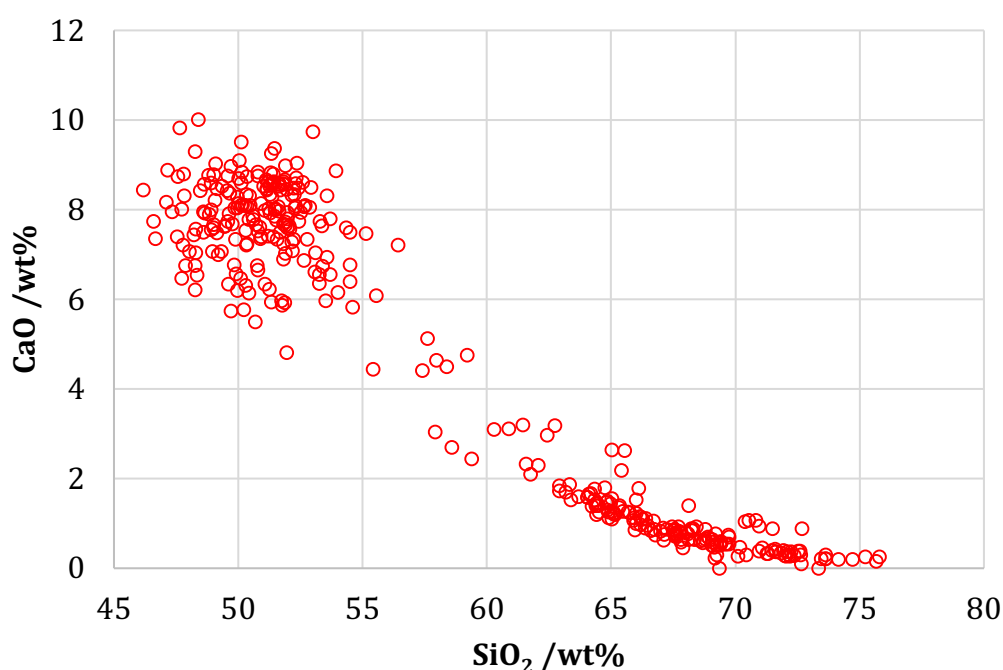
52 More recently, Iacovino et al. (2016) used additional ion microprobe (SIMS) constraints on
53 dissolved volatiles in melt inclusions and trace element behaviour, to argue that the
54 Millennium Eruption could have released up to 45 Tg of S, 20 Tg of Cl, and 58 Tg of F, with
55 more than 90% of S and Cl being sourced in the pre-eruptive excess gas (bubbles). Lower
56 amounts could arise if volatiles were lost during magma residence in the crust as a result of
57 fractionation processes and bubble migration beyond the crystallising melt before eruption.
58 In terms of sulfur, this upper limit would rank the Millennium Eruption only below the
59 Tambora 1815 and Rinjani 1257 eruptions in the Common Era. Such a high estimate, however,
60 is hard to reconcile with the absence of a strong summer cooling in the northern hemisphere
61 as attested by tree-ring proxies (Oppenheimer et al., 2017). Independent evidence for a low
62 S-yield is found in Arctic ice core glaciochemical records, which contain shards of both rhyolite
63 and trachyte matched to the Millennium Eruption (Sun et al., 2014). The corresponding sulfur
64 deposition suggests a low S yield to the stratosphere of order 2 Tg (Sigl et al., 2022).

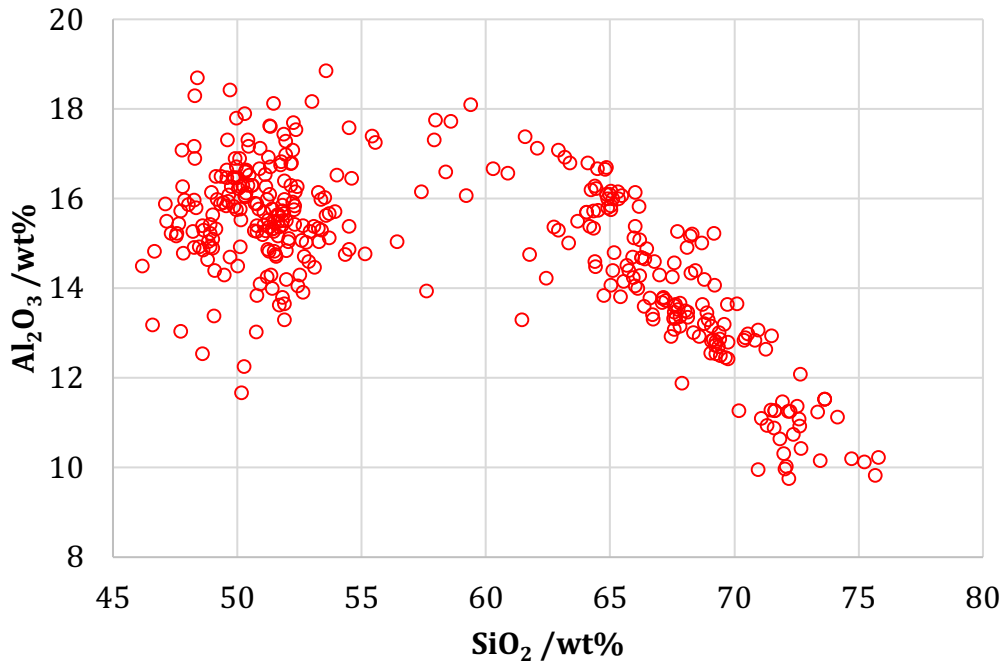
65 In the light of these conflicting estimates, we aim here to re-evaluate, from a petrologic
66 perspective, the volatile yields to the atmosphere of the Millennium Eruption. This requires
67 careful assessment of pre-eruptive conditions of the feeding reservoir (depth, temperature,
68 chemical conditions and abundance of any gas phase; e.g., Scaillet et al., 2003; Oppenheimer
69 et al., 2014). We draw on details of the petrology and texture of Millennium Eruption products
70 and apply experimental constraints and knowledge of volatile solubilities, fluid/melt
71 partitioning, and thermodynamic behaviour to determine pre- to syn-eruptive conditions for
72 the dominant rhyolitic magma.

73 2. Petrological inferences of P-T- fO_2 pre-eruptive conditions of Millennium Eruption 74 rhyolite

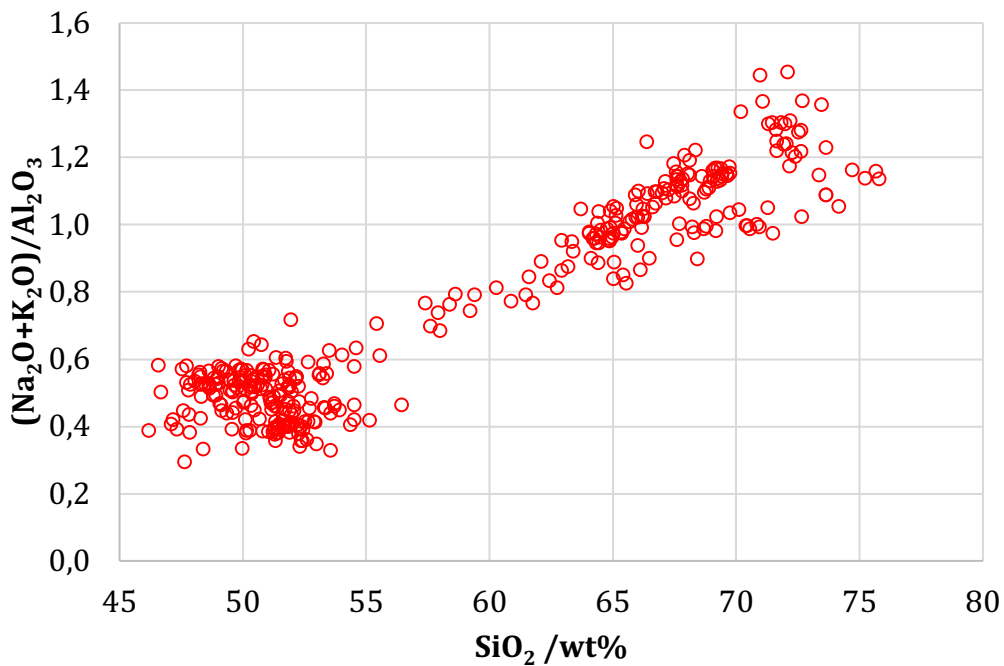
75 Here we use available thermometric estimates, along with phase equilibrium and geochemical
76 data, to constrain the P-T-H₂O conditions of magma storage. The majority of the Millennium
77 Eruption deposit consists of crystal-poor (2–3 wt%) alkali and Fe-rich rhyolite (Horn and
78 Schmincke, 2000). The lesser quantity of trachyte erupted is represented in the upper section
79 of the stratigraphy. The erupted rocks define a typical peralkaline trend, with alkali contents
80 increasing with differentiation (i.e., increasing SiO₂ content), but decreasing Al₂O₃ and CaO
81 contents. This corresponds to an increase in magma peralkalinity (NK/A=(Na₂O+K₂O)/Al₂O₃, in
82 moles), the rhyolite end-member classifies as comendite with NK/A=1.2–1.5 (Fig. 1) and FeO=4
83 wt% (Macdonald, 1974).

84 The mineralogy of the rhyolite is characterised by alkali feldspar, quartz, clinopyroxene and
85 olivine, accessory minerals being ilmenite, apatite, fluorite and sulphides. The ferromagnesian
86 silicates are close to the Fe endmembers (hedenbergite and fayalite; Zou et al., 2014),
87 reflecting both the extremely low Mg content of the whole rock, and low redox state typical
88 of peralkaline silicic magmas (Scaillet and Macdonald, 2003). Coexistence of almost pure
89 fayalite and quartz, and lack of magnetite imply an oxygen fugacity (fO_2) below that of the
90 Fayalite-Magnetite-Quartz (FMQ) solid buffer (which is 0.7 log units below the reference Ni-
91 NiO buffer, or NNO–0.7). Iacovino et al. (2016) drew on olivine-quartz-ilmenite equilibria to
92 calculate pre-eruptive temperature and fO_2 of 720°C and FMQ–1.2, respectively, the latter
93 consistent with estimates for most peralkaline rhyolites, which lie in the range NNO–1 to
94 NNO–2 (e.g., Di Carlo et al., 2010; White et al., 2009; Romano et al., 2020).





96



97

98 **Figure 1:** Selected major element variations with SiO_2 in CPV rocks. Whole rock data compiled
 99 by Zhang et al., 2018.

100 The major element compositions of Millennium Eruption rhyolites are close to those of
 101 Kenyan peralkaline rhyolites (Table 1), for which detailed phase equilibria have been
 102 established under carefully controlled $f\text{O}_2$ conditions (Scaillet and Macdonald, 2001; 2006).
 103 The experiments show that alkali feldspar and quartz stabilities are little affected by changes
 104 in magma composition, being only slightly depressed by the increase in peralkalinity (Fig. 2).

105 The temperature of crystallisation of both phases steadily increases with decreasing melt
 106 water content (H_2O_{melt}) from around 650°C at H_2O saturation (about 5–6 wt% at 150 MPa) up
 107 to over 800°C at $H_2O_{\text{melt}} < 2\text{--}3$ wt%. In all compositions investigated, both phases co-crystallise
 108 over a narrow H_2O_{melt} interval.

109 **Table 1.** Whole-rock compositions for the Millennium Eruption comendite compared with
 110 comendite from Olkaria (Kenya).

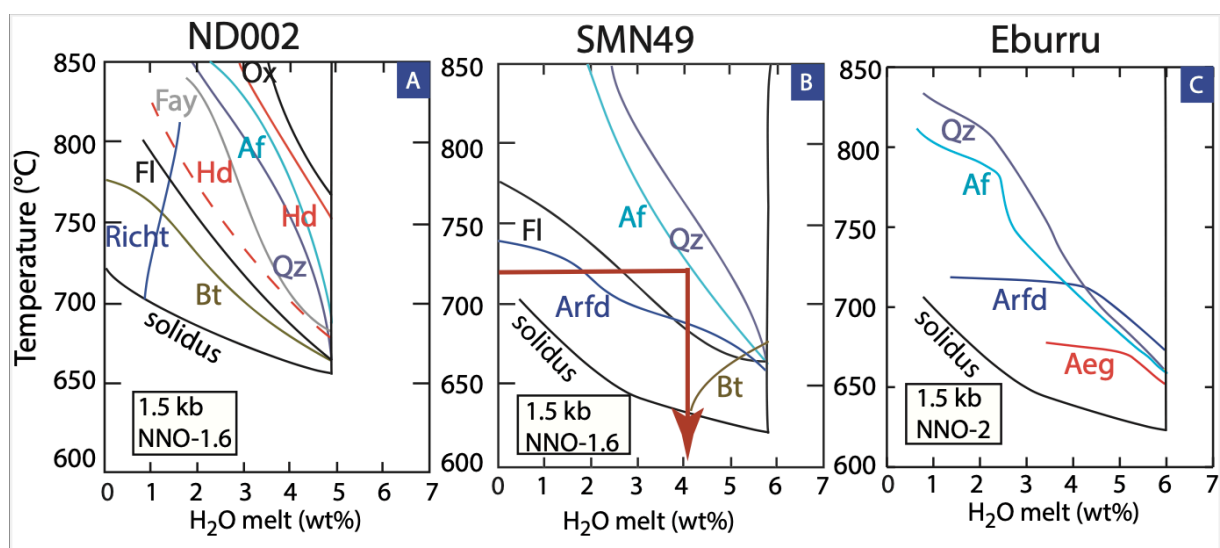
	PKTU-TP*	PEK-26*	PEK-56*	PEK-62*	Kenya**
SiO₂	73.68	74.67	74.66	74.59	74.17
TiO₂	0.225	0.219	0.214	0.21	0.17
Al₂O₃	11.38	10.47	10.51	10.58	10.89
FeO*	4.08	4.24	4.21	4.21	3.98
MnO	0.079	0.078	0.077	0.077	0.06
MgO	0.01	0.04	0.03	0.02	0
CaO	0.28	0.26	0.23	0.22	0.29
Na₂O	5.58	5.56	5.6	5.58	5.81
K₂O	4.69	4.46	4.46	4.51	4.34
P₂O₅	0.008	0.009	0.008	0.007	-
TOTAL	100	100	100	100	100

111 *Analyses from Iacovino *et al.*, 2016; **Analysis for sample SMN49 from Scaillet and
 112 Macdonald (2001), whose phase equilibrium relationships are shown in Fig. 2b.

113

114 Analyses of the H_2O_{melt} of feldspar-hosted melt inclusions (MI) in the comendite (Horn and
 115 Schmincke, 2000) indicate 4–6 wt% H_2O_{melt} , with an average of 5.2 wt%. The H_2O_{melt} in MI of
 116 other phenocrysts is either similar (fayalite) or lower (hedenbergite), the latter case possibly
 117 reflecting MI entrapment early in the crystallisation sequence in peralkaline rhyolites (Scaillet
 118 and Macdonald, 2001; 2006; Di Carlo et al., 2010), or, more likely, post-eruptive H diffusive
 119 loss. Taking an H_2O_{melt} of 5 wt%, along with the constraint of co-precipitation of feldspar and
 120 quartz, indicates a pre-eruptive temperature of about 675°C, or even as low as 650°C if the
 121 pre-eruptive H_2O_{melt} was closer to 6 wt% (Fig. 2b, comendite SMN49 similar to CPV). Iacovino
 122 et al (2016) report lower H_2O contents, between 1 and 4.2 wt%, averaging 2.4 wt%, which
 123 would correspond to a pre-eruptive temperature of 800°C, or higher (Fig. 2). The QUILF
 124 estimate of 720°C (Iacovino et al., 2016) suggests water contents of 4 wt% (Fig. 2b). In the
 125 following, we investigate a pre-eruptive temperature range of 650–700°C which satisfies melt
 126 water content constraints determined in MI by both studies. Analyses of CO_2 in melt inclusions
 127 yield a maximum of 23 ppm CO_2 in rehomogenised melt inclusions, most MI lacking
 128 detectable CO_2 via SIMS (Iacovino et al., 2016).

129



130

131 **Figure 2:** Phase relations of three peralkaline rhyolites (Scaillet and Macdonald, 2001; 2006).
 132 From left to right, N002-Naivasha, SMN49-Naivasha, and Eburru. Curves are labelled with
 133 phase abbreviations as follows: Ox: oxides; Af: alkali feldspar; Fay: fayalite; Hd: hedenbergite;
 134 Fl: fluorite; Bt: biotite; Richt: richterite; Arfd: aferdsonite; Aeg: aegirine. In panel B, the red
 135 arrow shows the melt H_2O content corresponding to a crystal-poor comendite at about 720°C
 136 and saturated in both quartz and feldspar.

137

138 At these conditions, comendite rhyolites are close to their liquidus. For instance, a H_2O -
 139 saturated comendite run ($H_2O_{\text{melt}}=5.8$ wt%) at 661°C, 150 MPa, yields magma crystallinities of

140 1–4 wt% (Scaillet and Macdonald, 2001, 2003), very close to that of Millennium Eruption
141 rhyolites (Horn and Schmincke, 2000). In contrast, a $H_2O_{\text{melt}} = 3.4$ wt% at 730°C and 50 MPa
142 would imply a crystallinity exceeding 15 wt%, while $H_2O_{\text{melt}} = 3$ wt% corresponds to 40 wt%
143 crystals (Scaillet and Macdonald, 2001, 2003), abundances that are not consistent with natural
144 phase proportions. Our temperature estimate is somewhat lower than, but compatible with,
145 that of Zou et al. (2014) who used an alkali feldspar-glass geothermometer to calculate a
146 temperature of 732°C. Altogether, these temperatures are among the coolest so far estimated
147 for an individual Plinian rhyolitic eruption of this magnitude. For instance, the range is 100–
148 150°C lower than the temperature of the metaluminous, but otherwise comparable, nearly
149 aphyric rhyolite erupted in 2008 from Chaitén volcano (Castro and Dingwell, 2009).

150 The H_2O_{melt} measured in MI provides a minimum estimate for the depth of the reservoir.
151 Available solubility laws for H_2O in silicic melts (Zhang, 1999) indicate pressures of around
152 100–120 MPa for H_2O_{melt} of 5–6 wt%. Taking a density of 2700 kg m⁻³ for the crustal rocks
153 above the reservoir, this corresponds to a depth of 4–5 km. We note that this range coincides
154 with that inferred for a magma body from diverse geophysical evidence, including volcano-
155 tectonic earthquake hypocentres recorded during the 2002–2005 crisis, the modelled source
156 of ground deformation (Xu et al., 2012), and seismic velocities in the crust (Hammond et al.,
157 2020). A further pressure estimate comes from the Cl contents of melt inclusions, which
158 cluster around 0.4 wt% (Horn and Schmincke, 2000; Iacovino et al., 2016). This value is similar
159 to that of a brine-saturated comendite melt at about 100 MPa (Métrich and Rutherford, 1992),
160 which suggests that the Millennium Eruption rhyolitic magma, if gas saturated, coexisted with
161 a brine in the reservoir.

162 The development of a shallow reservoir feeding peralkaline silicic volcanoes appears to be
163 characteristic of this composition of rhyolite magmas (Mahood, 1984), possibly related to
164 extensional tectonics. Note that a pressure of magma storage at 40 MPa, as suggested by
165 Iacovino et al. (2016), would imply Cl contents of about 0.6–0.7 wt% (Métrich and Rutherford,
166 1992), significantly higher than those observed, either in MI or matrix glass.

167 **3. Amount of excess gas in the Millennium Eruption magma reservoir**

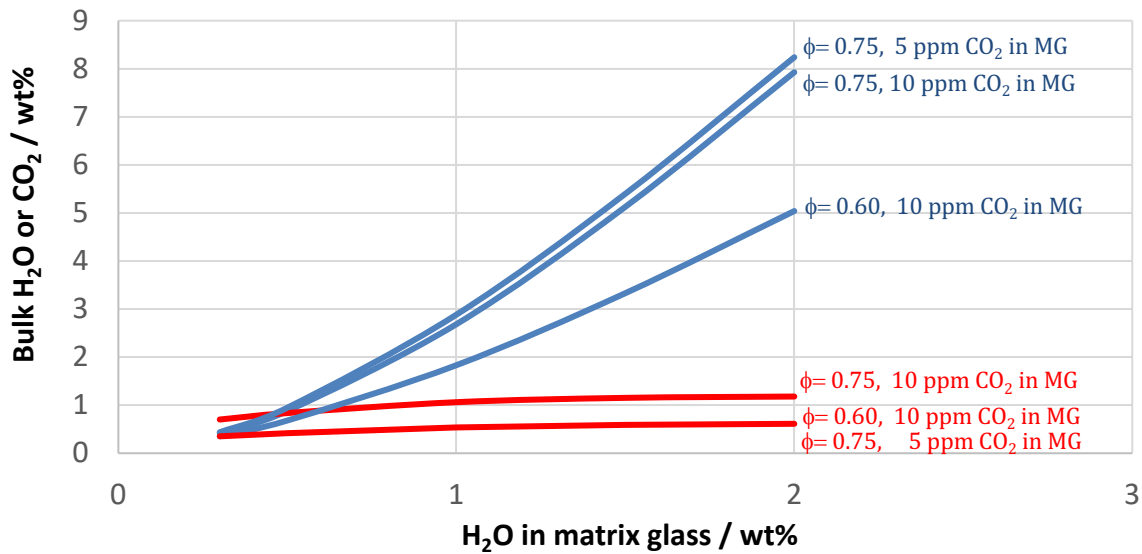
168 Determining the amount of excess gas in the reservoir is critical for petrological assessments
169 of volatile yields to the atmosphere during explosive eruptions (e.g. Scaillet et al., 2003).
170 Previous work has used the behaviour of trace or volatile elements during crystallisation (e.g.,
171 Wallace and Gerlach, 1994; Wallace et al., 1995), assuming consanguinity between melt
172 inclusions trapped in crystals (e.g. Papale, 2005). A similar approach has been used by Iacovino
173 et al. (2016), albeit based on the conservation of elements during fractional crystallisation of
174 trachyte to comendite. The tacit assumption underlying the calculations is that volatiles
175 concentrate in the residual liquid until reaching gas-saturation, upon which a free or excess
176 gas phase develops and accumulates as crystallisation proceeds. Using this approach, Iacovino
177 et al. (2016) inferred that the excess gas phase in the reservoir amounted to 3.8 wt% (of the

178 magma in the reservoir), which would correspond to a volume fraction of 43% were the
179 reservoir at 40 MPa, or, and more reasonably, 23% if at 100 MPa. This assumes (i) that the
180 parental trachyte was not already gas-saturated (in particular without CO₂), and (ii) that no
181 gas loss occurred during its accumulation in the upper reaches of the reservoir prior to
182 eruption.

183 Here we use an alternative approach drawing on the vesicularity of pumice ejecta from the
184 Millennium Eruption. The terminal porosity of pumices is the sum of pre-existing bubbles in
185 the reservoir and of syn-eruptive degassing. Bubbles grow during decompression, as a result
186 of volatile exsolution and cease expanding when fragmentation occurs in the conduit, at the
187 glass-transition temperature, owing to viscous resistance (e.g., Rust and Cashman, 2004), and
188 when volatile diffusion becomes too slow. At this stage, the residual matrix holds a finite
189 amount of water and other volatiles, such as S, Cl and CO₂. Measurement of those residual
190 volatiles in fresh matrix glass (MG) of Plinian silicic eruptions shows that water content (H₂O-
191 MG) can reach up to 1.5–2.0 wt%. CO₂ in matrix glass (CO₂-MG) while less often measured, is
192 generally below 30 ppm (e.g., Newmann et al., 1988; Barnes et al., 2014; Gardner et al., 2017;
193 Giachetti et al., 2020). Sulfur and halogens remain at levels close to pre-eruptive abundances,
194 underscoring their low diffusivities in hydrous rhyolites (e.g., Gerlach et al., 1996).

195 Compilation of residual water content in matrix glass of explosive rhyolitic eruptions
196 worldwide shows a prominent peak at around 2 wt% (Wadsworth et al., 2022). The origin of
197 water in volcanic glasses is a matter of debate, since secondary hydration is known to occur,
198 especially after prolonged surface exposure (e.g. Giachetti et al., 2015). However, the fact that
199 effusive eruptions clearly define a population with lower H₂O-MG compared with explosive
200 ones, strongly suggests that the peak in H₂O-MG of the latter is largely juvenile in origin. In
201 addition, experimental and numerical simulations (e.g. Hort and Gardner 2000), as well as
202 observations (e.g. Taylor et al., 1983; Newmann et al., 1988), suggest that for the most (early)
203 part, degassing of silicic melts before fragmentation in the upper reaches of the conduit occurs
204 near equilibrium for H₂O and CO₂ and in closed system. For these reasons, we assume that the
205 pressure of fragmentation can be approximated to first order by the sum of partial pressures
206 of the main volatiles, water and CO₂. The latter is given by the use of solubility models of
207 corresponding species (e.g. Blank et al., 1993; Zhang, 1999; Liu et al., 2005). This information,
208 combined with the porosity, enables calculation of the bulk volatile content of magma
209 (melt+bubbles) at fragmentation, neglecting the volatile content of crystals which contribute
210 little to degassing to the atmosphere. We take the density of melt as 2600 kg m⁻³ and
211 approximate the density of gas as that of pure water at the pressure and temperature of
212 fragmentation, assuming perfect gas behaviour, which is reasonable at the low P (<50 MPa)
213 and high T (>650°C) of fragmentation.

214



215

216 **Figure 3.** Relationships between H₂O (blue) and CO₂ (red) contents in matrix glass and bulk
 217 volatile contents calculated at fragmentation for different porosities and CO₂ contents in
 218 matrix glass (CO_{2-MG}). Note that the curves for the bulk CO₂ at porosities of 0.6 and 0.75 are
 219 superimposed.

220 Figure 3 illustrates the relationships between H₂O_{melt} in residual glass and bulk H₂O and CO₂
 221 contents at fragmentation, calculated at 700°C for two porosities (φ 0.75 and 0.6) and CO_{2-MG}
 222 of 5 and 10 ppm, which is within the range found by, for instance, Newmann et al. (1988),
 223 Watkins et al. (2012), Gardner et al. (2017) and Barnes et al. (2014). It shows that CO₂-bulk
 224 (melt+bubbles) content ranges from 0.3 to slightly over 1 wt%, whereas H₂O-bulk ranges from
 225 about 0.5 wt% to over 8 wt%, depending on porosity.

226 The next calculation step is carried out by recompressing the magma, keeping constant its
 227 bulk volatile content, and maintaining the equilibrium of species fugacities between melt and
 228 gas phases, which enables estimation of the amount of H₂O and CO₂ left over in the gas in the
 229 reservoir. As an illustration, at fragmentation the basic equation for H₂O is:

230
$$H_2O_{\text{bulk}} = H_2O_{\text{MG}} + H_2O_{\text{gas}} \quad (1)$$

231 In the reservoir, H₂O_{MG} is replaced by H₂O_{melt}, constrained from melt inclusion analyses.

232
$$H_2O_{\text{bulk}} = H_2O_{\text{melt}} + H_2O_{\text{gas}} \quad (2)$$

233 In both cases, the condition of equilibrium requires that:

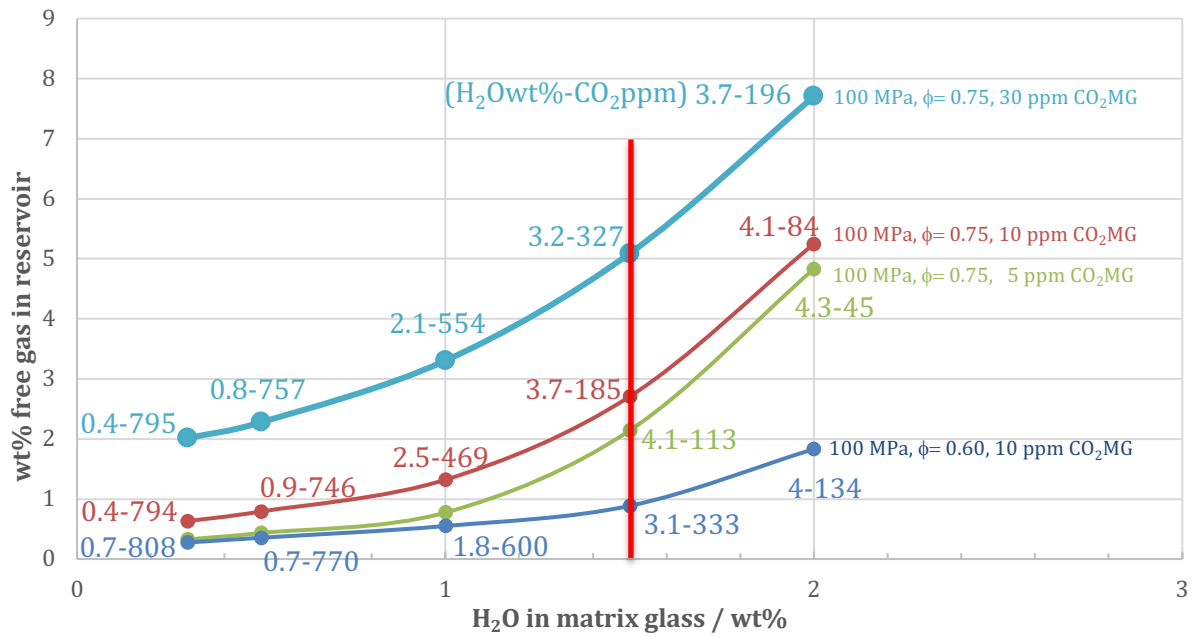
234
$$fH_2O_{\text{melt}} = fH_2O_{\text{gas}} \quad (3)$$

235 The same set of equations can be written for CO₂. If there is no CO₂, equations (1) and (2) can
 236 be solved directly. Adding CO₂ requires considering the diluting effect of this species on fH₂O,

237 which is done by varying the amount of excess gas that permits varying the fugacities of H₂O
238 and CO₂ until mass balance and the condition of equilibrium criteria are both satisfied. As a
239 result, there is only one solution of wt% excess gas in the reservoir that reproduces H₂O_{melt}
240 and CO_{2melt} values as inferred from MI, once P , T and H₂O_{bulk} and CO_{2bulk} are fixed. Given that
241 natural MI have a range of pre-eruptive H₂O and CO₂ contents, this procedure identifies a field
242 of permissible values of wt% excess gas, rather than a unique solution.

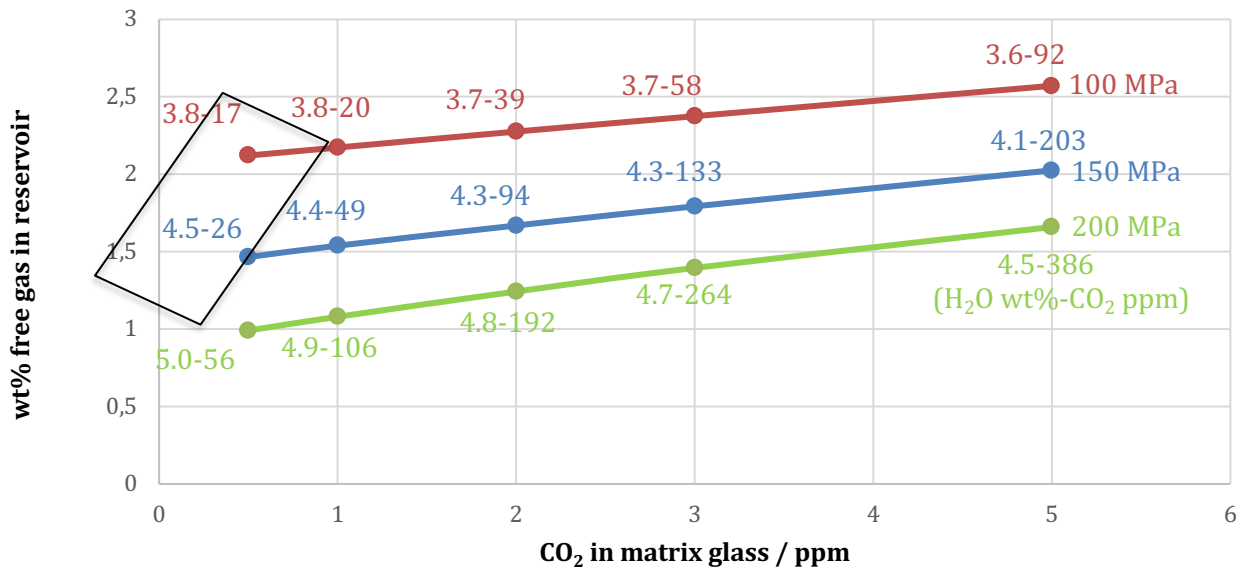
243 The results are shown in Fig. 4, using starting conditions as in Fig. 2. As expected, for any set
244 of final pressure and CO_{2-MG} conditions, increasing H₂O_{-MG} leads to an increase in the amount
245 of gas present in the reservoir: the computed amount of free gas at the reservoir P - T
246 conditions (700°C and 100–200 MPa) varies between below 1 wt% for a low content of H₂O_{MG}
247 up to over 5 wt% for a H₂O_{MG} of 2 wt% and CO_{2-MG} at or below 10 ppm. Increasing the CO_{2-MG}
248 to 30 ppm increases the amount of free gas to over 7 wt%. Decreasing the porosity from 0.75
249 to 0.60 significantly decreases the amount of gas, by a factor of two to three, depending on
250 H₂O_{-MG}.

251 The computed curves are also labelled with the corresponding contents of H₂O and CO₂ in the
252 melt. Along each curve, as H₂O_{-MG} increases, the H₂O_{melt} increases, while the CO_{2melt} decreases.
253 These figures can be directly compared with the concentrations found in melt inclusions,
254 assuming they record reservoir conditions. The work summarised above indicates that pre-
255 eruptive H₂O_{melt} was approximately 4 wt%, with CO_{2melt} barely detectable (≤ 20 ppm), pointing
256 to pre-eruptive gas contents lying on the H₂O-rich side of the diagram. Figure 5 shows the
257 calculations obtained using an average H₂O_{-MG}=1.5 wt%, as determined by Horn and
258 Schmincke (2000), and a porosity of 0.75. It indicates that an amount of free gas slightly above
259 2 wt% for a reservoir at 100 MPa, 1.5 wt% at 150 MPa, and 1 wt% at 200 MPa, is required to
260 maintain H₂O_{melt} ≥ 4 wt% and CO_{2melt} < 30 ppm (as inferred from MI) at reservoir conditions
261 (Fig. 5). A CO_{2-MG} of 30 ppm corresponds to higher free gas content in the reservoir (>5 wt%,
262 Fig. 4) but would imply an H₂O_{MG} of at least 2 wt% to yield a pre-eruptive H₂O_{melt} approaching
263 4 wt%, and the corresponding CO_{2melt} would be much higher (close to 200 ppm) than that
264 measured in MI. We therefore conclude that CO_{2MG} of the Millennium Eruption is likely to be
265 5 ppm at most, and possibly below 1 ppm (Fig. 4B).



266

267 **Figure 4:** Relationships between H_2O in matrix glass at fragmentation and the amount of
 268 excess gas, calculated at 100 MPa, for different porosities and CO_2 contents of matrix glass, as
 269 shown on the right of the figure. The vertical red line indicates the average H_2O content of
 270 Millennium Eruption rhyolite matrix glass as determined by Horn and Schmincke (2000).
 271 Numbers next to symbols give the corresponding pre-eruptive H_2O_{melt} (wt%) and CO_{2melt} (ppm)
 272 contents.



273

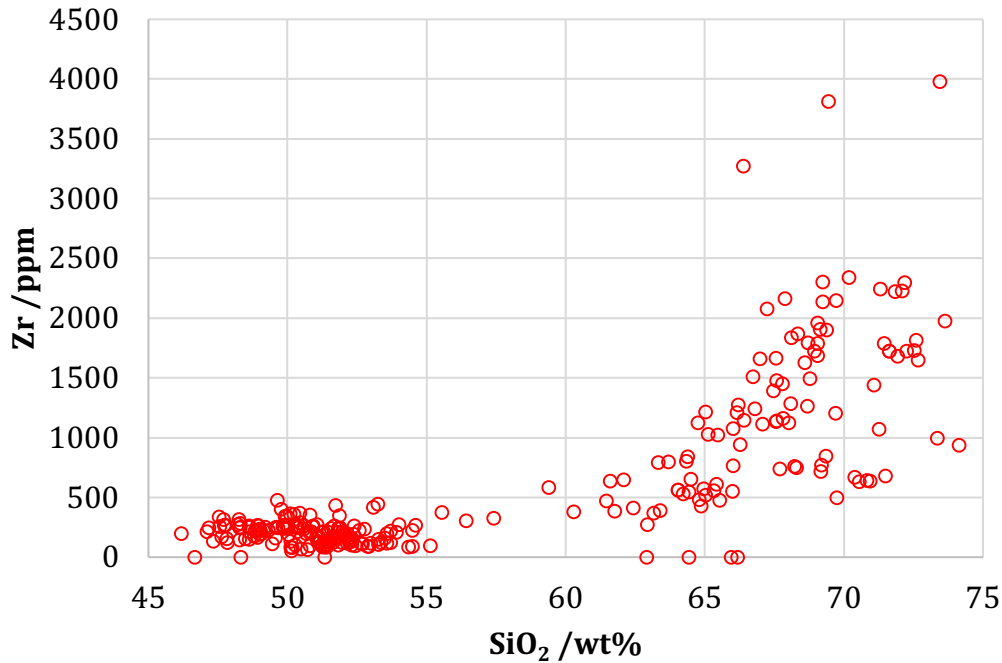
274 **Figure 5:** Relationships between CO_2 in matrix glass at fragmentation and the amount of
 275 excess gas, calculated for different reservoir pressures, for a H_2O in matrix glass of 1.5 wt%,
 276 and a porosity of 0.75. Numbers next to symbols give the corresponding pre-eruptive H_2O_{melt}

277 (wt%) and $CO_{2\text{melt}}$ (ppm) contents. The oblique rectangle spans the conditions corresponding
278 to H_2O and CO_2 contents determined in melt inclusions.

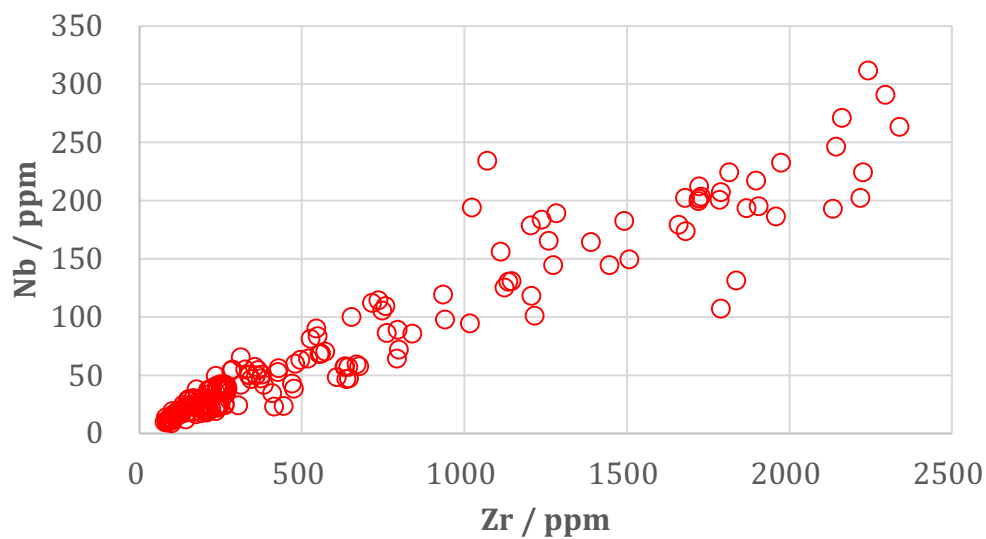
279 Computed gas contents with an H_2O_{MG} of 0.3 wt%, as reported by Iacovino et al. 2016, are in
280 all cases lower than 1 wt% (Fig. 4). More importantly, the calculated pre-eruptive H_2O_{melt} , is
281 also < 1 wt%, well below that analysed in melt inclusions, while $CO_{2\text{melt}}$ is close to 800 ppm,
282 altogether corresponding with crystal contents exceeding 85 wt% at 700°C, or conditions
283 below solidus at 650°C. This indicates that pumices with low H_2O_{MG} must have lost a
284 significant amount of dissolved water, either after fallout, or and more likely within the
285 conduit during ascent of the magma. It is possible these fragments experienced more shearing
286 at the flow margins, thereby enhancing permeability (e.g. Okumura et al., 2009; Carrichi et al.,
287 2011; Kushnir et al., 2017), and gas loss. Overall, on the basis of the above calculations, we
288 conclude that the Millennium Eruption reservoir contained 1-2 wt% of free gas (Fig. 5), which
289 had an X_{H_2O} of at least 0.9, and possibly >0.95. Next we address the concentrations of minor
290 volatiles in such a gas.

291 4. Composition of the gas phase in Millennium Eruption reservoir

292 The abundance of H_2O of melt inclusions, along with the reduced character of the magma,
293 dictates that H_2 was also abundant in the reservoir (Di Carlo et al., 2010), and that any S
294 present was speciated as H_2S . An unknown is the role of CO_2 . However, as stated above,
295 analyses of CO_2 in melt inclusions yield a maximum of 23 ppm CO_2 (Iacovino et al., 2016). This
296 is in agreement with other peralkaline centres (e.g., Neave et al., 2012), where CO_2 is present
297 in low amounts or below the detection level (about 20–100 ppm). This most probably reflects
298 the protracted fractionation needed to produce peralkaline silicic derivatives from more mafic
299 parents, during which most of the CO_2 is lost from the plumbing system before the rhyolites
300 are produced (Di Carlo et al., 2010). A five-fold increase, between trachyte and rhyolite, is
301 observed in incompatible trace elements such as Nb, Sn, Zr, U, Th, or W in peralkaline series
302 (Civetta et al., 1998 ; Macdonald et al., 2008), as illustrated for Zr and Nb in CPV whole rock
303 analyses (Fig. 6). This indicates that comendite production requires about 80 wt%
304 crystallisation of parental trachyte magma, as inferred also by Iacovino et al. (2016). We
305 conclude therefore that, even if the mafic parental magmas of Millennium Eruption rhyolites
306 held some CO_2 during early stages of fractionation, its abundance was negligible in the
307 rhyolitic reservoir.



308



309

310 **Figure 6.** Evolution of Zr during fractionation from basalt to trachyte to comendite at CPV.
 311 Whole rock data compiled by Zhang et al., 2018. Nb is taken to illustrate the highly
 312 incompatible behaviour of a trace element during crystallisation of basalt to trachyte (about
 313 65 wt% SiO₂, 70 ppm Nb and 500 ppm Zr) to comendite.

314 4.1. The case for sulfur

315 The case for sulfur is analogous to that for halogens, albeit for different reasons. Experiments
 316 have shown that peralkalinity increases sulfur solubility in silicic melts (Scaillet and
 317 Macdonald, 2006b). As a result, S behaves broadly as an incompatible element in mafic to
 318 silicic fractionation producing peralkaline magmas, at least to the point of gas saturation. The
 319 gas/melt partition coefficient of S (D_S) in comendite melts in the fO_2 range NNO–1 to NNO–2

320 (Scaillet and Macdonald, 2006) is 200–300 at 800°C. A decrease of 100°C decreases D_S by a
 321 factor of ten in metaluminous rhyolites (Scaillet et al., 1998), hence in the temperature range
 322 650–700°C we infer a D_S of about 20–30, similar to that established for reduced metaluminous
 323 silicic magmas owing to the expanded stability field of pyrrhotite, which locks up the majority
 324 of available S (Scaillet et al., 1998). 80% of MI and MG reported by Horn and Schmincke (2000)
 325 had S contents below the detection limit (250 ppm), while MI analyses of Iacovino et al. (2016)
 326 indicated an average S content of 110 ± 3 ppm, altogether suggesting a maximum S content of
 327 about 0.2–0.3 wt% for the average pre-eruption gas. This is about 10–20 times less than that
 328 inferred for the 1991 Mt. Pinatubo dacite (2–6 wt% S, Scaillet et al., 1998, 2003). Considering
 329 the S content of 455 ± 90 ppm in the 20% MI where S could be detected would suggest an S
 330 content of the gas of less than 0.4 wt%.

331 Given that the above figure comes from an extrapolation beyond the calibrated range, we also
 332 constrain the S content of the gas via a thermodynamic approach. We use the following
 333 equilibrium between pyrrhotite (FeS_{po}) and Fe^{2+} in the liquid (FeO_{liq}):



335 whose equilibrium constant is:

$$336 \quad K_1 = a_{\text{FeO}_{\text{liq}}} * (f_{\text{S}_2})^{1/2} / a_{\text{FeS}_{\text{po}}} * (f_{\text{O}_2})^{1/2} \quad (5)$$

337 We take advantage of the fact that pyrrhotite is a common sulphide in reduced rhyolites (e.g.
 338 Whitney, 1984), including in the Millennium Eruption comendite (Iacovino et al., 2016).
 339 Thermodynamic data (e.g. Robie and Hemingway, 1995; Barin, 1995) allow calculation of K_1 .
 340 We take the Gibbs free energy of formation of FeO_{liq} and FeS_{po} and heat capacities from
 341 Gaillard et al. (2003) and Barin (1995), respectively; and the molar volumes of solids from
 342 Robie and Hemingway (1995) and liquid FeO from Lange (1994). The f_{O_2} value is that
 343 determined by Iacovino et al. (2016). The main unknown in this approach comes from the
 344 term $a_{\text{FeO}_{\text{liq}}}$. For the Millennium Eruption comendite we build upon the fact that the rhyolite
 345 is saturated with an Fe-rich olivine (fayalite) and quartz so that the following equilibrium holds:



347 whose equilibrium constant is given by:

$$348 \quad K_2 = (a_{\text{FeO}_{\text{liq}}})^2 * a_{\text{SiO}_{2\text{-qz}}} / a_{\text{Fe}_2\text{SiO}_{4\text{-ol}}} \quad (7)$$

349 The Gibbs free energies of formation of fayalite and quartz are taken from Barin (1995) which
 350 along with that for FeO_{liq} from Gaillard et al. (2003), and the partial molar volume of FeO_{liq}
 351 from Lange (1994), allow us to compute K_2 (using standard states for solids and liquids at given
 352 P and T). To calculate $a_{\text{FeO}_{\text{liq}}}$, we first assume that quartz is pure ($a_{\text{SiO}_2}=1$). For olivine, the
 353 data of Zou et al (2014) show that Ol is nearly pure fayalite ($X_{\text{Fe}_2\text{SiO}_4} = 0.98$), which, with the

354 model of O'Neill et al. (2003), implies an activity coefficient close to 1 (hence $a_{\text{FeO}} = X_{\text{FeO}}$).
 355 Solving equation (7) for a $P = 100$ MPa and $T = 700^\circ\text{C}$ gives an $a_{\text{FeO}_{\text{liq}}} = 0.031$ (0.021 for 650°C).
 356 Rearranging (5), we have:

$$357 \quad f_{\text{S}_2} = (a_{\text{FeS}_{\text{po}}} * (f_{\text{O}_2})^{1/2} * K_1 / a_{\text{FeO}_{\text{liq}}})^2 \quad (8)$$

358 and using the activity for FeO_{liq} , the f_{O_2} as determined by Iacovino et al (2016) and the K_1 value
 359 as explained previously, yields an $f_{\text{S}_2} = 1.9 \times 10^{-7}$ bar, for $\text{Fe}_{0.877}\text{S}$ pyrrhotite (Barin, 1995) which
 360 corresponds to $a_{\text{FeS}_{\text{po}}} = 0.37$ (Toulmin and Barton, 1964). At 650°C , the f_{S_2} is 4×10^{-8} bar (note
 361 that the lack of pyrrhotite in rhyolite would imply that calculated f_{S_2} are maxima).

362 The next step is to calculate the corresponding fugacity of H_2S ($f_{\text{H}_2\text{S}}$), the dominant S-bearing
 363 species in reduced magmas. To do so we use the following equilibria:



365 and



367 Equilibrium (10) allows calculation of f_{H_2} , knowing f_{O_2} (Iacovino et al., 2016) and $f_{\text{H}_2\text{O}}$, the
 368 latter being given by thermodynamic model of Zhang (1999), which relates water content of
 369 the melt (4 wt%) to its fugacity. Use of calculated f_{H_2} and f_{S_2} and standard thermodynamic
 370 data for (9), yields an $f_{\text{H}_2\text{S}}$ of 0.28 MPa. The conversion of $f_{\text{H}_2\text{S}}$ into $X_{\text{H}_2\text{S}_{\text{gas}}}$ (mole fraction of
 371 H_2S in the gas) is achieved with the following standard relationship:

$$372 \quad X_{\text{H}_2\text{S}_{\text{gas}}} = f_{\text{H}_2\text{S}} / \gamma_{\text{H}_2\text{S}} * P_{\text{tot}} \quad (11)$$

373 Here, P_{tot} is total pressure (=100 MPa), $\gamma_{\text{H}_2\text{S}}$ (=1.05) is the fugacity coefficient of H_2S gas species
 374 which is here calculated using a modified Redlich-Kwong equation of state (MRK-EOS), using
 375 parameters given by Holloway (1987). The resulting $X_{\text{H}_2\text{S}_{\text{gas}}} = 0.0023$, which corresponds to an
 376 S content of 0.4 wt%, lies at the upper end of the range inferred from extrapolating the
 377 experiments of Scaillet and Macdonald (2006) to lower temperatures, but is almost four times
 378 less than the estimate (1.8 wt%) of Iacovino et al. (2016). Performing the above set of
 379 calculations at a pre-eruptive temperature of 650°C would further decrease the S content of
 380 the pre-eruptive gas to 0.3 wt%. These figures yield a partition coefficient of S between gas
 381 and melt of 30–40 (for comendite rhyolite at $650\text{--}700^\circ\text{C}$ and FMQ–1.2).

382 The above constraints on gas phase composition represent a rigorous framework for
 383 interpreting geochemical signals associated with unrest (see below), but also enable
 384 evaluation of the volatile yields to the atmosphere of the Millennium Eruption. The elevated
 385 $\text{H}_2\text{O}_{\text{melt}}$ of Millennium Eruption rhyolites indicates an H_2O -rich environment, promoting gas
 386 saturation, as suggested also by Cl systematics. Since the 1980 El Chichón eruption (Luhr et
 387 al., 1984), excess gas has been called upon to resolve the so-called 'excess sulfur' problem

388 especially in arc settings (e.g. Westrich and Gerlach, 1991; Métrich and Mandeville, 2010), for
389 which remote sensing methods detect 10–20 times more S than that which could have been
390 supplied by syn-eruptive melt degassing.

391 Previous geochemical modelling has shown that silicic reservoirs may hold up to 5–6 wt% gas
392 at their apices at around 150–200 MPa (Wallace et al., 1999), corresponding to 20–25 vol% at
393 this pressure. Higher gas contents seem to be precluded by the fact that bubbles start to form
394 an interconnected network allowing continuous gas escape from the reservoir beyond this
395 threshold (Wallace, 2001; 2005). Storage at low pressure, around 100 MPa such as in the case
396 of the Millennium Eruption rhyolite, significantly decreases water density relative to the
397 common storage pressure of 200 MPa observed in arc settings (0.3 g/cm³ vs 0.5 g/cm³,
398 respectively) which should reduce the maximum gas retainable in the reservoir.

399 Neglecting crystallinity, the atmospheric S (or Cl) yield in Tg of an eruption emitting A km³
400 (DRE) of magma with a density of ρ kg/m³, stored in a reservoir with B wt% gas which has C
401 wt% S (or Cl) is given by:

$$402 \quad S \text{ yield (Tg)} = 10^{-4} \times A \times \rho \times B \times C \quad (10)$$

403 Assuming that the Millennium Eruption reservoir contained 1–2 wt% gas with 0.3–0.4 wt% S,
404 gives a sulfur yield to the atmosphere of 1.7–4.5 Tg. To this amount should be added 2.6 Tg of
405 S due to syn-eruptive degassing of comendite, and 0.2 Tg of S from the minor trachyte
406 component (calculated assuming syn-eruptive degassing of 2 km³ of trachyte magma having
407 lost 42 ppm S (Iacovino et al. 2016), which gives a total amount of S ranging between 4.5 and
408 7.3 Tg, or half as much (2.2–3.6 Tg) using the eruption magnitude of Yang et al. (2021). The
409 lower figures are 2–4 times lower than that associated with the 1991 eruption of Mt. Pinatubo
410 (10 Tg S, Bluth et al., 1992). Our lower estimate is consistent with the evidence for a
411 comparatively low S yield estimated from polar ice records (Sigl et al., 2015; 2022).

412 The significantly higher S yield (up to 42 Tg) calculated by Iacovino et al. (2016) derive
413 essentially from assuming conservation of volatile elements during fractionation of trachyte
414 to comendite, which led them to compute an excess gas phase of 3.8 wt%. Our analysis shows,
415 however, that this gas phase amounts to 1–2 wt%, suggesting that at least half of it may be
416 lost during crustal residence of silicic magmas prior to eruption. The calculated bulk S content
417 of comendite magma ranges between 150 and 190 ppm, depending on the amount of fluid (1
418 and 2 wt%, respectively). This is less than that which could have been delivered by the parental
419 trachyte (which has 197 ppm S, Iacovino et al., 2016): assuming that S was entirely passed to
420 the comendite after about 80 wt% of trachyte fractionation, there would be 985 ppm of S in
421 comendite. The 4–5 fold decrease in S amount of the erupted comendite magma reflects loss
422 of this element during fractionation, either through sequestration in sulfides (pyrrhotite,
423 molybdenite) as shown by Iacovino et al. (2016), or owing to pre-eruptive gas loss from the
424 reservoir.

425 While the precursor magmas were volatile-rich, in particular in H₂O and halogens, their
426 reduced character, low temperature, shallow storage pressure, and the topology of Cl bearing
427 fluids, all combined to inhibit extensive outgassing of atmospherically-relevant species. Our
428 results emphasise the importance of estimating the outgassing from past eruptions on a case
429 by case basis.

430 **4.2. The case for chlorine**

431 As with many other peralkaline rhyolites, those of CPV are quite halogen-rich compared with
432 their metaluminous counterparts, suggesting the possibility of high syn-eruptive emissions of
433 halogens to the atmosphere. The possibility that the magma was brine-saturated in the
434 reservoir enables a first-order calculation of the Cl content of the gas phase. The H₂O-NaCl
435 system is characterised by a solvus at pressures below 200 MPa (Bodnard et al., 1985) where
436 the H₂O-rich gas coexists with a Cl-rich phase (brine). At 700°C and 100 MPa, i.e., conditions
437 approaching those inferred for the Millennium Eruption comendite, the gas phase is
438 topologically constrained to have no more than 1–2 wt% Cl (Bodnard et al., 1985). At this
439 temperature, the crest of the NaCl-H₂O solvus is at 120 MPa, beyond which NaCl and H₂O are
440 fully miscible, though the presence of K and Fe will expand the solvus towards higher pressure
441 (Liebscher, 2007).

442 Two additional factors indicate that the contents of Cl in the gas phase estimated above are
443 upper bounds. First, the solubility of Cl of silicate melts at brine saturation increases with
444 decreasing pressure, notably in peralkaline rhyolites (Métrich and Rutherford, 1992), which
445 requires that during ascent, degassing at equilibrium must produce increasingly Cl-poor gases.
446 Secondly, the limbs of the H₂O-NaCl solvus strongly expand as pressure decreases, such that
447 the gas becomes more H₂O-rich during ascent: for instance, at 50 MPa, the Cl content of the
448 hydrous gas drops by more than one order of magnitude relative to that at 100 MPa.

449 Although previous work (Horn and Schmincke, 2000) evaluated halogen yields by comparing
450 MG versus MI abundances, a close inspection reveals that Cl values in both MG and MI of
451 Plinian fallouts are essentially the same in light of uncertainties (0.41±0.06 wt% vs 0.44±0.11
452 wt%, respectively). This points to minimal syn-eruptive degassing, consistent with our
453 topological argument. This conclusion is also borne out by the data reported by Iacovino et al
454 (2016) which show that Cl in MG is even slightly higher than in MI, though still within error of
455 it (4166±225 ppm vs 3974±215 ppm, respectively). According to Iacovino et al. (2016), almost
456 all (> 95 wt.%) Cl (and S) expelled by the magma resided in pre-existing fluid, stressing the
457 importance of a correct estimate of the amount of that phase in the reservoir.

458 Though not analysed in CPV rocks, the study of Br in evolved magmas (Bureau and Métrich,
459 2003) shows this element to be essentially undegassed during eruption of peralkaline silicic
460 melts (Br contents in melt inclusion and matrix glass being identical). Hence, despite their
461 halogen-rich character, alkali-rich silicic magmas stored at shallow levels may not be
462 correspondingly large emitters of halogens to the atmosphere on eruption. For a magma

463 volume of 22 km³ (DRE), an excess gas of 2 wt%, and a conservative Cl content of gas of 1 wt%,
464 about 10 Tg Cl would have been lofted to the atmosphere (see below for the details of
465 calculation), or half this amount if the eruption magnitude is halved (Yang et al., 2021). This
466 amount of Cl is half that of Iacovino et al. (2016), essentially reflecting that our estimate of
467 free gas in the reservoir is half the value of 3.8 wt.% of Iacovino et al. (2016).

468

469 5. Considerations on future unrest of CPV

470 Radiometric dating (Wei et al., 2007) indicates that volcanism in the CPV area began around 4
471 Ma ago, with emplacement of basalts forming large shields and plateaus. This was followed
472 by a cone construction period (<1 Ma) dominated by eruption of trachytes, and then by the
473 ignimbrite stage as typified by the Millennium Eruption, which characterises activity for the
474 last several thousands of years. The overall temporal evolution of magma composition
475 indicates that the temperature of the plumbing system has progressively declined, since
476 abundant trachyte-comendite generation requires cooling of the parental basaltic magmas.

477 Comendites are dominantly produced by crystal fractionation of alkali basalt, via a trachyte
478 stage (Macdonald et al., 2008; 2021). The 10–30 km³ of near aphyric comendite discharged
479 with the Millennium Eruption implies efficient separation from a trachytic magma mush at
480 depth, whose volume should be approximately 50–100 km³, on the basis of the fivefold
481 increase in incompatible elements between trachyte and rhyolite (Fig. 5). Mush compaction
482 has been advocated as one mechanism for production of crystal-poor rhyolites (Bachmann
483 and Bergantz, 2004). The area of the caldera is about 36 km², which we take as the minimum
484 planimetric area of the underlying reservoir (Wei et al., 2013). This implies that the thickness
485 of the segregated layer of melt was 600–700 m. Considering its volume, the thickness of the
486 underlying trachyte magma body is probably of order of a few kilometres.

487 Owing to its elevated crystallinity (70–80%) by the time of comendite production, heat losses
488 from such a body would be mostly conductive. Assuming a half thickness of 2 km implies a
489 conductive cooling time of about 160 ka. A simple application of the model of McKenzie
490 (1984), shows that the corresponding timescale of melt segregation of a 4 km compacting
491 mush pile with 20–30 vol % liquid, varies from 90 ka (for a melt viscosity of 10⁴ Pa s) to 530 ka
492 (for a viscosity of 10⁵ Pa s), with corresponding thicknesses of the segregated melt layer
493 reaching 500 and 750 m, respectively. It is not clear, however, that compaction readily
494 operates in silicic reservoirs (see Holness, 2018), and in fact the mechanisms of melt extraction
495 from silicic to intermediate mushes remain obscure (e.g., Bachmann and Huber, 2019).

496 We note that the cooling and segregation timescales given above are comparable, though the
497 latter are not as fast as diffusion chronometry suggests, including for magmatic reservoirs of
498 dimension comparable to that of CPV, for which melt extraction timescales of decades to
499 months have been inferred (e.g., Santorini; Druitt et al., 2012). The viscosity of natural (i.e.,

500 iron-rich) peralkaline rhyolites is poorly known, but experiments on model compositions (i.e.,
501 Fe-free) indicate that peralkalinity dramatically decreases silicic melt viscosities (Dingwell et
502 al., 1998). Based on previous assessment of rhyolite viscosities worldwide (Scaillet et al.,
503 1998), which indicate a range from 10^4 to 10^5 Pa s, we suggest that CPV rhyolite magmas have
504 a viscosity close to 10^4 Pa s. For this value, the calculated timescale is compatible with
505 residence timescales inferred from zircon geochronology for the Millennium Eruption rhyolite,
506 which range up to 10 ka prior to eruption (Zou et al., 2010; 2014), indicating a long-lived
507 rhyolitic magma body, which has been stagnating for several thousand or tens of thousands
508 of years. Such a protracted residence may have favoured volatile escape from the roof of the
509 reservoir.

510 The large silicic reservoir has clearly acted as a trap for any rising basaltic magmas during the
511 latter period of CPV's evolution. While very little is known about activity of CPV since the
512 Millennium Eruption, there is some evidence that it has continued to erupt rhyolites (Wei et
513 al., 2013). If this is correct, it would suggest sustained mobility of the silicic reservoir, and
514 hence the potential for future rhyolitic eruptions. An episode of increased seismicity and
515 deformation, and compositional changes in hydrothermal fluids between 2002 and 2005 was
516 interpreted as magmatic unrest (Hahm et al., 2007; Xu et al., 2012). Our analysis shows that
517 fluids escaping from such an associated reservoir will be H₂O-, H₂- and H₂S-rich, with
518 comparatively minor halogens. Remobilisation of such a body would not be expected to result
519 in an increase in diffusive CO₂ flux on the volcano. In the case that there is a significant increase
520 in CO₂ at the surface, this might suggest arrival of mafic magma (basalt or trachyte) in the
521 upper reaches of the plumbing system, and the possible re-opening (or by-passing) of the
522 barrier imposed by the silicic system to more mafic eruptions.

523

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