# Persistent gas emission originating from a deep basaltic magma reservoir of an active volcano: the case of Aso volcano, Japan

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# Contributions to Mineralogy and Petrology

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| Abstract: | Volcanic gas emission is considered to reflect the degassing of magma beneath volcanoes. The combined observations of gas measurement and petrological study are expected to constrain the volatile concentrations and storage depths of the pre-eruptive and primitive magma. Aso volcano (Japan) is a constantly-monitored, persistently-degassing volcano, and an ideal site to acquire gas and petrologic data. We analyzed the melt inclusions and phenocryst minerals of Holocene basaltic eruption products, and reported their major and volatile element concentrations. The samples showed abundant evidence of magma mixing, such as reverse mineral zoning, and highly variable mineral and glass compositions. $SiO_2$ measured in melt inclusions varied from 46.0 to 65.8 wt. %. High-volatile concentration, S up to 3750 |

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| Response to Reviewers: | Dear Prof. Grove and reviewers: |
|---|---|
| | Thank you for your thoughtful and constructive feedback regarding our manuscript titled "Persistent gas emission originating from a deep basaltic magma reservoir of an active volcano: the case of Aso volcano, Japan". Please find attached our revised manuscript and responses to the reviewer's comments. We have carefully read all comments and revised the manuscript accordingly. |
| | In this revision, we rearranged the discussion order and added sentences to make it clearer. As suggested by the reviewers, we have also examined another degassing model and compared with our melt inclusion data, which is now enclosed into supplementary material. In addition, following the reviewer's suggestion, we have added a new summary figure for conclusion. Our manuscript has been greatly improved in other respects as well by the reviewers contributions. |
| | Lastly, thank you again for giving us the opportunity to strengthen our manuscript with your valuable comments and queries. We have worked hard to incorporate your feedback and hope that the revised version is now suitable for publication. |
| | Sincerely, Masataka Kawaguchi |

# Persistent gas emission originating from a deep basaltic magma reservoir of an active volcano: the case of Aso volcano, Japan

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## Abstract

Volcanic gas emission is considered to reflect the degassing of magma beneath volcanoes. The combined observations of gas measurement and petrological study are expected to constrain the volatile concentrations and storage depths of the pre-eruptive and primitive magma. Aso volcano (Japan) is a constantly-monitored, persistently-degassing volcano, and an ideal site to acquire gas and petrologic data. We analyzed the melt inclusions and phenocryst minerals of Holocene basaltic eruption products, and reported their major and volatile element concentrations. The samples showed abundant evidence of magma mixing, such as reverse mineral zoning, and highly variable mineral and glass compositions. $SiO_2$ measured in melt inclusions varied from 46.0 to 65.8 wt. %. High-volatile concentration, S up to 3750 ppm, were only found in mafic melt inclusions hosted by high-Fo olivine phenocrysts (~Fo82). The pre-eruptive storage depths were determined from volatile concentrations: 2 km and 4 km depth for Strombolian eruption and sub-Plinian eruption, respectively. The volatile-rich primitive magma, one endmember of the mixed-magma, originated from a deeper level (>10 km) than these magma reservoirs. Initial volatile concentrations of the primitive magma were determined using multiple constraints: >4.68 wt. % $H_2O$, 400 - 750 ppm $CO_2$, 3750 ppm S, 716 ppm Cl, and 324 ppm F. The observed variation of volcanic gas composition was best explained by the mixing of the gas segregated from at least a depth of 10 km, with that from the shallow reservoirs. This study illustrated the method to identify the primitive mafic magma responsible for deep volatile flux in a mature volcano with complex magmatic processes.

## Keywords

Melt inclusion, Volatile element, Magma mixing, Primitive magma, Storage depth, Excess degassing.

## Introduction

Arc volcanoes are known for their explosive eruptions driven by abundant dissolved volatile elements in their magma. It has been recognized that gas exsolution is the key player triggering rapid magma ascent and eruption (Roggensack *et al.* 1997; Pioli *et al.* 2009; Edmonds and Wallace 2017). Therefore, volcanic gas emission is considered to reflect the degassing of magma beneath volcanoes, and is one of the commonly observed and monitored activities, even in the quiescent period. Such persistent degassing of active volcanoes has been seen in arc volcanoes of the world (e.g. Miyakejima, Shinohara *et al.* 2003; Stromboli, Burton *et al.* 2007). Typically, volatile element behavior in magmas is governed by their solubility, and the amounts of volatile elements issued from magma are closely related to their pre-eruptive abundance. Thus, it is critical to determine the depths at which magmas were present, and their initial compositions through the studies of volcanic products. To investigate pre-eruptive volatile concentration and possibly primitive concentration, the study of melt inclusions is a

74 powerful tool since the melt is trapped in a host crystal at depth, and isolated from
75 interaction with surrounding magma (e.g. Anderson 1973; Sisson and Layne 1993;
76 Wallace 2005). In fact, melt inclusions are not perfectly isolated from surrounding
77 magmas since $H^+$ can diffuse through the host olivine (e.g. Gaetani *et al.* 2012) and $CO_2$
78 can be redistributed in shrinkage bubbles (e.g. Tucker *et al.* 2019). Therefore, $H_2O$ and
79 $CO_2$ measurements in melt inclusions are regarded as minimum values indicating the
80 condition of last equilibration. However, several studies have pointed out discrepancies
81 between total masses of emitted gas measurements and melt inclusion-estimation of
82 dissolved gas in glasses (e.g. Wallace 2005; Shinohara 2008). This is commonly referred
83 to as "excess degassing", and is observed in subduction zone volcanism (e.g. Métrich and
84 Wallace 2008; Roberge et al. 2009; Wallace and Edmonds 2011; de Moor et al. 2017). It
85 appears necessary to reconcile the melt inclusion-based volatile budget with the surface
86 observation and this is the task we want to tackle in this study.

87 Aso volcano (Japan) is the ideal study site to compare gas emissions and
88 petrological samples, including melt inclusions. It is a constantly monitored persistent
89 degassing volcano since the 1970s, emitting more than 100 - 200 tons of $SO_2$ a day, even
90 during the quiescent period (e.g. Mori *et al.* 2013; Shinohara *et al.* 2018; Japan
91 Meteorological Agency (JMA) 2020). In addition, Holocene eruptions from Aso
92 produced olivine-bearing tephra samples, ideal for finding quenched melt inclusions. For
93 example, a recent melt inclusion study of historical Aso eruption products reported a
94 shallow storage depth of erupted magma and a large excess of $SO_2$ degassing from Aso
95 volcano (Saito *et al.* 2018). However, this previous study did not report volatile element
96 concentrations of a primitive magma. Moreover, geophysical studies revealed multiple
97 magma reservoirs with depths down to 24 km (below sea level: bsl) (Sudo and Kong
98 2001; Sudo *et al.* 2006; Abe *et al.* 2010; Hata *et al.* 2016).

99 In this study, we analyzed the bulk tephra of less evolved erupted products,
100 matrix glasses, melt inclusions (glass and host minerals) to obtain information on the pre-
101 eruptive magma process, storage depth and characteristics of primitive magma of Aso
102 volcano. This paper reports the first petrological description of the deep magma reservoirs
103 of Aso volcano using melt inclusion data and corroborating gas composition model. Our
104 petrological constraints on a magma plumbing system give us the primitive $H_2O$, $CO_2$, F,
105 Cl, and S concentrations of Aso, a persistently-degassing active volcano.

## Samples and methods

### *Geological setting of Aso volcano and its cones*

108 Aso volcano, located in central Kyushu Island of the Southwest Japan Arc, is
109 one of the most active volcanoes of the volcanic front related to the Philippine sea plate
110 subduction (Nakada and Kamata 1991; Kamata 1998; Miyoshi *et al.* 2008a, b). It has
111 been active for at least 0.8 million years (e.g. Watanabe *et al.* 1989). Its activity is
112 characterized by two different types of volcanisms: caldera-forming gigantic pyroclastic-
113 flow eruptions (from 270 ka to 89 ka), and post-caldera extrusive activities (<89 ka) (Ono

3

114 and Watanabe 1985). In the post-caldera stage, various types of magma (basalt to rhyolite)
115 were erupted from, at least, 17 observable vents in the caldera (Watanabe 2001; Miyoshi
116 *et al.* 2005).

117 Holocene activities are well described in tephrostratigraphic studies
118 (Miyabuchi and Watanabe 1997; Miyabuchi 2009, 2010, 2017). The tephra is mostly
119 basaltic and limited to the ejections from central cones. The last silicic eruption deposited
120 Aso central cone pumice 1 (ACP1; Takada 1989) at 4.0 ka (Miyabuchi and Watanabe
121 1997; Hirata *et al.* 2020). ACP1 is the only silicic product in Holocene, which is dacitic
122 banded pumice related to the effusion of Akamizu andesite lava flow (Miyabuchi 2017).
123 Subsequently, volcanic activity of Kishimadake (3.7 ka), Ojodake (3.5 ka), Komezuka
124 and Kamikomezuka cones (3.0 ka) was derived from basaltic to basaltic andesite magmas
125 (Fig. 1; Miyabuchi and Watanabe 1997; Miyabuchi 2010; Hirata *et al.* 2020). Nakadake
126 cone is formed in three stages: old volcanic (22 − 7.3 ka), young volcanic (7.3 − 3.7 ka)
127 and youngest pyroclastic stages (<3.7 ka; Ono and Watanabe 1985; Miyabuchi 2009).
128 Today, Nakadake is the only active central cone since the last eruption of Kamikomezuka
129 (*ca.* 3.0 ka). All basaltic rocks in the post-caldera stage of Aso volcano evolved to low-
130 Mg high-alumina basalt (MgO < 6.1 wt.%; Kuno 1960; Sisson and Grove 1993).

131 The magma chambers beneath Aso caldera have been described by geophysical
132 surveys. Abe *et al.* (2010) reported a large low-velocity layer (LVL) from a depth of 11
133 to 25 km (for consistency hereafter, all the depths in the paper are referred as depths from
134 the vent of the edifice, adding 1 km to the depth below sea level), by receiver function
135 tomography. Hata *et al.* (2016) identified the magma pathway from 21 km deep beneath
136 the caldera by electromagnetic survey, and reported two anomaly centers (C1 and C2)
137 separated by 3 km in horizontal distance. C1 is located 5 km beneath Kishimadake cone,
138 which corresponds to the main magma chamber feeding present-day Nakadake eruptions.
139 This is in good agreement with earlier studies that reported the C1 chamber between 4
140 and 10 km depth, by deformation analysis of the volcano (Sudo *et al.* 2006) and seismic
141 low-velocity anomaly (Sudo and Kong 2001). C2 is located 3 km beneath Nakadake cone.
142 However, this C2 anomaly is geographically offsetted from the crater of Nakadake, and
143 instead, a crack-like conduit extending from 0.3 to 2.8 km. A continuing passage was
144 identified beneath this cracked-conduit, based on a region of lack of seismic reflectors at
145 a depth from 2.5 to 4.5 km beneath the crater based on a 3-D seismic reflection analysis
146 (Tsutsui and Sudo 2004). In this paper, we call this shallow magma passage as C2.

147

148

149 ***Tephra and scoria descriptions***
150 We collected tephra deposits of eruptions from Kishimadake (*ca.* 3.7 ka),
151 Ojodake (*ca.* 3.5 ka), Kamikomezuka (*ca.* 3.0 ka) and Nakadake (the youngest pyroclastic
152 cone; <3.7 ka). Tephra samples were specifically collected to avoid the diffusive volatile-
153 loss and daughter mineral crystallization within melt inclusions (Danyushevsky *et al.*
154 2002; Lloyd *et al.* 2013). Furthermore, we focused on recent (3.7 ka to present) eruption

155 activities of basalt to basaltic andesite composition involving olivine phenocrysts. The
156 sample set was therefore used to obtain information about crustal magma evolution and
157 the volatile characteristics of magmas. All tephra samples contain phenocrysts of
158 plagioclase, olivine, clinopyroxene, orthopyroxene, and opaque minerals. Detailed
159 descriptions of these tephras are found in Miyabuchi (2009, 2010).

160     Five tephra samples used in this study correspond to the eruptions of four cones:
161 Kishimadake scoria (KSS), Ojodake scoria (OJSU and OJSL), Kamikomezuka scoria
162 (KKO), and Nakadake scoria (NKD14). Specifically, KSS, OJSU, and OJSL were
163 collected from a tephra deposit site (A9418 section reported by Watanabe 1991;
164 Miyabuchi and Watanabe 1997; Fig. 1). KSS was collected from the lowest unit of sub-
165 Plinian scoria-fall deposits in the N6 stage. It is a vesicular basaltic black scoria with a
166 maximum size of 4.8 cm (Miyabuchi and Watanabe 1997). OJSU and OJSL were
167 collected from the uppermost and lowest unit of sub-Plinian scoria-fall deposits in the N4
168 stage, respectively. OJSU and OJSL are reddish-brown, weakly altered basaltic scoria,
169 with a maximum size of 4.6 cm (Miyabuchi and Watanabe 1997). These deposits
170 represent sub-Plinian eruption events, which are the biggest eruption events in Holocene
171 (each with approximately 0.06 km$^3$, VEI 3, Miyabuchi 2009). KKO was collected from
172 Kamikomezuka cone, because the tephra deposit away from the edifice has not been
173 identified presently. We sampled the black scoria from the outer part of the edifice from
174 a road-cut outcrop, avoiding oxidized reddish scoria. KKO is poorly sorted, non-welded,
175 vesicular scoria, ranging from cm-size to cow-dung bomb (tens of cm). NKD14 was
176 collected from the crater rim of Nakadake cone's first crater, immediately after the
177 eruption of Nov. 27, 2014. The samples were cm-size, well-vesiculated, black scoria. The
178 eruption of Nakadake cone in the period 2014 - 2015 is the first magmatic eruption in 24
179 years (Ikebe *et al.* 2008; JMA 2016). In the most violent phase, Strombolian eruptions
180 occurred with ejections of scoria lapilli and bombs at Nakadake cone's first crater (Yokoo
181 and Miyabuchi 2015).

182

183 *Melt inclusion preparation*
184     These 5 tephra samples were used for petrological observation and chemical
185 analysis (*i.e.* bulk rock, phenocrysts and melt inclusions). Samples were washed in an
186 ultrasonic bath, and only lapilli-size scoria (up to 6 cm) were chosen. Five grams of each
187 sample were powdered using a ball milling machine with an alumina cup and a ball, for
188 bulk rock X-ray fluorescence analysis (XRF). Olivine, pyroxene, and plagioclase crystals
189 were handpicked under an optical microscope from scoria crushed by hand and sieved
190 (from 0.25 to 1 mm). The picked crystals were mounted in resin and polished until the
191 melt inclusion was exposed. They were then measured using an electron probe micro-
192 analyzer (EPMA) and a reflectance Fourier transform infrared spectroscope (FTIR).
193 Selected olivine crystals hosting melt inclusions of KSS and NKD14 were removed from
194 the resin after EPMA and FTIR analyses, then mounted together in indium for secondary
195 ion mass spectrometry (SIMS).

*Analytical methods*

Bulk rock major and trace elements

Bulk rock major and trace elements were determined by XRF on flux-fused disks using a Philips PANalytical MagiX PRO spectrometer at the Kitakyushu Museum of Natural History and Human History. The detailed analytical procedures are described by Mori and Mashima (Mori and Mashima 2005). Accuracy was reported as ±0.1 % relative for $SiO_2$ and for trace elements, and varied from 5 to 25 ppm (Table 1).

Major and volatile elements in melt inclusion, mineral and glass

Major elements, S, and Cl concentrations were determined in melt inclusions, host minerals and groundmass glasses using a JXA8800R electron probe microanalyzer at the Earthquake Research Institute (ERI), University of Tokyo. The analytical settings were 15kV acceleration voltage, 12 nA beam current, with counting times for Na, Al, K, Fe, Mg, Si, Ti, V, Mn, and Ca at 20 s, and 30 s for Ni, Cr in mafic minerals and for S and Cl in hydrous melt. Beam diameter was set at 10 μm for glass and plagioclase, and focused (1 μm) for other minerals. During melt inclusion and groundmass glass analysis, Na and K were always measured in the first analytical cycle to minimize alkali loss (Devine *et al.* 1995). All analyses applied oxide ZAF correction. Analytical uncertainties are <0.7% relative for Si, <1% relative for Al, Fe, Mg, and Ca, <5% relative for Ti and Na, <10% relative for K, and <20% relative for Mn, V, Ni, Cr, S, and Cl.

In addition to the EPMA analysis, the core and rim compositions of phenocrysts were analyzed by energy-dispersive X-ray spectroscopy (EDS, AZtec system; Oxford Instruments) connected to a JEOL JSM-7001F field-emission electron microscope (FE-SEM) at Kumamoto University, using 15 kV acceleration voltage and 1 nA beam current. The beam diameter settings were the same as the EPMA setting at the University of Tokyo for all the host minerals. Analytical uncertainties are typically 0.5% relative for $SiO_2$, 1% relative for $Al_2O_3$, 1.5% relative for FeO, 0.5% relative for MgO, 2% relative for $TiO_2$ and $Na_2O$, 1.5% relative for $K_2O$, 1% relative for CaO. Other minor elements such as MnO and $P_2O_5$ can be as high as 20% relative.

Water concentrations in melt inclusions were determined by FTIR micro-reflectance spectroscopy using a JASCO FT-IR-660 plus, equipped with an IRT-30VC analytical microscope at the ERI, following the procedures described by Yasuda (2014). The IR spectra were obtained using $15 \times 15$ to $60 \times 60$ μm$^2$ rectangular apertures, and by accumulating 220 to 1500 scans, over a range of 400 to 7800 cm$^{-1}$. A gold mirror was used as a reflectance reference. Water concentrations were quantified using an empirical linear relationship for basalt to rhyolite compositions for total $H_2O$ concentrations, measured in the 3650 cm$^{-1}$ wavelength region. The analytical uncertainty ($2\sigma$) of the FTIR reflectance spectroscopy was < 0.3 wt. %. While the detection limit of the method

234 strongly depended on the sample, we estimated the detection limits as 0.14 wt. % (Yasuda
235 2014).

236        $H_2O$, $CO_2$, F, S, and Cl concentrations in selected melt inclusions were
237 determined by a SIMS (Cameca IMS-1280HR of Kochi Institute, JAMSTEC, Japan)
238 following the procedure described by Shimizu *et al.* (2017). This analytical method favors
239 a weaker primary current (up to 0.5 nA) than in previous studies (1-1.5 nA primary
240 current; Le Voyer *et al.* 2010; Helo *et al.* 2011; Rose-Koga *et al.* 2012, 2014; 20 nA
241 primary current in Hauri *et al.* 2002) and uses in-house standards covering the
242 concentration range found in the natural samples in this study. In short, a 20 keV (10 keV
243 at the ion source and 10 keV at the sample surface) $Cs^+$ ion beam of 300–500 pA was
244 defocused to be 10-15 μm in diameter. Secondary ions were accelerated at 10 kV. A -10
245 keV electron beam with a diameter of ~100 μm was applied for electrostatic charge
246 compensation of the analysis area. The field aperture was set at the size corresponding to
247 5 x 5 μm on the sample surface. Mass resolving power was set at ~6000 to separate mass
248 interferences (for example, to separate $^{34}S^1H$ interference on $^{35}Cl$ requires 5120 MRP;
249 Burdo and Morrison 1971). Negative secondary ions of $^{12}C$, $^{16}OH$, $^{19}F$, $^{30}Si$, $^{31}P$, $^{32}S$, and
250 $^{35}Cl$ and the mass position of 11.9 amu were measured by an axial electron multiplier
251 using the peak switching method. An analysis consisted of 10 cycles, and the total
252 measurement time for each analysis was ~6 min. Repeated analysis of a secondary
253 basaltic glass standard from East Pacific Rise, EPR-G3 (Shimizu *et al.* 2017), yielded a
254 relative standard deviation (1σ) for $H_2O$, $CO_2$, F, Cl, and S of 1.4, 3.2, 1.5, 2.5, and 0.9%,
255 respectively. This SIMS analysis was conducted after EPMA analysis. Therefore,
256 although we were careful to polish the sample with alumina powder again before SIMS
257 analysis, measured $CO_2$ concentrations were reported in the supplementary material but
258 not used due to possible carbon contamination. The measured values for S and Cl agreed
259 within 25% between EPMA and SIMS analysis. So when volatile elements were
260 measured by two methods, we adopted SIMS values rather than EPMA because analytical
261 uncertainty of these elements by SIMS are generally lower (e.g. Rose-Koga *et al.* 2020).
262 In this study, we did not find satisfactory agreement between $H_2O$ determined by FTIR
263 and by SIMS (uncertainty of FTIR measurements is close to 40%) so in the following,
264 we only consider $H_2O$ concentrations measured by SIMS, based on the better detection
265 limit and precision of the method.

266 <u>Sulfur speciation analysis</u>

267        Selected inclusions were analyzed for S$K\alpha$ peak positions to constrain the $fO_2$
268 conditions of the glasses. The wavelength of S$K\alpha$ radiation [λ(S$K\alpha$)] for melt inclusions
269 was measured using the EPMA following the procedures described by Yasuda *et al.*
270 (2001), based on the method of Wallace and Carmichael (1994) and Carroll and
271 Rutherford (1988). Sulfur speciation as the proportion of $S^{6+}$ over a total S content was
272 determined by measuring a relative shift from the peak position of an anhydrite mineral

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273 (Carroll and Rutherford 1988), with an assumption that $S^{2-}$ and $S^{6+}$ are the only two
274 relevant species in silicate melt (Jugo *et al.* 2010). To avoid sulfur oxidation due to
275 prolonged beam exposure (*i.e.* Rowe *et al.* 2007), we conducted a measurement with
276 multiple spots for each melt inclusion. Therefore, we added up the wavelength scan data
277 of individual spots to determine the precise peak position. A Gaussian curve fitting was
278 used for sulfur peak deconvolution. Analytical uncertainty ranges from 5 to 10% relative
279 (Table S1).
280
281 *Data processing: Post-entrapment crystallization correction*
282       Major and volatile element data for all melt inclusions hosted in olivine were
283 corrected for the effects of post-entrapment crystallization (PEC; e.g. Danyushevsky et
284 al. 2000) by incremental calculation of equilibrium olivine (0.1 wt. % step) adding into
285 the residual melt, until the melt reaching equilibrium with host olivine (Toplis 2005),
286 following the procedures described in Danyushevsky *et al.* (2000). The melt $Fe^{2+}/Fe^{Total}$
287 ratios were calculated from the empirical equation of Kilinc *et al.* (1983), assuming a
288 constant $fO_2$ ($\Delta$FMQ +1.0) based on measured $SK\alpha$ peak shifts of all eruptions (Jugo *et
289 al.* 2010). Temperatures of olivine-melt equilibrium were calculated using the olivine-
290 saturated melt thermometer of Sugawara (2000), corrected for the effect of water on
291 olivine liquidus temperature according to Médard and Grove (2008). We assumed an
292 average $H_2O$ concentration of NKD14 and KSS analyzed by SIMS for melt inclusions
293 that were not analyzed individually for $H_2O$. Note, $K_D$ and temperature were recalculated
294 at each increment of olivine addition. The melt inclusions were not corrected for post-
295 entrapment diffusive Fe-loss (Danyushevsky et al. 2000), as total FeO concentrations in
296 melt inclusions are either the same or higher than those in bulk rocks. Corrected volatile
297 concentrations were adjusted assuming volatiles are perfectly incompatible to host
298 minerals and corrected values are used in the figures and reported in Table 2 (raw
299 uncorrected data in supplementary material S1).
300       Plagioclase-, clinopyroxene-, and orthopyroxene-hosted melt inclusions were
301 not corrected for PEC because there is no universally accepted procedure, although some
302 attempts have been reported (Yasuda *et al.* 2001; Neave *et al.* 2017; Hartley *et al.* 2018).
303 Among these samples, only the melt inclusions in equilibrium with host minerals were
304 used for the magmatic temperature calculation, in which the exchange coefficients were
305 within expected range of basaltic composition: $K_D(Fe-Mg)_{cpx-liq}$ = 0.28 ± 0.08, $K_D$(Fe-
306 $Mg)_{opx-liq}$ = 0.29 ± 0.06, and $K_D(An-Ab)_{pl-liq}$ = 0.27 ± 0.01 or 0.1 ± 0.05 (depending on
307 the calculated temperature; Putirka 2008).

308 **Results**
309       The analysis of five scoria from Aso edifices produced data of major elements
310 for bulk rocks along with 204 melt inclusion data (major and volatile element
311 concentrations) and host mineral compositions. More than 890 point-analyses were made
312 to determine major element compositions of groundmass glasses and phenocrysts (core

8

313 and rim; Tables 1 – 3 and S1 – S3).

314

### *Petrography*

316     All samples were porphyritic with approximately 40 vol.% crystals. Plagioclase,
317 clinopyroxene, olivine plus minor orthopyroxene, and opaque minerals were present. In
318 all samples, plagioclase phenocrysts commonly showed dusty zone and honeycomb
319 texture (Fig. 2a), and all orthopyroxene phenocrysts had reaction rims of olivine and
320 clinopyroxene (Fig. 2b). Aggregates of phenocrysts (i.e. plagioclase, clinopyroxene,
321 olivine, and opaque minerals) were frequently found in all samples (Fig. 2c). The
322 groundmass consisted of microlites of plagioclase, clinopyroxene, olivine, and magnetite.
323 The groundmass of KSS occasionally showed the heterogeneous mingling texture where
324 crystals are relatively abundant (Fig. 2d).

325

### *Host mineral compositions*

327     The olivine phenocrysts were grouped into two types based on the core Fo
328 contents [$Mg / (Fe + Mg) \times 100$ in mole], as low-Fo (62 to 72) and high-Fo (72 to 82)
329 (Fig. 3a). High-Fo olivine was observed only in KKO, OJSU, OJSL, and KSS. Low-Fo
330 olivine was found in all samples. As Fo content of the phenocryst rims ranged from 68 to
331 78 in KKO, OJSU, OJSL, and KSS, and from 64 to 67 in NKD14 (Table S3), generally
332 low-Fo olivine phenocrysts were reversely zoned, whereas olivine phenocrysts in NKD14
333 were homogeneous. All high-Fo olivine phenocrysts were normally zoned.
334 Clinopyroxene and orthopyroxene phenocryst cores in all samples were in the range of
335 65-76 and 61-71, respectively ($Mg\# = [Mg / (Fe + Mg) \times 100$ in mole]). The majority of
336 clinopyroxene phenocrysts in KKO, OJSU, OJSL, and KSS were reversely zoned. Mg#
337 of NKD14 varied little, at ~70. The compositions in the rims of olivine and clinopyroxene
338 phenocrysts were the same as the minerals found in reaction rims of orthopyroxene
339 phenocrysts. The plagioclase phenocrysts were also divided into two types based on the
340 normal and reverse zoning patterns. The An content [$Ca / (Ca + Na) \times 100$ in mole] of
341 the plagioclase phenocryst cores was within the 55-93 range.

342

### *Major and volatile elements in melt inclusions*

344     The tephra samples of this study were basaltic to basaltic andesite with $SiO_2$
345 ranging from 51.5 to 54.3 wt. % (large circles in Fig. 3c). Melt composition in inclusions
346 varied significantly more than that of the bulk tephra composition: $SiO_2$ ranging from
347 46.0 to 65.8 wt. %. This range mostly overlapped with the compositional variation of
348 post-caldera volcanic products (grey circles in Fig. 3c). The melt inclusion compositions
349 of NKD14 were generally similar to evolved matrix glass and varied little, and were
350 distinguished from the melt inclusions of KKO, OJSU, OJSL, and KSS.
351     In our sample set, the core composition of host olivines were clearly divided
352 into two groups with Fo72 representing the divide (Fig. 3a). We interpreted that olivines
353 have grown from two distinctively different lavas, which we called mafic and felsic.

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354 Based on the anti-correlation of $SiO_2$ concentration in olivine-hosted melt inclusions with

355 host Fo content, we concluded that magma composition can be divided into two groups

356 above and below 55 wt.% $SiO_2$. The high $SiO_2$ corresponded to low-Fo olivine and low

357 $SiO_2$ corresponded to high-Fo olivine. Thus, in the following we grouped all the melt

358 inclusions lower than 55 wt.% $SiO_2$ in a mafic group, and others in a felsic group. S

359 concentration in melt inclusions correlates well with host Fo content and is anti-correlated

360 with $SiO_2$ (Fig. 3a) and $K_2O$, indicating a mafic volatile-rich (with S up to 3750 ppm and

361 Cl up to 1311 ppm) magma, and a felsic volatile-poor magma (Fig. 3b). NKD14

362 inclusions were notably different, with less than 434 ppm S, indicating extensive

363 degassing. Melt inclusion Cl concentrations varied from 530 ppm to 1311 ppm (Table 2

364 and Table S1; SIMS value is preferred to EMP value when both are reported). F

365 concentrations were determined only on a subset of olivine-hosted melt inclusions and

366 therefore there are fewer data. F concentrations varied between 258 and 853 ppm (Table

367 2 and Table S1). F and Cl correlates with $SiO_2$ and $K_2O$ and anti-correlate with host Fo

368 content. $H_2O$ concentrations measured in melt inclusions vary between 0.47 to 2.89 wt.%

369 (NKD14-Olivine-4-m4 and KSS-Olivine-4-m11, respectively; Table 2 and Table S1).

## Discussion

370

### *Evidence for magma mixing*

371

372 Zoning in magmatic minerals characterizes their crystallization in a magma

373 chamber and can trace the history of magma cooling (e.g. Costa *et al.* 2008), and magma

374 mixing (e.g. Sakuyama 1979). Among the tephra samples in this study, phenocrysts in

375 every sample indicate textural evidence of magma mixing that could have been produced

376 by the introduction of hotter magma: for example, the reverse zoning and disequilibrium

377 texture, such as the honey-comb texture of plagioclase and reaction rim of orthopyroxene

378 (Fig. 2a and 2b; Tsuchiyama 1985). The coexistence of normally zoned plagioclase and

379 olivine phenocrysts with these disequilibrium phenocrysts suggests that magma mixing

380 of at least two distinct components has occurred (e.g. Sakuyama 1979). This

381 interpretation is supported by the compositional variation of the melt inclusions; felsic

382 melt inclusions are hosted in reversely zoned phenocrysts such as plagioclase,

383 clinopyroxene, orthopyroxene, and low-Fo olivine. Mafic melt inclusions are hosted in

384 high-Fo olivine and some of plagioclase (Fig. 3).

385 The presence of orthopyroxenes surrounded by reaction rims and An-rich zones

386 in the middle part of plagioclases in NKD14 (Fig. 2f) indicates that the 2014 magma is

387 also the result of mixing. Such petrological features are found in magmatic products of

388 every Nakadake eruption (Miyoshi *et al.* 2005). Thus, we consider that all the Nakadake

389 eruption products are the result of magma mixing, rather than the derivatives from a single

390 parental magma. In addition, Miyoshi *et al.* (2005) also show that the compositional

391 variation in the trace elements in the post-caldera basaltic rocks of Aso volcano is

392 consistent with a magma mixing model and not with a fractional crystallization process.

393 Therefore, at least two types of magmas are present beneath the Nakadake cone, and feed

394 its eruption.

395

### *Characterization of mixing endmembers*

397 　　We conducted a two-component mixing model calculation of two distinct
398 magmas, one silicic endmember and one mafic endmember, based on the major element
399 variation of melt inclusions (see Supplementary document S4). The model used the most
400 primitive basaltic melt (Melt ID: 2-m1 hosted in an olivine) and the most $SiO_2$-rich dacitic
401 melt (Melt ID: d2-m1 hosted in a plagioclase) of KSS as the mafic and silicic endmember,
402 respectively. The major element variation was well reproduced with the mixing model
403 for melt inclusions of all host minerals (Fig. S4-5). While the major variance of
404 concentration variations was explained by a simple mixing process, in close inspection of
405 trends, it is likely that crystal fractionation contributed to the dispersion from the mixing
406 model. It should also be noted that the mixing model required the presence of independent
407 mixing endmembers, it does not constrain their origin.

408 　　It is important to note that there is a surface expression of this silicic
409 endmember in the Aso eruption products, while the mixing endmember is set by a melt
410 inclusion. Major element compositions of ACP1 dacitic pumice (Takada 1989), the only
411 Holocene felsic product erupted three hundred years before that of KSS, are similar to the
412 endmember, and this indicates the presence of the silicic magma. Furthermore, the
413 presence of a banded pumice was reported in ACP1 prior to KSS (Miyabuchi 2017). This
414 banded texture is evidence of magma mingling and therefore the mixing trend is unlikely
415 a result of assimilation and crystal fractionation of single parental magma. The cores of
416 reversely zoned phenocrysts of KSS scoria samples were formed at equilibrium
417 conditions with the silicic endmember. Therefore, the temperature of silicic endmember
418 magma was determined with a two-pyroxene thermometer by pairing core compositions
419 (Putirka 2008). The estimated temperatures of the silicic endmember are 1010-1025ºC
420 for KKO, OJSU, OJSL, and KSS (± 13˚C, 1σ for samples, while standard error of the
421 thermometer is ±38 ˚C). We adopted this estimated range as the temperature of the silicic
422 endmember magma. These estimated temperatures are higher than those of typical dacitic
423 magma with 4 - 5 wt. % $H_2O$ (e.g. 770 – 915 ˚C for Mount St. Helens, Gardner *et al.*
424 1995) and lower than that estimated for a completely anhydrous dacitic magmas, for
425 example Puna Geothermal Venture Wellfield, Hawaii have the highest temperature
426 estimates 1050ºC (Teplow *et al.* 2009). This silicic endmember magma (T between 1010-
427 1025ºC) will mix with the mafic endmember (most likely hotter) magma at temperature
428 presumably higher than 1010-1025ºC.

429 　　Basaltic lava corresponding to the pure mafic endmember is absent among the
430 eruption products of the entire post caldera stage (Miyoshi *et al.* 2005), while it is found
431 in olivine-hosted melt inclusion. Many tephras of this study also contain normally zoned
432 phenocrysts with high-Fo and high-An cores. As for the case of the silicic endmember, it
433 is possible to assume the equilibrium of these cores with the mafic endmember melt. We
434 therefore calculated the magmatic temperature of the pure mafic endmember, using

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435 Sakuyama's method (Sakuyama *et al.* 2014), which involves the combined application of
436 a plagioclase-melt hygrometer (Lange *et al.* 2009) and an olivine-saturated melt
437 geothermometer (Sugawara 2000; Médard and Grove 2008). This method accounts for
438 the $H_2O$-dependency of the olivine thermometer by simultaneously solving for $H_2O$ and
439 temperature using an additional constraint from the plagioclase hygrometer. The resulting
440 temperature of mafic endmember magma varies between 1051 – 1063 ˚C, depending on
441 the assumed pressure condition of the magma chamber (0.1 - 0.5 GPa, respectively). In
442 addition, the entrapment temperature of the endmember inclusion (KSS-2-m1) is 1092
443 ˚C based on the olivine-liquidus thermometer (Table S1, Sugawara 2000; Médard and
444 Grove 2008). Considering the uncertainties of the thermometry methods, these
445 temperature estimates are likely representing the range for the mafic magma. By taking
446 the high temperature result (~1090 ˚C), the temperature difference between mafic and
447 felsic (1010-1025 ˚C) endmembers is at least 65 ˚C.
448     The mixing trend among volatile elements is present and generally consistent
449 with the trend of major elements. However, in detail, there are systematic disparities from
450 the mixing curve (Supplementary document S4). Notably, abundances of $H_2O$, S, and Cl
451 for NKD14 sample, are depleted compared to the mixing trend traced by KSS melt
452 inclusions (Fig. S4-4). This is best explained by significant degassing occurring
453 during/after magma mixing. Furthermore, there is no single melt inclusion uniquely
454 representing suitable mafic endmember volatile concentrations. The sample KSS-2-m1 is
455 selected as the major element endmember, but its $H_2O$ contents are not the highest values.
456 From the inspection of the trend, we inferred that the mafic endmember must have higher
457 volatile content thus most likely lost water after its entrapment. If melt inclusions formed
458 at a deeper depth, and were stored in a shallower magma chamber, it is expected that $H^+$
459 diffusion through the olivine would equilibrate the melt inclusion with the surrounding
460 magma (Portnyagin *et al.* 2008; Chen *et al.* 2011; Gaetani *et al.* 2012; Bucholz *et al.*
461 2013; Ferriss *et al.* 2016). Complete re-equilibrated melt inclusion would have erased the
462 mixing trend. It is not the case here, we have found suitable endmember volatile element
463 concentrations that satisfy the general trend. Because the mafic endmember magma is
464 expected to be volatile-rich, it's $H_2O$ concentration has to be higher than the $H_2O$ of the
465 mixed-magma (e.g. that of the melt inclusions). The maximum estimated $H_2O$
466 concentration (4.68 wt. %) based on the hygrometer discussed above is therefore taken as
467 the concentration for the volatile-rich mafic endmember. This value of 4.68 wt.% $H_2O$ is
468 higher, by about 2 wt. %, than the highest $H_2O$ concentration measured in the melt
469 inclusion. Sakuyama's method implicitly ignores the $CO_2$ activity in magma, and predicts
470 lower $H_2O$ content when considering $CO_2$-bearing system (by 0.9 wt. % less $H_2O$,
471 assessed from an experimental result of Melekhova *et al.* 2017). Furthermore, this volatile
472 content is the value at the condition of olivine - plagioclase crystallization, most likely of
473 the cooling magma in the crust. At this point, we have no other constraint on the $H_2O$
474 concentration of the mafic endmember and the primary magma could have an even higher
475 $H_2O$ content.

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### *Volatile concentrations of primitive basaltic melt*

The melt inclusions similar to the mafic endmember of the mixing model showed element concentrations with primitive character, such as low incompatible element concentrations (low $K_2O$, Cl, and F), and higher volatile element such as S. However, $H_2O$ concentration is likely equilibrated to a lower pressure conditions, and $CO_2$ concentration in melt inclusion appears to be low. While these melt inclusions are hosted in high Fo olivine, the $H_2O$ and $CO_2$ abundances are not of primitive character. On the contrary, as F, S, and Cl are not expected to diffuse through the host olivine, and at the time of entrapment, they retain the value closest to the primitive magma. In an attempt to constrain the mafic endmember composition, compositional trends are examined with ratios of S, Cl, and F over $K_2O$. These ratios are less affected by crystallization within melt inclusions and before entrapment, assuming the strong incompatibility of $K_2O$ in magmatic minerals near basaltic liquidus (Fig. 4). Because the composition of the mafic endmember points towards that of the primitive magma, the maximum values are taken from Fig. 4a, b, and c, as the primitive volatile ratios: $S/K_2O$ = 0.711, $Cl/K_2O$ = 0.170, and $F/K_2O$ = 0.047.

Dissolved S concentrations, up to 3750 ppm in the mafic group melt inclusions, are higher than many melt inclusions from subduction-like hydrous basalt (Fig. 5a; S mostly between 900 and 2500 ppm; e.g. Wallace 2005), while high S content appears to occur in oxidized magmas (Roggensack 2001; Webster *et al.* 2010). Our primitive magma S estimate is therefore 3750 ppm, the highest measured concentration in a melt inclusion of the mafic group. We also noted that S concentration of half of the melt inclusions are supersaturated in sulfide, plotting above the sulfur concentration at sulfide saturation (SCSS, Fig. 5b), while no sulfide is found in the melt inclusions or in the groundmass. These sulfide supersaturated melt inclusions must be at high $fO_2$ condition, so that the concentration of sulfide-precipitating $S^{2-}$ in magma is lower than SCSS. In fact, it has been shown that arc basalt magmas have higher oxygen fugacities than MORB magmas (e.g. Wallace 2005; Kelley and Cottrell 2009). In addition to this, the redox state of the melt inclusions was determined and ranges from FMQ + 0.68 to FMQ + 1.41 (Average = 1.05, $1\sigma$ = 0.17, corresponding to $S^{6+}/S_{total}$ = 0.14 - 0.85, Table S1). Such oxidizing conditions allow for (i) higher S solubility in the mafic magma (Carroll and Rutherford 1985; Jugo *et al.* 2010) and (ii) the presence of both $S^{2-}$ and $S^{6+}$ in the melt. Fig. 5b also shows a dashed line expected for the SCSS corrected for abundance of $S^{2-}$ species ($S^{6+}/S_{total}$ = 0.85). Such first order correction puts all of our melt inclusion to be below sulfur saturation, consistent with our observation. Also, S concentrations of all the melt inclusions are under-saturated with respect to anhydrite saturation (SCAS was from 5300 to 6000 ppm, Li and Ripley 2009; Baker and Moretti 2011). The elevated S concentrations in the undersaturated oxidized melt are therefore considered to represent, less-degassed, non-sulfide-fractionated, S concentrations, at least at the condition of the shallow storage depth.

Similarly, we also consider that the mafic endmember Cl and F concentrations are representative of primary concentrations, as the exsolution pressure of Cl and F is at shallower depths (~100 MPa for Cl and ~10 MPa for F; Spilliaert *et al.* 2006) than for other volatile species. Cl concentration in the Aso primitive magma was 716 ppm (took the value of the mafic end member melt inclusion: KSS-2-m1) which is higher than that of MORB (Fig. 6; max 500 ppm Cl, Le Voyer *et al.* 2015), as it is interpreted as the addition of Cl to the subarc mantle from the subducting slab (e.g. Straub and Layne 2003). On the contrary, F concentration in the primitive magma was 324 ppm, which is the same order of magnitude as that of MORB (max 500 ppm, Le Voyer *et al.* 2015). This suggests that F addition to the subarc mantle was insignificant.

The Cl/F ratios of melt inclusions globally reflect the composition of the slab-agent added to the mantle source as F fractionate from Cl depending on the physical character of the flux leaving the slab (Le Voyer *et al.* 2010; Van den Bleeken and Koga 2015; Narvaez *et al.* 2018). Observed Cl/F ratio of melt inclusions from Aso volcano are relatively high (from 1 to 2.5, Fig. 6) compared with that of MORB (Saal *et al.* 2002; Wanless and Shaw 2012; Wanless *et al.* 2014, 2015; Le Voyer *et al.* 2017; Shimizu *et al.* 2019). Because Cl/F values in arc magma are characterized by several parameters such as the composition of slab, nature of the fluid and fractionating minerals in residual slab, and the degree of melting of arc magma, the physical character of slab derived flux is determined with a set of assumptions. In any case, the primitive magmas with MORB-like F concentration and a high Cl/F value (2.2) are found among the melt inclusions of calc-alkaline arc magmas in a typically "cold" subduction setting (Straub and Layne 2003; Rose-Koga *et al.* 2014). The halogen characteristics of our Aso melt inclusions were in the range of typical arc magma, and the value of the primitive magma was close to the melt inclusions of Iwate volcano, a prototypical example of the arc magma derived from aqueous fluid driven from a cold oceanic crust (Rose-Koga *et al.* 2014). This indication is consistent with studies based on high bulk B/Nb ratios indicating aqueous fluid additions from the subducting Philippine sea plate in the source of the Aso basalt-basaltic andesite rocks (Miyoshi *et al.* 2008a, b). Other studies based on Sr, Nd, and Pb isotope variations of Quaternary lavas in the northern Kyushu area also support the model of slab-derived aqueous fluid addition from the subducted Philippine sea plate beneath Aso volcano (Shibata *et al.* 2014).

***Storage depth of the magma mixture***

Solubility of volatiles in magma strongly depends on pressure and temperature conditions, and the chemical composition of the magma (e.g. Dixon *et al.* 1995). In this section, we discuss the storage depth of the mixed-magma based on $H_2O$ concentration. For example, measured volatile concentrations of melt inclusions are considered to be re-equilibrated to a condition of a magma storage. Alternatively, it is also possible to

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556 determine $H_2O$ concentrations estimated from plagioclase rim and groundmass glass pairs
557 (geo-hygrometer, Lange *et al.* 2009), likely corresponding to the value of the mixed
558 magma during the plagioclase rim growth. The $H_2O$ concentrations of such mixed
559 magmas are, ~2 wt.% for NKD14 and KKO, and ~3 wt.% for OJSU, OJSL and KSS
560 (Table 4). Here, the hygrometer calibrated for the total fluid pressure is equal to $P(H_2O)$,
561 neglecting the role of $CO_2$. Yet, these values are comparable to those measured in the
562 melt inclusions, and indicate a magma chamber pressures of 0.5 kbar for NKD14 and
563 KKO, and 1.0 kbar for OJSU, OJSL, and KSS (*i.e.* 2.1 and 4 km deep, respectively, Fig.
564 7, note the depth is calculated using a density of 2200 kg/m$^3$ for the first 1 km and 2700
565 kg/m$^3$ for the crust at greater depths (Komazawa 1995), by solving for the depth, h [m],
566 P = g {2200 (1000) + 2700 (h-1000)}). Because $CO_2$ concentrations in the felsic group
567 melt inclusions are notably low (0 - 77 ppm, Table S1), it makes negligible changes to
568 the calculated equilibrium pressure (~20 MPa, using RhyoliteMELTS/MagmaSat,
569 Ghiorso and Gualda 2015). These pressures correspond to the depths of magma storage
570 after mixing, since (1) the last growth rim of plagioclase must have occurred after mixing,
571 as both normal and reverse zoning plagioclase have the same rim composition. (2) It is
572 less likely that plagioclase rim significantly grew during sub-Plinian and Strombolian
573 eruption. Melt inclusion $H_2O$ concentrations range from 0.47 to 2.89 wt. %, indicating
574 the minimum equilibrium pressure in agreement with the plagioclase-rim method. Two
575 magma chambers, C2 and C1, detected by geophysical studies are also located at similar
576 depths, 1 - 4 and 3 - 10 km, respectively (Tsutsui and Sudo 2004; Sudo *et al.* 2006; Hata
577 *et al.* 2016; Fig. 7). At the depths, because the solubility of $CO_2$ is so low, the conclusion
578 presented here would remain the same even if the hygrometer calculation does not
579 account for $CO_2$.

580 The magma of the mafic endmember is expected to have more than 4.68 wt. %
581 $H_2O$, and it is therefore derived from a greater depth than these C1 and C2 storage depths.
582 The corresponding equilibrium pressure is approximately 2.7 kbar (SolEx, Witham *et al.*
583 2012; note MagmaSat give 2.3 kbar, Ghiorso and Gualda 2015; with $CO_2$ of 340 ppm
584 reported in a melt inclusion from Nakadake by Saito *et al.* 2018) that is about 10 km deep
585 below the edifice. As gas bubbles were seen in melt inclusions, large amounts of $CO_2$
586 incorporated in such shrinkage bubbles significantly increases the entrapment pressure
587 estimation (e.g. Moore *et al.* 2015). Therefore, our pressure estimations are minimum and
588 true entrapment pressures of the basaltic magma certainly occurred at a depth greater than
589 10 km. Recent melt inclusion studies reported more than 40-90 % of the initial $CO_2$ that
590 was dissolved in the melt at the time of entrapment was lost to shrinkage bubbles, with
591 an average loss of 75-80 % (Hartley *et al.* 2014; Moore *et al.* 2015; Wallace *et al.* 2015).
592 If 90 % of initial $CO_2$ is present in the shrinkage bubble and a maximum $CO_2$ value of
593 340 ppm is assumed in the melt (from Saito *et al.* 2018), then the expected initial value
594 of the melt would reach 3400 ppm. This value is in the same order of magnitude as the
595 initial $CO_2$ concentration in a typical primary arc magma (Aster *et al.* 2016), and in this
596 case the saturation pressure would exceed 5 kbar (~19 km depth equivalent). However,

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597 at the time of this study, bubble sizes were not documented with impossibility to go back
598 to measuring them *a posteriori* since most are now polished away. In this case, we chose
599 not to use the $CO_2$ data of the melt inclusions. Hata *et al.* (2016) also reported a magma
600 pathway from depths deeper than 11 km, feeding the deeper C1 reservoir. Also, the
601 presence of a seismic low-velocity layer at 11 - 25 km depth was reported and attributed
602 to a magma ponding location beneath the Aso caldera (Abe *et al.* 2010). These
603 observations are in good agreement with our petrological implication for the presence of
604 volatile-rich basaltic magma beneath C1 magma reservoir at a depth greater than 10 km.
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### *Persistent degassing from a deeper magma reservoir (>10km)*

608 <u>Excess degassing of $SO_2$ and $CO_2$ from Nakadake 2014 eruption</u>

609 Decomposition of magma mixing endmembers and the subsequent
610 identification of the primitive magma composition provide critical information for
611 investigating volcanic emission of gas and its mass balance. For the 2014 eruption of Aso
612 volcano, the mass of erupted magma is insufficient to account for the mass of the observed
613 $SO_2$ gas emissions (Saito *et al.* 2018), which is commonly reported in many active
614 volcanoes and is called "excess degassing". For Aso, approximately $90 - 140$ times more
615 magma than the erupted tephra mass is needed to account for the observed total $SO_2$
616 emission of $1.4 - 2.2 \times 10^5$ tons for the period of 70 days from Nov. 2014 to Feb. 2015
617 (Table 5 and; also Saito *et al.* 2018). As demonstrated in the sections above, NKD magma
618 is a mixed magma, so the gas phase must have come from the degassing of mafic and
619 felsic endmember magmas. For this reason, we have used the highest volatile element
620 concentrations determined for Nakadake samples (*i.e.* mixed magmas) for the sulfur
621 budget calculation (Supplementary material S4). This calculation simply demonstrates
622 that the mixed magmas are inadequate sources of the observed volcanic gas flux. The
623 most commonly proposed explanation for this excess is the existence of a gas/fluid phase
624 in the magma, possibly containing C-O-H-S and co-existing with the magma prior to the
625 eruption (e.g. Anderson 1973; Wallace 2001; Scaillet and Pichavant 2003; Shinohara
626 2008). The magmatic volatile component must originate from the volatile-rich magma
627 corresponding to the basaltic/mafic endmember. This magma must degas at a deeper
628 depth than that indicated by the equilibrium solubility depth of NKD samples (~2 km at
629 the depth of C2). Therefore, the degree of S excess should be re-assessed with a deeper,
630 volatile-rich, basaltic magma. It should be noted that the observation of S-excess is
631 common (*e.g.* Wallace and Edmonds 2011) and we simply point out here that the eruption
632 of Nakadake edifice of Aso also shows such excess.
633 There are geophysical observations indicating that degassing is fed by volcanic
634 activities corresponding to depths deeper than ~2 km. The $SO_2$ gas emission of Aso
635 volcano is continuously monitored during the eruptive and the quiescent periods. The

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636 amount of $SO_2$ emission during the quiescent period (alternatively, "persistent
637 degassing"; Shinohara 2008) is more than $100 - 200$ tons/day from 1975 to 2006 (Mori
638 *et al.* 2013). Ground deformation measurements since 1937 revealed deformation
639 (deflation) of the deeper C1 magma reservoir synchronous to gas emission from
640 Nakadake cone during the quiescent period (Sudo *et al.* 2006). This C1 deformation,
641 located approximately 3 km West of Nakadake, causes no significant deformation on the
642 surface around the crater. This degassing is therefore interpreted as open-system
643 degassing of the C1 magma reservoir through stable conduit passages to Nakadake crater
644 (Yamamoto *et al.* 1999; Sudo *et al.* 2006). Furthermore, deflation of the C1 reservoir was
645 seen to slow down from 2008 to early 2014, before acceleration of inflation of the C1
646 reservoir from July 2014, shortly before the eruption in November (Ohkura *et al.* 2015;
647 JMA 2016). These changes were accompanied by a sudden increase in persistent $SO_2$ gas
648 emission in September 2013, considered as a precursor to the 2014 - 2015 eruptive period
649 (JMA 2016). These temporal and spatial relationships of geophysical observation and
650 degassing activities strongly indicate the role of the deeper C1 reservoir during degassing.
651 However, to sustain replenishment of the Cl reservoir, the magma must be supplied from
652 an even deeper depth (greater than 10 km; Sudo *et al.* 2006; Hata *et al.* 2016). For example,
653 the slowing down of deflation in 2008 and subsequent inflation in 2014 can be interpreted
654 as events relating to magma replenishment of the Cl reservoir (Ohkura *et al.* 2015, 2017).
655 We also found excess degassing of $CO_2$ for this eruption period. Using the
656 maximum pre-eruptive $CO_2$ concentration of 340 ppm measured in a melt inclusion of
657 Nakadake eruption products (Saito *et al.* 2018), and assuming there is no pre-eruptive
658 vapor phase approximately $1700 - 2700$ times more dissolved $CO_2$ is required to account
659 for the observed $0.77 - 1.2 \times 10^6$ tons of $CO_2$ emission (Table 5). In the case of Aso, the
660 gas phase must be derived from a depth greater than that of the C1 reservoir.

661 Modelling degassing of the deep magma reservoir

662 In the sections above, the equilibrium depths of volatile concentration in
663 magma were used to indicate magma storage depth, where stagnated-magma and gas
664 remain at equilibrium. Equilibrium gas composition at that depth should be the source of
665 the gas composition observed at the surface, only if the gas segregated and travelled to
666 the surface without precipitating solids or re-dissolving gas in between. In detail, the
667 speciation of mixed gas is a function of pressure, temperature, and oxygen fugacity, but
668 the gas system composition can be considered closed. With this hypothesis, it is possible
669 to determine the depth at which the observed gas composition is in equilibrium with a
670 magma (e.g. Burton *et al.* 2007; Allard 2010).
671 Fig. 8 is a result of such a calculation using SolEx (Witham *et al.* 2012),
672 showing the variations in $H_2O/S$, $CO_2/S$, and $Cl/S$ molar ratios of gas in equilibrium with
673 a magma as a function of pressure. The observed $H_2O/S$ gas composition of the 2014
674 eruption (shown as horizontal dotted red lines) intersects with the equilibrium gas

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675 composition (plain lines Fig. 8) between 2.6 to 3.3 kbars. These pressures correspond to
676 10 - 13 km depth below the edifice. The family of curved lines represent the results of the
677 model with varying initial $CO_2$ concentration (400, 750, and 1000 ppm), as the initial $CO_2$
678 concentration was unknown (but for sure higher than 340 ppm). For the range of
679 degassing trajectory, the observed Cl/S values (horizontal dotted blue line) intersect with
680 the model calculations between 2.6 and 3.8 kbars. $H_2O$/S and $CO_2$/S are less sensitive to
681 the variation of the initial $CO_2$ concentration. It should be noted that the closed system
682 degassing path here is used to find a unique pressure condition at which the observed high
683 temperature gas composition is at the equilibrium with a mafic magma. The systematics
684 shows that only $CO_2$ concentrations between 400 and 750 ppm can produce the observed
685 gas composition at pressures between 2.6 to 3.3 kbars, satisfying the observed ranges of
686 $H_2O$/S, $CO_2$/S, and Cl/S all at once.

687 Therefore, the observed gas composition must have been derived from the
688 depth of about 10 to 13 km (~2.6 to 3.3 kb) at which it was in equilibrium with a magma
689 with the initial magmatic $CO_2$ concentration between 400 to 750 ppm (Fig. 8). The
690 determination of initial $CO_2$ is strongly tied to the Cl and S partitioning into $H_2O$-$CO_2$
691 fluid, and we think that these values may need to be revised once we have a better
692 understanding of Cl and S element partitioning. Lastly, this conclusion is highly model
693 dependent. Here, we chose to use SolEx for its agreement with the variation of S in the
694 melt inclusions. However, one must be cautious with the use of SolEx, because it is shown
695 to fail to reproduce degassing trajectories of other volcanoes (e.g., Werner et al. 2020).

696 Fig. 9 shows the observed gas composition emitted from Aso volcano in the
697 quiescent period and eruptive period. The gas data shown in Fig. 8 correspond to the
698 eruptive period data (orange). While Fig. 8 demonstrated the occurrence of deep gas
699 segregation, it does not explain the range of gas composition observed before and, even,
700 during the eruption of the Nakadake cone. We modelled the variation in gas composition
701 using (1) a degassing trend (solid line), the same model as that used in Fig. 8, and it fits
702 the data with some scatter and (2) a mixing line (dotted line) between a deep reservoir,
703 for example at the storage depth around 10 km, and a shallow reservoir (C2 or top of C1).
704 Both explain the data (Fig. 9). Thus, on the one hand, it is possible to consider the
705 variation in gas composition as the variation in gas segregation depth. On the other hand,
706 the observed gas composition variation potentially represents the different degrees of
707 mixing between discharged gas from NKD14 magma at shallow depth and segregated
708 gas from a deep reservoir (*i.e.* gas segregation depth at 10 km; Fig. 8 and 10). Case 1 is
709 less likely to apply here. Because of the closed-system degassing model (solid line), the
710 ascending primitive magma would have been expected to be in equilibrium with gas all
711 the time until it reaches near the surface. Therefore, the gas composition representing the
712 low pressure must have been in equilibrium with the mafic magmas at the shallowest
713 depth. However, no volcanic product of primitive composition was found during the
714 eruption of Nakadake cone. Instead, observed volcanic products were all the result of
715 mixing. As case 1 is unlikely, we conclude that the mixing of gases (case 2) is the process

explaining the observed compositional variation. The gas mixing could have been possible, for example, by bubble accumulation at the roof of a magma chamber (Jaupart and Vergniolle 1988, 1989).

*Implications for understanding current Aso volcanic activity*

This study identified the role of a volatile-rich, primitive magma during volcanic degassing (Fig. 10). During ascent, the volatile-rich primitive magma started to degas at a depth between 11 and 13 km (2.8 to 3.5 kbars, SolEx) based on the initial volatile concentration. The gas and magma reached 10 km depth maintaining equilibrium. At that depth, the gas segregated from the magma and moved to the surface without any significant modification. The separation of gas from magma was potentially caused by stopping of magma ascent, which contributed to overpressuring of C1 observed by the deformation of the edifice. The magma then moved upwards and mixed with silicic magma in the C1 magma reservoir. While the exact depth of mixing was undetermined, the mixed magma was eventually stored at depths of C1 and C2 (for example 2 km (C2) for NKD14 and KKO samples, and 4 km (C1) for OJSU, OJSL, and KSS samples).

The segregated deep gas mixed with the shallow gases upon its ascent at shallower levels. We were unable to constrain the exact mechanism of the deep gas transport to the shallow depth without significant interaction. One possibility is the presence of porosity providing connected gas passages. However, this mechanism implies the rigid structure at a temperature lower than magmatic conditions, and this contradicts with the observation of the high temperature gas indicating magmatic degassing. Alternatively, a convection within C1 and C2 potentially serves a "gas pump". In this scenario, a shallow mixed magma (devoid of volatile elements) descends by convection to the bottom of C1 where gas segregation is occurring. Upon the return of such magma to shallow depth, it drags the gas component with it. Such parcel of magma may further pull gas bubbles from the shallow depth and result in a bulk system of mixed gas. If the magma degases completely, the resulting gas composition will be identical to the result of the gas mixing. This scenario would fail if some batch of magma do not degas and remain in some depth; it requires complete degassing. Shinohara (2018) proposed a model which suggested that the observed chemical variation in gases during eruption was caused by mixing of gases derived from magmas at different depths. This model is consistent with our gas mixing model. Our model furthered understanding of Aso activity, by (1) quantifying the volatile concentration of primitive mafic magma, and (2) by determining its degassing, segregation, and storage depths.

## Summary and conclusion

Petrological analyses of melt inclusions in basaltic tephras from the late Holocene eruption of Aso volcano provided us with insights into the process of the persistent degassing in a magma plumbing system.

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(1) The compositions of melt inclusions in phenocrysts from recent eruption products (Nov. 2014) of Nakadake cone were homogeneous, evolved and degassed (S < 434 ppm), while compositions of melt inclusions in phenocrysts from Kishimadake and other related cones (ca. 3.0 − 3.7 ka) showed variable compositions with two extreme endmembers. One was mafic ($SiO_2$ < 55wt.%) and volatile-rich, and the other was felsic ($SiO_2$ > 55wt.%) and relatively degassed. Mafic melt inclusions were hosted in high-Fo olivine and some plagioclase, whereas felsic melt inclusions were hosted in plagioclase, clinopyroxene, orthopyroxene and low-Fo olivine.

(2) Reverse mineral zoning, and highly variable mineral and glass compositions indicated a mixing process during which volatile-rich basaltic magma was injected in a degassed shallower magma.

(3) The estimated depths of pre-eruptive magma were approximately 2 km (C2 magma reservoir) for Strombolian eruption of Nakadake cone (Nov. 27, 2014) and Kamikomezuka cone (3.0 ka) and approximately 4 km (top of C1 magma reservoir) for sub-Plinian eruption of Ojodake and Kishimadake cones in 3.5 − 3.7 ka. These depths corresponded to the partially melted zones characterized by geophysical investigations (e.g. Hata *et al.* 2016). Furthermore, volatile-rich primitive magma originated from a deeper level (greater than 10 km) than these two magma reservoirs.

(4) Even with the highest S concentration of NKD14, it was impossible to account for the excess S gas emission. This suggests an addition of gas derived from the deep magma reservoir (greater than 10 km depth).

(5) Initial volatile concentrations of the volatile-rich primitive magma were determined from the systematics of melt inclusion, plagioclase compositions, and degassing model: >4.68 wt.% $H_2O$, 3750 ppm S, 716 ppm Cl and 324 ppm F.

(6) Emitted gas compositions constrained the initial $CO_2$ concentration ranges in the magma, between 400 and 750 ppm.

(7) The variation observed in volcanic gas composition was best explained by the mixing of the gas segregated at 10 km depth with those from the shallow reservoirs.

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**Figure caption**

**Fig. 1** Locations of volcanic cones and sampling sites of the study. Main map shows topography of Aso volcano with a 50 m contour interval. Volcanic cones are indicated by solid triangles. Sampling sites are indicated by solid circles. Location of Aso volcano is indicated in an inset in the top left corner, showing Japanese islands with plate boundaries: solid line, active subduction plate boundary, and dashed line, diffused plate boundary. Stratigraphic log shows corresponding eruption stages and nature of volcanic deposits in A9418 site (Miyabuchi and Watanabe 1997). Kishimadake scoria (KSS) and Ojodake scoria (OJSL and OJSU) were collected at the indicated units. Kamikomezuka scoria (KKO) and Nakadake scoria (NKD14) were collected at the location indicated by field symbols. KKO in parenthesis indicates the relative eruption age (top of N4 stage).

**Fig. 2** Microscope photographs (a-d) and backscatter electron images (e, f) of representative phenocrysts and textures from Holocene basaltic tephra products in Aso central cones. (a) Plagioclase (Pl) phenocrysts with honeycomb texture in KKO, under cross-polarized light. Clinopyroxene (Cpx) and olivine (Ol) phenocrysts also present. (b) An orthopyroxene (Opx) phenocryst with reaction rim consisted of clinopyroxene and olivine in KSS, under cross-polarized light. (c) An aggregate of phenocryst consisted of plagioclase, clinopyroxene and olivine in KSS, under cross-polarized light. (d) A microlite-rich part of groundmass in KSS with abundant crystals, under plain-polarized light. (e) High-Fo olivine phenocryst and its melt inclusions observed in KSS. (f) A texture of plagioclase phenocryst with (optically) dusty zone, in the middle part of the crystal, observed in NKD14.

**Fig. 3** Major element and volatile concentrations in melt inclusions from Holocene basaltic tephra products in Aso central cones. Melt inclusion data from minerals other than olivine are shown as open symbols. The melt inclusion data are compared to bulk tephra and average groundmass glass compositions, solid circles, and solid squares, respectively. The distribution of Fo content in all olivine cores is shown as a relative density function on the left side of (a). The dashed line in Figure 3a and 3b indicates the value Fo72. Bulk lava compositions of late-Holocene volcanic products, reported previously, are also shown as solid grey circles in (c) (Miyoshi *et al.* 2005; Miyabuchi 2010, 2017; Saito *et al.* 2018). All oxide concentrations were normalized to 100 wt. %, excluding volatile element abundance.

**Fig. 4** Ratios of volatiles/$K_2O$ vs. $K_2O$ in melt inclusions and groundmass glasses (the same symbols as Fig. 3). All volatile elements showed a systematic decrease (a, $H_2O/K_2O$; b, $S/K_2O$; c, $Cl/K_2O$) with respect to increasing $K_2O$. High volatile/$K_2O$ corresponds to high volatile concentration as well as low $K_2O$.

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**Fig. 5** (a) Variations in S and total FeO concentrations of melt inclusions and groundmass glasses. Symbols are the same as Fig. 3. Melt inclusions hosted in olivine show abrupt decrease in S content, and the change lacks correlation with FeO. (b) Measured S concentration in olivine-hosted melt inclusions as a function of sulfur concentration at sulfide saturation (SCSS). In this figure, the samples at the saturation can be seen on the solid grey line (1:1 line). The dashed line shows the SCSS corrected for abundance of $S^{2-}$, which was 0.85, the maximum value. All data plots below the corrected SCSS. SCSS is calculated according to Fortin *et al.* (2015) using the trapping temperature ($T_{trap}$) of the melt inclusion (Table S1) at 0.05 GPa (for NKD14) and 0.1 GPa (for KKO, OJSU, OJSL, and KSS) based on estimated volatile saturation pressure of the pre-eruptive magma reservoir. For melt inclusions without measured $H_2O$ concentration, we attributed average $H_2O$ concentrations (by SIMS) of NKD14 and KSS.

**Fig. 6** Variations in Cl and F concentrations of melt inclusions (KSS and NKD14) plotted in decadic log scale. The KSS and NKD14 data are compared with the volatile rich mafic primitive magma, represented by a large blue diamond. The two areas are indicated to show the Cl and F concentrations in primitive arc basalt and MORB, which were measured in olivine-hosted melt inclusions (taken from Van den Bleeken and Koga 2015). MORB melt inclusions were plotted as solid light-grey circles (Saal *et al.* 2002; Wanless and Shaw 2012; Wanless *et al.* 2014, 2015; Le Voyer *et al.* 2017; Shimizu *et al.* 2019) including Cl-rich data of assimilated MORB samples by seawater derived component. Melt inclusions from Iwate volcanoes, one of low F concentration arc lava from Japan arc, is shown as an example of a cold subduction zone (red plus sign, Rose-Koga *et al.* 2014). The lines show the constant Cl/F values, and the values are indicated above the line.

**Fig. 7** Pre-eruptive temperatures and water concentrations calculated from the compositions of plagioclase rim and groundmass glass. The squares represent the estimated range of temperature and $H_2O$ concentration. The calculation was based on a combination of a plagioclase-olivine-liquid hygrometer (Lange *et al.* 2009) and olivine-saturated liquid geothermometer (Sugawara 2000; Médard and Grove 2008) according to Sakuyama *et al.* (2014), assuming the crustal conditions (0.1 − 0.5 GPa). Standard deviations (1σ) of the difference in temperature and $H_2O$ concentration between estimation and expectations using this method were 23 ˚C and 0.6 wt. %, respectively. The dashed lines represent water saturation isobars for groundmass glass composition of KSS calculated according to Moore *et al.* (1998); the corresponding pressures (kbar) and the depths (km) are indicated to the left of the line. The depth in the crust was calculated assuming a density of 2200 kg/m$^3$ for less than 1 km depth and a density of 2700 kg/m$^3$ for depth greater than 1 km (Komazawa 1995). The red and blue colors show the range of the magma storage depths: red, C1 from 3 to 10 km depth, and blue, C2 from 1 to 4 km depth beneath Nakadake's first crater (Sudo and Kong 2001; Sudo *et al.* 2006; Hata

1253 *et al.* 2016).

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**Fig. 8** Evolution of $H_2O/S$, $CO_2/S$, and $Cl/S$ molar ratios of magmatic gases in equilibrium with the primitive basaltic melt plotted against pressure. Horizontal dotted lines indicate measured gas compositions of $H_2O/S = 22.5$, $CO_2/S = 6$, and $Cl/S = 0.07$ (S as total sulfur) with the variation observed with propagated measurement uncertainties shown by shaded regions. The values correspond to high-pressure gas component A reported in previous studies (Shinohara 2013; Shinohara *et al.* 2018). $SO_2$ and $H_2S$ components were added to calculate the total S. Horizontal colored bars at the top of the panel show pressure ranges corresponding to the C1, C2, and LVL. To evaluate the evolution of the gas composition of the basaltic magma from a great depth, we modelled the equilibrium compositions of gas and magma for a closed system magma ascent using SolEx (Witham *et al.* 2012). Grey field indicates the pressure range of $2.3 - 2.9$ kbars, at which conditions the modeled gas compositions (solid and dashed curves) intersect with measured gas ratios. Thus, the observed gas composition potentially originated at these depths. We chose the primitive magma composition (discussed in the text) with values of FMQ+1.4 and 1090 °C based on the individual melt analyses. We tested initial $CO_2$ contents of 400, 750 and 1000 ppm for the calculation, as the $CO_2$ concentration was unknown to us. In combination with $H_2O/S$ and $Cl/S$, the initial $CO_2$ concentration from 400 to 750 ppm produced the gas composition evolution curves that agree at a similar depth.

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**Fig. 9** Observed volcanic gas compositions emitted from Aso volcano compared with modelled variation in $CO_2/SO_2$ and $H_2O/CO_2$ molar ratios. Observed gas compositions are those during quiescent periods (fumarole and lake gases) and during eruptive periods (Shinohara *et al.* 2018). Some data points were reported as poor quality observations due to atmospheric $H_2O$, and they are plotted as smaller symbols. Solid curve is a modeled gas composition of closed-system ascent of primitive magma with 750 ppm initial $CO_2$ concentration, which is the same as that used in Fig. 8. The gas compositions on the curve indicate the different depths of gas segregation, and thus, the variation among observations can be attributed to a variation in segregation depths. Dashed curve shows a mixing curve between a $CO_2$-rich gas in equilibrium with the deep primitive magma at 2.6 kbar (crossed circle) and a gas discharged from NKD14 magma at shallow depth (asterisk) representing the gas stored at the shallow reservoir. The shallow gas component was calculated from the difference in volatile concentrations between pre-eruptive melt and groundmass glass.

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**Fig. 10** Schematic summary of the magma and gas evolution in the Aso plumbing system. Magma passage is indicated by the color ranging red-orange-yellow. The gas is white, and the grey zone corresponds to the conductivity anomaly (Hata *et al.* 2016). C1, C2, and LVL (black thick bars) are the zones of magma stagnations determined by geophysical methods (Yamamoto *et al.* 1999; Sudo and Kong 2001; Tsutsui and Sudo

1294    2004; Sudo *et al.* 2006; Abe *et al.* 2010; Hata *et al.* 2016).

Figure 1

Figure 1

Figure 2 — Click here to access/download;Figure;Fig2.pdf
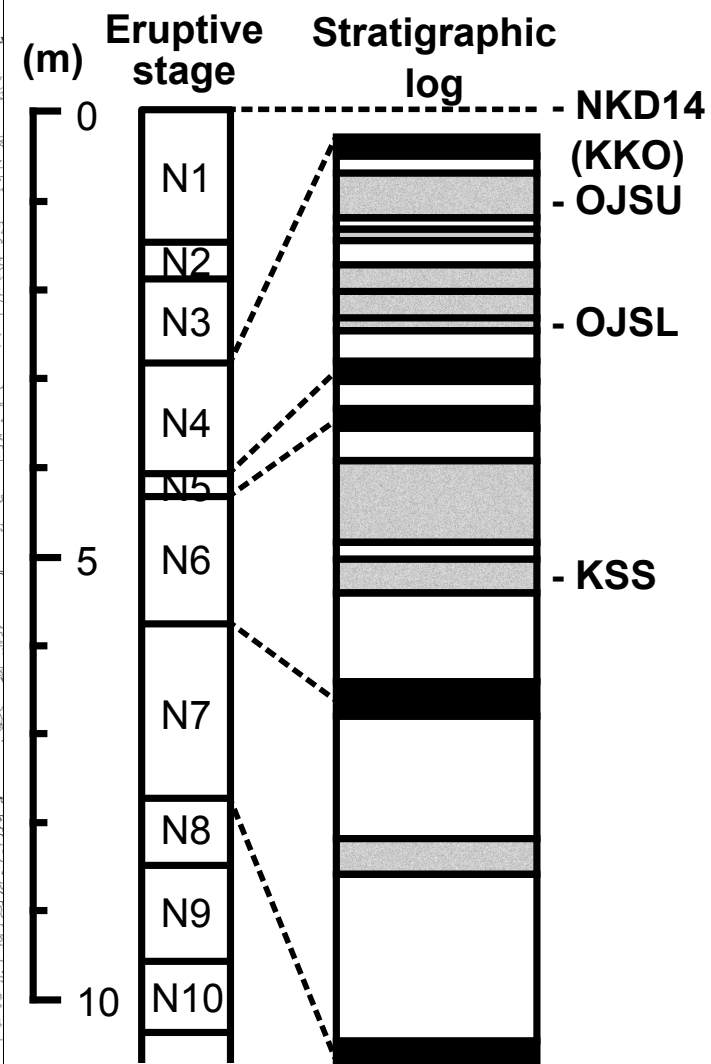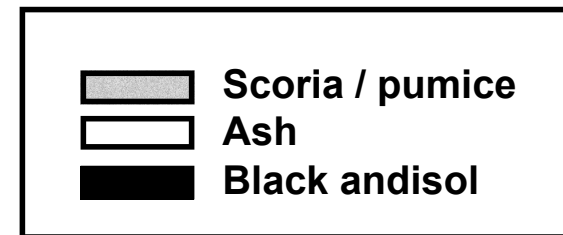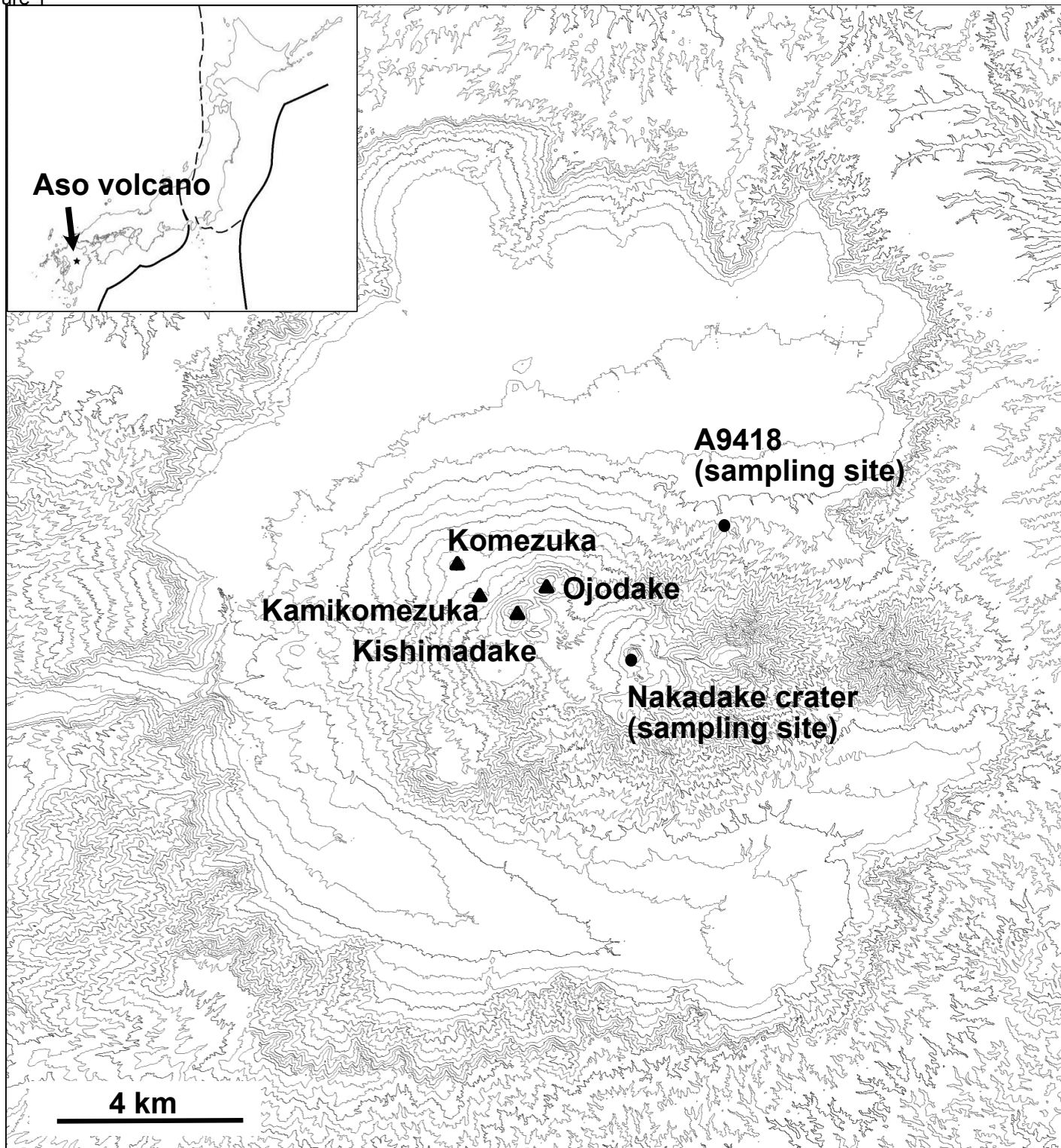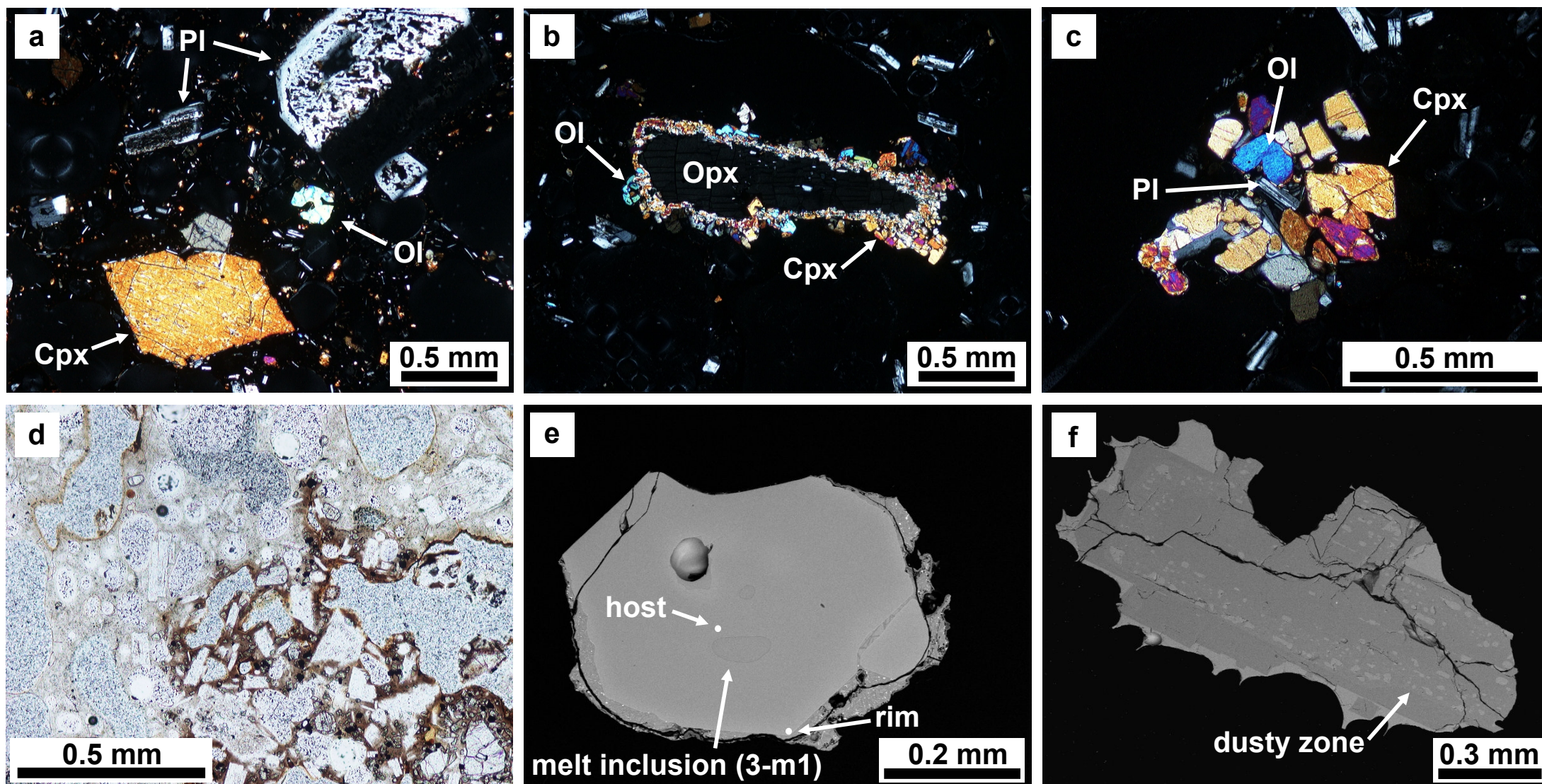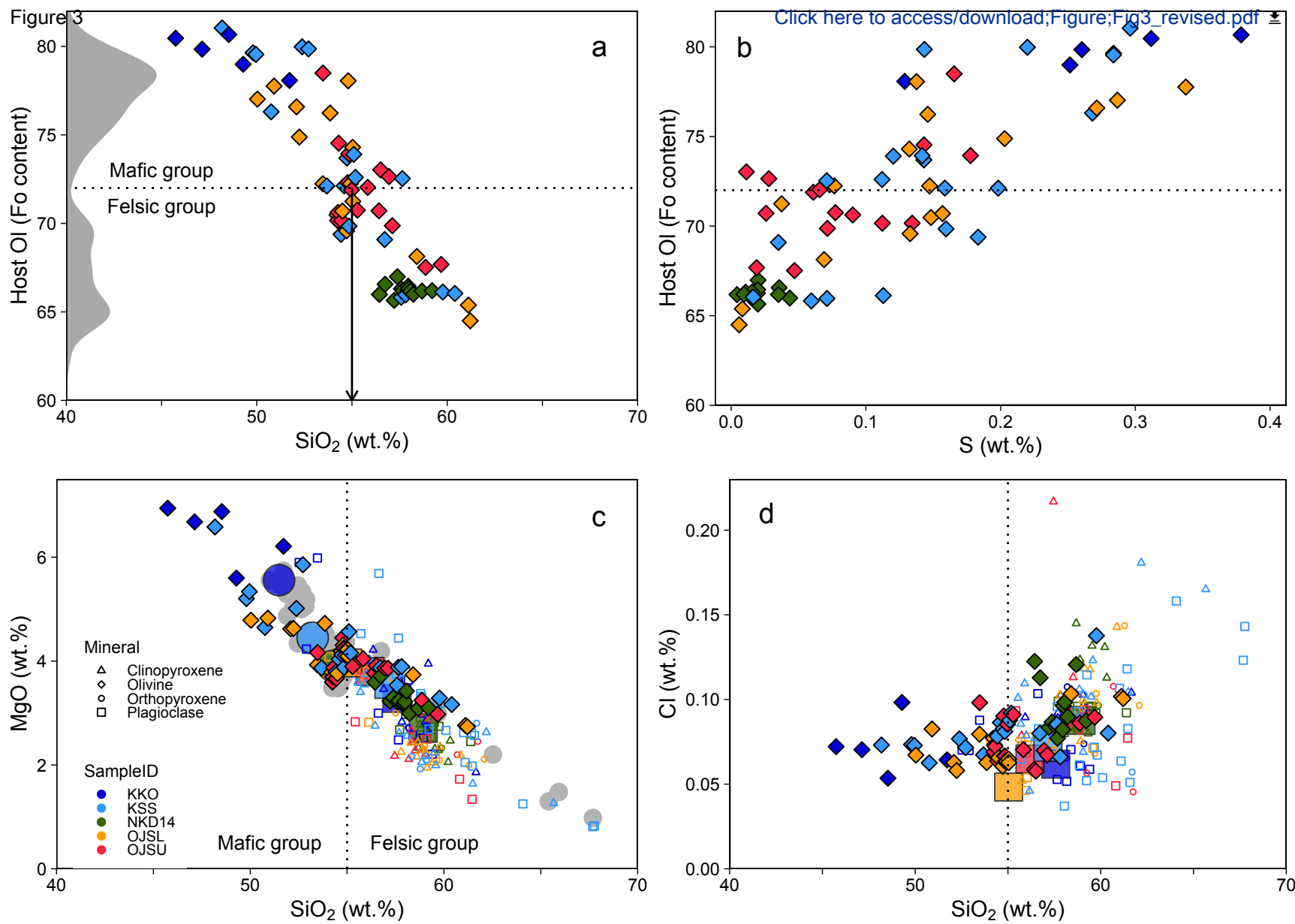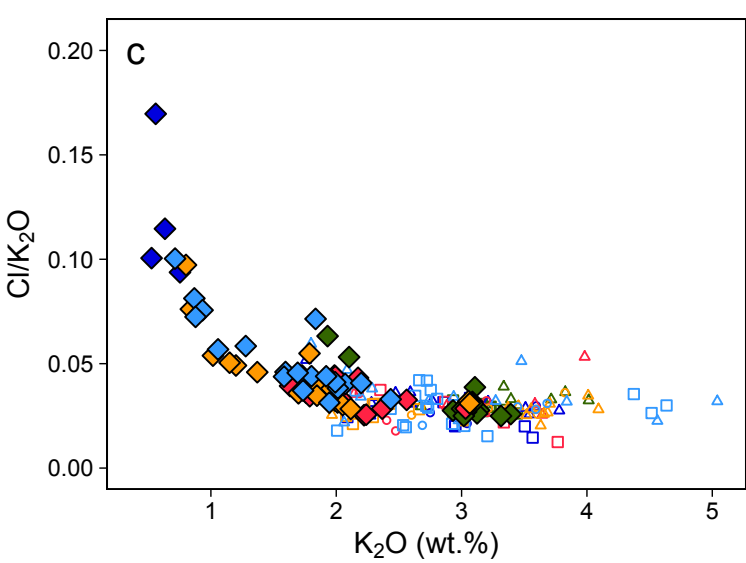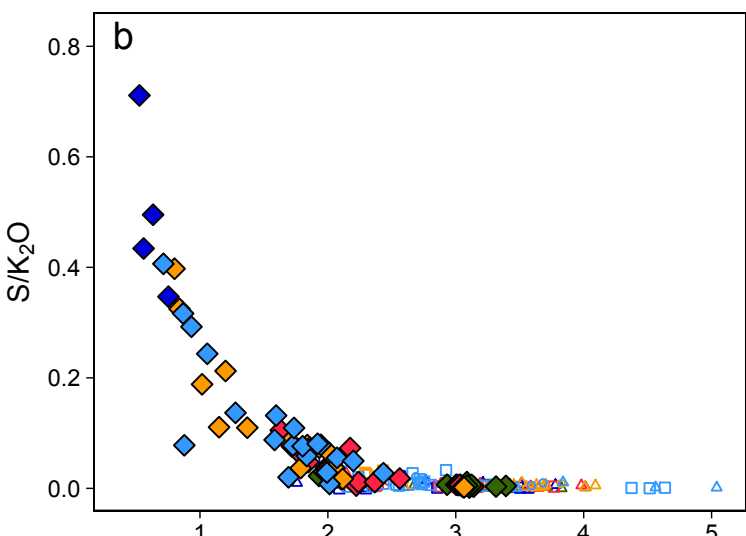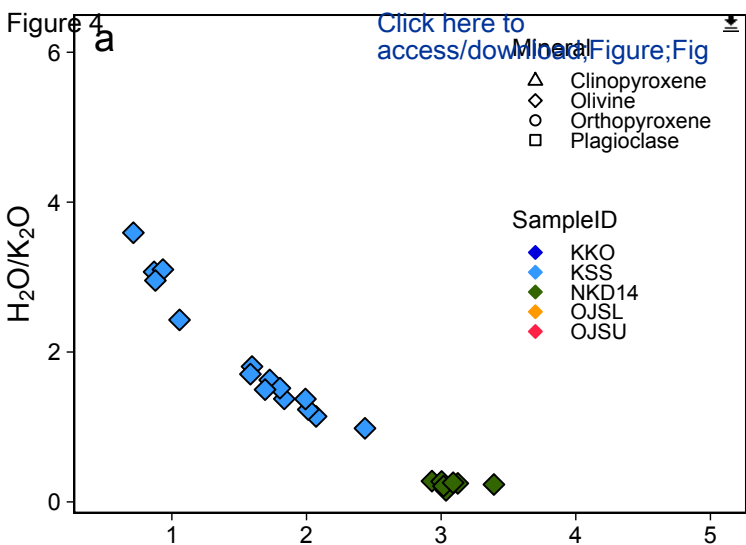
Figure 3

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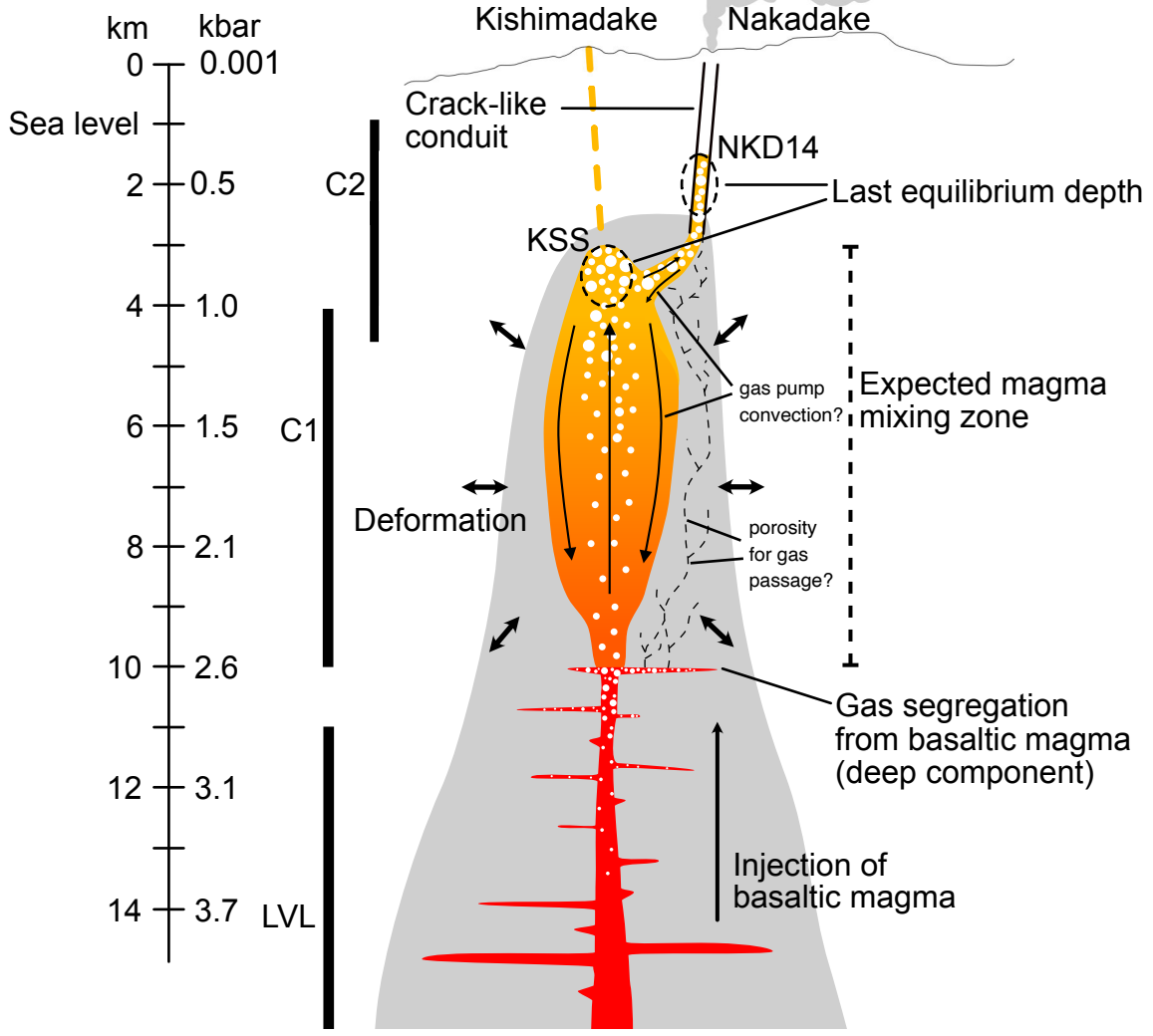
Table 1 Major and trace element compositions of bulk tephra samples.

| Volcanic cone | Nakadake | Kamikomezuka | Kishimadake | | |
|---|---|---|---|---|---|
| Sample | NKD14 | KKO | KSS | RSTD (%)[b] | Detection limit |
| *Majore elements (wt.%)* [a] | | | | | |
| $SiO_2$ | 54.26 | 51.49 | 53.22 | 0.1 | |
| $TiO_2$ | 0.94 | 0.94 | 1.00 | 0.3 | |
| $Al_2O_3$ | 17.84 | 18.52 | 18.48 | 0.1 | |
| FeO* | 8.78 | 10.07 | 9.62 | 0.1 | |
| MnO | 0.16 | 0.18 | 0.17 | 0.3 | |
| MgO | 3.91 | 5.56 | 4.45 | 0.1 | |
| CaO | 8.77 | 9.38 | 8.71 | 0.1 | |
| $Na_2O$ | 3.05 | 2.49 | 2.61 | 0.2 | |
| $K_2O$ | 2.00 | 1.16 | 1.51 | 0.3 | |
| $P_2O_5$ | 0.28 | 0.21 | 0.22 | 0.4 | |
| Total** | 99.75 | 99.93 | 99.50 | | |
| *Trace elements (ppm)* | | | | | |
| Sc | 26 | 31 | 30 | 2.4 | 4.6 |
| V | 260 | 320 | 283 | 0.5 | 5.4 |
| Cr | n.d. | 11 | 12 | 8.9 | 3.7 |
| Ni | n.d. | 21 | 18 | 6.2 | 5.1 |
| Cu | 209 | 202 | 131 | 0.7 | 5.3 |
| Zn | 81 | 88 | 81 | 0.7 | 2.9 |
| Rb | 58 | 31 | 45 | 0.7 | 1.4 |
| Sr | 566 | 588 | 598 | 0.2 | 2.7 |
| Y | 26 | 21 | 23 | 2.3 | 2.5 |
| Zr | 139 | 88 | 121 | 0.6 | 2.4 |
| Nb | 7 | 5 | 7 | 6.3 | 1.5 |
| Ba | 369 | 277 | 328 | 0.7 | 9.8 |
| La | 18 | 13 | 15 | 11.2 | 6.1 |
| Ce | 82 | 33 | 33 | 4.2 | 5.4 |
| Nd | 25 | 16 | 18 | 7.3 | 5.5 |
| Pb | 13 | 7 | 18 | 3.8 | 2.4 |

[a] All oxides were normalized to 100 wt.%.

[b] Relative standard deviation (RSTD) of major elements were from Mori and Mashima (2005). RSTD of trace elements were calculated for KSS using the relationship between RSTD and concentration reported in Mori and Mashima (2005).

* Total iron as FeO calculated by following equation: $FeO = 0.8998*Fe_2O_3$.

** Total of the raw data.

Table 2: PEC corrected and normalized to 100%, major element and volatile concentrations in representative melt inclusions.

| Sample | NKD14 | | | | | | KKO | | | | | | OJSU | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Host mineral[a] | OL | OL | OL | PL | CPX | OPX | OL | OL | PL | PL | CPX | OPX | OL | OL | PL | PL | CPX |
| Melt ID | 1-m1 | 2-m1 | 4-m4 | a3-m1 | c5-m1 | 4-m6 | 2-m1 | 3-m3 | a2-m1 | Cb3-m1 | d2-m1 | 1-m2 | 1-m5 | 1-m13 | 1-m1 | 1-m4 | 1-m2 |
| $SiO_2$ (wt.%)[b] | 59.21 | 56.44 | 57.22 | 57.71 | 60.22 | 59.88 | 48.53 | 49.29 | 57.65 | 52.53 | 61.65 | 59.09 | 59.68 | 54.30 | 59.11 | 55.74 | 57.45 |
| $TiO_2$ | 1.33 | 1.01 | 1.35 | 1.48 | 1.45 | 1.25 | 0.86 | 1.07 | 1.15 | 1.25 | 1.39 | 1.36 | 0.97 | 1.15 | 1.10 | 1.33 | 1.60 |
| $Al_2O_3$ | 14.43 | 14.82 | 14.33 | 14.61 | 14.23 | 14.37 | 18.08 | 19.52 | 17.10 | 13.35 | 13.69 | 14.90 | 14.42 | 16.77 | 16.91 | 15.34 | 15.47 |
| $FeO^{Total}$ | 10.08 | 11.63 | 10.63 | 11.16 | 10.06 | 9.45 | 11.85 | 10.50 | 8.34 | 13.85 | 9.31 | 9.24 | 9.45 | 9.88 | 7.39 | 10.14 | 10.04 |
| MnO | 0.23 | 0.22 | 0.21 | 0.23 | 0.18 | 0.24 | 0.13 | 0.19 | 0.15 | 0.28 | 0.21 | 0.19 | 0.19 | 0.17 | 0.14 | 0.21 | 0.19 |
| MgO | 3.10 | 3.59 | 3.23 | 2.68 | 2.05 | 2.33 | 6.88 | 5.60 | 2.48 | 5.90 | 1.86 | 2.76 | 2.98 | 3.87 | 2.50 | 3.84 | 2.17 |
| CaO | 5.13 | 6.50 | 6.38 | 5.83 | 4.90 | 5.24 | 10.37 | 10.60 | 6.86 | 8.85 | 4.71 | 5.87 | 5.72 | 8.50 | 5.92 | 7.51 | 5.27 |
| $Na_2O$ | 2.86 | 3.49 | 3.03 | 2.55 | 2.97 | 3.63 | 2.61 | 2.48 | 2.44 | 1.81 | 3.16 | 3.40 | 3.02 | 3.10 | 3.49 | 3.11 | 3.09 |
| $K_2O$ | 3.16 | 1.94 | 3.09 | 3.23 | 3.36 | 3.35 | 0.53 | 0.58 | 3.62 | 1.98 | 3.78 | 2.78 | 3.14 | 1.95 | 2.97 | 2.46 | 4.07 |
| $P_2O_5$ | 0.48 | 0.37 | 0.53 | 0.52 | 0.57 | 0.26 | 0.16 | 0.17 | 0.21 | 0.20 | 0.23 | 0.40 | 0.44 | 0.31 | 0.46 | 0.31 | 0.64 |
| S (EPMA) | 0.010 | 0.044 | 0.022 | 0.009 | 0.013 | 0.019 | 0.378 | 0.251 | 0.004 | 0.097 | 0.022 | 0.014 | 0.019 | 0.143 | 0.011 | 0.041 | 0.021 |
| Cl (EPMA) | 0.087 | 0.122 | 0.085 | 0.099 | 0.131 | 0.096 | 0.054 | 0.098 | 0.053 | 0.070 | 0.104 | 0.074 | 0.090 | 0.072 | 0.094 | 0.073 | 0.217 |
| $H_2O$ (SIMS) | - | - | 0.48 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| S ppm (SIMS) | - | - | 199 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Cl ppm (SIMS) | - | - | 835 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| F ppm (SIMS) | - | - | 727 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| $P_2O_5$ (SIMS) | - | - | 0.49 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| $H_2O/K_2O$ | - | - | 0.154 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| $S/K_2O$ | 0.003 | 0.022 | 0.006 | 0.003 | 0.004 | 0.006 | 0.711 | 0.434 | 0.001 | 0.049 | 0.006 | 0.005 | 0.006 | 0.073 | 0.004 | 0.017 | 0.005 |
| $Cl/K_2O$ | 0.028 | 0.063 | 0.027 | 0.031 | 0.039 | 0.029 | 0.101 | 0.170 | 0.015 | 0.035 | 0.028 | 0.027 | 0.028 | 0.037 | 0.032 | 0.029 | 0.053 |
| $F/K_2O$ | - | - | 0.024 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| PEC%[c] | 1.3 | 1.6 | 1.4 | - | - | - | 5.6 | 0.1 | - | - | - | - | 0.7 | 0.1 | - | - | - |
| Host Mg#/An[a] | 66.2 | 66.0 | 65.6 | 66.8 | 69.6 | 69.2 | 80.7 | 79.0 | 66.7 | 89.6 | 69.2 | 68.9 | 67.7 | 74.5 | 65.7 | 80.8 | 69.6 |

Table 2 (continued)

| Sample | OJSL | | | | | | | | KSS | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Host mineral[a] | OPX | OL | OL | PL | PL | CPX | CPX | OPX | OL | OL | OL | PL | PL | CPX | CPX | OPX |
| Melt ID | 1-m2 | 1-m2 | 1-m3 | 1-m1 | 1-m6 | 1-m6 | O1-m7 | 1-m8 | 2-m1 | 3-m4 | 4-m6 | c1-m1 | d2-m1 | a2-m1 | b5-m1 | 3-m2 |
| $SiO_2$ (wt.%)[b] | 61.75 | 52.24 | 61.21 | 56.12 | 59.57 | 58.65 | 60.87 | 62.08 | 48.18 | 56.92 | 60.40 | 59.81 | 67.77 | 55.90 | 59.58 | 58.78 |
| $TiO_2$ | 0.76 | 1.08 | 0.79 | 1.48 | 1.19 | 1.24 | 1.27 | 1.21 | 0.99 | 0.56 | 1.25 | 0.98 | 1.01 | 1.37 | 1.41 | 1.36 |
| $Al_2O_3$ | 14.16 | 16.91 | 13.34 | 16.56 | 16.37 | 15.31 | 15.22 | 14.53 | 17.89 | 13.04 | 12.71 | 16.61 | 15.89 | 16.09 | 14.99 | 14.51 |
| $FeO^{Total}$ | 8.68 | 11.50 | 9.60 | 9.41 | 8.01 | 9.66 | 7.55 | 7.67 | 11.72 | 10.28 | 10.56 | 7.31 | 4.20 | 10.25 | 9.44 | 10.48 |
| MnO | 0.16 | 0.16 | 0.20 | 0.20 | 0.13 | 0.18 | 0.16 | 0.16 | 0.18 | 0.17 | 0.27 | 0.20 | 0.10 | 0.23 | 0.24 | 0.17 |
| MgO | 2.45 | 4.63 | 2.74 | 2.82 | 2.13 | 2.44 | 2.18 | 2.11 | 6.58 | 3.13 | 3.16 | 3.19 | 0.83 | 3.55 | 1.99 | 1.92 |
| CaO | 5.45 | 9.35 | 5.49 | 7.01 | 5.78 | 5.50 | 4.59 | 4.68 | 10.99 | 6.14 | 5.97 | 6.94 | 2.99 | 7.28 | 5.09 | 5.27 |
| $Na_2O$ | 3.91 | 2.77 | 2.89 | 2.78 | 3.36 | 2.96 | 3.58 | 3.40 | 2.50 | 2.81 | 3.15 | 2.24 | 2.04 | 3.16 | 2.79 | 3.08 |
| $K_2O$ | 2.55 | 1.08 | 3.25 | 2.76 | 3.11 | 3.50 | 4.12 | 3.74 | 0.73 | 1.84 | 2.10 | 2.42 | 4.77 | 1.84 | 3.87 | 3.83 |
| $P_2O_5$ | 0.12 | 0.29 | 0.49 | 0.86 | 0.36 | 0.56 | 0.45 | 0.41 | 0.23 | 0.35 | 0.43 | 0.30 | 0.41 | 0.34 | 0.60 | 0.60 |
| S (EPMA) | 0.033 | 0.203 | 0.006 | 0.026 | 0.007 | 0.021 | 0.008 | 0.013 | 0.180 | 0.068 | 0.017 | 0.008 | 0.006 | 0.081 | 0.042 | 0.038 |
| Cl (EPMA) | 0.045 | 0.058 | 0.101 | 0.078 | 0.071 | 0.103 | 0.143 | 0.096 | 0.071 | 0.153 | 0.085 | 0.067 | 0.143 | 0.109 | 0.123 | 0.118 |
| $H_2O$ (SIMS) | - | - | - | - | - | - | - | - | 2.62 | 2.52 | 2.58 | - | - | - | - | - |
| S ppm (SIMS) | - | - | - | - | - | - | - | - | 2962 | 1075 | 164 | - | - | - | - | - |
| Cl ppm (SIMS) | - | - | - | - | - | - | - | - | 731 | 1311 | 801 | - | - | - | - | - |
| F ppm (SIMS) | - | - | - | - | - | - | - | - | 331 | 853 | 578 | - | - | - | - | - |
| $P_2O_5$ (SIMS) | - | - | - | - | - | - | - | - | 0.22 | 0.40 | 0.50 | - | - | - | - | - |
| $H_2O/K_2O$ | - | - | - | - | - | - | - | - | 3.591 | 1.375 | 1.232 | - | - | - | - | - |
| $S/K_2O$ | 0.013 | 0.188 | 0.002 | 0.009 | 0.002 | 0.006 | 0.002 | 0.003 | 0.406 | 0.059 | 0.008 | 0.003 | 0.001 | 0.044 | 0.011 | 0.010 |
| $Cl/K_2O$ | 0.018 | 0.054 | 0.031 | 0.028 | 0.023 | 0.030 | 0.035 | 0.026 | 0.100 | 0.071 | 0.038 | 0.028 | 0.030 | 0.059 | 0.032 | 0.031 |
| $F/K_2O$ | - | - | - | - | - | - | - | - | 0.045 | 0.047 | 0.028 | - | - | - | - | - |
| PEC%[c] | - | 2.3 | 0.1 | - | - | - | - | - | 8.7 | 1.3 | 0.3 | - | - | - | - | - |
| Host Mg#/An[d] | 70.4 | 74.9 | 64.5 | 81.8 | 66.4 | 71.1 | 69.2 | 66.7 | 81.0 | 66.1 | 66.0 | 76.7 | 56.8 | 76.4 | 69.4 | 66.2 |

[a] OL: olivine, PL: plagioclase, CPX: clinopyroxene, OPX: orthopyroxene. [b] All major oxides were normalized to 100 wt.% as volatile-free. [c] Degree of post-entrapment crystallization (wt.%) based on the addition of equilibrium olivine. Oxide concetrations presented in this table were corrected values. [d] Mg# = Mg/(Fe+Mg), An = Ca/(Ca+Na), in mole%.

Table 3 Major element and volatile contents in groundmass glasses.

| Volcanic cone | Nakadake | | Kamikomezuka | | Ojodake | | | | Kishimadake | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample | NKD14 | | KKO | | OJSU | | OJSL | | KSS | |
| | Avr. | Std. | Avr. | Std. | Avr. | Std. | Avr. | Std. | Avr. | Std. |
| $N =$ [a] | 17 | | 8 | | 14 | | 13 | | 18 | |
| $SiO_2$ (wt.%)[b] | 58.94 | 0.30 | 57.58 | 0.46 | 56.19 | 0.95 | 55.03 | 0.33 | 57.15 | 0.63 |
| $TiO_2$ | 1.39 | 0.05 | 1.56 | 0.06 | 1.32 | 0.06 | 1.30 | 0.05 | 1.24 | 0.05 |
| $Al_2O_3$ | 14.66 | 0.35 | 14.14 | 0.23 | 15.01 | 0.43 | 15.40 | 0.55 | 15.77 | 0.32 |
| $FeO^{Total}$ | 9.60 | 0.26 | 12.11 | 0.43 | 10.36 | 0.35 | 10.87 | 0.42 | 9.40 | 0.36 |
| MnO | 0.21 | 0.02 | 0.23 | 0.02 | 0.21 | 0.02 | 0.22 | 0.02 | 0.21 | 0.02 |
| MgO | 2.70 | 0.15 | 3.28 | 0.15 | 3.80 | 0.19 | 3.96 | 0.22 | 3.55 | 0.17 |
| CaO | 6.05 | 0.23 | 6.67 | 1.12 | 7.29 | 0.34 | 7.84 | 0.28 | 7.29 | 0.36 |
| $Na_2O$ | 2.87 | 0.23 | 2.15 | 0.66 | 3.33 | 0.18 | 3.28 | 0.31 | 2.73 | 0.22 |
| $K_2O$ | 3.09 | 0.09 | 2.01 | 0.45 | 2.22 | 0.10 | 1.86 | 0.29 | 2.30 | 0.15 |
| $P_2O_5$ | 0.48 | 0.04 | 0.28 | 0.05 | 0.26 | 0.04 | 0.23 | 0.03 | 0.36 | 0.05 |
| S | 0.008 | 0.011 | 0.003 | 0.005 | 0.012 | 0.018 | 0.006 | 0.008 | 0.006 | 0.006 |
| Cl | 0.088 | 0.013 | 0.062 | 0.016 | 0.065 | 0.014 | 0.048 | 0.008 | 0.072 | 0.012 |

[a] Number of analyses.
[b] All major oxides were normalized to 100 wt.% excluding S and Cl.

Table 4 Results of thermo-barometric calculation for mixed magma

| Volcanic cone | Nakadake | Kamikomezuka | Ojodake | | Kishimadake |
|---|---|---|---|---|---|
| Sample | NKD14 | KKO | OJSU | OJSL | KSS |
| An content (Pl-rim) | 63 | 70 | 77 | 79 | 78 |
| Temperature (˚C)[b] | 1039 - 1047 | 1062 - 1070 | 1036 - 1046 | 1033 - 1044 | 1027 - 1037 |
| $H_2O$ in melt (wt.%) | 1.97 - 2.26 | 1.54 - 1.83 | 2.83 - 3.10 | 3.01 - 3.30 | 2.91 - 3.20 |

[a] Mode of plagioclse-rim composition

[b] Temperature and $H_2O$ content are estimated based on groundmass glasses and plagioclase compositions after Sakuyama et al. (2014). Ranges of estimated values corespond with the range of assuming crustal condition (0.1 - 0.5 GPa).

Table 5 Comparison of the measured volatile emission with petrological estimation for Nakadake 2014 eruption

| | $H_2O$ | $CO_2$ | $SO_2$ | HCl |
|---|---|---|---|---|
| Total emitted mass (ton)[a] | $1.2 \times 10^6$ | $7.7 \times 10^3$ | $1.4 \times 10^5$ | $5.6 \times 10^3$ |
| Pre-eruptive concentration in melt (ˇ | 1.08 | 0.034 | 0.069* | 0.196* |
| Exsolved volatile from magma (ton) | 14000 | 440 | 1600 | 1400 |

[a] Total mass of each volatile species were computed from observed gas composition of $CO_2/SO_2 = 8$, $H_2O/SO_2 = 30$ and $HCl/SO_2 = 0.07$ in mole (Shinohara 2013, 2018) assuming observed average $SO_2$ emission rate of 2000 - 3100 ton/day from November 18, 2014 to Janurary 9, 2015 (JMA 2016, 2020) for 70 days.

[b] Pre-eruptive volatile concentrations were estimated for an average $K_2O$ concentration of groundmass glass times the maximum volatiles/$K_2O$ ratios of NKD14 melt inclusions. For pre-eruptive $CO_2$ concentration, we chose the highest reported value (340 ppm) of Nakadake eruption products (Saito et al. 2018).

[c] Total masses of exsolved volatiles from erupted magma were calculated using the total mass of erupted products of $2.0 \times 10^6$ ton during the eruption of 2014 - 2015 (Yokoo and Miyabuchi 2015) assuming all S degassed as $SO_2$.

*Values with asterisk are shown as S and Cl.

# Reply to reviewer's comments

First of all, we thank the reviewers for detailed and insightful comments. We carefully read the comments and answered to all in this reply summary. To distinguish the comments from replies, we quoted the comment as an indented paragraph or in double quotation marks in italic. Please note that the reviewer comments refer to the page and line numbers of our initial submitted document, while our replies refer to line numbers of the newly revised document. The modified text as it reads now in the revised manuscript is quoted in blue.

Our manuscript got three reviews and four major points were raised by all the reviewers so we are making a common response to the three issues that were:

1) Regarding the choice of magma degassing model, some reviewers were skeptical about the accuracy of SolEx. They have asked if we can explain, provide arguments in favor of, the choice of SolEx? Why not D-Compress?

2) The term felsic and mafic correspond to two groups of samples that are not well defined. This makes the text hard to follow and consequently some parts of discussion appear *ad hoc*.

3) The concentration of volatile elements in the volatile-rich end-member is re-assessed in the middle section of the discussion. The reason for the re-calculation of the volatile concentration in mafic endmember is not clear, especially for $H_2O$ concentration.

4) The authors have measured $CO_2$ by SIMS and although they argue it could be contaminated by prior carbon coating for EMPA analysis, yet the authors claim they are low in the text. These values should be reported in the tables.

In addition to these points, we realized that our discussion may have been unclear. Because of this, we have added a new figure (Fig. 10), summarizing the conclusion derived from the discussion. We sincerely hope that the paper improved the clarity.

**Response to (1)**: In this paper, we compared published Aso volcanic gas composition with modelled gas composition at depths. Here, we used the SolEx model to achieve such comparison. As pointed out by all reviewers, S behavior during magmatic degassing is a complex process and it appears that there is no one model applicable for all volcanic degassing, and accuracy of some models were questioned as well. It is possible that our approach to apply an existing model may be premature and misleading. In this revision, we investigated further and came to a conclusion that SolEx still suits our situation best. "Lastly, this conclusion is highly model dependent. Here, we chose to use SolEx for its agreement with the variation of S in melt inclusions. However, one must be cautious with the use of SolEx, because it is shown to fail to reproduce degassing trajectories in other volcanoes (e.g., Werner et al. 2020)" [see Line 692-695].

As suggested by the reviewers, we now have calculated the compositional variations modelled by the model D-compress (Burgisser et al. 2015), and compared the results with the observed compositional trend (the figure shown below). The degassing paths modelled by D-compress (red lines) show moderate decrease of S with a decrease of $H_2O$ (left panel), whereas the paths of SolEx (black lines) show dramatic depression of sulfur with the initial decrease of $H_2O$, and fits globally with the observed trend. The SolEx results indicate negligible degassing of Cl (right panel), which is also consistent with our observation. However, some previous studies reported the inconsistency between SolEx paths and observed melt compositions (e.g. Werner et al. 2020). Furthermore, unlike D-compress, which accounts for chemical potential of gas species, SolEx treats the behavior of S with variable partition coefficient with pressure while not accounting for other parameters, such as oxygen fugacity change with decompression. Lastly, because the compositional trend of volatile elements in the melt inclusions is a result of degassing, mixing, and probably crystal fractionation, the disparity of melt composition from the degassing path is likely due to such processes. On top of this, diffusive H-loss of melt inclusion can reduce $H_2O$ while keeping S concentration. Similarly, many Cl points are shifted to a higher value

compared to the SolEx path, which can be explained by mixing and crystal fractionation as Cl is incompatible in minerals. Here, our point is that the trend of the volatile element depletion is better explained by SolEx than D-compress, while it is far from a perfect fit.

An ideal case, would be to use the method for predicting gas evolution using pressure-dependent bulk partitioning coefficients derived from the observed trend (Werner et al. 2020; Johnson et al. 2010; Sisson and Layne 1993; Spilliaert et al. 2006). However, this method requires a well-documented sample set representing the degassing and crystallization, but without mixing. In our case, the variation of major and some volatile elements is clearly controlled by mixing, while $H_2O$ and $CO_2$ are degassed. It was not possible to separate these processes, and derive degassing controlled S partition coefficient, like in those studies. Thus, we did not pursue this approach, and accepted to use SolEx for the degassing modelling of our sample.
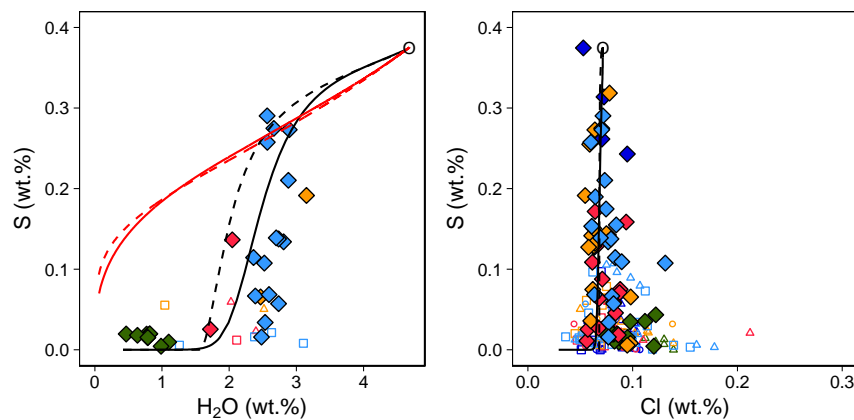


Figure caption: Red and black lines correspond to the modelled degassing paths of D-compress and SolEx, respectively. Solid and dashed line indicates the closed-system and the open-system degassing, respectively. Initial volatile concentration used for the degassing model is plotted as an open circle, with $H_2O$=4.68 %, S = 3750 ppm, Cl = 716 ppm (Our mafic endmember composition before degassing). The paths shown in the figures is the case with 650 ppm initial $CO_2$. Changing the initial $CO_2$ concentration did not change the paths significantly. Measured volatile concentrations of individual melt inclusion and average values of groundmass glasses are plotted as the same symbols as in Figure 3. $H_2O$ concentrations of groundmass glasses are assumed to be 0.01wt.%.

**Response to (2):** The definition of the two groups, mafic and felsic, is based on their host olivine composition. In our sample set, the core composition of the host olivines are clearly divided into two groups with Fo72 representing the divide (see the histogram below). We interpreted that olivines are grown from two distinctively different lavas, which we called mafic and felsic. Based on the anti-correlation of $SiO_2$ concentration in olivine-hosted melt inclusions with host Fo content, we concluded that magma composition can be divided into two groups above and below 55 wt.% $SiO_2$. The high $SiO_2$ corresponds to low-Fo olivine and low $SiO_2$ corresponds to high-Fo olivine. Thus, we grouped all melt inclusions lower than 55 wt.% $SiO_2$ in a mafic group, and others in a felsic group.

Olivine core (all samples)
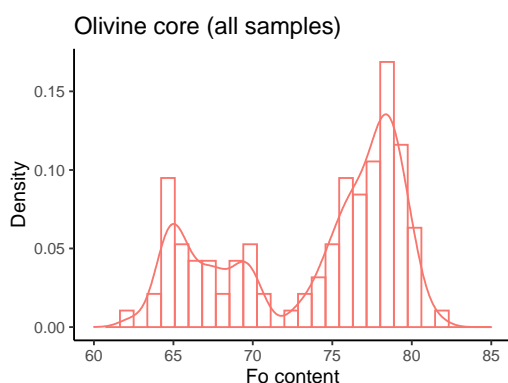


Thank you for pointing out the cut-off value of Fo74 as being unclear. While we mention the value in the text that was misquoted (as Fo74), the correct value is Fo72. We corrected the Fo value in the main texts to "…as low-Fo (62 to 72) and high-Fo (72 to 82)…" [Line 328] . In addition, we modified Figure 3a to include the relative density distribution of olivine core composition. On top of it, a dashed line representing Fo72 is added to Figure 3a and 3b to indicate the separation between the two MI groups. In the caption of Figure 3, we added the sentence, "The distribution of Fo content in all olivine cores is shown as a relative density function on the left side of (a). The dashed line in Figure 3a and 3b indicates the value Fo72.".

To clarify the definition of the groups, we added a new passage in the manuscript. The new text now reads [L 351-358], "In our sample set, the core composition of host olivines were clearly divided into two groups with Fo72 representing the divide (Fig. 3a). We interpreted that olivines have grown from two distinctively different lavas, which we called mafic and felsic. Based on the anti-correlation of $SiO_2$ concentration in olivine-hosted melt inclusions with host Fo content, we concluded that magma composition can be divided into two groups above and below 55 wt.% $SiO_2$. The high $SiO_2$ corresponded to low-Fo olivine and low $SiO_2$ corresponded to high-Fo olivine. Thus, in the following we grouped all the melt inclusions lower than 55 wt.% $SiO_2$ in a mafic group, and others in a felsic group."

**Response to (3):** The volatile concentration of the mafic endmember is defined based on the hygrometer of the plagioclase – melt – olivine equilibrium. This is necessary because MI data are influenced by magma degassing as $H_2O$ concentration in melt inclusion is easily modified by diffusion of $H^+$ through host olivine (Portnyagin et al. 2008, Chen et al. 2011, Gaetani et al. 2012, Bucholz et al. 2013). Thus, water content in MI is re-equilibrated to a degassed magma after entrapment. The measured water content in melt inclusions does not represent the water concentration at the depth of the deep magma chamber. To clarify, we rearranged the section "Characterization of mixing endmembers" and added sentences to better express what we meant. The exact changes are as follow:

- First these comments made us realise that the source of confusion originates from the mixing calculation applied to $H_2O$ concentration while we were clearly aware of the post-entrapment loss. In retrospect, the mixing model does not need to include $H_2O$. In the revised manuscript, we suppressed all the discussions concerning the $H_2O$ in the context of mixing. Furthermore, to clarify the definition of the mafic endmember, we change the order of sections. Now "Characterization of mixing endmembers" is followed by "volatile concentrations of the primitive magma" then "storage depth of magma mixture"
- We also addressed the issue by re-organizing a section of the discussion, "Characterization of mixing endmembers", by separating the discussion concerning the endmember compositions in major elements and volatile elements. Then, in the paragraphs discussing the characterization of the end-member of volatile elements, we explicitly discussed the effect of degassing in melt inclusions and why MI volatile data are not used.
- In the section "Characterization of mixing endmembers" in the discussion, "former" page 10 line 15 – 17, the sentences "For volatile elements, …. during/after magma mixing." are deleted from the paragraph and moved to the end of this section. This separates the discussion of major elements from volatile elements. The new paragraph now reads: "The mixing trend among

volatile elements is present and generally consistent with the trend of major elements. However, in detail, there are systematic disparities from the mixing curve (Supplementary document S4). Notably, abundances of $H_2O$, S, and Cl for NKD14 samples are depleted compared to the mixing trend traced by KSS melt inclusions (Fig. S4-5). This is best explained by significant degassing occurring during/after magma mixing. Furthermore, there is no single melt inclusion uniquely representing suitable mafic endmember volatile concentrations. The sample KSS-2-m1 is selected as the major element endmember, but its $H_2O$ contents are not the highest values. From the inspection of the trend, we inferred that mafic endmember must have higher volatile content thus most likely lost water after its entrapment. If melt inclusions formed at a deeper depth were stored in a shallower magma chamber, it is expected that H+ diffusion through olivine equilibrates melt inclusion with surrounding magma (Portnyagin et al. 2008, Chen et al. 2011, Gaetani et al. 2012, Bucholz et al. 2013, Ferris et al., 2016). Complete re-equilibration of the melt inclusions would have erased the mixing trend. However, we have found suitable endmember volatile element concentrations that satisfy the general trend. Because the mafic endmember magma is expected to be volatile-rich, it's $H_2O$ concentration has to be higher than the $H_2O$ of the mixed magma (e.g. melt inclusions). The maximum estimated $H_2O$ concentration (4.68 wt. %) based on the hygrometer discussed above is therefore taken as the concentration for the volatile-rich mafic endmember. This value of 4.68 wt.% $H_2O$ is higher, by about 2 wt. %, than the highest $H_2O$ concentration measured in the melt inclusion. Sakuyama's method implicitly ignores the $CO_2$ activity in magma, and predict lower $H_2O$ content when considering $CO_2$-bearing system (by 0.9 wt. % less, assessed from an experimental result of Melekhova et al., 2017). Furthermore, this volatile content is the value at the condition of olivine - plagioclase crystallization, most likely of the cooling magma in the crust. At this point we have no other constraint on the $H_2O$ concentration of the mafic endmember and the primary magma could have an even higher $H_2O$ content." [Line 448-475].
- The discussion concerning the volatile element concentration in the mafic endmember appears in two other sections, "Storage depth of the magma mixture", and "Volatile concentrations of primitive basaltic melt". We carefully examined redundancy, paid extra attention to improve the clarity of our interpretation.
- Lastly, we added a sentence in the supplementary material S4 "$H_2O$ concentration of mafic endmember was taken from the maximum plagioclase-olivine-liquid hygrometer-estimated value (4.68 wt.%) rather than from the measured melt inclusion because of possible diffusive H-loss (e.g. Portnyagin et al. 2008)."

**Response to (4)**: the $CO_2$ measurements by SIMS were added to Table 2 and S1. The $CO_2$ concentrations measured in the melt inclusions vary from 10 to 411 ppm. Although we wrote that these concentrations are generally low, we have doubts on the higher $CO_2$ values. We advise for caution interpreting the values in the range of a few hundreds ppm because of possible carbon contamination, since the EMP analyses (therefore carbon coating) were performed prior to volatile measurements by SIMS. In any case we did not use the melt inclusion measured $CO_2$ data in the discussion.

# Specific replies to reviewer's comments:

## Reviewer #1: Kayla Iacovino

*K. Iacovino review of "Persistent gas emission originating from a deep basaltic magma reservoir of an active volcano: the case of Aso volcano, Japan" by Kawaguchi et al. for Contributions to Mineralogy and Petrology.*

*Dear Editor,*

*This manuscript represents an increasingly important approach to understanding volcanic degassing; that is, it is one of a growing number of studies to look in depth at both the petrology of erupted products (petrography; compositional analysis of matrix glass and phenocrysts; and major and volatile element compositional analysis of melt inclusions) as well as modeling of the surface gas data. The data collected in this work seem to be of top quality, and I have no qualms with the results of chemical analyses (including the descriptions of the analyses performed). However, I find that key sections of this paper are complicated in ways that make it impossible to understand the use of these data. For example, while melt inclusion volatile concentrations are measured, key volatile concentrations of various magma reservoirs are also calculated in multiple ways. It is unclear why the authors have calculated so many of these values, instead of relying more heavily on their hard-won and quite thorough dataset.*

*Below I detail specific areas of concern where I think the manuscript could be improved with additional clarity in both a.) what samples are being referred to when; and b) why certain choices were made by the authors. Overall, the body of work is impressive, and I find the final analyses intriguing. But, I cannot comment intelligently on whether I am convinced with the final argument, since I am so confused by key details along the way. I recommend that this manuscript be accepted pending major revisions to the text. Some new calculations may be required OR the authors must better justify the values they chose for various modeling exercises.*

Response: We thank you very much for the support of the paper and the model. We took your comment carefully into account, and revised the discussion section as detailed in the following replies, especially examining what we have stated what is referred to and why certain choices are made.

## Specific comments

*Volatile concentrations: which are which?*
*The authors present a large number of values for H2O, CO2, S, F, and Cl concentrations in various magma reservoirs. Some of these are based on measured values in melt inclusions, while others are based on various calculated values. It is unclear to me throughout the text which reservoir is being referred to at any given time. I \*think\* there are three main reservoirs: a shallow region which contains a mixed magma created by the mixing of a mafic end-member and a silicic end-member plus a deeper region which is referred to as either a primitive or primary source region. I attempted to keep a running tally of the values ascribed to each of these magma bodies as I read the text but was unable to accurately do so. I think a table AND a figure showing the values broken down based on these three reservoirs with symbols for measured (MI) and calculated (hygrometer, K2O ratio modeling…) values would be very helpful.*

*The different "sets" of values that I encountered include:*
1. *Measured melt inclusion values for various subsets of the data (although it is never made clear which samples within each sample number are grouped into which of the three reservoirs listed above)*
2. *Primitive reservoir values modeled using the plagioclase hygrometer (some of which are discounted by the authors)*
3. *Primitive reservoir values modeled using the ratio of volatiles to K2O concentration*
4. *Values from another paper (Saito et al., 2018) that show up and which are used in the final analysis despite new values presented in this paper*

Response: The reason why we constantly mention different sets of values, volatile concentration in particular, is the reflection of the complexity of the processes. On the one hand, we have the measured

values, yet these are the results of modifications due to magma transport and storage. As we develop the discussion to distinguish processes (mixing, deep and shallow storages), inevitably we need to introduce other geochemical indications that may be the reflections of our model hypothesis.

We acknowledge that our discussion was not organized enough to present our idea clearly. Especially since the issues mentioned here were also pointed out by other reviewers. We addressed it as one of the four points listed at the beginning of this summary.

> *Introduction and methods sections*
> *These sections are fantastic and well written, and I suggest no changes here.*

> *Results section*
> ***Section on host mineral compositions****: Here is where my confusion begins. The MI-bearing olivines (e.g., those shown in figure 3) come from 5 different sampled locations (the five sample numbers) and are grouped into two groups: high Fo_olivine with low SiO2_MI and low Fo_olivine with high SiO2_MI. These groups are separated at Fo=74. However, figure 3a does not seem to indicate that there are two distinct groups of ol, and it makes me wonder why the authors chose this seemingly arbitrary Fo value to define their groups.*

Response: We wrote a common reply for the three reviewers at the beginning of the document. This is addressed in "Response to (2)" of the list.

> ***Section on major and volatile elements in melt inclusions:*** *As with the previous section, this one details volatile concentrations in two "groups": mafic and felsic. It is not immediately clear to me which samples in Fig 3 fall into which groups. Specific volatile concentrations are called out here, but for example, which sample in Fig 3 represents the "felsic volatile-poor magma" with S<1069 ppm? Since the distinction between these groups seems arbitrary to me, I lose the meaning of the most volatile-rich sample from the felsic group.*

Response: As we have revised the presentation of the mafic and felsic groups (see "Response to (2)), we hope the discussion on volatile elements is clearer. We also modified figure 3, adding a background color to identify immediately the mafic and felsic groups.

> ***Section on storage depth of magma mixture:*** *Here it is very unclear as to which samples are being referred to at any given time.*

Response: we revised the text carefully to be more specific about what sample we were talking about. We hope that the section now reads well. Also, we switched the position of two sections, "***Volatile concentrations of primitive basaltic melt"*** now comes before "***Storage depth of the magma mixture"*** for clarity of discussion.

> *A plagioclase hygrometer is used here to calculate the $H_2O$ concentration of the mixed magma (I think?). I think I understand the rationale for this, although it should be more clearly stated. E.g., MI measured values give $H_2O$ in end-member magmas, so the hygrometer calculated values using feldspar rims and matrix glass should correspond to the mixed value.*

Response: Measurements of $H_2O$ in melt inclusions are not used for determining the $H_2O$ concentrations of the endmembers. Instead, the $H_2O$ determined by the hygrometer is the $H_2O$ concentration of the mixed magma, because plagioclase rim - melt are equilibrated after mixing. The $H_2O$ concentration of the endmember has to be higher than the $H_2O$ of the mixed magma, therefore higher than the $H_2O$-determined by the hygrometer. The $H_2O$ concentration of the volatile-rich endmember is 4.68 wt.% (and this is still a minimum value) corresponding to the highest calculated value with the hygrometer determined from the plagioclase core. To clarify the significance of the results of the hygrometers, we

added a sentence in (former) page 11, line 13. It reads: "For example, measured volatile concentrations of melt inclusions are considered to be re-equilibrated to a condition of a magma storage. Alternatively, it is also possible to determine $H_2O$ concentrations estimated from plagioclase rim and groundmass glass pairs (geo-hygrometer, Lange et al. 2009), likely corresponding to the value of the mixed magma during the plagioclase rim growth. The $H_2O$ concentration of such mixed magmas are, ~2 wt.% for NKD14 and KKO, and ~3 wt.% for OJSU, OJSL and KSS (Table 4)." [Line 554-560]

> *$H2O$ concentrations are converted to storage depths. VERY IMPORTANT: which model was used to calculate saturation pressures?*

Response: The conversion from $H_2O$ concentrations to saturation pressure was based on the water solubility model of Moore et al. (1998). Estimated $H_2O$ concentrations and temperatures were plotted in Figure 4, then saturation pressures were read from solubility contours. The corresponding depths of these pressures were calculated based on the reported crustal density structure in the Aso area (2200 kg/m3 for depths <1km and 2700 kg/m3 for greater depths; Komazawa, 1995). We have revised and made sure that all the information is explicitly cited in the text.

> *Line 22-23 on this page: 1) "Melt inclusion $H2O$ measurements ranged from 0.47 to 2.97 wt% (SIMS)" For which samples? 2) In table 2, measured $H2O$ in MI goes up to 4.57 (measured by FTIR). Do you discount this FTIR value? 3) Also noteworthy that I think the authors should decide how to compare FTIR and SIMS data. Currently, both are presented, but it is unclear if one method is favored over another?*

Response: **(1)** The sample names are NKD14-Olivine-4-m4 corresponding to 0.47 wt. % $H_2O$ and KSS-Olivine-4-m11 corresponding to 2.89 wt. %. Sample names are added to the sentence [Line 369]. **(2)** The comparison of $H_2O$ measurements by FTIR and SIMS data: although we reported $H_2O$ concentrations done with both methods, FTIR by reflectance is prone to overestimation of $H_2O$ concentration due to the baseline correction of spectra. Therefore, in the entire manuscript only the SIMS $H_2O$ measurements are used for discussion and considered reliable. As some inclusions are only measured by FTIR, we couldn't compare them with SIMS measurements and we do not have a concrete reason to discard the data neither. So we decided to report the data with a caution of potentially large uncertainty close to a factor of 2. We added the following sentence as a footnote to the Table S1 "In this study, we did not find satisfactory agreement between $H_2O$ determined by FTIR and by SIMS (uncertainty of FTIR measurements is close to 40%) so in the following, we only consider $H_2O$ concentrations measured by SIMS, based on the better detection limit and precision of the method." [Line 262-265]. **(3)** Regarding the measurements of $H_2O$ concentration, FTIR and SIMS measurements are unusually in weak agreement (within 40%, see first figure below), with one obvious outlier (KSS-OL-4-m7). As already written in (2), one explanation to this disagreement is overestimation of $H_2O$ in reflectance FTIR analysis due to the contamination of reflective components derived from the host minerals. Again in response to this, we only consider SIMS $H_2O$ measurements in the entire manuscript, for the sake of consistency, and the range of $H_2O$ cited everywhere in the text is always that of SIMS measurements.
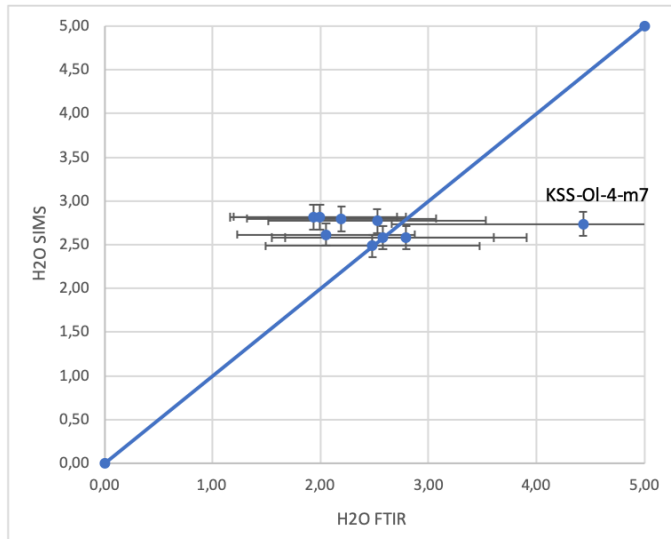
*Lines 26-28 on this page: I don't understand why the $CO_2$ concentration in the matrix glass has any meaning here. The matrix glasses are completely degassed. If anything, the $CO_2$ concentration in the MI should be considered (even given the presence of vapor bubbles). By the way, how is $CO_2$ measured in glasses? It seems like it is not measured, but here it is reported that matrix glasses have very low $CO_2$.*

Response: Yes, your remark is absolutely correct. It was our error. We deleted the text referring to $CO_2$ measurements in the matrix. The section of "Storage depth and . . . " is completely re-written, suppressing such incoherence.

*Second paragraph in this section: 1) Why is $H_2O$ concentration calculated using the plagioclase hygrometer for the mafic end-member? Surely it makes more sense to rely on measured MI concentrations here? 2) Also, why Is a $CO_2$ value of 200 ppm used to model the saturation pressure? 3) What is the rationale for the crustal densities of 2400 kg/m3 and 2700 kg/m3?*

Response:
**1)** The reason that we calculated using the plagioclase-olivine-melt hygrometer is to have the $H_2O$ concentration of the mixed magma. The risk with $H_2O$ measurements in olivine-hosted melt inclusion as we already explained, is that melt inclusions could have suffered $H_2O$ loss by proton diffusion (e.g. Portnyagin et al. 2008). We modified the text accordingly to explain this. Considering that olivine-plagioclase crystallization comes after olivine-only crystallization, the value from the plagioclase hygrometer cannot be the primary concentration (at most its maximum value represents a minimum $H_2O$ of the endmember). It represents a deep magma saturation value but not the $H_2O$ concentration before crystallization.

**2)** In the revised text, we have changed completely how we refer to measured $CO_2$ data. This is mainly due to the fact that our measurements are potentially influenced by carbon contamination of the EMP carbon coating and we do not have any good way to discriminate the bad data. While we incorporated $CO_2$ data in the supplementary data, in the text we only mention them as the indication of low $CO_2$ abundance. The concentration referred to here, is suppressed.

**3)** Both crustal densities of 2200 kg/m3 and 2700 kg/m3 were the reported values based on the gravimetric analysis of Aso volcano by Komazawa (1995). To avoid any confusion, we have explicitly cited the source and provided a complete description how we converted the entrapment pressure to depth. "note the depth is calculated using a density of 2200 kg/m3 for the first 1 km and 2700 kg/m3 for the crust at greater depths (Komazawa, 1995), by solving for the depth, h [m], P = g {2200 (1000) + 2700 (h-1000)}." [Line 564-566]

*Section on volatile concentrations of primitive basaltic melt: (1)It is unclear to me why new volatile concentrations are calculated here, since some of the language here makes it seem like*

Response: **(1)** The $H_2O$ and $CO_2$ measurements in the melt inclusions from the mafic group are not interpreted as representing the volatile composition of the mafic endmember, after the revision, because melt inclusions have been affected by degassing. We hope the message is clear now that we reorganized this section.

**(2)** The choice of $K_2O$ concentration was on the basis of the lowest concentration. However, such estimates create significant disparities with F and Cl concentration measured. We chose to simplify the discussion regarding the determination of mafic endmember composition, during the revision. We now tie the endmember composition of S, Cl, and F to the melt inclusion values.

**(3)** $H_2O$ was measured by 2 methods FTIR (reflectance) and SIMS. We reported both in the table but the agreement between the 2 methods is poor because the FTIR method overestimates $H_2O$ concentrations. To remain conservative, we only trust and consider the $H_2O$ measurements that were obtained by SIMS.

> *Second paragraph in this section and Figure 6: the calculation of SCSS is very confusing to me. Based on the text, it seems like the first calculation (at a reduced condition?) was incorrectly calculated. If fO2 is known, why are curves for two different fO2 values plotted? Then, I don't understand how these data are plotted; were SCSS values calculated independently for each MI sample? Finally, why are the S concentrations in "undersaturated oxidized melt" considered to represent primary concentrations? What does "primary" mean in this context? The deepest primitive reservoir? Which S concentrations correspond this "undersaturated oxidized melt"?*

Response: SCSS equation of Fortin et al. (2015) does not include the term of $fO_2$ explicitly. Rather, the author specifies he determines FeO abundance from the total FeO with the correct redox state while the sulfur concentration in the melt is as $S^{2-}$. As commented here, we could calculate the fO2 corrected line but it would be a deviation from Fortin's equation. For the clarity, we decided to develop the discussion in this manner. We revised the figure 5 caption to include more detail about these points. SCSS can be calculated with melt composition, P, and T. This allows us to plot SCSS vs. measured S content. The grey line on the figure thus indicates the 1:1 line. When measured S is equal to SCSS, such melt inclusion would plot on the line. The word primary is used to state that magma did not experience sulfur phase saturation and fractionation since the formation of the magma.

> **Figure 4:** *This might be a good place to plot all of the various H2O concentrations (measured and calculated).*

Response: Figure 4 was modified accordingly with plotting individual measured melt inclusions and calculated $H_2O$ concentrations. FTIR data is excluded.

> **Section on persistent degassing from a deeper magma reservoir (>10km):** *Here, some new volatile concentrations are introduced, but I'm not sure where they are from. An "initial S concentration" of 690 ppm and a "maximum pre-eruptive CO2 concentration" of 340 ppm are given. Are both of these values from Saito et al., (2018)? I can understand using CO2 values from this work, as it appears those were not measured in this study (although this should be explicitly stated earlier in the manuscript), but why use that value for S? What reservoir does it correspond to? The deep primitive reservoir? Odd, since the S concentrations measured in this study are much greater than 690 ppm.*

Response: Reading the comment, we realised that our organization of the discussion was too meandering. In this revision, we simply tied $CO_2$ budget to a result from a previous study (Saito et al., 2018), as our measurements of $CO_2$ content is only reliably concluded as low (0-77 ppm) among the mixed magmas (inclusions with intermediate compositions).

In line 357-379, we have a revised paragraph discussing $CO_2$ concentration mafic endmember. Now, we state clearly here that we do not know the exact value, and consider 340 ppm as the observed high value, probably indicating the depth of equilibration. Later in the section "Modelling degassing of the deep magma reservoir", we make further advances on possible source $CO_2$ contents by comparing with the gas observation. In this paper, one of our goals is to demonstrate the possible $CO_2$ constraints in such a complex system.

There is another passage (line 381, section "Excess degassing of $SO_2$ and $CO_2$ from Nakadake 2014 eruption") where we introduce a different volatile content (Table 5). The point of this discussion simply illustrates the occurrence of excess degassing by investigating recent 2014 eruption with its magmatic product and observed gas output. The magma of the 2014 eruption is the mixed magma. Therefore, the corresponding possible source composition is independently assessed (supplementary S4). As we considered this part as a passage to support the needs of deep gas sources, we did not see the importance of developing a full discussion, and in consequence caused confusion. As it is mentioned in the footnote of Table 5, the value of 690 ppm S was calculated for NKD14 based on their maximum $S/K_2O$ ratios and average $K_2O$ concentration of the groundmass glass because we explained the excess degassing of NKD14 magma in this first section "Excess degassing of $SO_2$ and $CO_2$ from Nakadake 2014 eruption" in "Persistent degassing from a deeper magma reservoir (>10 km)".

One of the reasons making confusion is the usage of the term "initial volatile concentration". To distinguish from the "initial" meaning volatile concentrations in primary magma, we changed to use "pre-eruptive" for volatile concentration at the pre-eruptive magma reservoir and modified the text accordingly.

> ***Section on modelling degassing of the deep magma reservoir:*** *It is never stated here which model is used to perform these calculations, which is paramount. DCOMPRESS?*

Response: Indeed, thank you, we forgot to specify the model we used. The modified text now reads: "Fig. 8 is the result of such a calculation using SolEx (Witham et al. 2012), showing the variations in $H_2O/S$, $CO_2/S$ and $Cl/S$ molar ratios of gas in equilibrium with a magma as a function of pressure." [Line 671-673]

> *"Equilibrium gas composition at depth should be the same as the gas composition observed at the surface, if the gas segregated and travelled to the surface without any modification in between." Senso stricto, this is not true. Due to P-dependent fugacity coefficients, the speciation of a gas will change from depth to surface (even at constant fO2). This does not matter for this study if and only if surface gas measurements were made in terms of total S. Based on the information in the supplement, it appears that S may have been measured as SO2. Technically, if total C in the gas was measured as CO2, this also presents a problem as a gas will speciate between (primarily) CO2 and CO (plus other probably minor C species). However, the amount of CO is usually quite low, so I am okay with this approximation for carbon. For sulfur, however, the fO2 of the system can have a big effect on SO2 concentration, since S is split primarily between SO2 and H2S (plus other probably minor S species). I can't say off the top of my head weather the bulk gas composition will be significantly affected, but this felt worthy of pointing out.*

Response: Absolutely. We have completely overseen the changes of gas speciation between the depth and the surface, and indeed Shinohara et al. (2018) reports measurements of $SO_2/H_2S$, but not $CO_2/CO$. We revised and made sure to calculate the gas ratios as molar $H_2O/(total S)$, $CO_2/(total S)$, and $Cl/(total S)$, and rewrote the discussions, and modified Fig. 8, and 9 where gas compositions were compared with magmatic sulfur input.

*Overall, I find it difficult to comment on the conclusions drawn in this section, since I am unclear as to which dissolved volatile concentrations were used to represent which magma reservoirs. I think an additional table AND a figure showing the various volatile concentrations measured or calculated for these reservoirs will help alleviate this, PLUS some necessary clarification in the text. Other than this confusion, the manuscript was well written. I think that some more thought into how to organize and present the volatile data can go a long way toward strengthening the manuscript.*

*This work is very interesting to me, and I am available to re-review this manuscript should that be desired.*

Response: We thank the reviewer again for the positive encouragement. In conclusion, we have added a figure (Fig10) summarising the discoveries made in this study using a schematic diagram. We hope this would improve the readability of the paper.

# Reviewer #2: Daniel Rasmussen

## 1. Summary

*Kawaguchi et al. provide a detailed study of melt inclusions from Aso volcano. They evaluate compositions of melt inclusions, host crystals, and bulk tephras, as well as phenocryst textures. They find that melt inclusion major elements give evidence of magma mixing as the primary means of variation in melt composition. Volatile elements were used to investigate magma storage depths, and the authors argue for shallow, pre-eruptive storage at depths of 2 and 4 km, and they suggest that mafic magmas feeding the system originate at depths >10 km. They use SolEx to model magma degassing paths, and a comparison of their model results with observed gas emissions indicates that mixing of shallow and deep gases occurs.*

*This paper was a pleasure to read, and it will be an important contribution. The authors have conducted a careful, thorough study. The dataset presented here represents a monumental effort (200 melt inclusions!). The data are robust. The writing is very clear, and I was amazed by the level of polish. Broadly, the authors have been careful in their interpretation of the data. However, I have identified some areas that need improvement or further clarification below. Specifically, the main findings of the paper relate to magma mixing, magma storage depth, and origins of gas emissions. In all three of these areas, there are weaknesses in some aspects of the arguments.*

## 2. Major comments

1. *The authors rely heavily on a model of magma mixing ("liquid"-"liquid" mixing) to describe the chemical compositions and textures of minerals, and the major-element trends in melt inclusions. No consideration is given for alternative scenarios (magma-crystal mixing, crystallization). The paper would benefit from the authors making a stronger case for the mixing scenario they consider and/or describing some of the alternatives. More information on my concerns can be found in my specific comments on Pages 8 and 9 of the manuscript.*

Response: This was the point we contemplated for the organization of the paper. We absolutely agree that magma evolution is complex and it is rarely controlled only by a single process. With this in mind, our choice to place mixing as a central process to explain the magma transport may have appeared too simplistic. However, we maintain the idea that the major compositional variation reflects that of mixing, while crystallization contributes to a minor dispersion. The mixing might have been a mixing process of magma crystal mixture, certainly, but melt inclusion is expected to represent magma only. Even if magma-crystal mixtures had been present, inclusions probably record only the mixing of magma. In the revision, we paid attention to discuss competing magmatic processes, while insisting on why we prefer the magma-magma mixing model.

2. *There are weak arguments that surround the suggested shallow region of magma storage. The authors discuss saturation pressures that are relevant for a pure-H2O system when the system in question is a mixed-volatile (i.e., H2O and CO2) system. Pressures derived using assuming the melt and vapor only had H2O are minimums. If CO2 is added to the melt (and coexisting vapor), the saturation-pressure estimates increase. The authors state that there was no CO2 in the systems when the crystals formed because at the depths of the imaged reservoirs, CO2 solubility is low (Page 11, lines 26-28). That may be true. However, then the petrological data are not being used as an independent confirmation of the geophysically determined magma storage depths. Rather, the interpretation of the petrological data relies on the assumption that the depths recorded by the samples are the same as the geophysical depths. Their data could be used as an independent constraint on magma depth if they can convincingly argue that the magma did not have much CO2 in it at the time the crystals in question formed without relying on the geophysical data.*

Response: First of all, we insist that the abundance of $CO_2$ in the melt inclusions were low especially for the felsic group melt inclusion (0 - 77 ppm). While we agree with all the points raised here by the reviewer, because of the low $CO_2$ in the melt inclusions, the change of the pressure of equilibration is minor. As with the presence of bubbles in the inclusions, the concentration of volatile element in melt is equilibrated with the pressure condition just before the eruption, thus the shallow storage in this case, and as it is not the discussion of the entrapment pressure, it is unnecessary to account for the $CO_2$ in the bubble.

Ultimately, as commented here, the weakness of our argument was rooted in luck of independent evidence showing low $CO_2$. In this revision, we decided to include SIMS $CO_2$ data, with a cautionary note for high concentration measurements for potential C contamination. However, it is clearly shown that the mixed magmas are low in $CO_2$. We added a sentence stating "Because $CO_2$ concentrations in the felsic group melt inclusions are notably low (0 - 77 ppm, Table S1), it makes negligible changes to the calculated equilibrium pressure." [Line 566-568].

3. *The authors base several of their interpretations on modeling that was performed using melt inclusion H2O contents without adequately exploring the potential role of diffusive exchange of H⁺ (i.e., water loss or gain) between the melt inclusion and exterior melt. The authors indicate that they selected samples to minimize the effects of this process during quench, and they indicate the possibility of water loss in page 11. However, there are ample opportunities for the process to have occurred prior to quench. Are the measured H2O contents consistent with their mixing model? Or could they be described by a model of ascent, degassing, and crystallization? Diffusive exchange of H⁺ is a widely*

*known and understand challenge when working with melt inclusion data which must be very clearly addressed.*

Response: This point was raised by all reviewers. We addressed this at the beginning of this reply letter, point (3).

4. *The authors argue that the "initial" CO2 contents of the magma is 250-500 ppm. This is very low for an arc magma. The basis for this argument is the comparison of observed gas emissions with the results of SolEx modeling. Degassing model predictions are highly dependent on the model, the parameters, and the scenario. The authors do not adequately justify their modeling. For further information, see my comments on page 15.*

Response: Again, we can only accept this comment. The discussion surrounding $CO_2$ strongly depends on the choice model as pointed out here. As for the reply to this, we examined the alternative model available at this moment (see the beginning of this reply document, point 1). As we found that SolEx after all, appears to follow our compositional trend better, we decided to keep the original interpretation. However, we revised the section of "degassing" and carefully described the limit of our interpretation.

5. *If the paper goes back to review, it would be helpful for the authors to make the line numbers continuous (i.e., not start over at the beginning of each page).*

Response: We apologize for the inconvenience caused by the line numbering and our revised manuscript now has continuous line numbering

## 3. Line comments

*Abstract: The authors have been very consistent with their use of verb tense. From what I can tell, the entire paper is written in past tense. I do not recommend the authors change any of the tenses in this paper. However, for future papers, the authors should consider using other tenses. Here is a general guideline from Nature: "In your scientific paper, use verb tenses (past, present, and future) exactly as you would in ordinary writing. Use the past tense to report what happened in the past: what you did, what someone reported, what happened in an experiment, and so on. Use the present tense to express general truths, such as conclusions (drawn by you or by others) and atemporal facts (including information about what the paper does or covers). Reserve the future tense for perspectives: what you will do in the coming months or years. Typically, most of your sentences will be in the past tense, some will be in the present tense, and very few, if any, will be in the future tense."*
 *(https://www.nature.com/scitable/topicpage/effective-writing-13815989/)*

Response: We appreciate very much the advice here. In fact, correct usage of verb tense is difficult to master.

*Page 2, Line 11: Melt inclusions.*

Response: Corrected, thank you. [new line, Line 45] Also we have re-examined the singular-plural usage carefully throughout the manuscript.

*Page 2, Line 12: Phenocrysts. What was their Fo?*

Response: Corrected thank you. [Line 46]

*Page 2, Line 34: Suggest replacing "characterized" with "governed".*

Response: Corrected thank you. [Line 69]

> *Page 2, Line 38: Suggest replacing "melt inclusion" with "the study of melt inclusions".*

Response: Corrected thank you. [Line 73]

> *Pages 2-3, Lines 37-1: Today, it is very well known that melt inclusions are not completely isolated from chemical interaction with their host crystal and the external melt. The authors should make a brief comment of this here with one or two references.*

Response: Yes indeed, we added the following sentence and references in the text [Line 76-80] : "In fact, melt inclusions are not perfectly isolated from surrounding magmas since $H^+$ can diffuse through the host olivine (e.g. Gaetani et al., 2012) and $CO_2$ can be redistributed in shrinkage bubbles (e.g. Tucker et al., 2019). Therefore, $H_2O$ and $CO_2$ measurements in melt inclusions are regarded as minimum values indicating the conditions of last equilibration."

> *Page 3, Lines 1-6: The excess sulfur problem has been known for a long time, and several studies have given explanations to explain the observation. Some should be cited here.*

Response: We agree and we cited more references for example: Métrich and Wallace 2008, Wallace and Edmonds 2011, de Moor et al. 2017 [Line 83-84]

> *Page 3, Line 20: Suggest replacing "magma" with "glass".*

Response: Corrected thank you. [Line 100]

> *Page 4, Lines 27-29: It is great that you have made note of your consideration for post-eruptive cooling. It is also important that you describe the clast size of the tephra samples you worked with. Did you focus on loose crystals in the ash size fraction of tephra samples?*

Response: Yes, indeed. The clast size of the tephra sample is written in the following paragraph [Line 160 - 181]. We only used lapilli-size scoria (up to 6 cm) [Line 185-186].

> *Page 4, Lines 32-33: Do you have a sense of the relative abundance of each of these phases?*

Response: We have no data about the relative abundance of these minerals in our samples. However, Miyoshi et al. (2005) reported the phenocryst mode of basalt – basaltic andesite lava (<54 wt.% $SiO_2$) erupted from Kishimadake, Ojodake, Komezuka, and Nakadake volcanoes: 32 – 39 vol.% plagioclase, 7 – 9 vol.% clinopyroxene, <1 vol.% orthopyroxene, 1 – 2 vol.% olivine, 1 – 2 vol.% opaque minerals. To point the reader to the right information, we added "Detailed descriptions of these tephras are found in Miyabuchi *et al.* (2005)." [Line 158 - 159]

> *Page 4, Line 36 (and throughout): In some cases, the authors use the Oxford comma. In others, they do not. Its use should be systematic. I would recommend using it.*

Response: Thank you for pointing out the inconsistency. We have revised all the occurrences and corrected accordingly.

> *Page 5, Line 5: Suggest changing "was not identified today" to "has not been identified presently."*

Response: Corrected thank you.

> *Page 5, Lines 34-35: It would be better to express the accuracies as percent errors. An uncertainty of 5-25 ppm may be a lot more significant for an element like Nb than it is for something like Sr.*

In the text we cited the range to indicate the standard deviations. The detailed variations are in fact in Table 1. For this revision, we decided to report relative standard deviations.

> *Page 6, Lines 19-27: Do you have a sense of the detection limit for the reflectance technique? It probably depends somewhat on the specifics of the sample, but a rough estimate would be helpful to include here.*

Response: Our understanding of the reflectance technique for FTIR made us realised how difficult and how user-dependent the estimation of the baseline of FTIR spectra is. As already explained, we therefore took the conservative decision to only trust the SIMS data for $H_2O$ measurements. We nonetheless reported the FTIR $H_2O$ measurement in the supplementary material. While the detection limit of the method strongly depends on the sample, we estimated detection limits as 0.14 wt. % [Line 233-235].

> *Page 6, Lines 19-27: It appears that you performed SIMS on some of the same melt inclusions that you obtained water content measurements using FTIR. It is important to describe how the two measurements compare. It appears that, in some cases, the agreement is good, while in others is pretty poor.*

Response: Like we replied to the reviewer 1, we adopted SIMS $H_2O$ values rather than FTIR. Similarly, we systematically favored SIMS volatile data to EMPA measurements, SIMS being more precise.

> *Pages 6-7, Lines 28-6: Did you measure secondary (check) standards? Do you have a sense of the precision and accuracy of the SIMS analyses?*

Response: Yes, we measured a secondary standard, EPR-G3 an aphyric basalt from the East Pacific Rise. We added the sentence "Repeated analysis of a secondary basaltic glass standard from East Pacific Rise EPR-G3 (Shimizu et al., 2017) yielded a relative standard deviation for $H_2O$, $CO_2$, F, Cl, and S of 1.4, 3.2, 1.5, 2.5, and 0.9%, respectively". [Line 252-255].

> *Page 7, Lines 34-37: Are the FeO concentrations significantly elevated about the bulk rock?*

Response: We realised our writing raised this question. In fact, FeO in the inclusions is mostly the same as the bulk rock or higher. High FeO melt inclusions were also lower in $SiO_2$ consistent with magma evolution. As it was not our aim to develop the discussion regarding the precision of FeO content in the melt inclusion, we did not elaborate more information here. Instead, we changed the sentence to "The melt inclusions were not corrected for post-entrapment diffusive Fe-loss (Danyushevsky et al. 2000), as total FeO concentrations in melt inclusions are either the same or higher than those in bulk rocks." [Line 294-296]

> *Page 8, Lines 5-6: How was equilibrium with the host tested?*

Response: The melt inclusions that are in equilibrium with their host were identified by filtering our data. Specifically, the melt inclusion - host pair must satisfy an expected range of Kd, typical for basaltic compositions. The modified text now reads: "Among these samples, only the melt inclusions in equilibrium with host minerals were used for the magmatic temperature calculation, in which the

exchange coefficients were within expected range of basaltic composition: ($KD(Fe-Mg)cpx-liq = 0.28 \pm 0.08$, $KD(Fe-Mg)opx-liq = 0.29 \pm 0.06$, and $KD(An-Ab)pl-liq = 0.27 \pm 0.01$ or $0.1 \pm 0.05$ (depending on the calculated temperature; Putirka 2008)." [Line 303-307]

> *Page 8, Lines 9-10: Suggest changing wording to "major and volatile element concentrations".*

Response: Corrected thank you.

> *Page 9, Line 16: Here and elsewhere "olivine-hosted" should be hyphenated.*

Response: Corrected thank you.

> *Page 9, Line 30: Normally zoned olivine phenocrysts are not described in the "Host mineral compositions section". Are these common? Does normal zoning occur in the high-Fo olivine only?*

Response: Yes, all high-Fo olivine observed in KKO, OJSU, OJSL, and KSS are normally zoned and common. As described in former page 8 line 37, some plagioclase phenocrysts were also normally zoned. In conclusion, normal zoning occurred in the high-Fo olivine and high-An plagioclase only. We added the sentence into former page 8 line 30: "All high-Fo olivine phenocrysts were normally zoned." [Line 333]

> *Page 9, Lines 29-34: I wonder if describing the mixing as something that occurs between two "liquids" is too reductive. (1) Does the mixing need to be between two liquids? Could you have one magma carrying some crystals interact with xenocrysts or antecrysts? In other words, could you explain the observations listed in lines 31-34 with a mafic magma bearing crystals interacting with a more evolved pile of crystals? Also, if the "liquids" are suggested to be bearing crystals (and/or other phases), I would recommend calling them "magmas".*

Response: Yes indeed, it is better to use "magma" and we changed the text accordingly. In fact, we don't have a clear evidence to judge if mixing was just between "liquids". As the reviewer said, we can not exclude the incorporation of xenocrysts or antecrysts into the ascending magma. However, given the presence of banded pumice in ACP-1 (e.g. Miyabuchi 2017) erupted prior KSS eruption, it seems conceivable that melt would have been present. Even if the silicic endmember magma was the remnant of such mixed ACP-1, the mixing of two distinct extreme magmas is not geochemically wrong. Furthermore, considering the high temperature of the silicic endmember and the fact inclusion traps the liquid only, we stand by our choice of mixing liquids. Thanks to the reviewer's comment we leave this possibility open for food for thoughts without having any good argument here to constrain it. In any case, for the flow of discussion it is not the right place to state "liquid" here [Line 372-384]. Reference to liquid-liquid mixing is suppressed here and moved further down in the discussion.

We modified the text to clarify our interpretation in this discussion, "It is important to note that there is a surface expression of this silicic endmember in the Aso eruption products, while the mixing endmember is set by a melt inclusion. Major element compositions of ACP1 dacitic pumice (Miyabuchi 2017), the only Holocene felsic product erupted three hundred years before that of KSS, are similar to the felsic endmember, and this indicates the presence of the silicic magma. Furthermore, the presence of a banded pumice was reported in ACP1 prior to KSS (Miyabuchi 2017). This banded texture is evidence of magma mingling and therefore the mixing trend is unlikely a result of assimilation and crystal fractionation of single parental magma." [Line 408-415]

*Page 10, Lines 4-6: Perhaps you could make a brief statement why the two types of magmas that mix are proposed to not be derived from a single parent. It is easy to imagine a scenario where magma mixing occurs between two magmas that have a similar parent.*

Response: Certainly. We modified the first paragraph of the discussion expanding to mention the point raised here. "While the major variance of concentration variations was explained by a simple mixing process, in close inspection of trends, it is likely that crystal fractionation contributed to the dispersion from the mixing model. It should also be noted that the mixing model required the presence of independent mixing endmembers, it does not constrain their origin." [Line 403-407]

*Page 10, Lines 16-17: Some of the variation in water could be due to diffusive equilibration of $H^+$, right?*

Response: Yes for example most MI from KSS have $H_2O$ concentrations between 2.36 and 2.89 wt.%, with the exception of one Mi (KSS 3-m3) which has probably suffered diffusive equilibration of proton and has a lower $H_2O$ concentration (1.52 wt.%). For this reason, we did not include $H_2O$ in the mixing model.

*Page 10, Lines 9-17: Can the major elements be described by a crystallization model? In the major element data alone, is mixing required? Mixing requires linear trends on major element plots. Some major element plots (see below, note these were made used the uncorrected major element data of melt inclusions) do not seem to show linear trends. Rather, there is some evidence of "kinked" paths, which are commonly attributed to crystallization.*
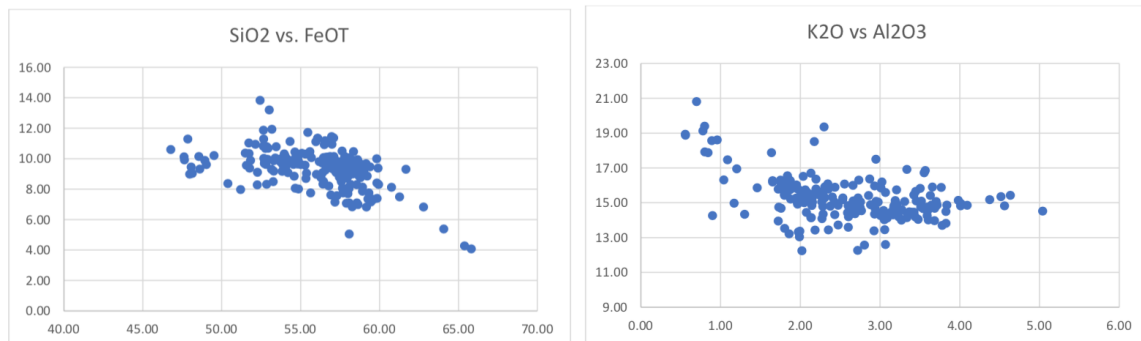


Response: Thank you. We tested the idea of a fractional crystallization on the figure the reviewer produced but with the corrected MI data and we added the fractional crystallization model. The trend in corrected major element FeO vs $SiO_2$ is closer to linear now (no kink, figure below). However, a simple cristallisation trend (produced by Rhyolite MELTS, fractional crystallization from 1150 °C) disagrees with the composition variation here. So maybe fractional crystallization happens but it is not the main process justifying the composition variation. Therefore, we maintain our mixing model to explain the melt inclusion variations but we now mention the fractional crystallization because we can not rule it out entirely, but we add that it does not play an essential role in this variation.
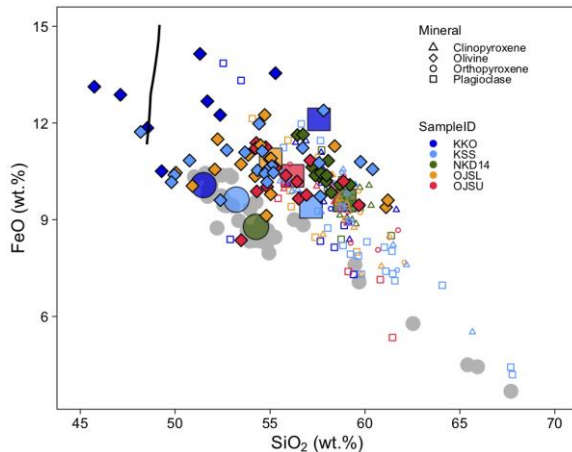
Response: Yes, indeed. The cited uncertainty is of the sample variations. The standard error of Putirka's two pyroxene thermometer is ±38 ˚C. The text is modified as " . . . are 1010-1025ºC for KKO, OJSU, OJSL, and KSS (± 13˚C  1σ  of samples, while standard error of the thermometer is ±38 ˚C; Table 4)".  [Line 419-421]

Response: Yes, the low temperature (770 – 915 ˚C) found for the dacitic magma from Mount St Helens might have been due to higher $H_2O$ contents (4 to 5 wt.%) compared to $H_2O$ range that we have in this study (0.5 to 2.9wt.%). Actually, our temperature estimates (1010-1025ºC) are in between that found for this previous hydrous dacite (Mount St Helens) and that found for an anhydrous dacite (Puna Geothermal Venture Wellfield, Hawaii; Teplow *et al.* 2009; 1050ºC). We modified the text accordingly. [Line 422-428]

For volcanological sense, we do not have a concrete explanation on what would cause the production of the high temperature magmas. We just report here that it does exist beneath Aso.

Response: Yes, this was certainly our point as well. First, we discussed the diffusive water exchange of olivine-hosted melt inclusion and stressed that melt inclusions have lost water. In the revision, we wrote more statements recognising this. Furthermore, Sakuyama's method exactly recognizes the issue and is based on the major element composition of melt inclusion and plagioclase. Using the latter method, temperature and $H_2O$ concentration are calculated simultaneously. Lastly, we also applied a simple olivine thermometer to the melt inclusion with the highest water content to have a comparable value to Sakuyama's method. We think that the convergence of these two methods is an indication of the successful determination of magma temperature.

*Page 11, Lines 11-28: The saturation pressures presented are the pressure of saturation of a pure- H2O vapor. However, this is a mixing volatile system. If you start to add CO2 to the melt (and coexisting vapor), the pressures presented become minimums. The authors argue that if magma storage occurs at 2 and 4 km, then it is unlikely that the system contained much CO2 because the saturation pressures calculated for an H2O-only system are consistent with those depths. That may be true. However, that means that the petrological data are not being used as an independent constraint on those depths. Rather, the authors are just arguing that their data can be consistent with it if no (or very little) CO2 existed in the melt (and coexisting vapor) that the samples record. This problem could be resolved by presenting measurements of CO2, which the authors say they performed using SIMS, yet there is no mention of the results of these analyses.*

Response: The SIMS $CO_2$ measurements were done after the EMP analyses, and we conservatively thought that the carbon coating contamination could have ruined the data. However, the $CO_2$ we measured in the melt inclusions is low (<450ppm; mostly 10-30 ppm for mixed felsic magmas). We decided to follow the reviewers' request and reported the $CO_2$ SIMS measurements in the supplementary material. Table S1 is modified to include $CO_2$.

*Page 11, Lines 27-28: The CO2 content of the groundmass is irrelevant. Clearly, the groundmass has degassed its CO2. What is more important is determining the CO2 that existed in the melt at the conditions of the entrapment of your melt inclusions (or formation of plagioclase).*

Response: yes absolutely, we agree. We deleted this erroneous sentence from our text.

*Page 12, Line 22: The first clear demonstration of rapid water equilibration in olivine-hosted melt inclusions is Portnyagin et al. (2008). The most up-to-date reference on the diffusivity of $H^+$ in olivine is Ferriss et al. (2016). Both references should be cited here.*

Response: Yes thank you, we added the references.

*Page 12, Lines 29-31: SCSS was calculated using the pressures of the shallow reservoir, but the high S contents are observed in melt inclusions hosted in high-Fo olivine (i.e., Fo~80) that I thought were entrapped at much greater depths? The depth of the "pre-eruptive magma reservoir" is not important here. The depth of melt inclusion entrapment is key.*

Response: There can be a pressure effect but here we think the higher S concentrations in melt inclusions reflects mainly a change in redox conditions. The pressure change does not affect S solubility as much as the oxidation change. The melt are oxidised and have more dissolved S.

We added a sentence to clarify such limitations: "The elevated S concentrations in the undersaturated oxidized melt are therefore considered to represent, less-degassed, non-sulfide-fractionated, S concentrations, at least at the condition of the shallow storage depth." [Line 513-516]

*Page 13, Lines 2-3: The authors are considering the sulfur contents of the melt inclusions relative to saturation of an S-bearing phase. It is not clear to me how they are arguing that their S contents are primary. If you are below SCAS (or SCSS), S can still degas. S partitions strongly into vapor. What is the evidence that S has not degassed from the high-S melt inclusions?*

Response: We have no counter argument against this point. We were too eager to extend the interpretation. We dropped the claim that we demonstrated the undegassed S content. The value was rather the best we could find.

> *Page 14, Lines 13-14: I thought the authors were arguing that their least-degassed melt inclusions recorded primary S contents (e.g., page 13, lines 2-3)? Here they indicate that they need a "deeper, volatile-rich basaltic magma" to assess the S excess. Can this be assessed using their deep, volatile- rich melt inclusions?*

Response: As pointed here, that is exactly how we would like to develop our discussion. In the paragraph in question, we are just establishing S-excess to illustrate the necessity of the deep source.

> *Pages 13-15, Lines 37-7: The discussion here is very interesting. I think it would benefit from further discussion of possible mechanisms of degassing (e.g., second boiling, magma ascent and decompression) and the relationship of observed SO2 and CO2 emissions.*

Response: At this point of the discussion, our goal was to establish the observation of excess degassing. Instead, we introduced the mechanism of degassing in the revised conclusion.

> *Page 15, Lines 16-31: SolEx is often inaccurate and unreliable (e.g., Werner et al., 2020). The issue is that SolEx uses an extremely limited range of experimental data to model the degassing of S, which is a complex function of melt composition, fO2, temperature, pressure, etc. The authors need to justify their use of SolEx. One way the authors could do this would be by comparing SolEx predictions for volatile contents of the melt with their observations (i.e., melt inclusions). Have the authors considered using D-compress? There are a lot more knobs to turn when performing modeling with D-compress, but I think many would consider that model capable of producing results that are more accurate.*

Response: Refer to the answers at the beginning of the reply.

> *Figure 8: The authors model degassing as "closed system", yet they suggest excess sulfur is derived from a deeper magma. This would mean that the gas that exsolved from the deep melt become decoupled from its melt. The authors acknowledge this when they discuss the segregation of a deep gas (e.g., page 15, line 35). Later (page 16, lines 18-20) the authors suggest that at 9 km, the system changes from open to closed. Therefore, their modeled degassing path does not apply at depths <9 km. Regardless, the authors have not justified the assumption that degassing occurs in a closed system at depths >9 km.*

Response: Based on our idea of Fig. 8, the closed system model is used to find a unique condition at which observed gas compositions agree with the prediction of the model. Chemically, we envisioned the scenario to decouple the deep gas from the magma at depth, and thus the system became open. Because our intention was to find thermodynamic equilibrium, we did not justify why degassing should be closed below 9 km. Rather we consider that even if magma might have gone through some kind of open system degassing below 9 km, if the gas became stagnant at 9 km and re-equilibrated with magma, we can still argue for the condition of equilibrium.

> *Figure 8: Perhaps the authors could add a second x-axis that indicates depth? It would be helpful for the reader.*

Response: Fig. 8 was modified and the depth tick marks are added.

> *Page 15, Lines 27-29: By "initial magmatic CO2 concentration", do the authors mean the primary CO2 contents (i.e., CO2 concentration of the melt when it entered the lower crust)? If so, this would be very low for an arc magma. Most would argue that, in general, primary arc magmas have at least 1000s of ppm CO2. The modeling the authors present here does not seem robust enough to make such a bold claim. The results of the degassing model are highly sensitive to several factors, such as choice of model (e.g., SolEx vs. D-compress), style of degassing (e.g., open, closed), degassing scenario (e.g., second-boiling, ascent), whether or not the gas emitted at the surface reflects gas derived from a single depth or if it is a mix of gases from multiple depths, etc. Most of these factors are not discussed with relation to the estimate of initial CO2 contents.*

Response: It seems we did not express ourselves better here. First, $CO_2$ content should be considered as an estimate highly dependent on the model. We think our deduction is correct as long as the model works. In the revision, we stress this point. As for low $CO_2$ in Aso, we think it is possible as total $CO_2$ flux of Aso appears to be lower than other arc volcanoes. Certainly, this maybe a transient, only contemporary, observation. Again, we agree that we do not have a constraint to say anything definitive about primitive $CO_2$ content, contrary to what we stated initially. We have revised the point: "Therefore, the observed gas composition must have been derived from the depth of about 9 km (~2.4 kb) at which it was in equilibrium with a magma with the initial magmatic $CO_2$ concentration between 400 to 750 ppm (Fig. 8). The total $CO_2$ flux of Aso is described to be lower than of other arc volcanoes, and this may be an indication why our estimated $CO_2$ content in Aso magma is lower than those of many other arcs (e.g. 1000 - 2000 ppm; Wallace 2005). The determination of initial $CO_2$ is strongly tied to the Cl and S partitioning into $H_2O$-$CO_2$ fluid, and we think that these values may need to be revised once we have a better understanding of Cl and S element partitioning. Lastly, this conclusion is highly model dependent. Here, we chose to use SolEx for its agreement with the variation of S in the melt inclusions. However, we must be careful with the use of SolEx, because it is shown to fail to reproduce degassing trajectories in other volcanoes (e.g., Werner et al. 2020)." [Line 687-695]

> *Page 16, Lines 9-12: If gas mixing occurred, how does this impact the interpretations of Figure 8?*

Response: We think the conclusion of Fig. 9 holds independently of Fig. 8. The key is to explain the mechanism at which the deep gas travels to the surface without experiencing significant modifications. Such discussion is added to the end. [Line 733-751]

> *Pages 16-17, Lines 35-3: It would be helpful to use ranges of chemical compositions to elaborate on terms like "mafic" and "felsic". Also, it would be helpful to show the ranges of crystal endmember mole fractions for the olivine, plag, cpx, and opx hosts.*

Response: A lack of explicit definition of mafic and felsic was pointed out by other reviewers, and addressed in the beginning of this reply (point 2).

> *Figure 8: The authors indicate that the observed gas component they investigate is "high-pressure gas component A". Was there also a low-pressure gas component identified in the Shinohara studies?*

Response: Yes, Shinohara et al. (2018) reported low-pressure gas component B and C having low $CO_2$/$SO_2$ molar ratio of 1.6 observed during eruption. All these gas components were also plotted in Figure 9.

# Reviewer #3: Nicole Métrich

*Comments on the manuscript entitled "Persistent gas emission originating from a deep basaltic magma reservoir of an active volcano: the case of Aso volcano, Japan", submitted to Contributions to Mineralogy and Petrology by Masataka Kawaguchi and co-authors.*

*The authors have conducted a standard study of the mineralogy and melt inclusions for modelling the magma differentiation and degassing at Aso, a very active volcano. The tephra samples which have been studied cover a span of time from ~ 4 ka to present-day.*

*Major elements, S and Cl were analyzed with electron microprobe and $H_2O$ by FTIR in melt inclusions hosted in olivine, cpx and plagioclase. Water, S, Cl and F were also analyzed by SIMS in a subset of MIs hosted in olivine. Magma mixing well explains the evolution trends recorded by MIs and the mineral zoning. The possible depths of magma storage at Aso have been assessed from the dissolved $H_2O$ amounts ($P_{H_2O}$ is calculated using Volatilecalc), and from literature data for $CO_2$. The petrological results are discussed and compared to the seismic records. Both support Aso magma ponding at various levels in the crust beneath Aso. The last part of the manuscript is dedicated to the modelling of the gas emissions. This paper deserves to be published in Contributions to Mineralogy and Petrology and fits well with the objectives of the journal. The data are of high quality and the target volcano of interest. My main comments are related to the sulfur degassing, the modelling of the magma mixing, and the pressure determinations. In my point of view the manuscript could be improved in its form, and some references could be added that would strengthen the discussion.*

*My comments are detailed hereafter. I suggest moderate revisions.*

## Comments

*P3, l1. Excess degassing is known at open -vent systems (i.e., Stromboli, Etna, Villarica, Popo..) and the approach using melt inclusions to describe and quantify the degassing path of magmas is widely discussed as reviewed, as an example by Métrich and Wallace (2008, RiMG69), and Wallace and Edmonds (2011; RiMG 73). There is also a nice paper on sulfur degassing (gas and MIs measurements) at Erta Ale and Masaya by de Moor et al., (2017, Gcubed).*

Response: The reviewer is correct, we added the proposed citations in the introduction to this well-known "sulfur excess degassing" question. We hadn't given enough credit to previous work.

*P7. "SIMS analysis was conducted after EPMA analysis". Could $H_2O$ have been lost and the SIMS analyses of $H_2O$ biased to some extents? It could explain the low concentrations measured in olivine KSS-4-m7: 4.4 wt% (FTIR) vs 2.74 (SIMS) as an example.*

Response: To our knowledge it has never been reported that H2O analysis by SIMS is affected by prior EPMA measurements. We take notes of beam position in the melt inclusion and are careful not to re-position the beam of the SIMS on or near the EPMA beam spot. Therefore, we do not think this is the right argument to explain the FTIR vs SIMS measurement discrepancy for some of the samples. However, it is true that in this study, we heavily rely on the SIMS measurements due to the disappointing correlation between EMP and SIMS (within 25%) and basically the no correlation between FTIR and SIMS. We now have clearly stated our position regarding our analytical preference in the "analytical methods" section, "major and volatile elements in melt inclusions".

*P8, 127. Remove Fo before 62-74*

Response: Thank you, we have suppressed Fo.

*P9. Section major and volatile elements.*
*-1. A few words to describe how H2O and halogens are evolving as written for sulfur could be informative.*

Response: Thank you for the suggestion. We added the following text, "F and Cl correlates with $SiO_2$ and $K_2O$ and anti-correlate with host Fo content." [Line 367-368]

*-2. "The tephra samples of this study were basaltic to basaltic andesite with SiO2 .. (large circles in Fig. 3c). Melt composition in inclusions varied significantly more than that of the bulk tephra composition...".* This sentence could be easily re-arranged in order to present Figure 3 first. This Figure 3 is very important for the understanding of the paper. Adding two plots with Cl, and H2O vs MgO could be worth.

Response: we added in figure 3, Cl and S versus $SiO_2$ and Fo of host olivine, respectively.

*-3. It is written, in the description of the mixing model (ESM2), that MIs in plagioclase and cpx were not considered in the modelling of mixing. However, in Fig.3b most MIs in olivine, plagioclase and cpx form a cluster. For the NKD 14 sample these MIs and the matrix glasses have similar compositions. It means that the post-entrapment evolution is minimum and that these mineral phases crystallized in the same magma batch or in closely similar magma batches. It is fully consistent with the NKD 14 sample which would result from the mixing between basalt and dacite and in which the crystals are in equilibrium with the residual melt.*

Response: We apologize for the confusing story. Actually, we tested all melt inclusions including those hosted in plagioclase and pyroxenes, and we now wrote "All melt inclusions (even those hosted in other crystals than olivine), whole rocks, groundmass glasses and everything plots along the linear trend of olivine-hosted melt inclusions (Fig. S4-3)." Figures were just showing the results of olivine hosted melt inclusion only. However, the sentence we were using might have been unclear. Therefore, we modified text and figures to include the results of melt inclusions hosted in other minerals.

We replaced the text in the second paragraph "It should be noted that the model was verified by the melt compositions of melt inclusions hosted in olivine and hosted in other minerals. However only olivine hosted melt inclusions have an established procedure for the correction of the post-entrapment

crystallization.", and now reads: "The major element variation was well reproduced with the mixing model for melt inclusions of all host minerals (Fig. S4-5)" [Line 402-403] Furthermore, we exchanged captions of Fig. S4-3 and Fig. S4-4 because it was inverted.

> *-4. From Fig. 3d MIs in KSS olivine record a significant depletion in sulfur (from ~ 0.3 wt% down to <0.05 wt% @ nearly constant MgO that is not due to mixing (at least in my point of view). I am wondering if KSS-MIs recording such a trend are fully enclosed. Could they be instead embayments?*

Response: thank you, yes indeed after your comment we double checked the "melt inclusion" and found that there were three embayments (KSS-OL-3-m3, KKO-OL-3-m1, and KKO-OL-OP2-m2) We verified visually that they were indeed embayments. We now signal that all embayment data are suppressed     from the Table S1 of the supp. material.

> *In this figure there are two trends of evolution: one is due but most likely to degassing since sulfide immiscibility is not observed, without crystallization and the other to mixing of magma batches differing by their composition and extent of degassing. Adding a transmitted light photomicrograph of a typical olivine-hosted melt inclusion would be important.*

Response: As we have acknowledged in the reply to the reviewer 2, we were too assertive about the mixing process without carefully evaluating other processes. In the revision, for the simplicity of the discussion we decided not to discuss the mixing process for $H_2O$ and $CO_2$. For S, Cl, and F, we retained the presence of the mixing trend, however we also mentioned the role of degassing, and crystallisation.

Three images of olivine hosted-melt inclusions are added to the supplementary documents S4.

> *Fig .2e shows that the olivine and its MI have been carefully prepared but does provide any information on the MI itself (bubble size, morphology..). Moreover looking at the Table S1, the analysis of this olivine (KSS 3-m1) is not so good (total = 96.5%), MgO is most likely underestimated.*

Response: Unfortunately, the textural information of melt inclusions were not recorded during the preparation. This work started during the second year Master of the first author Kawaguchi and was done in Kumamoto University. It is now *a posteriori* not possible to provide information regarding bubble size. The form of inclusions were consistent with the type of primary inclusions, meaning not align in a plane with many other melt inclusions.

Olivine host composition is measured by EPMA with WDS mode. In fact, we see the total is generally poor. Here, we accepted the data with the total more than 98 % and less than 102 %. Since stoichiometry is good, we now reported only cation for poor total olivine data set and only used Fo content for PEC correction. The table does not include the other worse totals now.

> *-5. For clarity it could be written that the volatile (at least S) concentrations that are considered are the SIMS data (even if in the Table only the SIMS data are reported after PEC correction).*

Response: As we replied in previous question of reviewer 1, we added the sentence in the main text to clarify that we adopted SIMS values because of high analytical precision.

*What could justify the difference between SIMS and EMP analyses of sulfur whereas for SIMS and EMP data for Cl are in good agreement? As an example the S content of the MI (KSS-2m1) chosen as the basaltic end-member is 0.31 wt% (SIMS) and <0.2 wt% (EMPA).*

Response: As we already answered, the measured values for S between EPMA and SIMS analysis agree within 25%. When melt inclusions are measured by both method EMP and SIMS, we favored SIMS data because of high analytical precision.

*What about $H_2O$?*

Response: we adopted SIMS $H_2O$ values because of high precision of analysis, they are the only $H_2O$ measurements we trust here.

*P9. Discussion: evidence of magma mixing. What is the significance of the MIs compositions (major and volatile elements) in reversely zoned crystals? A short description of the MIs in the dedicated section should be inserted to describe a little bit better these MIs. Is there any evidence of cracks and overpressure, of melting/crystallization at the glass/mineral interface. Are calculations of PEC% relevant in the case of reversely zoned olivine crystals?*

Response: We scrutinized the olivine and inclusions and checked for cracks and decrepitation, but to the best of our knowledge we did not identify any of those. While we did not make an explicit reference, there is a correlation between olivine zoning and the inclusion composition. Normally zoned olivine has high-Fo core (Fig. 3), thus the mafic group on the basis of our grouping (< 55 % $SiO_2$). Reversely zoned olivine has low-Fo and belong to the felsic group. As the revised the text, we described the compositional correlation carefully, we believe it illustrates the systematics better now.

PEC is calculated between the melt inclusion and small immediate vicinity of the surrounding olivine. The fact that the olivine is reversely zoned has nothing to do with the correction at the time of the eruption. The reverse zoning likely happened sometimes after the entrapment of the melt inclusion.

*P10, l10-13. Could the calculated mixing curves be reported in the plots ($H_2O$-S-Cl) of Fig. 5?*

Response: In the revised text, we decided not to include volatile elements in the mixing model, mainly due to difficulty separating degassing from mixing. Fig. 5 was kept but the mixing line was not added.

*P10, l35. "The mafic endmember magma is expected to be volatile- rich, notably in sulfur (up to 4000 ppm; Fig. 3)." Yes but the end-member which has been chosen for the modeling of the magma mixing process contains 0.29 wt% S? Moreover, in the Figure 3d and as it is written p 9 and in the abstract, the S concentration reaches 3745 ppm in one MI (KKO sample) and most of them are <3745 ppm.*

Response: The reviewer is right. The value of "4000 ppm" written in the text was a mistake, "3750 ppm" is right. Thus, we replaced the number in the text with "3750 ppm". This corresponds to the highest S concentration measured in a KKO olivine-hosted melt inclusion and we took this value as the S composition of the mafic endmember. We explicit this in the text.

*P11, l14-17. I think that it is important to write here that $P_{H2O}$ is assumed to be equivalent to the total pressure of fluids, neglecting the role of $CO_2$.*

Response: Yes absolutely. Now it reads "Here the total pressure of fluids is in fact equivalent to $PH_2O$, neglecting the role of $CO_2$." [Line 560-561]

*P1, l25. Are the depths of 2 and 4 km, below sea level? or below the vents?*

Response: Yes these 2 numbers are below sea level every time because they come from the magnetotelluric work of Hata. When we calculated the lithostatic pressure we did it from the vent so we added 1km which corresponds to the height of the volcano (so 3 to 5 km below the vent). In the revised document, the depths are referenced to the common point= the vent.

*P11, l35. VolatileCalc is calibrated for MORB at low pressure. The authors could make their pressure calculations using Shishkina et al., (Chem Geol 2014), who provide an extensive experimental dataset on the $CO_2$ concentrations in basalts. As fully proved in this paper the solubility of $CO_2$, contrary to $H_2O$, widely varies with the melt compositions.*

Response: As pointed out here, we have explored alternative saturation pressure calibration available in the community (Supplementary material S4). In the revision, we mention the range of pressure that we found. SolEx and MagmaSat (Ghiorso and Gualda 2015) are shown to be comparable. [Line 582-583]

*P11, l35: " the mafic-endmember $H_2O$ concentration as 4.43 – 4.68 wt.%. Thus, the initial primitive $H_2O$ concentration is at least 4.5 wt. %.". In the modeling of mixing reported in ESM2 the end-member are KSS-2m1 and KSS-2d-m1. The former contains 2.9 wt% $H_2O$ and 0.29 wt% S (SIMS corrected data). I am confused here.*

Response: Yes indeed, our writing was not clear enough. We used the maximum $H_2O$ determined with the hygrometer (4.68wt.%) as the $H_2O$ concentration of the mafic endmember. The S concentration of the mafic endmember is the maximum S concentration measured in the melt inclusion 3750 ppm. We modified the text accordingly.

*P11, l38. "2400 kg/m$^3$ for the first km and... " first km of what?*

Response: we meant the first 1 km of crust. We modified text and it reads "*2200 kg/m$^3$ for less than 1 km deep in the crust*" to clarify. Furthermore, we have revised the near surface density to 2200 g/m$^3$ after carefully inspecting Komazawa's figure. [Line 564]

*P11-12. "Gas bubbles in MIs...increases the pressure entrapment...". Not the bubble, the $CO_2$ trapped in the bubble because the total fluid pressure = $PH_2O+PCO_2$.*

Response: We modified text, and now reads: "As gas bubbles were seen in melt inclusions, large amounts of $CO_2$ incorporated in such shrinkage bubbles significantly increases the entrapment pressure estimation (e.g. Moore *et al.* 2015)." [Line 585-587]

*More than 40–90% of the initial $CO_2$ that was dissolved in the melt inclusions at the time of trapping was lost to shrinkage bubbles, with an average loss of 75-80% (Wallace et al., 2015; Moore et al. 2015; Hartley et al., 2014). Hence the initial dissolved amount of $CO_2$ in Aso MIs could imply a much higher total fluid pressure*

*(P<sub>CO2</sub>+P<sub>H2O</sub>) than 300 MPa (~10 km depth equivalent). The discussion needs to be more elaborated here to demonstrate that there is a good agreement between the petrology and the depth of the seismic-low velocity layer at Aso. I also suppose that the magma ponding zone is not unique between 10 and 24 km beneath Aso, and that magma batches could mix altogether at various depths?*

Response: The argument of the reviewer is correct and we took it into account in our discussion. On former page 12 line 3, we added the following text "Recent melt inclusion studies reported more than 40-90 % of the initial $CO_2$ that was dissolved in the melt at the time of entrapment was lost to shrinkage bubbles, with an average loss of 75-80 % (Wallace et al. 2015; Moore et al. 2015; Hartley et al. 2014). If 90 % of initial $CO_2$ is present in the shrinkage bubble and a maximum $CO_2$ value of 340 ppm is assumed in the melt (from Saito et al. 2018), then the expected initial value of the melt would reach 3400 ppm. This value is in the same order of magnitude as the initial $CO_2$ concentration in a typical primary arc magma (Aster et al. 2016), and saturation pressure would exceed 5 kbar (~19 km depth equivalent) However, at the time of this study, bubble sizes were not documented with impossibility to go back to measuring them *a posteriori* since most are now polished away. In this case we chose not to use the $CO_2$ data of the melt inclusions." [Line 589-599]

Regarding the magma ponding zone, we don't have any information to argue for multiple ponding zones. Therefore, further discussion is currently difficult.

*P12, l35. As written above, the S concentration reaches 3745 ppm in one MI (KKO sample) and most of them are <3745 ppm (not 4000 pm). Such an amount is not higher but typical of subduction-related magmas -related basalt in which sulfur is dissolved dominantly or totally dissolved as sulfate. As another example, the $H_2O$-rich MIs of Augustine volcano display similar high S concentration (i.e.,Webster et al., 2010; in The 2006 eruption of Augustine volcano, Alaska, US Prof paper 1769).*

Response: It was our error to stress the high S content. We revised the text, "Dissolved S concentrations, up to 3750 ppm in the mafic endmember melt inclusions, are higher than many in subduction-like hydrous basalt (Fig. 6a, mostly S between 900 and 2500 ppm; e.g. Wallace 2005), while similar high S content appears to occur in oxidized magmas (Roggensack 2001; Webster et al., 2010)." [Line 493-496]

*P12, l17-19. I am confused also here. How are calculated these ratios? There is no sulfur concentration as high as 5050 ppm? What are they representative of?*

Response: We admit it was confusing. Now we only use the maximum ratios $S/K_2O$ (0.711), $Cl/K_2O$ (0.170) and $F/K_2O$ (0.047) as representative of the primitive composition, and we did not demonstrate a strong ground to choose a concentration of $K_2O$. The endmember composition is now defined by melt inclusion values. The text now reads: "Because the composition of the mafic endmember points towards that of the primitive magma, the maximum values are, taken as the primitive volatile ratios: $S/K_2O = 0.711$, $Cl/K_2O = 0.170$, and $F/K_2O = 0.047$." [Line 489-492]

*P12, l23-24. "In fact, as shown in the previous section, we assessed the mafic-endmember $H_2O$ concentration as 4.43 – 4.68 wt.%. Thus, the initial primitive $H_2O$ concentration is at least 4.5 wt. %". This sentence is redundant. Could it be just one section where the volatile ($H_2O$, S, Cl) contents of the end-member are clearly described: what is the best candidate (KKO, KSS)? Why is it representative of THE parental melt of the ASO series?*

Response: Absolutely agree. We decided to rewrite the section about "Characterization of mixing endmembers", and "Volatile concentrations of primitive basaltic melt". We have paid particular attention to suppress redundancy.

> *P14, l10-14. What is the pressure of sulfur exsolution in such magma? The question of the sulfur supply from deep basalt magmas is detailed in Wallace and Edmonds (2011).*

Response: In the passage here, we did not specify the exact depth as the discussion is developed later Fig. 8. As the conclusion of the paper, we think S is degassed between 9 - 10 km and we added a summary figure to synthesize our finding to the reader.

> *P15, l1-7. It is well known that $CO_2$ is almost totally exsolved as a gas phase at pressure less than 500 MPa (see Wallace and co-authors).*

Response: Indeed, that is the point of our discussion as well. Now, in our new revision, we simplified the discussion regarding $CO_2$. $CO_2$ is nearly all degassed at shallow depth, and all the inclusions have low $CO_2$. We have no information regarding the $CO_2$ at the source. Taking high values of $CO_2$, it is possible to infer the depths of equilibrium, however the inclusions were degassed already. Our conclusion is that observed gas composition is consistent with the equilibrium pressure of 2.2-2.3 kb which is derived from 400-750 ppm initial $CO_2$. Our finding is therefore coherent with the point mentioned here. Yes, the major degassing and segregation occurs at depth shallower than 5 kb.

> *P16, l19. What are the gas species exsolved at 300MPa (±equivalent to 9 km)? I suppose that it 9 km below the vents? Geophysicists generally indicate depth below sea level.*

Response: yes the 9 km here is from the vent. The difference between vent and sea level is 1000m the height of the volcano, so 9km from the vent, means 8 km below sea level. As SolEx model ignores gas speciation completely, the gas species at the depth must be $H_2O$-$CO_2$-(dissolved S, Cl, and F).

## Other remarks

> *Table S1. Analysis OP2-M1. Is there an error in the $Na_2O$ concentration (0.63 wt%) that is very low?*

The data with the $Na_2O$ outlier was suppressed from the Table.

> *Table S3 some of the analyses have a relatively low total (among others: OJSU olivine a2c& a4c: 95.8; c1c: 96.2; c5c: 91.2) or >102wt%.*

Response: we have deleted these low total data after check the stoichiometry. Data of olivine and plagioclase presented in S3 are those measured by an EDS detector in SEM. Since stoichiometry of minerals are good, even for these with low total, we remained these EDS data as 100 wt.% normalized value unless total is too low (±4 wt.%), and suppressed all low total data. For WDS data, while stoichiometry of minerals is excellent, we decided to suppress data with low or high total (>102 wt.% or <98 wt.%).
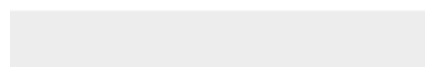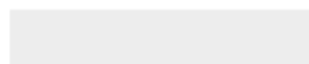
> *Fig. 4. Temperature*
> *ESM 2: $C^i_{obs} - C^i_B$ written two times*

Response: The spelling error is corrected, so is the error of the equation.

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