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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.* 2013). 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.

106　**Samples and methods**
107　*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

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).

196

Analytical methods

Bulk rock major and trace elements

199   Bulk rock major and trace elements were determined by XRF on flux-fused
200 disks using a Philips PANalytical MagiX PRO spectrometer at the Kitakyushu Museum
201 of Natural History and Human History. The detailed analytical procedures are described
202 by Mori and Mashima (Mori and Mashima 2005). Accuracy was reported as ±0.1 %
203 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

205   Major elements, S, and Cl concentrations were determined in melt inclusions,
206 host minerals and groundmass glasses using a JXA8800R electron probe microanalyzer
207 at the Earthquake Research Institute (ERI), University of Tokyo. The analytical settings
208 were 15kV acceleration voltage, 12 nA beam current, with counting times for Na, Al, K,
209 Fe, Mg, Si, Ti, V, Mn, and Ca at 20 s, and 30 s for Ni, Cr in mafic minerals and for S and
210 Cl in hydrous melt. Beam diameter was set at 10 μm for glass and plagioclase, and
211 focused (1 μm) for other minerals. During melt inclusion and groundmass glass analysis,
212 Na and K were always measured in the first analytical cycle to minimize alkali loss
213 (Devine *et al.* 1995). All analyses applied oxide ZAF correction. Analytical uncertainties
214 are <0.7% relative for Si, <1% relative for Al, Fe, Mg, and Ca, <5% relative for Ti and
215 Na, <10% relative for K, and <20% relative for Mn, V, Ni, Cr, S, and Cl.
216   In addition to the EPMA analysis, the core and rim compositions of phenocrysts
217 were analyzed by energy-dispersive X-ray spectroscopy (EDS, AZtec system; Oxford
218 Instruments) connected to a JEOL JSM-7001F field-emission electron microscope (FE-
219 SEM) at Kumamoto University, using 15 kV acceleration voltage and 1 nA beam current.
220 The beam diameter settings were the same as the EPMA setting at the University of Tokyo
221 for all the host minerals. Analytical uncertainties are typically 0.5% relative for SiO_2, 1%
222 relative for Al_2O_3, 1.5% relative for FeO, 0.5% relative for MgO, 2% relative for TiO_2
223 and Na_2O, 1.5% relative for K_2O, 1% relative for CaO. Other minor elements such as
224 MnO and P_2O_5 can be as high as 20% relative.
225   Water concentrations in melt inclusions were determined by FTIR micro-
226 reflectance spectroscopy using a JASCO FT-IR-660 plus, equipped with an IRT-30VC
227 analytical microscope at the ERI, following the procedures described by Yasuda (2014).
228 The IR spectra were obtained using 15×15 to 60×60 μm^2 rectangular apertures, and by
229 accumulating 220 to 1500 scans, over a range of 400 to 7800 cm^{-1}. A gold mirror was
230 used as a reflectance reference. Water concentrations were quantified using an empirical
231 linear relationship for basalt to rhyolite compositions for total H_2O concentrations,
232 measured in the 3650 cm^{-1} wavelength region. The analytical uncertainty (2σ) of the FTIR
233 reflectance spectroscopy was < 0.3 wt. % (Yasuda 2014). While the detection limit of the

234 method strongly depended on the sample, we estimated the detection limits as 0.5 wt. %.

235 H$_2$O, CO$_2$, F, S, and Cl concentrations in selected melt inclusions were
236 determined by a SIMS (Cameca IMS-1280HR of Kochi Institute, JAMSTEC, Japan)
237 following the procedure described by Shimizu *et al.* (2017). This analytical method favors
238 a weaker primary current (up to 0.5 nA) than in previous studies (1-1.5 nA primary
239 current; Le Voyer *et al.* 2010; Helo *et al.* 2011; Rose-Koga *et al.* 2012, 2014; 20 nA
240 primary current in Hauri *et al.* 2002) and uses in-house standards covering the
241 concentration range found in the natural samples in this study. In short, a 20 keV (10 keV
242 at the ion source and 10 keV at the sample surface) Cs$^+$ ion beam of 300–500 pA was
243 defocused to be 10-15 μm in diameter. Secondary ions were accelerated at 10 kV. A -10
244 keV electron beam with a diameter of ~100 μm was applied for electrostatic charge
245 compensation of the analysis area. The field aperture was set at the size corresponding to
246 5 x 5 μm on the sample surface. Mass resolving power was set at ~6000 to separate mass
247 interferences (for example, to separate ^{34}S^{1}H interference on ^{35}Cl requires 5120 MRP;
248 Burdo and Morrison 1971). Negative secondary ions of ^{12}C, ^{16}OH, ^{19}F, ^{30}Si, ^{31}P, ^{32}S, and
249 ^{35}Cl and the mass position of 11.9 amu were measured by an axial electron multiplier
250 using the peak switching method. An analysis consisted of 10 cycles, and the total
251 measurement time for each analysis was ~6 min. Repeated analysis of a secondary
252 basaltic glass standard from East Pacific Rise, EPR-G3 (Shimizu *et al.* 2017), yielded a
253 relative standard deviation (1σ) for H$_2$O, CO$_2$, F, Cl, and S of 1.4, 3.2, 1.5, 2.5, and 0.9%,
254 respectively. This SIMS analysis was conducted after EPMA analysis. Therefore,
255 although we were careful to polish the sample with alumina powder again before SIMS
256 analysis, measured CO$_2$ concentrations were reported in the supplementary material but
257 not used due to possible carbon contamination. The measured values for S and Cl agreed
258 within 25% between EPMA and SIMS analysis. So when volatile elements were
259 measured by two methods, we adopted SIMS values rather than EPMA because analytical
260 uncertainty of these elements by SIMS are generally lower (e.g. Rose-Koga *et al.* 2020).
261 In this study, we did not find satisfactory agreement between H$_2$O determined by FTIR
262 and by SIMS (uncertainty of FTIR measurements is close to 40%) so in the following,
263 we only consider H$_2$O concentrations measured by SIMS, based on the better detection
264 limit and precision of the method.

265 <u>Sulfur speciation analysis</u>

266 Selected inclusions were analyzed for S$K\alpha$ peak positions to constrain the *fO$_2$*
267 conditions of the glasses. The wavelength of S$K\alpha$ radiation [λ(S$K\alpha$)] for melt inclusions
268 was measured using the EPMA following the procedures described by Yasuda *et al.*
269 (2001), based on the method of Wallace and Carmichael (1994) and Carroll and
270 Rutherford (1988). Sulfur speciation as the proportion of S^{6+} over a total S content was
271 determined by measuring a relative shift from the peak position of an anhydrite mineral
272 (Carroll and Rutherford 1988), with an assumption that S^{2-} and S^{6+} are the only two

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

307 **Results**
308   The analysis of five scoria from Aso edifices produced data of major elements
309 for bulk rocks along with 204 melt inclusion data (major and volatile element
310 concentrations) and host mineral compositions. More than 890 point-analyses were made
311 to determine major element compositions of groundmass glasses and phenocrysts (core
312 and rim; Tables 1 – 3 and S1 – S3).

313
314 *Petrography*
315   All samples were porphyritic with approximately 40 vol.% crystals. Plagioclase,
316 clinopyroxene, olivine plus minor orthopyroxene, and opaque minerals were present. In
317 all samples, plagioclase phenocrysts commonly showed dusty zone and honeycomb
318 texture (Fig. 2a), and all orthopyroxene phenocrysts had reaction rims of olivine and
319 clinopyroxene (Fig. 2b). Aggregates of phenocrysts (i.e. plagioclase, clinopyroxene,
320 olivine, and opaque minerals) were frequently found in all samples (Fig. 2c). The
321 groundmass consisted of microlites of plagioclase, clinopyroxene, olivine, and magnetite.
322 The groundmass of KSS occasionally showed the heterogeneous mingling texture where
323 crystals are relatively abundant (Fig. 2d).
324
325 *Host mineral compositions*
326   The olivine phenocrysts were grouped into two types based on the core Fo
327 contents [Mg / (Fe + Mg) × 100 in mole], as low-Fo (62 to 72) and high-Fo (72 to 82)
328 (Fig. 3a). High-Fo olivine was observed only in KKO, OJSU, OJSL, and KSS. Low-Fo
329 olivine was found in all samples. As Fo content of the phenocryst rims ranged from 68 to
330 78 in KKO, OJSU, OJSL, and KSS, and from 64 to 67 in NKD14 (Table S3), generally
331 low-Fo olivine phenocrysts were reversely zoned, whereas olivine phenocrysts in NKD14
332 were homogeneous. All high-Fo olivine phenocrysts were normally zoned.
333 Clinopyroxene and orthopyroxene phenocryst cores in all samples were in the range of
334 65-76 and 61-71, respectively (Mg# = [Mg / (Fe + Mg) × 100 in mole]). The majority of
335 clinopyroxene phenocrysts in KKO, OJSU, OJSL, and KSS were reversely zoned. Mg#
336 of NKD14 varied little, at ~70. The compositions in the rims of olivine and clinopyroxene
337 phenocrysts were the same as the minerals found in reaction rims of orthopyroxene
338 phenocrysts. The plagioclase phenocrysts were also divided into two types based on the
339 normal and reverse zoning patterns. The An content [Ca / (Ca + Na) × 100 in mole] of
340 the plagioclase phenocryst cores was within the 55-93 range.
341
342 *Major and volatile elements in melt inclusions*
343   The tephra samples of this study were basaltic to basaltic andesite with SiO_2
344 ranging from 51.5 to 54.3 wt. % (large circles in Fig. 3c). Melt composition in inclusions
345 varied significantly more than that of the bulk tephra composition: SiO_2 ranging from
346 46.0 to 65.8 wt. %. This range mostly overlapped with the compositional variation of
347 post-caldera volcanic products (grey circles in Fig. 3c). The melt inclusion compositions
348 of NKD14 were generally similar to evolved matrix glass and varied little, and were
349 distinguished from the melt inclusions of KKO, OJSU, OJSL, and KSS.
350   In our sample set, the core composition of host olivines were clearly divided
351 into two groups with Fo72 representing the divide (Fig. 3a). We interpreted that olivines
352 have grown from two distinctively different lavas, which we called mafic and felsic.
353 Based on the anti-correlation of SiO_2 concentration in olivine-hosted melt inclusions with

354 host Fo content, we concluded that magma composition can be divided into two groups
355 above and below 55 wt.% SiO_2. The high SiO_2 corresponded to low-Fo olivine and low
356 SiO_2 corresponded to high-Fo olivine. Thus, in the following we grouped all the melt
357 inclusions lower than 55 wt.% SiO_2 in a mafic group, and others in a felsic group. S
358 concentration in melt inclusions correlates well with host Fo content and is anti-correlated
359 with SiO_2 (Fig. 3a) and K_2O, indicating a mafic volatile-rich (with S up to 3750 ppm and
360 Cl up to 1311 ppm) magma, and a felsic volatile-poor magma (Fig. 3b). NKD14
361 inclusions were notably different, with less than 434 ppm S, indicating extensive
362 degassing. Melt inclusion Cl concentrations varied from 530 ppm to 1311 ppm (Table 2
363 and Table S1; SIMS value is preferred to EMP value when both are reported). F
364 concentrations were determined only on a subset of olivine-hosted melt inclusions and
365 therefore there are fewer data. F concentrations varied between 258 and 853 ppm (Table
366 2 and Table S1). F and Cl correlates with SiO_2 and K_2O and anti-correlate with host Fo
367 content. H_2O concentrations measured in melt inclusions vary between 0.47 to 2.89 wt.%
368 (NKD14-Ol-e3-4-m4 and KSS-Olivine-4-m11, respectively; Table 2 and Table S1).

Discussion

Evidence for magma mixing

371   Zoning in magmatic minerals characterizes their crystallization in a magma
372 chamber and can trace the history of magma cooling (e.g. Costa *et al.* 2008), and magma
373 mixing (e.g. Sakuyama 1979). Among the tephra samples in this study, phenocrysts in
374 every sample indicate textural evidence of magma mixing that could have been produced
375 by the introduction of hotter magma: for example, the reverse zoning and disequilibrium
376 texture, such as the honey-comb texture of plagioclase and reaction rim of orthopyroxene
377 (Fig. 2a and 2b; Tsuchiyama 1985). The coexistence of normally zoned plagioclase and
378 olivine phenocrysts with these disequilibrium phenocrysts suggests that magma mixing
379 of at least two distinct components has occurred (e.g. Sakuyama 1979). This
380 interpretation is supported by the compositional variation of the melt inclusions; felsic
381 melt inclusions are hosted in reversely zoned phenocrysts such as plagioclase,
382 clinopyroxene, orthopyroxene, and low-Fo olivine. Mafic melt inclusions are hosted in
383 high-Fo olivine and some of plagioclase (Fig. 3).
384   The presence of orthopyroxenes surrounded by reaction rims and An-rich zones
385 in the middle part of plagioclases in NKD14 (Fig. 2f) indicates that the 2014 magma is
386 also the result of mixing. Such petrological features are found in magmatic products of
387 every Nakadake eruption (Miyoshi *et al.* 2005). Thus, we consider that all the Nakadake
388 eruption products are the result of magma mixing, rather than the derivatives from a single
389 parental magma. In addition, Miyoshi *et al.* (2005) also show that the compositional
390 variation in the trace elements in the post-caldera basaltic rocks of Aso volcano is
391 consistent with a magma mixing model and not with a fractional crystallization process.
392 Therefore, at least two types of magmas are present beneath the Nakadake cone, and feed
393 its eruption.

394
395 *Characterization of mixing endmembers*
396   We conducted a two-component mixing model calculation of two distinct
397 magmas, one silicic endmember and one mafic endmember, based on the major element
398 variation of melt inclusions (see Supplementary document S4). The model used the most
399 primitive basaltic melt (Melt ID: 2-m1 hosted in an olivine) and the most SiO_2-rich dacitic
400 melt (Melt ID: d2-m1 hosted in a plagioclase) of KSS as the mafic and silicic endmember,
401 respectively. The major element variation was well reproduced with the mixing model
402 for melt inclusions of all host minerals (Fig. S4-5). While the major variance of
403 concentration variations was explained by a simple mixing process, in close inspection of
404 trends, it is likely that crystal fractionation contributed to the dispersion from the mixing
405 model. It should also be noted that the mixing model required the presence of independent
406 mixing endmembers, it does not constrain their origin.
407   It is important to note that there is a surface expression of this silicic
408 endmember in the Aso eruption products, while the mixing endmember is set by a melt
409 inclusion. Major element compositions of ACP1 dacitic pumice (Takada 1989), the only
410 Holocene felsic product erupted three hundred years before that of KSS, are similar to the
411 endmember, and this indicates the presence of the silicic magma. Furthermore, the
412 presence of a banded pumice was reported in ACP1 prior to KSS (Miyabuchi 2017). This
413 banded texture is evidence of magma mingling and therefore the mixing trend is unlikely
414 a result of assimilation and crystal fractionation of single parental magma. The cores of
415 reversely zoned phenocrysts of KSS scoria samples were formed at equilibrium
416 conditions with the silicic endmember. Therefore, the temperature of silicic endmember
417 magma was determined with a two-pyroxene thermometer by pairing core compositions
418 (Putirka 2008). The estimated temperatures of the silicic endmember are 1010-1025ºC
419 for KKO, OJSU, OJSL, and KSS (± 13˚C, 1σ for samples, while standard error of the
420 thermometer is ±38 ˚C). We adopted this estimated range as the temperature of the silicic
421 endmember magma. These estimated temperatures are higher than those of typical dacitic
422 magma with 4 - 5 wt. % H_2O (e.g. 770 – 915 ˚C for Mount St. Helens, Gardner *et al.*
423 1995) and lower than that estimated for a completely anhydrous dacitic magmas, for
424 example Puna Geothermal Venture Wellfield, Hawaii have the highest temperature
425 estimates 1050ºC (Teplow *et al.* 2009). This silicic endmember magma (T between 1010-
426 1025ºC) will mix with the mafic endmember (most likely hotter) magma at temperature
427 presumably higher than 1010-1025ºC.
428   Basaltic lava corresponding to the pure mafic endmember is absent among the
429 eruption products of the entire post caldera stage (Miyoshi *et al.* 2005), while it is found
430 in olivine-hosted melt inclusion. Many tephras of this study also contain normally zoned
431 phenocrysts with high-Fo and high-An cores. As for the case of the silicic endmember, it
432 is possible to assume the equilibrium of these cores with the mafic endmember melt. We
433 therefore calculated the magmatic temperature of the pure mafic endmember, using
434 Sakuyama's method (Sakuyama *et al.* 2014), which involves the combined application of

435 a plagioclase-melt hygrometer (Lange *et al.* 2009) and an olivine-saturated melt
436 geothermometer (Sugawara 2000; Médard and Grove 2008). This method accounts for
437 the H_2O-dependency of the olivine thermometer by simultaneously solving for H_2O and
438 temperature using an additional constraint from the plagioclase hygrometer. The resulting
439 temperature of mafic endmember magma varies between 1051 – 1063 ˚C, depending on
440 the assumed pressure condition of the magma chamber (0.1 - 0.5 GPa, respectively). In
441 addition, the entrapment temperature of the endmember inclusion (KSS-2-m1) is 1092
442 ˚C based on the olivine-liquidus thermometer (Table S1, Sugawara 2000; Médard and
443 Grove 2008). Considering the uncertainties of the thermometry methods, these
444 temperature estimates are likely representing the range for the mafic magma. By taking
445 the high temperature result (~1090 ˚C), the temperature difference between mafic and
446 felsic (1010-1025 ˚C) endmembers is at least 65 ˚C.

447 The mixing trend among volatile elements is present and generally consistent
448 with the trend of major elements. However, in detail, there are systematic disparities from
449 the mixing curve (Supplementary document S4). Notably, abundances of H_2O, S, and Cl
450 for NKD14 sample, are depleted compared to the mixing trend traced by KSS melt
451 inclusions (Fig. S4-4). This is best explained by significant degassing occurring
452 during/after magma mixing. Furthermore, there is no single melt inclusion uniquely
453 representing suitable mafic endmember volatile concentrations. The sample KSS-2-m1 is
454 selected as the major element endmember, but its H_2O contents are not the highest values.
455 From the inspection of the trend, we inferred that the mafic endmember must have higher
456 volatile content thus most likely lost water after its entrapment. If melt inclusions formed
457 at a deeper depth, and were stored in a shallower magma chamber, it is expected that H^+
458 diffusion through the olivine would equilibrate the melt inclusion with the surrounding
459 magma (Portnyagin *et al.* 2008; Chen *et al.* 2011; Gaetani *et al.* 2012; Bucholz *et al.*
460 2013; Ferriss *et al.* 2018). Complete re-equilibrated melt inclusion would have erased the
461 mixing trend. It is not the case here, we have found suitable endmember volatile element
462 concentrations that satisfy the general trend. Because the mafic endmember magma is
463 expected to be volatile-rich, it's H_2O concentration has to be higher than the H_2O of the
464 mixed-magma (e.g. that of the melt inclusions). The maximum estimated H_2O
465 concentration (4.68 wt. %) based on the hygrometer discussed above is therefore taken as
466 the concentration for the volatile-rich mafic endmember. This value of 4.68 wt.% H_2O is
467 higher, by about 2 wt. %, than the highest H_2O concentration measured in the melt
468 inclusion. Sakuyama's method implicitly ignores the CO_2 activity in magma, and predicts
469 lower H_2O content when considering CO_2-bearing system (by 0.9 wt. % less H_2O,
470 assessed from an experimental result of Melekhova *et al.* 2017). Furthermore, this volatile
471 content is the value at the condition of olivine - plagioclase crystallization, most likely of
472 the cooling magma in the crust. At this point, we have no other constraint on the H_2O
473 concentration of the mafic endmember and the primary magma could have an even higher
474 H_2O content.

475

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, 1σ = 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

517   are representative of primary concentrations, as the exsolution pressure of Cl and F is at
518   shallower depths (~100 MPa for Cl and ~10 MPa for F; Spilliaert *et al.* 2006) than for
519   other volatile species. Cl concentration in the Aso primitive magma was 716 ppm (took
520   the value of the mafic end member melt inclusion: KSS-2-m1) which is higher than that
521   of MORB (Fig. 6; max 500 ppm Cl, Le Voyer *et al.* 2015), as it is interpreted as the
522   addition of Cl to the subarc mantle from the subducting slab (e.g. Straub and Layne 2003).
523   On the contrary, F concentration in the primitive magma was 324 ppm, which is the same
524   order of magnitude as that of MORB (max 500 ppm, Le Voyer *et al.* 2015). This suggests
525   that F addition to the subarc mantle was insignificant.
526   The Cl/F ratios of melt inclusions globally reflect the composition of the slab-
527   agent added to the mantle source as F fractionate from Cl depending on the physical
528   character of the flux leaving the slab (Le Voyer *et al.* 2010; Van den Bleeken and Koga
529   2015; Narvaez *et al.* 2018). Observed Cl/F ratio of melt inclusions from Aso volcano are
530   relatively high (from 1 to 2,5, Fig. 6) compared with that of MORB (Saal *et al.* 2002;
531   Wanless and Shaw 2012; Wanless *et al.* 2014, 2015; Le Voyer *et al.* 2017; Shimizu *et al.*
532   2019). Because Cl/F values in arc magma are characterized by several parameters such
533   as the composition of slab, nature of the fluid and fractionating minerals in residual slab,
534   and the degree of melting of arc magma, the physical character of slab derived flux is
535   determined with a set of assumptions. In any case, the primitive magmas with MORB-
536   like F concentration and a high Cl/F value (2.2) are found among the melt inclusions of
537   calc-alkaline arc magmas in a typically "cold" subduction setting (Straub and Layne
538   2003; Rose-Koga *et al.* 2014). The halogen characteristics of our Aso melt inclusions
539   were in the range of typical arc magma, and the value of the primitive magma was close
540   to the melt inclusions of Iwate volcano, a prototypical example of the arc magma derived
541   from aqueous fluid driven from a cold oceanic crust (Rose-Koga *et al.* 2014). This
542   indication is consistent with studies based on high bulk B/Nb ratios indicating aqueous
543   fluid additions from the subducting Philippine sea plate in the source of the Aso basalt-
544   basaltic andesite rocks (Miyoshi *et al.* 2008a, b). Other studies based on Sr, Nd, and Pb
545   isotope variations of Quaternary lavas in the northern Kyushu area also support the model
546   of slab-derived aqueous fluid addition from the subducted Philippine sea plate beneath
547   Aso volcano (Shibata *et al.* 2014).
548

549   ***Storage depth of the magma mixture and mafic endmember magma***

550   Solubility of volatiles in magma strongly depends on pressure and temperature
551   conditions, and the chemical composition of the magma (e.g. Dixon *et al.* 1995). In this
552   section, we discuss the storage depth of the mixed-magma based on H_2O concentration.
553   For example, measured volatile concentrations of melt inclusions are considered to be re-
554   equilibrated to a condition of a magma storage. Alternatively, it is also possible to
555   determine H_2O concentrations estimated from plagioclase rim and groundmass glass pairs

556 (geo-hygrometer, Lange *et al.* 2009), likely corresponding to the value of the mixed
557 magma during the plagioclase rim growth. The H_2O concentrations of such mixed
558 magmas are, ~2 wt.% for NKD14 and KKO, and ~3 wt.% for OJSU, OJSL and KSS
559 (Table 4). Here, the hygrometer calibrated for the total fluid pressure is equal to $P(H_2O)$,
560 neglecting the role of CO_2. Yet, these values are comparable to those measured in the
561 melt inclusions, and indicate a magma chamber pressures of 0.5 kbar for NKD14 and
562 KKO, and 1.0 kbar for OJSU, OJSL, and KSS (*i.e.* 2.1 and 4 km deep, respectively, Fig.
563 7, note the depth is calculated using a density of 2200 kg/m^3 for the first 1 km and 2700
564 kg/m^3 for the crust at greater depths (Komazawa 1995), by solving for the depth, h [m],
565 P = g {2200 (1000) + 2700 (h-1000)}). Because CO_2 concentrations in the felsic group
566 melt inclusions are notably low (0 - 77 ppm, Table S1), it makes negligible changes to
567 the calculated equilibrium pressure (~20 MPa, using RhyoliteMELTS/MagmaSat,
568 Ghiorso and Gualda, 2015). These pressures correspond to the depths of magma storage
569 after mixing, since (1) the last growth rim of plagioclase must have occurred after mixing,
570 as both normal and reverse zoning plagioclase have the same rim composition. (2) It is
571 less likely that plagioclase rim significantly grew during sub-Plinian and Strombolian
572 eruption. Melt inclusion H_2O concentrations range from 0.47 to 2.89 wt. %, indicating
573 the minimum equilibrium pressure in agreement with the plagioclase-rim method. Two
574 magma chambers, C2 and C1, detected by geophysical studies are also located at similar
575 depths, 1 - 4 and 3 - 10 km, respectively (Tsutsui and Sudo 2004; Sudo *et al.* 2006; Hata
576 *et al.* 2016; Fig. 7). At the depths, because the solubility of CO_2 is so low, the conclusion
577 presented here would remain the same even if the hygrometer calculation does not
578 account for CO_2.
579   The magma of the mafic endmember is expected to have more than 4.68 wt. %
580 H_2O, and it is therefore derived from a greater depth than these C1 and C2 storage depths.
581 The corresponding equilibrium pressure is approximately 2.7 kbar (SolEx, Witham *et al.*
582 2012; note MagmaSat give 2.3 kbar, Ghiorso and Gualda 2015; with CO_2 of 340 ppm
583 reported in a melt inclusion from Nakadake by Saito *et al.* 2018) that is about 10 km deep
584 below the edifice. As gas bubbles were seen in melt inclusions, large amounts of CO_2
585 incorporated in such shrinkage bubbles significantly increases the entrapment pressure
586 estimation (e.g. Moore *et al.* 2015). Therefore, our pressure estimations are minimum and
587 true entrapment pressures of the basaltic magma certainly occurred at a depth greater than
588 10 km. Recent melt inclusion studies reported more than 40-90 % of the initial CO_2 that
589 was dissolved in the melt at the time of entrapment was lost to shrinkage bubbles, with
590 an average loss of 75-80 % (Hartley *et al.* 2014; Moore *et al.* 2015; Wallace *et al.* 2015).
591 If 90 % of initial CO_2 is present in the shrinkage bubble and a maximum CO_2 value of
592 340 ppm is assumed in the melt (from Saito *et al.* 2018), then the expected initial value
593 of the melt would reach 3400 ppm. This value is in the same order of magnitude as the
594 initial CO_2 concentration in a typical primary arc magma (Aster *et al.* 2016), and in this
595 case the saturation pressure would exceed 5 kbar (~19 km depth equivalent). However,
596 at the time of this study, bubble sizes were not documented with impossibility to go back

597 to measuring them *a posteriori* since most are now polished away. In this case, we chose
598 not to use the CO_2 data of the melt inclusions. Hata *et al.* (2016) also reported a magma
599 pathway from depths deeper than 11 km, feeding the deeper C1 reservoir. Also, the
600 presence of a seismic low-velocity layer at 11 - 25 km depth was reported and attributed
601 to a magma ponding location beneath the Aso caldera (Abe *et al.* 2010). These
602 observations are in good agreement with our petrological implication for the presence of
603 volatile-rich basaltic magma beneath C1 magma reservoir at a depth greater than 10 km.
604
605
606 ***Persistent degassing from a deeper magma reservoir (>10km)***

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

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

16

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

660 <u>Modelling degassing of the deep magma reservoir</u>

661   In the sections above, the equilibrium depths of volatile concentration in
662 magma were used to indicate magma storage depth, where stagnated-magma and gas
663 remain at equilibrium. Equilibrium gas composition at that depth should be the source of
664 the gas composition observed at the surface, only if the gas segregated and travelled to
665 the surface without precipitating solids or re-dissolving gas in between. In detail, the
666 speciation of mixed gas is a function of pressure, temperature, and oxygen fugacity, but
667 the gas system composition can be considered closed. With this hypothesis, it is possible
668 to determine the depth at which the observed gas composition is in equilibrium with a
669 magma (e.g. Burton *et al.* 2007; Allard 2010).
670   Fig. 8 is a result of such a calculation using SolEx (Witham *et al.* 2012),
671 showing the variations in H_2O/S, CO_2/S, and Cl/S molar ratios of gas in equilibrium with
672 a magma as a function of pressure. The observed H_2O/S gas composition of the 2014
673 eruption (shown as horizontal dotted red lines) intersects with the equilibrium gas
674 composition (plain lines Fig. 8) between 2.6 to 3.3 kbars. These pressures correspond to

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

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

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

(1) The compositions of melt inclusions in phenocrysts from recent eruption

756 products (Nov. 2014) of Nakadake cone were homogeneous, evolved and
757 degassed (S < 434 ppm), while compositions of melt inclusions in
758 phenocrysts from Kishimadake and other related cones (ca. 3.0 – 3.7 ka)
759 showed variable compositions with two extreme endmembers. One was
760 mafic (SiO_2 < 55wt.%) and volatile-rich, and the other was felsic (SiO_2 >
761 55wt.%) and relatively degassed. Mafic melt inclusions were hosted in
762 high-Fo olivine and some plagioclase, whereas felsic melt inclusions were
763 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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1174

1175   **Figure caption**
1176

1177   **Fig. 1** Locations of volcanic cones and sampling sites of the study. Main map shows
1178   topography of Aso volcano with a 50 m contour interval. Volcanic cones are indicated by
1179   solid triangles. Sampling sites are indicated by solid circles. Location of Aso volcano is
1180   indicated in an inset in the top left corner, showing Japanese islands with plate boundaries:
1181   solid line, active subduction plate boundary, and dashed line, diffused plate boundary.
1182   Stratigraphic log shows corresponding eruption stages and nature of volcanic deposits in
1183   A9418 site (Miyabuchi and Watanabe 1997). Kishimadake scoria (KSS) and Ojodake
1184   scoria (OJSL and OJSU) were collected at the indicated units. Kamikomezuka scoria
1185   (KKO) and Nakadake scoria (NKD14) were collected at the location indicated by field
1186   symbols. KKO in parenthesis indicates the relative eruption age (top of N4 stage).
1187

1188   **Fig. 2** Microscope photographs (a-d) and backscatter electron images (e, f) of
1189   representative phenocrysts and textures from Holocene basaltic tephra products in Aso
1190   central cones. (a) Plagioclase (Pl) phenocrysts with honeycomb texture in KKO, under
1191   cross-polarized light. Clinopyroxene (Cpx) and olivine (Ol) phenocrysts also present. (b)
1192   An orthopyroxene (Opx) phenocryst with reaction rim consisted of clinopyroxene and
1193   olivine in KSS, under cross-polarized light. (c) An aggregate of phenocryst consisted of
1194   plagioclase, clinopyroxene and olivine in KSS, under cross-polarized light. (d) A
1195   microlite-rich part of groundmass in KSS with abundant crystals, under plain-polarized
1196   light. (e) High-Fo olivine phenocryst and its melt inclusions observed in KSS. (f) A
1197   texture of plagioclase phenocryst with (optically) dusty zone, in the middle part of the
1198   crystal, observed in NKD14.
1199

1200   **Fig. 3** Major element and volatile concentrations in melt inclusions from Holocene
1201   basaltic tephra products in Aso central cones. Melt inclusion data from minerals other
1202   than olivine are shown as open symbols. The melt inclusion data are compared to bulk
1203   tephra and average groundmass glass compositions, solid circles, and solid squares,
1204   respectively. The variation of Fo content in all olivine cores is also shown as relative
1205   density estimates on the left side of (a). Dashed line in Figure 3a and 3b indicates Fo72.
1206   Bulk lava compositions of late-Holocene volcanic products, reported previously, are also
1207   shown as solid grey circles in (c) (Miyoshi *et al.* 2005; Miyabuchi 2010, 2017; Saito *et*
1208   *al.* 2018). All oxide concentrations were normalized to 100 wt. %, excluding volatile
1209   element abundance.
1210

1211   **Fig. 4** Ratios of volatiles/K_2O vs. K_2O in melt inclusions and groundmass glasses (the
1212   same symbols as Fig. 3). All volatile elements showed a systematic decrease (a,

1213　H$_2$O/K$_2$O; b, S/K$_2$O; c, Cl/K$_2$O) with respect to increasing K$_2$O. High volatile/K$_2$O
1214　corresponds to high volatile concentration as well as low K$_2$O.

1215

1216　**Fig. 5** (a) Variations in S and total FeO concentrations of melt inclusions and groundmass
1217　glasses. Symbols are the same as Fig. 3. Melt inclusions hosted in olivine show abrupt
1218　decrease in S content, and the change lacks correlation with FeO. (b) Measured S
1219　concentration in olivine-hosted melt inclusions as a function of sulfur concentration at
1220　sulfide saturation (SCSS). In this figure, the samples at the saturation can be seen on the
1221　solid grey line (1:1 line). The dashed line shows the SCSS corrected for abundance of S^{2-},
1222　which was 0.85, the maximum value. All data plots below the corrected SCSS. SCSS is
1223　calculated according to Fortin *et al.* (2015) using the trapping temperature (T$_{trap}$) of the
1224　melt inclusion (Table S1) at 0.05 GPa (for NKD14) and 0.1 GPa (for KKO, OJSU, OJSL,
1225　and KSS) based on estimated volatile saturation pressure of the pre-eruptive magma
1226　reservoir. For melt inclusions without measured H$_2$O concentration, we attributed average
1227　H$_2$O concentrations (by SIMS) of NKD14 and KSS.

1228

1229　**Fig. 6** Variations in Cl and F concentrations of melt inclusions (KSS and NKD14) plotted
1230　in decadic log scale. The KSS and NKD14 data are compared with the volatile rich mafic
1231　primitive magma, represented by a large blue diamond. The two areas are indicated to
1232　show the Cl and F concentrations in primitive arc basalt and MORB, which were
1233　measured in olivine-hosted melt inclusions (taken from Van den Bleeken and Koga 2015).
1234　MORB melt inclusions were plotted as solid light-grey circles (Saal *et al.* 2002; Wanless
1235　and Shaw 2012; Wanless *et al.* 2014, 2015; Le Voyer *et al.* 2017; Shimizu *et al.* 2019)
1236　including Cl-rich data of assimilated MORB samples by seawater derived component.
1237　Melt inclusions from Iwate volcanoes, one of low F concentration arc lava from Japan
1238　arc, is shown as an example of a cold subduction zone (red plus sign, Rose-Koga *et al.*
1239　2014). The lines show the constant Cl/F values, and the values are indicated above the
1240　line.

1241

1242　**Fig. 7** Pre-eruptive temperatures and water concentrations calculated from the
1243　compositions of plagioclase rim and groundmass glass. The squares represent the
1244　estimated range of temperature and H$_2$O concentration. The calculation was based on a
1245　combination of a plagioclase-olivine-liquid hygrometer (Lange *et al.* 2009) and olivine-
1246　saturated liquid geothermometer (Sugawara 2000; Médard and Grove 2008) according to
1247　Sakuyama *et al.* (2014), assuming the crustal conditions (0.1 – 0.5 GPa). Standard
1248　deviations (1σ) of the difference in temperature and H$_2$O concentration between
1249　estimation and expectations using this method were 23 ˚C and 0.6 wt. %, respectively.
1250　The dashed lines represent water saturation isobars for groundmass glass composition of
1251　KSS calculated according to Moore *et al.* (1998); the corresponding pressures (kbar) and
1252　the depths (km) are indicated to the left of the line. The depth in the crust was calculated
1253　assuming a density of 2400 kg/m^3 for less than 1 km depth and a density of 2700 kg/m^3

1254 for depth greater than 1 km (Komazawa 1995). The red and blue colors show the range
1255 of the magma storage depths: red, C1 from 3 to 9 km depth, and blue, C2 from 1 to 3 km
1256 depth beneath Nakadake's first crater (Sudo and Kong 2001; Sudo *et al.* 2006; Hata *et al.*
1257 2016).

1258

1259 **Fig. 8** Evolution of H_2O/S, CO_2/S, and Cl/S molar ratios of magmatic gases in equilibrium
1260 with the primitive basaltic melt plotted against pressure. Horizontal dotted lines indicate
1261 measured gas compositions of $H_2O/S = 22.5$, $CO_2/S = 6$, and $Cl/S = 0.07$ (S as total sulfur)
1262 with the variation observed with propagated measurement uncertainties shown by shaded
1263 regions. The values correspond to high-pressure gas component A reported in previous
1264 studies (Shinohara 2013; Shinohara *et al.* 2018). SO_2 and H_2S components were added to
1265 calculate the total S. Horizontal colored bars at the top of the panel show pressure ranges
1266 corresponding to the C1, C2, and LVL. To evaluate the evolution of the gas composition
1267 of the basaltic magma from a great depth, we modelled the equilibrium compositions of
1268 gas and magma for a closed system magma ascent using SolEx (Witham *et al.* 2012).
1269 Grey field indicates the pressure range of $2.3 - 2.9$ kbars, at which conditions the modeled
1270 gas compositions (solid and dashed curves) intersect with measured gas ratios. Thus, the
1271 observed gas composition potentially originated at these depths. We chose the primitive
1272 magma composition (discussed in the text) with values of FMQ+1.4 and 1090 ˚C based
1273 on the individual melt analyses. We tested initial CO_2 contents of 400, 750 and 1000 ppm
1274 for the calculation, as the CO_2 concentration was unknown to us. In combination with
1275 H_2O/S and Cl/S, the initial CO_2 concentration from 400 to 750 ppm produced the gas
1276 composition evolution curves that agree at a similar depth.

1277

1278 **Fig. 9** Observed volcanic gas compositions emitted from Aso volcano compared with
1279 modelled variation in CO_2/SO_2 and H_2O/CO_2 molar ratios. Observed gas compositions
1280 are those during quiescent periods (fumarole and lake gases) and during eruptive periods
1281 (Shinohara *et al.* 2018). Some data points were reported as poor quality observations due
1282 to atmospheric H_2O, and they are plotted as smaller symbols. Solid curve is a modeled
1283 gas composition of closed-system ascent of primitive magma with 800 ppm initial CO_2
1284 concentration, which is the same as that used in Fig. 8. The gas compositions on the curve
1285 indicate the different depths of gas segregation, and thus, the variation among
1286 observations can be attributed to a variation in segregation depths. Dashed curve shows a
1287 mixing curve between a CO_2-rich gas in equilibrium with the deep primitive magma at
1288 2.6 kbar (crossed circle) and a gas discharged from NKD14 magma at shallow depth
1289 (asterisk) representing the gas stored at the shallow reservoir. The shallow gas component
1290 was calculated from the difference in volatile concentrations between pre-eruptive melt
1291 and groundmass glass.

1292

1293 **Fig. 10** Schematic summary of the magma and gas evolution in the Aso plumbing system.
1294 Magma passage is indicated by the color ranging red-orange-yellow. The gas is white,

1295 and the grey zone corresponds to the conductivity anomaly (Hata *et al.* 2016). C1, C2,
1296 and LVL (black thick bars) are the zones of magma stagnations determined by
1297 geophysical methods.

Aso volcano

4 km

Scoria / pumice
Ash
Black andisol

A9418
(sampling site)

Komezuka

Kamikomezuka

Ojodake

Kishimadake

Nakadake crater
(sampling site)

(m)

Eruptive
stage

Stratigraphic
log

0

N1

N2

N3

N4

N5

N6

N7

N8

N9

N10

5

10

- NKD14
(KKO)
- OJSU

- OJSL

- KSS

a

Mineral
△ Clinopyroxene
◇ Olivine
○ Orthopyroxene
□ Plagioclase

SampleID
◆ KKO
◆ KSS
◆ NKD14
◆ OJSL
◆ OJSU

b

SCSS ($S^{6+}/S_{total} = 0.85$)

S : SCSS = 1 : 1