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2 **Origin of volatiles emitted by Plinian mafic eruptions of the Chikurachki volcano, Kurile**
3 **arc, Russia: trace element, boron and sulphur isotope constraints**

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27

28 **Abstract** – Chikurachki is a 1816-m high stratovolcano on Paramushir Island, Kurile arc,
29 Russia, which has repeatedly produced highly explosive eruptions of mafic composition. The
30 present work is aimed at constraining the origin of volatile components (CO₂, H₂O, F, S, and Cl),
31 along with B and S isotopic compositions in a series of phenocryst-hosted melt inclusions and
32 groundmass glasses from basaltic andesite pyroclasts of the 1853, 1986, and prehistoric Plinian
33 eruptions of the volcano. The ranges of volatile concentrations in melt inclusions (47–1580 µg/g
34 CO₂, 0.4–4.2 wt.% H₂O, 399–633 µg/g F, 619–3402 µg/g S and 805–1240 µg/g Cl) imply a
35 sudden pressure release from ~460 through ~35 MPa that corresponds to ~1.2–16-km-depth
36 range of magma ascent upon decompression. We conclude that rapid ascent of the volatile-rich
37 basaltic magmas from ~16-km initial depth accompanied by near-surface bubble nucleation and
38 growth, and subsequent magma fragmentation appear to be a primary reason for the Plinian
39 character of the Chikurachki eruptions. Significant negative correlations of S with K, Zr, Nb, Ba,
40 La, Ce, Pr ($R = -0.8$ to -0.9), no clear relationships of S with H₂O, CO₂ and Cl, but strong
41 positive correlations of S/K₂O with H₂O/K₂O, Cl/K₂O and F/K₂O preclude magma degassing to
42 be the only process affecting volatile concentrations dissolved in the melt. The $\delta^{34}\text{S}$ values of the
43 studied inclusion and groundmass glasses range from -1.6 to $+12.3\%$, decrease with decreasing
44 S, show significant positive correlations with H₂O/K₂O, Cl/K₂O and F/Zr, and negative
45 correlations with a number of incompatible trace elements. Neither open- nor close-system
46 magma degassing can account for the observed range of $\delta^{34}\text{S}$. The $\delta^{11}\text{B}$ values of the melt
47 inclusions range from -7.0 to $+2.4\%$ with 13–23 µg/g B. The relationships of $\delta^{11}\text{B}$ with B/K₂O
48 and B/Nb are inconsistent with magma contamination at shallow crustal depths. Linear character
49 of 1/S vs. $\delta^{34}\text{S}$ relationship suggests two-component mixing. The possible mixing end-members
50 could be the magmas having similar major and trace element compositions, but strongly
51 contrasting volatile contents and S isotopes. Based on the behaviour of fluid-mobile vs. fluid-
52 immobile incompatible trace elements, we conclude that the subduction component likely

53 represents a mixture of subduction sediment-derived melt with up to 60% of slab-derived fluid.
54 Admixture of ~1–8% of the inferred subduction component to the depleted mantle wedge source
55 is required to account for the compositional range of the Chikurachki melt inclusions, and
56 ~0.4–10% to account for the composition of Kurile arc mafic magmas.

57

58 **Keywords**

59 Plinian mafic eruptions, Chikurachki volcano, Melt inclusions, Magmatic volatiles, Stable
60 isotopes, Ion microprobe

61

62 **Research Highlights**

- 63 • Origin of volatiles that caused Plinian basaltic eruptions of Chikurachki was studied.
- 64 • Degassing cannot account for the observed ~14‰ range of $\delta^{34}\text{S}$ in melt inclusions.
- 65 • Behaviour of volatiles and $\delta^{11}\text{B}$ in inclusion glasses precludes crustal contamination.
- 66 • Volatiles and $\delta^{34}\text{S}$ of the glasses were mainly controlled by two-component mixing.
- 67 • The subduction component was a 4:6-mixture of slab-derived melt and fluid.

68

69

70 **1. Introduction**

71 Strongly explosive (Plinian) eruptions are characterised by high eruption rates, high
72 eruption columns and widely dispersed fallout deposits, representing an efficient mechanism to
73 transport volatiles from the Earth's interior to the upper atmosphere (Walker, 1973, 1980;
74 Fischer and Schmincke, 1984; Wilson and Walker, 1987; Francis, 1993). Injection of water,
75 halogens and sulphur into the atmosphere leads to the formation of solid and liquid aerosols,
76 which may significantly affect global climate and the stability of the ozone layer (Brasseur and
77 Granier, 1992). Plinian eruptions are mainly associated with water-rich intermediate and silicic
78 magmas (andesite through dacite), whereas highly explosive eruptions of mafic composition
79 (i.e., resembling basalt or basaltic andesite) are less common. Examples of Plinian mafic
80 eruptions occur at Klyuchevskoy, Tolbachik, Chikurachki and Tyatya in the Kamchatka and
81 Kurile arcs, Russia (Fedotov and Markhinin, 1983; Ovsyannikov and Muravyev, 1992; Belousov
82 et al., 2003, 2015, 2017; Hasegawa et al., 2011), Masaya and Cerro Negro, Nicaragua (Williams,
83 1983; Roggensack et al., 1997), Arenal, Costa Rica (Soto and Alvarado, 2006; Szramek et al.,
84 2006), Llaima, Chile (Ruth et al., 2016), Sumisu Rift, Japan (Gill et al., 1990), Ambrym,
85 Vanuatu (Robin et al., 1993), Tofua, Tonga (Caulfield et al., 2011), Taupo and Tarawera, New
86 Zealand (Walker, 1980; Walker et al., 1994), Shishaldin, Alaska (Szramek et al., 2010) and Etna,
87 Italy (Houghton et al., 2004; Sable et al., 2006). The lack of clear relationships between eruption
88 rate and style often associating with rapid change of eruptive behaviour of a volcano suggest that
89 many different parameters such as conduit geometry, magma viscosity, changing conditions of
90 magma ascent and fragmentation, and even the dynamics of syn-eruptive microlite growth may
91 strongly affect the eruption figure (e.g., Fischer and Schmincke, 1984; Carey and Sparks, 1986;
92 Houghton et al., 2004; Szramek et al., 2006, 2010; Houghton and Gonnermann, 2008).

93 The present work is a follow-up study to Gurenko et al. (2005a) and focuses on the
94 detailed investigation of the behaviour of volatile components (CO₂, H₂O, F, S, and Cl) along
95 with boron and sulphur isotopic compositions of the previously analysed olivine-,

96 orthopyroxene- and plagioclase-hosted melt inclusions and groundmass glasses erupted by the
97 Chikurachki volcano. Volatile-rich slab-derived melts and fluids play a central role in the origin
98 of arc magmatism by lowering the solidus of a peridotite mantle wedge and triggering partial
99 melting (e.g., [Gill, 1981](#); [McCulloch and Gamble, 1991](#); [Hawkesworth et al., 1993](#); [Pearce and](#)
100 [Peate, 1995](#)). Being a major inventory and a transport media of volatile components from
101 descending plate to the overlying mantle, these melts and fluids (along with the factors listed
102 above) may also have a link to the eruption style of volcanoes occurring in the subduction zone
103 (SZ) setting. Here we explore the role of two concurrent processes, namely, subduction-related
104 volatile flux versus possible gain of volatile components due to shallow crustal contamination of
105 magma, also in relation of their possible contribution to the enrichment/depletion of the magma
106 by sulphur and boron isotopes. Our new data provide additional constraints on the origin of
107 volatile components in the mafic magmas erupted by the Chikurachki volcano during Plinian
108 prehistoric and recent, 1853 and 1986 eruptions.

109 Another key problem in understanding the origin of arc magmas is the uncertainty in the
110 provenance of volatile components. For example, Cl and H₂O are thought to be primarily
111 (>95%) from the subducting slab (e.g., [Straub and Layne, 2003](#)), whereas S and F can originate
112 from metasomatically enriched subarc mantle or come directly from the slab (e.g., [Alt et al.,](#)
113 [1993](#); [Metrich et al., 1999](#); [Straub and Layne, 2003](#); [Churikova et al., 2007](#); [Selvaraja et al.,](#)
114 [2017](#)). Moreover, with increasing of subduction depth, the slab becomes progressively depleted
115 in H₂O and Cl, and to a lesser extent in S and F, implying efficient fractionation of H₂O and Cl
116 from S and F (e.g., [Chaussidon et al., 1987](#); [Metrich et al., 1999](#); [Straub and Layne, 2003](#)).
117 Understanding the origin of volatiles that triggers the Plinian eruption of Chikurachki may also
118 contribute to our understanding of fluid dynamics and mass transport in SZ settings, as well as
119 help in elucidating the relative contributions of different subduction components to the
120 generation of arc magmas.

121

122 2. Geological setting and samples

123 Chikurachki (50°19'24"N 155°27'39"E, 1816 m.a.s.l) is an active stratovolcano on Paramushir
124 Island, the northern Kuriles (**Fig. 1**). The volcanism of Chikurachki results from westward
125 subduction of the Pacific plate under the Okhotsk plate. The Late Holocene stratocone of the
126 volcano is built on a thick sequence of Pleistocene lava flows ([Gorshkov, 1967](#)). The recorded
127 activity on Chikurachki started around 7500 BC. According to the Kamchatka Volcanic Eruption
128 Response Team (KVERT), the most recent eruptions of 1958, 1961, 1964, 1973, 2002, 2003,
129 2004, 2005, 2007, 2008 were predominately of strombolian (mildly explosive), but recent
130 Plinian (highly explosive) eruptions occurred in 1853, 1986 (**Fig. 2**), and the last one in 2015.

131

132 2.2. Samples studied

133 This study is based on the analyses of glassy lapilli with porphyritic texture, which came
134 from the 1853 (sample CHK3/4), 1986 (sample CHK16) and two prehistoric (samples CHK13/1
135 and 13/2) tephra fallouts, resulting from documented, highly explosive eruptions of Chikurachki
136 ([Ovsyannikov and Muravyev, 1992](#); [Belousov et al., 2003](#)). We studied primary melt inclusions
137 hosted by olivine, orthopyroxene and plagioclase phenocrysts, most of which were naturally
138 quenched to glass. Chemical compositions of the studied inclusions and groundmass glasses
139 (major and trace element, and H₂O, S and Cl concentrations) were reported by [Gurenko et al.](#)
140 ([2005a](#)). Briefly, the erupted melts range from low- to medium-K tholeiitic basalts and andesites,
141 which are typical for Kurile lavas (**Fig. S2.1 – Supporting online material**). Variation diagrams
142 of FeO, CaO and K₂O vs. SiO₂ show that glass compositions follow simple trends of magma
143 fractionation (Fig. 5 in [Gurenko et al., 2005a](#)). The phenocrysts are dominated by euhedral,
144 elongated, twinned individual crystals of plagioclase (Pl, ~0.2–3.0 mm, 70–90 vol.%, An_{74–95})
145 that may also form glomerocrysts. Phenocrysts of subhedral to rounded olivine (Ol, Fo_{72–78}) and
146 orthopyroxene (Opx, *mg*-number = 72–75), both of 0.2–0.5 mm size, and euhedral to resorbed

147 clinopyroxene (Cpx, 0.3–1.0 mm, *mg*-number = 71–77) are present in subordinate amounts. The
148 groundmass is strongly vesiculated (20–30 vol.% vesicles) and consists of variable proportions
149 of rounded olivine, prismatic augite and isometric Fe-Ti oxide crystals mixed with needle-like
150 plagioclase microlites (up to 200 μ m).

151 The studied inclusion and groundmass glasses are slightly enriched in light rare earth
152 elements (LREE) relative to heavy rare earth elements (HREE); e.g., $[\text{La}/\text{Sm}]_n = 1.8\text{--}2.4$, where
153 the subscript n denotes the respective element concentrations normalised to those of N-MORB
154 taken from Hofmann (1988) (Fig. 3, Table S2.1 – Supporting online material). The glasses also
155 show significant depletions in high-field-strength elements (HFSE) relative to LREE but nearly
156 equal concentrations of HFSE relative to HREE normalised to N-MORB (e.g., $[\text{Nb}/\text{La}]_n =$
157 $0.19\text{--}0.29$, $[\text{Zr}/\text{Sm}]_n = 0.52\text{--}0.76$, $[\text{Y}/\text{Yb}]_n = 0.86\text{--}1.24$), and enrichments in Th and large-ion
158 lithophile elements (LILE) relative to Nb (e.g., $[\text{Ba}/\text{Nb}]_n = 41\text{--}69$, $[\text{Th}/\text{Nb}]_n = 7\text{--}30$, $[\text{K}/\text{Nb}]_n =$
159 $15\text{--}25$ and $[\text{Sr}/\text{Sm}]_n = 2.9\text{--}6.9$). The inclusions, and to lesser extent the groundmass glasses are
160 characterised by relatively high contents of volatile components (the concentrations of B, H₂O,
161 Cl and F shown in Fig. 3 are discussed in section 4.1), displaying positive anomalies in the
162 multi-element diagram relative to respective trace elements of similar incompatibility (e.g.,
163 $[\text{Cl}/\text{Nb}]_n = 21\text{--}54$, $[\text{B}/\text{K}]_n = 2.3\text{--}5.4$, $[\text{H}_2\text{O}/\text{Ce}]_n = 4.9\text{--}23$, $[\text{F}/\text{Nd}]_n = 2.2\text{--}3.2$, $[\text{F}/\text{Zr}]_n = 3.9\text{--}7.8$).
164 These values are generally in, or slightly exceeding, the range of volatile concentrations reported
165 for the Kurile island arc basalts and basaltic andesites (MgO >2.5 wt.%) by Bailey et al.
166 (1987a,b), Ishikawa and Tera (1997), Ikeda (1998), Ikeda et al. (2000), Takagi et al. (1999),
167 Ishikawa et al. (2001) (Fig. 3).

168

169 3. Analytical methods

170 Ion microprobe analyses were obtained with a CAMECA IMS 1280 ion microprobe at
171 the Northeast National Ion Microprobe Facility (Woods Hole Oceanographic Institution, Woods

172 Hole, USA) (for detailed description of the employed analytical protocols, see *Supporting online*
173 *material*).

174

175 **4. Results**

176 *4.1. Volatile concentrations*

177 The concentrations of CO₂, H₂O, F, S, and Cl in naturally quenched, glassy inclusions
178 hosted in Ol, Opx and Pl are listed in **Table S2.1** (*Supporting online material*), along with H₂O,
179 S and Cl reported by [Gurenko et al. \(2005a\)](#). The inclusions have a wide range of volatile
180 concentrations (39–653 µg/g CO₂, 0.4–4.2 wt.% H₂O, 428–638 µg/g F, 676–3450 µg/g S, and
181 805–1243 µg/g Cl) that corresponds to the volatile contents previously reported by [Gurenko et](#)
182 [al. \(2005a\)](#). Correction for post-entrapment crystallisation (PEC) of host mineral (up to 7.8 wt.%
183 Ol, 0.8 wt.% Opx, and no correction for Pl) results in the following ranges: 39–626 µg/g CO₂,
184 0.4–4.2 wt.% H₂O, 412–634 µg/g F, 639–3408 µg/g S, 805–1241 µg/g Cl, which appeared to be
185 nearly the same (given the maintained analytical uncertainty) as the uncorrected volatile
186 concentrations. This observation implies that the eruption and quenching of magma occurred
187 shortly after the inclusions have been entrapped by growing phenocrysts. Thus, the
188 concentrations of H₂O and CO₂ measured in the studied melt inclusions reflect the last vapour-
189 melt equilibrium in the magmatic system upon the eruption, returning a minimum pressure of
190 magma fractionation. According to the *VolatileCalc* solution model ([Newman and Lowenstern,](#)
191 [2002](#)), they correspond to H₂O-CO₂ gas pressure of 33 to 276 MPa or to the range of depth from
192 ~1 to ~9.5 km, assuming average and constant density of ~2900 kg/m³ of the upper crust (**Fig.**
193 **4A**).

194 Several recent studies ([Esposito et al., 2011](#); [Steele-Macinnis et al., 2011](#); [Hartley et al.,](#)
195 [2014](#); [Moore et al., 2015](#); [Wallace et al., 2015](#); [Mironov et al., 2015](#); [Aster et al., 2016](#)) have
196 demonstrated that 40 to 90% of the original CO₂ dissolved in the melt at the time of inclusion

197 entrapment can be lost to a shrinkage bubble during post-entrapment cooling. A correction
198 algorithm described by Wallace et al. (2015) was therefore used to reconstruct the original CO₂
199 and H₂O concentrations in the entrapped melts (see *Supporting online material*). These
200 calculations revealed that ~5 to 69% of the original CO₂ and 0.1 to 3.2% of the original H₂O
201 could have been lost to the shrinkage bubble, in agreement with the results of the above studies.
202 The following ranges of volatile concentrations were obtained after the correction: 47–1580 µg/g
203 CO₂, 0.4–4.2 wt.% H₂O, 399–633 µg/g F, 619–3402 µg/g S and 805–1240 µg/g Cl (**Table S2.1**
204 – *Supporting online material*). According to the *VolatileCalc* solution model (Newman and
205 Lowenstern, 2002), the corrected results correspond to the H₂O-CO₂ gas pressures between 35
206 and 456 MPa or to ~ 1.2–15.7-km-range of crustal depth (**Fig. 4B**).

207 The concentrations of S in melt inclusions are shown in comparison with mid-ocean ridge
208 basalts (MORB) and ocean island basalts (OIB) (**Fig. 5A**). Many of the Chirurachki glass
209 inclusions have similar or higher S concentrations than those of MORB or OIB, whereas all
210 groundmass glasses are depleted in S (<350 µg/g), consistent with sulphur loss presumably by
211 degassing. However, sulphur in the inclusion glasses shows significant negative correlations with
212 a number of trace and rare earth incompatible elements, such as K (–0.81), Ti (–0.59), Y (–0.61),
213 Zr (–0.82), Nb(–0.71), Ba (–0.83), La (–0.79), Ce (–0.88), Pr (–0.77), Nd (–0.71), Sm (–0.68),
214 Gd (–0.56), Dy (–0.73), Ho (–0.53), Er (–0.73), Yb (–0.66), Lu (–0.71), Th (–0.66), where the
215 respective correlation coefficient (*R*) values are given in brackets and *N* = 21, if not specified
216 (**Fig. 5B** and **Table S2.1** – *Supporting online material*). All these correlations are significant at
217 95% confidence level (for *N* = 18 and 21, a number of points in the correlations, a critical value
218 of the Pearson correlation coefficient at the 0.05-level of significance for a two-tailed test is 0.47
219 and 0.43, respectively). There are no significant correlations of S with H₂O, Cl and F. We
220 observe, however, strong positive correlation between these elements, if their concentrations are
221 normalised to K₂O (or any other melt- and fluid-immobile incompatible element) that minimises

222 possible effects of partial melting and/or magma fractionation (e.g., $R = 0.83$ for S/K₂O vs.
223 H₂O/K₂O correlation, **Fig. 5C**, $R = 0.80$ for S/K₂O vs. Cl/K₂O, **Fig. S2.1A** – *Supporting online*
224 *material*, $R = 0.85$ for S/K₂O vs. F/K₂O, **Fig. 5D**, and $R = 0.88$ for Cl/K₂O vs. H₂O/K₂O, **Fig.**
225 **5E**). Chlorine does not correlate with incompatible trace elements, except for Sr ($R = -0.56$; **Fig.**
226 **S2.1B** – *Supporting online material*), shows a significant correlation with fluorine ($R = 0.70$;
227 **Fig. S2.1C** – *Supporting online material*), which becomes much stronger, if we consider F/Zr vs.
228 Cl/Nb ratios ($R = 0.88$; **Fig. 5F**).

229

230 4.2. Sulphur isotopes

231 Sulphur isotopic compositions of the studied melt inclusions and one groundmass glass
232 are given in **Table S2.1** (*Supporting online material*) and presented in **Fig. 6**. The $\delta^{34}\text{S}$ values are
233 given in permil units (‰) relative V-CDT (the Vienna Canyon Diabolo Troilite, $^{34}\text{S}/^{32}\text{S} =$
234 0.0441626 ± 0.0000039 ; [Ding et al., 2001](#)). The $\delta^{34}\text{S}$ values of the inclusion glasses range from
235 -1.6 to $+12.3\%$, and decrease with decreasing S concentrations ($R = 0.85$; **Fig. 6A**). The S vs.
236 $\delta^{34}\text{S}$ relationship has a hyperbolic shape and is transformable into a strait line in the $1/\text{S}-\delta^{34}\text{S}$
237 space ($R = -0.84$; **Fig. 6B**), pointing towards two-component mixing scenario ([Langmuir et al.,](#)
238 [1978](#)), though the effect of magma degassing cannot be completely excluded (see further
239 discussion). The sample 13/1 matrix glass has $\delta^{34}\text{S} = +0.39 \pm 0.43\%$, 1 SE, contains very low S
240 concentration (107 $\mu\text{g/g}$ S) and strongly deviates from the linear array defined by melt inclusions
241 (**Fig. 6B**), being in contrast strongly degassed. Also, the $\delta^{34}\text{S}$ values show significant positive
242 correlations with H₂O (0.54), CO₂ (0.55) and Sr (0.5), as well as negative correlations with light
243 lithophile elements Li (-0.53 , $N = 10$), Be (-0.73 , $N = 10$) and B (-0.6), and other incompatible
244 elements, such as K (-0.8), Zr (-0.71), Nb (-0.64), Ba (-0.75), La (-0.69), Ce (-0.72), Pr
245 (-0.57), Sm (-0.63), Gd (-0.76), Dy (-0.71), Tb (-0.49), Er (-0.8), Lu (-0.79), Th (-0.53),
246 where the respective correlation coefficient (R) values are given in brackets and $N = 17$, if not

247 specified, and the critical value of the Pearson correlation coefficient is 0.48. The significance of
248 the correlations of $\delta^{34}\text{S}$ with volatile components becomes higher, if volatile concentrations are
249 normalised to incompatible elements as, for instance, $\text{H}_2\text{O}/\text{K}_2\text{O}$ (0.79), $\text{Cl}/\text{K}_2\text{O}$ (0.83) (**Fig.**
250 **6B,C**), F/Zr (0.84, **Fig. S2.1D** – *Supporting online material*).

251

252 4.3. Boron concentrations and B isotopic composition

253 The concentrations of boron (12.5–22.9 $\mu\text{g}/\text{g}$ measured, and 12.5–21.7 $\mu\text{g}/\text{g}$ corrected for
254 PEC) are similar to those previously reported by [Gurenko et al. \(2005a\)](#) (16.1–18.7 $\mu\text{g}/\text{g}$ B)
255 (**Table S2.1** – *Supporting online material*). The B/K ratios ranging from 0.0025 to 0.0057 are
256 systematically higher than those of primitive N-MORB (B/K of ~ 0.001) and OIB (B/K of
257 ~ 0.0003) ([Ryan and Langmuir, 1993](#); [Chaussidon and Jambon, 1994](#); [Gurenko and Chaussidon,](#)
258 [1997](#)) but are in the midrange of B concentrations reported for Kurile arc magmas with $\text{SiO}_2 < 60$
259 wt.% (4.5–36.6 $\mu\text{g}/\text{g}$ B; [Ryan et al., 1995](#); [Ishikawa and Tera, 1997](#)). Very similar concentrations
260 of B in the Chikurachki lavas (14.4–15.5 $\mu\text{g}/\text{g}$) were found, in particular, by [Ishikawa and Tera](#)
261 [\(1997\)](#), who also noted a clear across-arc variation of B/Nb ratios (and $\delta^{11}\text{B}$, as well). At the slab
262 depth of ~ 140 km corresponding to that of the Chikurachki volcano (e.g., [Tatsumi et al., 1994](#);
263 [Ishikawa and Tera, 1997](#); [Ishikawa et al., 2001](#) and references therein), the B/Nb ratios in the
264 Kurile lavas vary from ~ 6 to 18 ([Ishikawa and Tera, 1997](#)), and the present B/Nb range obtained
265 for the studied melt inclusions (from ~ 9 to ~ 22) is in agreement with these data.

266 The $\delta^{11}\text{B}$ values of the studied naturally quenched olivine-hosted melt inclusions range
267 from -7.0 to $+2.4\text{‰}$, calculated relative to NBS 951 standard with $^{11}\text{B}/^{10}\text{B} = 4.04558 \pm 0.00033$
268 ([Spivack and Edmond, 1986](#)) (**Table S2.1** – *Supporting online material*). The range is similar but
269 extends to more negative values than those of the Kurile arc lavas (from -3.8 to $+5.9\text{‰}$;
270 [Ishikawa and Tera, 1997](#)), being however within a broad interval of $\delta^{11}\text{B}$ -values of arc magmas
271 worldwide, from -21.3‰ (e.g., Mt. Shasta; [Rose et al., 2001](#)) to $+12\text{‰}$ (e.g., Izu arc; [Straub and](#)

272 Layne, 2002). In contrast to S isotopes, $\delta^{11}\text{B}$ values show neither a correlation with the
273 concentrations of B or 1/B values nor with major and incompatible trace elements. Similarly, a
274 wide $\delta^{11}\text{B}$ range of $\sim 20\text{‰}$ (from -21.3 to -1.1‰ at relatively narrow range of boron
275 concentrations ($0.67\text{--}1.64 \mu\text{g/g B}$) showing no clear correlation between each other was
276 described in the Mt. Shasta basaltic andesite rocks (Rose et al., 2001).

277

278 5. Discussion

279 5.1. $\text{H}_2\text{O}\text{-Cl}\text{-B}$ and $\delta^{11}\text{B}$ relationships and the magma contamination scenario

280 Assimilation of crustal rocks is a common process that can significantly modify pristine
281 chemical and isotopic compositions of parental arc magmas (e.g., Davidson, 1987; Thirlwall et
282 al., 1996; Hickey et al., 1986; Turner et al., 1997; Macpherson and Matthey, 1998; Vroon et al.,
283 2001; Bindeman et al., 2004; Walowski et al., 2016). Excess of halogens in mafic magmas, and
284 especially coherent variation of H_2O and Cl was shown to be a good proxy to assess the role of
285 assimilation of oceanic crust and/or addition of NaCl-rich brines or fluids during magma
286 fractionation (e.g., Anderson, 1974; Michael and Schilling, 1989; Jambon et al., 1995; Michael
287 and Cornell, 1998; Kent et al., 1999; Lassiter et al., 2002; Simons et al., 2002; le Roux et al.,
288 2006; Shimizu et al., 2009; Gurenko and Kamenetsky, 2011; Kendrick et al., 2013, Cabral et al.,
289 2014). However, as noted by le Roux et al. (2006), this approach is based on the assumption that
290 the concentration of K_2O in the magma remains unaffected by later processes. These authors
291 recommend using Cl/Nb and $\text{H}_2\text{O}/\text{Ce}$ ratios because Nb and Ce have similar incompatible
292 behaviour to Cl and H_2O , respectively, but are less affected by alteration, as compared to K.

293 In our case, a positive correlation of $\text{H}_2\text{O}/\text{K}_2\text{O}$ with Cl/ K_2O in the Chikurachki melt
294 inclusions (Fig. 5E) can be interpreted in favour of magma contamination. However, strong
295 positive correlations between $\text{H}_2\text{O}/\text{K}_2\text{O}$ and $\text{H}_2\text{O}/\text{Ce}$ ($R = 0.97$, not shown) and between Cl/ K_2O
296 and Cl/Nb ($R = 0.88$, not shown) suggest that K, Nb and Ce appear to behave coherently during

297 magma fractionation. Furthermore, the concentrations of K are unlikely to have been
298 compromised and could be equally used for normalisation. The results of concurrent modelling
299 of magma contamination using different compositions of probable crustal contaminants are
300 shown in **Fig. 7** and **8**. In the modelling, we use the same element concentrations and $\delta^{11}\text{B}$ values
301 of seawater (SW), 15%- and 50%-NaCl brine (15%-NaCl and 50%-NaCl, respectively), and
302 altered oceanic crust (AOC) mixing end-members, as in [Gurenko and Kamenetsky \(2011\)](#)
303 (**Table 1**). Given the narrow range of incompatible element concentrations in the studied melt
304 inclusions (**Fig. 3**), the concentrations of K_2O (0.804 wt.%), Nb (1.28 $\mu\text{g/g}$) and Ce (15.37 $\mu\text{g/g}$)
305 of a presumably “uncontaminated” arc magma (UAM) were defined as average of all melt
306 inclusions from **Table S2.1 – Supporting online material** (using PEC-corrected concentrations).
307 The boron content and B isotopic composition of UAM (0.9 $\mu\text{g/g}$ B, $\delta^{11}\text{B} = -3.7\text{‰}$)
308 corresponding to back-arc basin basalts presumably unaffected by later shallow-crustal
309 contamination were taken from [Chaussidon and Marty \(1995\)](#). The concentrations of H_2O and Cl
310 in UAM were calculated using those of the neighbouring elements of similar incompatibility but
311 showing no anomalies in the multi-element diagram (**Fig. 3**) to be in the lower left corner of the
312 respective panels in **Fig. 7**, thereby matching the lower end of the trends defined by the inclusion
313 compositions: $[\text{H}_2\text{O}]_n = ([\text{Ce}]_n \times [\text{Pr}]_n)^{0.5}$, equal to 0.256 wt.% H_2O , and $[\text{Cl}]_n = ([\text{Nb}]_n \times [\text{K}]_n)^{0.5}$,
314 equal to 128.5 $\mu\text{g/g}$ Cl. The chemical and isotopic compositions of seawater (SW) is relatively
315 uniform and well constrained, whereas the composition of seawater-derived NaCl-brines can be
316 calculated from that of SW (**Table 1**). In contrast, the composition of altered oceanic crust
317 (AOC) is variable. In particular, AOC from [Gurenko and Kamenetsky \(2011\)](#) is significantly
318 more H_2O -, Cl- and K_2O -rich than that used for similar calculations by [le Roux et al. \(2006\)](#). In
319 order to account for possibly wider ranges of H_2O , Cl, Nb and Ce, we considered two
320 compositions of AOC: AOC1 from [Gurenko and Kamenetsky \(2011\)](#) and AOC2 from [le Roux et](#)
321 [al. \(2006\)](#) (**Table 1**). Finally, we assigned a composition of siliceous marine sediment (SED),

322 which is considered as one possible, if not a single contamination component to account for the
323 negative $\delta^{11}\text{B}$ melt inclusion values, with 10.1 wt.% H_2O , 1.7 wt.% K_2O , 7.67 $\mu\text{g/g}$ Nb, 50.11
324 $\mu\text{g/g}$ Ce. The concentrations of H_2O , K_2O , Nb and Ca used in calculations are those of the
325 average sediment column of the Kurile trench from [Plank and Langmuir \(1998\)](#), and 1000 $\mu\text{g/g}$
326 Cl, 120 $\mu\text{g/g}$ B, and $\delta^{11}\text{B} = -10\text{‰}$ were taken from [Gurenko and Kamenetsky \(2011\)](#), given that
327 siliceous terrigenous sediments may be as low as -15‰ of $\delta^{11}\text{B}$ ([Leeman and Sisson, 1996](#)).

328 As noted by [Gurenko and Kamenetsky \(2011\)](#), it is not possible to unequivocally prove
329 magma contamination only on the basis of $\text{H}_2\text{O}/\text{K}_2\text{O}$ vs. $\text{Cl}/\text{K}_2\text{O}$ relationships (or using Cl- and
330 H_2O -to-incompatible-element normalised ratios). Similarly, if we consider solely the $\text{H}_2\text{O}/\text{K}_2\text{O}$
331 vs. $\text{Cl}/\text{K}_2\text{O}$ or $\text{H}_2\text{O}/\text{K}_2\text{O}$ -B/ K_2O variations in melt inclusions (equally, $\text{H}_2\text{O}/\text{Ce}$ vs. Cl/Nb or
332 $\text{H}_2\text{O}/\text{Ce}$ vs. B/Nb), they can be explained by contamination of magma by seawater or NaCl-rich
333 brines (**Fig. 7**). On the other hand, if in addition to H_2O and Cl we consider boron content and B-
334 isotope data then the relationships between $\text{Cl}/\text{K}_2\text{O}$ and B/ K_2O (equally, Cl/Nb vs. B/Nb; **Fig.**
335 **S2.2C – Supplementary online material**), or B/ K_2O (or B/Nb) vs. $\delta^{11}\text{B}$ (**Fig. 8**) confirm neither
336 significant contribution of these components, nor the contribution of AOC1, AOC2 and SED
337 components. Indeed, to account for the compositions of melt inclusions with strongly and
338 coherently varying $\text{H}_2\text{O}/\text{K}_2\text{O} = 0.3\text{--}8.9$ and $\text{Cl}/\text{K}_2\text{O} = 0.06\text{--}0.24$, it would require contamination
339 either by SW (up to 7%) or more concentrated NaCl-brine, or assimilation of AOC1 (up to 60%)
340 or both AOC1 + SW components (**Fig. 7A**). No significant effect of 15%-NaCl and 50%-NaCl
341 brine, as well as the role of AOC2 and SED can be recognised in this diagram. The same
342 conclusions can be derived from the $\text{H}_2\text{O}/\text{Ce}$ vs. Cl/Nb variations (**Fig. 7B**), with only a
343 difference that contamination by AOC1 (up to 70%) is required. However, if we consider mixing
344 of the same components in coordinates $\text{H}_2\text{O}/\text{K}_2\text{O}$ vs. B/ K_2O or $\text{H}_2\text{O}/\text{Ce}$ vs. B/Nb (**Fig. 7C,D**),
345 then the role of SW and AOC1, along with 15%-NaCl and AOC2 is not yet justified, but the
346 50%-NaCl end-member appears to be potentially significant. The amount of SED to add to UAM

347 appears to be up to 50% in **Fig. 7C** and up to 100% in **Fig. 7D**, both being unrealistic. Finally, if
348 we consider B/K₂O vs. $\delta^{11}\text{B}$ or B/Nb vs. $\delta^{11}\text{B}$ systematics (**Fig. 8**), then the role of seawater,
349 NaCl-brines and AOC1 is not confirmed at all, while the amount of AOC2 and SED to be
350 assimilated approaches to 100% (**Fig. 8B**).

351 In conclusion we note that Cl and F often behave as incompatible elements during partial
352 melting and magma fractionation (e.g., Fischer and Schmincke, 1984; Carroll and Webster,
353 1994; Jambon, 1994; Dalou et al., 2014). As shown by Dalou et al. (2014 and references
354 therein), a Cl/F ratio of >1 is expected in arc magmas resulting from partial melting of a depleted
355 mantle source mixed with an aqueous dehydration fluid because the Cl/F ratio in the subduction
356 slab fluids is usually high (e.g., ~4 in Mount Shasta rocks and up to 9.5 in Izu Bonin arc
357 magmas). In contrast, the low Cl/F ratios (<1; e.g., Central and South American arcs, Kermadec)
358 suggest that the magmas were produced by melting of a mantle source mixed with a hydrous slab
359 melt. In this context, it is essential to note that Cl/F ratios in the studied melt inclusions range
360 from 1.5 to 2.0, pointing towards predominant role of the subduction slab fluid in the origin of
361 Chickuracki magmas. Finally, the observed relationships of S/K₂O with K₂O-normalised
362 concentrations of H₂O, Cl and F (**Fig. 5C,D** and **Fig. 2.1A** – *Supporting online material*), as well
363 as the H₂O/K₂O vs. Cl/K₂O and F/Zr vs. Cl/Nb correlations (**Fig. 5E,F**) strongly suggest that the
364 variations of H₂O, S, Cl and F contents were not primarily affected by degassing or
365 contamination, but more likely related to the transport of these components to magma source
366 region by subduction slab fluids, in agreement with the previous studies of the Kurile-
367 Kamchatka arc volcanism (e.g., Hochstaedter et al., 1996; Ishikawa and Tera, 1997;
368 Kepezhinskas et al., 1997; Dorendorf et al., 2000; Churikova et al., 2001, 2007; Ishikawa et al.,
369 2001; Portnyagin et al., 2007, 2015, Konrad-Schmolke et al., 2016).

370

371 *5.2. Origin of sulphur concentration and S-isotope ranges*

372 Sulphur solubility in basaltic magmas was shown to be mostly a function of iron content
373 of the melt, if sulphur is predominately present in sulphide (S^{2-}) form (e.g., Connolly and
374 Haughton, 1972; Haughton et al., 1974; Mathez, 1976; Carroll and Rutherford, 1985; Wallace
375 and Carmichael, 1992;), but it also depends strongly on temperature, pressure, redox conditions,
376 H_2O content, and the composition of coexisting melt and vapour phase (Nagashima and Katsura,
377 1973; Katsura and Nagashima, 1974; Carroll and Rutherford, 1985, 1987; Luhr, 1990; Wallace
378 and Carmichael, 1992; Mavrogenes and O'Neill, 1999; Matjuschkin et al., 2016; Canil and
379 Fellows, 2017; Mavrogenes and Blundy, 2017). The solubility of sulphur is generally higher (at a
380 given f_{O_2}) in mafic (tholeiite and hawaiite), as compared to more SiO_2 -rich magmas (rhyodacite)
381 (e.g., Katsura and Nagashima, 1974).

382 As a sulphide-saturated melt becomes progressively oxidised, higher amount of sulphur
383 is required to be dissolved in the melt to cause saturation of the melt with sulphide (e.g., Carroll
384 and Webster, 1994 and references therein). This is also evident from the exponential character of
385 FeO-S relationships observed in the more S-rich inclusions (**Fig. 5A**). The sulphur valence state
386 changes from S^{2-} to S^{6+} within a limited range of oxygen fugacity, from NNO-1 to NNO+2
387 (Carroll and Rutherford, 1988; Wallace and Carmichael, 1994; Metrich and Clocchiatti, 1996;
388 Gurenko and Schmincke, 2000; Jugo et al., 2005a,b, 2010; Fiege et al., 2015). Further melt
389 oxidation causes a sulphide phase to become unstable. At these and more oxidised conditions
390 (i.e., f_{O_2} is greater than NNO+2), anhydrite ($CaSO_4$) may become stable and appear as
391 phenocrysts in the magma, as it was observed, for example, in some El Chichón and Mount
392 Pinatubo trachyandesite and dacite magmas (Luhr et al., 1984; Varekamp et al., 1984; Carroll
393 and Rutherford, 1987; Luhr, 1990; Bernard et al., 1991; Kress, 1997). Moreover, the solubility of
394 sulphate (SO_4^{2-}) is much higher than that of sulphide (S^{2-}) in mafic magmas and can reach up to
395 2.5 wt.% SO_3 (Carroll and Rutherford, 1985, 1987; Luhr, 1990; Metrich and Clocchiatti, 1996;
396 Gurenko and Schmincke, 2000; Jugo et al., 2005a,b; Fiege et al., 2015). Since S concentrations

397 in many of our inclusion glasses significantly exceed the level of S^{2-} solubility, and they show
398 no correlation with FeO (**Fig. 5A**), we contend that a significant proportion of sulphur is
399 dissolved as SO_4^{2-} species. This is consistent with generally higher oxidation state of subduction-
400 zone-related magmas, and also with previously estimated oxygen redox conditions of the
401 Chikurachki magmas (i.e., $\Delta NNO = +1$ to $+2$; [Gurenko et al., 2005a](#)). According to the
402 relationship given in [Wallace and Carmichael \(1994\)](#):

403

$$404 \quad \log (X_{SO_4^{2-}}/X_{S^{2-}}) = a \log fO_2 + b/T + c \quad (1)$$

405

406 where $X_{SO_4^{2-}}$ and $X_{S^{2-}}$ are mole fractions of SO_4^{2-} and S^{2-} sulphur species in the melt (i.e., $X_{SO_4^{2-}}$
407 $+ X_{S^{2-}} = 1$), T is temperature in Kelvin, and coefficients $a = 1.02$, $b = 25410$, and $c = -10$,
408 between 80 and 98% sulphur dissolved as SO_4^{2-} is expected in the basaltic melts representing the
409 studied Plinian 1986, 1853 and prehistoric eruptions of the Chikurachki volcano, thereby
410 explaining the elevated concentrations of sulphur in the studied melt inclusions.

411 The fact that sulphur isotopic composition (i.e., $\delta^{34}S$) strongly correlates with S
412 concentrations in the melt inclusions and groundmass glasses (**Fig. 6A,B**), as well as with K_2O -
413 normalised concentrations of H_2O and Cl (**Fig. 6C,D**) suggests that sulphur was more likely
414 introduced to the magma by the same process along with H_2O and Cl. One possible and
415 relatively simple explanation would be a contamination of magma by sulphate-bearing seawater-
416 derived material at shallow-crustal depth, as it was previously demonstrated on example of
417 Miocene basaltic hyaloclastites drilled during the ODP Leg 157 southwest of Gran Canaria
418 (Canary Islands, Spain) by [Gurenko et al., 2001](#). However, as discussed above, shallow-depth
419 contamination was not a factor controlling budget of volatile components in the studied
420 Chikurachki magmas. Thus, the origin of sulphur and its S-isotope signature could more likely

421 be ascribed to slab-derived fluids. Whether a consequent degassing of the magmas could result in
422 the observed, nearly 14‰-range of $\delta^{34}\text{S}$ values is a subject of further discussion.

423

424 5.2.1. S-isotope fractionation during magma degassing

425 Magma degassing is an alternative process, which is capable to significantly affect the
426 concentration and isotopic composition of sulphur in the melt by changing the proportion of the
427 reduced (S^{2-}) and oxidised (SO_4^{2-}) forms (e.g., Taylor, 1986; Marini et al., 2011; Mandeville et
428 al., 2009 and references therein). This is mostly because sulphide and sulphate species may
429 possess strongly contrasting $\delta^{34}\text{S}$ values, with an average fractionation factor of $+7.3 \pm 1.4\%$
430 between sulphate and sulphide (e.g., Sakai et al., 1982, 1984). According to Holloway and Blank
431 (1994), the variations of $\delta^{34}\text{S}$ values resulted from continuous volatile exsolution can be
432 modelled either as closed-system (Eq. 2) or as open-system (i.e., Rayleigh distillation) degassing
433 (Eq. 3):

434

$$435 \quad \delta^{34}\text{S}_f = \delta^{34}\text{S}_i + 1000 (1 - F) \ln \alpha_{\text{gas-melt}} \quad (2)$$

$$436 \quad \delta^{34}\text{S}_f = (\delta^{34}\text{S}_i + 1000) (F^{\alpha_{\text{gas-melt}} - 1}) - 1000 \quad (3)$$

437

438 where subscripts f and i refer to the final and initial isotopic compositions of S in the melt,
439 respectively, F is a fraction of sulphur remaining in the melt upon degassing, and $\alpha_{\text{gas-melt}}$ is a
440 gas-melt S-isotope fractionation factor defined as:

441

$$442 \quad \alpha_{\text{gas-melt}} = ({}^{34}\text{S}/{}^{32}\text{S})_{\text{gas}} / ({}^{34}\text{S}/{}^{32}\text{S})_{\text{melt}} \quad (4)$$

443

444 To calculate the parameter F in Eq. 2 and 3, we used S-concentrations in final ($[S]_f$) and
 445 initial ($[S]_i$) melts normalised to a concentration of an incompatible trace element (metal; $[Me]_f$
 446 and $[Me]_i$, respectively) by the following equation:

$$447$$

$$448 \quad F = ([S]_f \times [Me]_i) / ([S]_i \times [Me]_f) \quad (5)$$

449

450 using, in particular, the concentrations of Ce and K in the respective melts, and then the average
 451 was used. Two melt inclusions with the highest S concentrations and $\delta^{34}\text{S}$ values (3/4-4-1 and
 452 13/2-1-2, PEC- and exsolution-corrected values; **Table S2.1** – *Supporting online material*) were
 453 taken to calculate the initial melt composition ($[S]_i = 3287 \mu\text{g/g}$, $[\text{Ce}]_i = 9.54 \mu\text{g/g}$, $[\text{K}]_i = 3592$
 454 $\mu\text{g/g}$, and $\delta^{34}\text{S}_i = +11.2\%$).

455 Modelling of S isotopic fractionation caused by degassing is rather complicated because
 456 $\alpha_{\text{gas-melt}}$ can be either higher or lower than unity because it depends strongly on T , f_{O_2} and the
 457 proportion of SO_4^{2+} and S^{2-} species dissolved in the melt. Generally, a fractionation factor of ^{32}S
 458 and ^{34}S isotopes between gas phase and silicate melt ($\Delta^{34}\text{S}_{\text{gas-melt}}$) can be expressed as following
 459 (e.g., Sakai et al., 1982), assuming that isotopic equilibrium is maintained among all sulphur
 460 species in the gaseous and melt phases:

$$461$$

$$462 \quad \Delta^{34}\text{S}_{\text{gas-melt}} = \delta^{34}\text{S}_{\text{gas}} - \delta^{34}\text{S}_{\text{melt}} \approx 1000 \ln \alpha_{\text{gas-melt}} =$$

$$463 \quad = [X\delta^{34}\text{S}_{\text{SO}_2} + (1 - X)\delta^{34}\text{S}_{\text{H}_2\text{S}}] - [Y\delta^{34}\text{S}_{\text{sulfide}} + (1 - Y)\delta^{34}\text{S}_{\text{sulfate}}], \quad (6)$$

464

465 where X is the mole fraction of SO_2 in the SO_2 - H_2S gas phase (i.e., $X_{\text{SO}_2} + X_{\text{H}_2\text{S}} = 1$), and Y is the
 466 mole fraction of sulphur dissolved in the melt as sulphide, and $1 - Y$ mole fraction of sulphur
 467 dissolved as sulphate. After multiplying and collecting terms, Eq. 6 can be expressed as:

468

469 $1000 \ln \alpha_{\text{gas-melt}} = X 1000 \ln \alpha_{\text{SO}_2\text{-H}_2\text{S}} + Y 1000 \ln \alpha_{\text{sulphate-sulphide}} -$
 470 $- 1000 \ln \alpha_{\text{sulphate-H}_2\text{S}}$ (7)

471
 472 The temperature dependences of the fractionation factors in Eq. 7 can be approximated by the
 473 relationships studied by [Richet et al. \(1977\)](#) and [Miyoshi et al. \(1984\)](#) (for more detail see a
 474 compilation by [Taylor, 1986](#)):

475
 476 $1000 \ln \alpha_{\text{SO}_2\text{-H}_2\text{S}} = -0.42 \times 10^9/T^3 + 4.367 \times 10^6/T^2 - 0.105 \times 10^3/T - 0.41$ (8)

477 $1000 \ln \alpha_{\text{sulphate-sulphide}} = 7.4 \times 10^6/T^2 - 0.19$ (9)

478 $1000 \ln \alpha_{\text{sulphate-H}_2\text{S}} = 6.5 \times 10^6/T^2$ (10)

479
 480 where T is temperature in Kelvin. For the temperature range from 910 to 1180°C determined for
 481 the studied Chikurachki melt inclusions ([Gurenko et al., 2005a](#)), the $\Delta^{34}\text{S}_{\text{gas-melt}}$ fractionation
 482 factor is within the range of -2.1‰ to -0.9‰ (i.e., $\alpha_{\text{gas-melt}} = 0.9979\text{--}0.9991$). The calculations
 483 were done assuming $X = 0.98$ because usually the volcanic gases emitted at temperatures
 484 $\sim 1000^\circ\text{C}$ contain mostly SO_2 , whereas H_2S is present only in trace amount, as shown for Kilauea
 485 volcano, Hawaii, and Mnt. Etna, Sicily ([Symonds et al., 1994](#)) and according to the recent gas-
 486 melt equilibria model of [Burgisser and Scaillet \(2007\)](#) for oxidised (i.e., $\Delta\text{NNO} = +1.5$)
 487 conditions. The variations of X within $\pm 10\%$ (from 0.8 to 1) will cause an uncertainty in the
 488 resulting $\Delta^{34}\text{S}_{\text{gas-melt}} \approx \pm 0.2\text{--}0.3\text{‰}$. The Y value varied from 0.02 to 0.2, in agreement with the
 489 previously reported ΔNNO -range from +1 to +2, resulting in 80 to 98% sulphur dissolved as
 490 sulphate in the melt (see above).

491 The diagram of $\delta^{34}\text{S}$ versus F (**Fig. 9**) demonstrates that neither open- nor close-system
 492 degassing can account for the observed $\sim 14\text{‰}$ range in the Chikurachki melt inclusions. This is
 493 mostly because the outgassed SO_2 will preferentially drive out the lighter ^{32}S isotope under

494 conditions of high f_{O_2} so that the remaining melt will be progressively enriched in ^{34}S , as it was
495 first shown by Sakai et al. (1982) and also demonstrated by Mandeville et al. (2009) for the case
496 of climatic and pre-climatic eruptions of Mt. Mazama, Crater Lake, Oregon, but being
497 completely opposite to what is observed in **Fig. 6A** and **Fig. 9**. Negative correlations of S with
498 incompatible trace elements mentioned above (**Fig. 5B**) may suggest that magma fractionation
499 (resulting in enrichment of melt by incompatible trace elements) might have been accompanied
500 by S-depletion due to degassing. However, a weak correlation of S with CO_2 and no correlations
501 with other volatile components (like H_2O and Cl) imply that degassing, though being probably
502 important, was not a single process affecting the concentrations of the dissolved S. Furthermore,
503 the fact that the hyperbola-shaped relationship of $\delta^{34}\text{S}$ vs. S concentrations (**Fig. 6A**) is
504 transformable into a straight line in the $1/\text{S}-\delta^{34}\text{S}$ space (**Fig. 6B**) represents a strong argument in
505 favour of two-component mixing hypothesis (Langmuir et al., 1978), whereas host lapilli
506 groundmass glasses, which presumably suffered degassing, do not fit the line. We thus contend
507 that sulphur abundances, the entire S-isotope range, as well as the other volatile components
508 such as H_2O , Cl and F correlating with each other (**Fig. 5**) were largely controlled by two-
509 component mixing process. The possible mixing end-members could be the magmas having
510 similar major and trace element compositions but strongly contrasting volatile contents and S
511 isotopes.

512

513 *5.3. Trace element constraints on magma source components*

514 Mafic arc magmatism results from melting of a mantle wedge, whose solidus is lowered
515 by input of slab-derived hydrous melts and/or fluids (e.g., Gill, 1981; McCulloch and Gamble,
516 1991; Hawkesworth et al., 1993; Woodhead et al., 1993; Pearce and Peate, 1995). The
517 composition of mantle wedge is relatively well constrained and thought to be represented by a
518 MORB-type, or even more depleted upper mantle material (e.g., Woodhead et al., 1993;

519 [Kepezhinskas et al., 1997](#)). However, a relative contribution of slab-derived H₂O-rich fluids
520 and/or melts, as well as the proportion of the sediments relative to the mafic part of the oceanic
521 crust in the slab remains enigmatic. Numerous previous studies attempted to assess the effect of
522 fluid transport vs. slab melting in the origin of the Kurile-Kamchatka arc magmas (e.g.,
523 [Hochstaedter et al., 1996](#); [Ishikawa and Tera, 1997](#); [Kepezhinskas et al., 1997](#); [Khubunaya and](#)
524 [Sobolev, 1998](#); [Dorendorf et al., 2000](#); [Churikova et al., 2001, 2007](#); [Ishikawa et al., 2001](#);
525 [Portnyagin et al., 2007, 2015](#), [Konrad-Schmolke et al., 2016](#), among others). One of the main
526 purposes of the present study is to constrain a contribution of the above mentioned components
527 to the origin of the Chikurachki magmas using the behaviour of fluid-immobile (i.e., Nb, Zr, Ti,
528 Yb) vs. fluid-mobile (i.e., B, Ba, K, Sr, ±Th) elements.

529

530 *5.3.1. Mantle wedge composition*

531 In our model calculations, it is essential to assess chemical composition of the mantle
532 wedge. Generally, the HFSE and HREE are immobile in the fluid and not enriched in the oceanic
533 crust and in sedimentary components of the subduction slab, and the ratios of these elements can
534 be used as reasonable proxy to characterise the nature of the mantle wedge of a particular
535 volcano in the SZ setting (e.g., [Pearce, 1983](#); [Pearce and Peate, 1995](#)).

536 Several trace element characteristics of the studied Chikurachki melt inclusions allow us
537 to conclude that the composition of the mantle wedge is similar or even more depleted than the
538 source of typical N-MORB magmas. They are following: (i) the average N-MORB-normalised
539 concentrations of $[Nb]_n = 0.55 \pm 0.21$, $[Sm]_n = 1.16 \pm 0.37$, $[Zr]_n = 0.74 \pm 0.30$, $[Ti]_n = 0.74 \pm$
540 0.27 , $[Yb]_n = 0.83 \pm 0.29$ are close to, or lower, than unity; (ii) the element ratios $Zr/Nb = 35\text{--}49$,
541 $Zr/Yb = 16\text{--}25$, and $Nb/Yb = 0.35\text{--}0.7$ are similar to those of N-MORB (i.e., $Zr/Nb = 32$, Zr/Yb
542 $= 24$, $Nb/Yb = 0.76$; [Hofmann, 1988](#)); (iii) the studied melt inclusions plot in the field of MORB
543 in the [Pearce and Peate \(1995\)](#) Zr/Yb vs. Nb/Yb discrimination diagram (not shown). Thus, to
544 simplify our calculations, we assume the trace element concentrations of the Kurile arc mantle

545 wedge is the same as depleted N-MORB mantle of [Salters and Stracke \(2004\)](#) (**Table 1**). We
546 note that using more depleted composition of the mantle wedge will not significantly change the
547 calculation results, but slightly increase a role of the slab-derived components.

548

549 *5.3.2. Subduction slab melt vs. fluid as a volatile transport media*

550 The origin of arc magmas is tightly related to dehydration and/or melting of the slab,
551 where both melt and fluid components are added in different proportions, namely higher
552 proportion of fluid at shallower depths and *vice versa* when the slab penetrates deeper ([Hickey
553 and Frey, 1982; Cameron, 1985; Tatsumi et al., 1986; Crawford et al., 1989; Elliott et al., 1997](#)).
554 Experiments on element partitioning confirm that slab-derived H₂O-rich fluids may cause
555 remarkable enrichment by incompatible elements typical for volcanic arcs worldwide (e.g.,
556 [Brenan et al., 1995; Ayers et al., 1997; Stalder et al., 1998; Johnson and Plank, 1999](#)). Silica-rich
557 partial melts released from the subducting crust and/or sediment are also potential contributors to
558 the chemical balance ([Defant and Drummond, 1990; Drummond and Defant, 1990](#)).

559 Several studies proposed a concurrent addition of slab-derived melt and fluid components
560 in the arc magmas (e.g., [Kay, 1978; Rogers et al., 1985; Stern et al., 1984; Defant et al., 1991;
561 Stern and Kilian, 1996; Class et al., 2000; Yogodzinski et al., 2001](#)). In particular, it has been
562 concluded that hydrous fluids released in the arc front due to amphibole and serpentine
563 dehydration are enriched in boron, LILE, sulphur and chlorine and likely represent a main fluid
564 transport and reaction agent affecting mantle wedge of the Kurile and Kamchatka arcs (e.g.,
565 [Hochstaedter et al., 1996; Ishikawa and Tera, 1997; Churikova et al., 2001, 2007; Portnyagin et
566 al., 2007](#)). Moreover, [Churikova et al. \(2007\)](#) concluded that S, Cl and B could have been
567 transported by a fluid released from AOC-like subduction slab at shallow depth, whereas Li
568 appeared to be related to Li-F-rich fluids resulting from breakdown of volatile-rich minerals
569 (e.g., amphibole) at much greater depths (~400 km). Furthermore, [Churikova et al. \(2007\)](#) have
570 noted that some Kurile-Kamchatka arc magmas may also exhibit an adakitic signature, whereas

571 [Portnyagin et al. \(2015\)](#) argued that melting of the mantle wedge beneath Tolbachik was
572 triggered by slab-derived hydrous melts.

573 We think that in the case of Chikurachki, the significant positive correlations of H_2O/K_2O
574 vs. Cl/K_2O and F/Zr vs. Cl/Nb (**Fig. 5E,F**), Th/Nb vs. Ba/Nb ($R = 0.649$; see **Fig. 9** and
575 discussion below), as well as B/Nb vs. Li/Nb and Be/Nb ($R = 0.833$ and 0.796 , respectively,
576 except for one outlier; **Fig. S2.2** – *Supporting online material*) imply a complex nature of the
577 Kurile arc subduction component composed of both melt and fluid. The observed strong
578 correlations of Li/Nb and Be/Nb with B/Nb and F/Zr with Cl/Nb in the Chikurachki melt
579 inclusions suggest that these elements have a common source (i.e., slab component), support a
580 major role of a Cl-rich fluid and imply that B, Cl and F are likely to relate to a single transport
581 process, in contrast to the mechanism of B and Li decoupling suggested by [Churikova et al.](#)
582 [\(2007\)](#).

583

584 5.3.3. Trace element constraints

585 Thorium and LREE are enriched in the subducted slab, being however less mobile or
586 nearly immobile in the fluid phase, as compared to fluid-mobile elements, such as Li, B, Ba, Pb
587 and Sr. The difference in geochemical behaviour of these elements can be used to elucidate a
588 contribution of slab-derived melts vs. dehydration fluids in the origin of arc magmas (e.g.,
589 [Kamenetsky et al., 1997](#); [Class et al., 2000](#); [Hochstaedter et al., 2001](#)). Namely, the transport by
590 fluid would leave Th/Nb ratios virtually unchanged since both elements are immobile but affect
591 the ratios of fluid-mobile to fluid-immobile elements (e.g., Ba/Nb , B/Nb), and *vice versa*, if the
592 element transport would have been caused solely by the slab-derived melt. Systematic variations
593 of Th/Nb vs. Ba/Nb or B/Nb ratios would imply the contribution of both slab-derived melt and
594 fluid components.

595 We modelled the contribution of the anticipated subduction sediment-derived melt and
596 fluid components to the mantle wedge following the approach of [Hochstaedter et al. \(2001\)](#). The

597 AOC- and SED-derived fluids, as well as a partial melt from SED were considered as possible
598 end-members (**Table 2**). The element partitioning data used in the modelling are from
599 experimentally-determined bulk sediment-melt, sediment-fluid, rutile-melt and rutile-fluid
600 partition coefficients (Brenan et al. 1994, 1995; Stalder et al., 1998; Johnson and Plank, 1999;
601 Foley et al., 2000). The sediment subducted at the Kurile trench (its composition is taken from
602 Plank and Langmuir, 1998) is thought to contain up to 5% Ti-rich residual phase (i.e. rutile),
603 which has the potential to fractionate Nb from Th (Class et al., 2000), whereas 1% rutile was
604 assigned for AOC (Hochstaedter et al., 2001). Equilibrium batch melting and Rayleigh
605 fractionation equations (Shaw, 1970) were used to calculate the compositions of partial melt and
606 fluid in equilibrium with the subduction sediment, respectively. We assumed 5% partial melting
607 of the Kurile sediment to produce a sediment melt mixing end-member, and 2% fluid removal
608 from both the Kurile sediment and AOC to account for a possible sediment fluid end-member
609 (**Fig. 10**). We note also that because Ba, Nb and Th are chemical elements of very similar
610 incompatibility to minerals composing magma source rocks, as follows from their solid-melt
611 partition coefficients, they show little or no fractionation during partial melting and/or magma
612 fractionation. The calculated Ba/Nb and Th/Nb ratios of the multi-component magma source
613 region are thus relevant for the Th/Nb and Ba/Nb of the produced partial melts, and can be used
614 to assess the origin of the Chikurachki parental magmas.

615 In the model presented in **Fig. 10**, the Th/Nb vs. Ba/Nb variations observed in the
616 Chikurachki melt inclusions (presented alongside whole-rock chemical compositions of the
617 Kurile arc mafic lavas) can be explained by partial melting of a magma source composed of the
618 following three components (**Table 2**):

- 619
- 620 1. A mantle wedge (*MW*) component with trace element concentrations of depleted mantle after
621 [Salters and Stracke \(2004\)](#).

- 622 2. A composite dehydration fluid, which is enriched in Ba relative to Th or Nb and presents a 9:1
623 mixture of the fluid released from the altered oceanic crust (*AOCFluid*, the composition is
624 taken from [Hochstaedter et al., 2001](#)) and a fluid produced by dehydration of a subduction
625 sediment (*SedFluid*), whose trace element composition was calculated from that of the Kurile
626 sediment after [Plank and Langmuir \(1998\)](#) (for more detail see explanatory notes in **Table 2**).
627 The 9:1 proportion of *AOCFluid* to *SedFluid* was selected arbitrary, given a subordinate
628 amount of the sediment relative to a total mass of the slab, taking also into account that
629 sediment is more volatile-rich, as compared to its basaltic and ultramafic counterparts. We
630 note however that variations of *AOCFluid* to *SedFluid* ratio do not affect significantly the
631 calculation results.
- 632 3. A sediment-derived melt (*SedMelt*) with slightly elevated Th/Nb ratios and significantly lower
633 Ba/Nb ratios, as compared *AOCFluid* and *SedFluid* mixing end-members, whose trace
634 element composition was also calculated from the composition of the Kurile sediment (see
635 also explanatory notes in **Table 2**).

636

637 As it follows from our calculations, the composition of subduction component (*SUBD*) is
638 variable. It ranges from the composition of the pure *SedMelt* component (representing a lower
639 limit of the range) to that of *SedMelt* mixed with up to 60% composite slab-derived fluid
640 presenting, in turn, a 9:1-mixture of *AOCFluid* and *SedFluid*, crudely corresponding to the AOC
641 to SED proportion in the dehydrating model slab ([Tonarini et al., 2011](#)) and assuming also equal
642 amount of fluid released from both lithologies. The ~1–8% admixture of *SUBD* to *MW* appeared
643 to satisfactorily explain the entire compositional range of the Chikurachki melt inclusions, and
644 from ~0.4% to ~10% of *SUBD* to be mixed with *MW* to account for the range of the Kurile arc
645 magmas (**Fig. 10**). In conclusion, it is worth emphasising that the subduction component
646 contributed to the origin of the Tolbachik magmas ([Portnyagin et al., 2015](#)) appeared to be very
647 similar to *SUBD* inferred during the present study (**Fig. 9; Table 2**).

648

649 *5.3.4. Implications for chemical composition and amount of slab-derived fluid*

650 Here we evaluate a possible contribution of slab-derived fluid to the origin of volatile
651 components and boron in the studied magmas, assessing the observed B-isotope range. The light
652 lithophile element boron is a powerful proxy to trace fluid transport of chemical elements from
653 subducting slab to the mantle wedge because of strongly contrasting B concentrations and $\delta^{11}\text{B}$
654 values in these geochemical reservoirs. A significant fraction of initial boron is contained in the
655 uppermost few km of the subducting crust and sediments, being then progressively released as
656 subduction proceeds (e.g., [Leeman and Sisson, 1996](#)). Systematically higher $\delta^{11}\text{B}$ values in the
657 volcanic arc magmas, as compared to the exhumed subduction-related metamorphic rocks,
658 suggest that dehydration reactions cause significant decrease of $\delta^{11}\text{B}$ values of subducted crustal
659 material, implying strong fractionation of ^{10}B and ^{11}B isotopes as boron partitions in the fluid
660 (e.g., [Peacock and Hervig, 1999](#)). This conclusion was supported by later experimental study of
661 [Wunder et al. \(2005\)](#), who have demonstrated that a wide range of $\delta^{11}\text{B}$ in the arc magmas may
662 result from continuous breakdown of micas, if they are present in the down-dragged slab.
663 Finally, a serpentinitised mantle wedge at the slab-mantle interface represents another major
664 inventory of boron, being also a source of variable but generally positive $\delta^{11}\text{B}$ values (e.g.,
665 [Benton et al., 2001](#); [Straub and Layne, 2002](#); [Savov et al., 2005, 2007](#); [Scambelluri and Tonarini,](#)
666 [2012](#)).

667 Boron mobilised from the slab was shown to be systematically enriched in ^{11}B than the
668 parental AOC at 400–500°C, resulting in +5 to +10‰ enrichment of the fluid relative to the
669 solid ([Ishikawa and Nakamura, 1992](#); [Leeman and Sisson, 1996](#); [Rose et al. 2001](#); [Rosner et al.](#)
670 [2003](#); [Leeman et al., 2004](#); [Le Voyer et al., 2008](#)). Since the composition of slab-derived fluid
671 may vary strongly, depending on the composition of subducting crust and the degree of its
672 devolatilisation, a wide $\delta^{11}\text{B}$ range from –7‰ up to +15‰ (assuming +10‰ enrichment of the

673 fluid phase relative to the upper end of the $\delta^{11}\text{B}$ range given for AOC by [Smith et al., 1997](#)) is
674 very probable ([Rose et al. 2001](#); [Leeman et al., 2004](#); [Gurenko et al., 2005b](#); [Le Voyer et al.,](#)
675 [2008](#); [Tonarini et al., 2011](#), [Scambelluri and Tonarini, 2012](#)).

676 The effects of possible interaction of slab-derived fluids with depleted MORB-like
677 mantle source are illustrated in diagrams in coordinates of $\delta^{11}\text{B}$ vs. B/Nb and Ba/Nb ratios (**Fig.**
678 **11**). Given the $^{11}\text{B}/^{10}\text{B}$, B/Nb and Ba/Nb do not change significantly during partial melting or
679 magma fractionation, these ratios, being calculated for the magma source, can be directly
680 transferred to the resulting partial melts. The following mixing end-members were defined
681 (**Table 1**):

- 682
- 683 1. Mantle wedge (*MW*) was chosen to contain 1.2 $\mu\text{g/g}$ Ba, 0.21 $\mu\text{g/g}$ Nb, 0.06 $\mu\text{g/g}$ B and
684 $\delta^{11}\text{B} = -4\text{‰}$ ([Chaussidon and Marty, 1995](#); [Salters and Stracke, 2004](#)).
 - 685 2. Subducting slab fluid (*SSF*) varies significantly in chemical composition, depending on
686 the particular chemical and lithological composition of the slab and the dehydration
687 depth. In particular, [Tonarini et al. \(2011\)](#) have demonstrated that slab-derived fluids
688 released at the depth range from 30 to 120 km may contain from ~ 10 and ~ 200 $\mu\text{g/g}$ B
689 and vary between -10 to higher than $+20\text{‰}$ $\delta^{11}\text{B}$. Three contrasting fluid compositions
690 (*SSF1* through *SSF3*) were compiled based on the data of [Hochstaedter et al. \(2001\)](#),
691 [Rose et al. \(2001\)](#), [Straub and Layne \(2002\)](#), [Rosner et al. \(2003\)](#), [Leeman et al. \(2004\)](#),
692 [Gurenko et al. \(2005b\)](#), [Le Voyer et al. \(2008\)](#), [Tonarini et al. \(2011\)](#), [Scambelluri and](#)
693 [Tonarini \(2012\)](#), using also the compositions of *SED* and *AOC*-derived fluids calculated
694 during the present study (*SSF1*: trace elements concentrations are those as of *SEDFluid*,
695 containing 300 $\mu\text{g/g}$ B and $\delta^{11}\text{B} = +15\text{‰}$; *SSF2* is the 9:1 mixture of *AOCFluid* and
696 *SedFluid* as calculated above, containing 100 $\mu\text{g/g}$ B and $\delta^{11}\text{B} = +3\text{‰}$; and *SSF3* is equal
697 to *AOCFluid* with 50 $\mu\text{g/g}$ B and $\delta^{11}\text{B} = -8\text{‰}$). The decrease of B and Ba contents and

698 $\delta^{11}\text{B}$ values in the fluid components qualitatively reflects the increase of slab temperature
699 and degree of its devolatilisation.

700
701 As it follows from the calculations, the slab-derived fluid may represent a major agent affecting
702 the abundances of volatile and fluid-mobile elements, and B isotopes in the melt inclusions.
703 About 1–10% of SSF2 and SSF3 have to be added to MW in order to explain the ~9‰ range of
704 $\delta^{11}\text{B}$ values of the studied melt inclusions. We note that this estimation is very similar to that
705 inferred from the trace element modelling (1 to 8% addition of SUBD; **Fig. 9**). It is also worth
706 emphasising that the selected compositions of SSF2 and SSF3 are very close to the model fluid
707 compositions released from the South Sandwich Island arc uppermost slab at 90–120 km depth
708 (170–190 $\mu\text{g/g}$ B and $\delta^{11}\text{B} = -0.7$ to -3.9% ; [Tonarini et al., 2011](#)), but having less boron and
709 more negative $\delta^{11}\text{B}$ values. This discrepancy can be explained by somewhat stronger dehydration
710 of the residual Kurile slab because of the greater depth of the Wadati-Benioff zone beneath
711 Chikurachki (~130–140 km; e.g., [Ishikawa and Tera, 1997](#); [Ishikawa et al., 2001](#)).

712

713 *5.4. Magma ascent, degassing history and eruption style*

714 It is well known that conduit geometry, magma viscosity, degassing history, changing
715 conditions of magma ascent and fragmentation, and even the dynamics of syn-eruptive microlite
716 growth may strongly affect the eruption rate and style of a volcano (e.g., [Fischer and Schmincke,](#)
717 [1984](#); [Carey and Sparks, 1986](#); [Houghton et al., 2004](#); [Szramek et al., 2006, 2010](#); [Houghton and](#)
718 [Gonnermann, 2008](#)). Previously, [Gurenko et al. \(2005a\)](#) suggested intensive pre-eruptive
719 degassing of H_2O and S from the magma at the stage of phenocryst crystallisation, pointing on
720 the strongly varying to very low volatile contents in the melt inclusions trapped by phenocrysts
721 of the same or very close chemical composition. The authors suggested a scenario by which local
722 volumes of magma could be partially degassed before being trapped by growing crystals and

723 employed a mechanism of vertical cycling of magma within one or between several connected
724 reservoirs, being akin to the magma drainback phenomenon described in particular for Kilauea
725 Volcano, Hawaii (e.g., [Wallace and Anderson, 1998](#)). Our present data (i.e., numerous
726 correlations of volatile component concentrations and S isotope compositions preserved in the
727 studied melt inclusions with incompatible trace elements and between each other, inability of
728 magma degassing and crustal contamination to account for these variations coupled with the
729 suggested here two-component mixing scenario to explain $\delta^{34}\text{S}$ vs. S concentrations) could be
730 interpreted in support of the mechanism previously suggested by [Gurenko et al. \(2005a\)](#) to
731 control the variations of H₂O, S, Cl and F in the erupting magmas.

732 The required insignificant correction of melt inclusion compositions for post-entrapment
733 crystallisation of host mineral (i.e., less than 7.8 wt.% Ol, 0.8 wt.% Opx, and no correction for
734 Pl) also suggests that the eruption and quenching of magma likely occurred shortly after the
735 inclusions have been entrapped by growing phenocrysts. As previously discussed (e.g.,
736 [Roggensack et al., 1997](#); [Gurenko et al., 2005a](#); [Shinohara, 2008](#); [Ruth et al., 2016](#)), eventual
737 eruptions may be non-explosive, if magma degassing is effective at shallow crustal depth,
738 whereas rapid ascent of a volatile-rich magma may result in strong volatile release and highly
739 explosive character of eruptions. In this context, the range of volatile contents recorded by melt
740 inclusions and their relationships with other chemical components may indicate whether the
741 erupted magma underwent a prolonged stage of relatively passive degassing or degassing was
742 essentially a single-stage process upon the eruption. It is worth emphasising that most of the
743 historic eruptions from Chikurachki have been of the non-explosive character, possibly linked to
744 the episodes where volatile components were able to dissipate smoothly. Explosive eruptions, in
745 contrast, are thought to occur when access to shallow levels is blocked or when the flux of
746 magma from depth is too rapid for shallow degassing to prevent a catastrophic decompression
747 and explosive fragmentation of the magma. We thus think that rapid ascent of the volatile-rich

748 basaltic magmas from ~16-km initial depth (inferred from our CO₂-H₂O data; **Fig. 4B**) was a
749 primary reason caused the Plinian character of the Chikurachki eruptions.

750

751 **6. Summary and conclusions**

752 The present study focuses on the unravelling the origin and behaviour of volatile
753 components resulting in highly explosive (Plinian) basaltic eruptions of the Chikurachki volcano.

754 The following main conclusions were derived:

755

756 1. The obtained concentrations of volatile components in the studied melt inclusions agree well
757 with our previously reported data. After correction for post-entrapment crystallisation of the
758 host mineral, the concentrations of CO₂ and H₂O reveal minimum pressure of 33 to 276 MPa
759 (or ~9.5 to ~1 km depth), corresponding to the last equilibrium between melt and vapour
760 phases upon magma eruption and quenching. About 5–69% of the original CO₂ and
761 0.1–3.2% of H₂O were lost to the shrinkage bubble of melt inclusions after their entrapment
762 during phenocryst crystallisation. After correction, the obtained 47–1580 µg/g CO₂, 0.4–4.2
763 wt.% H₂O, 399–633 µg/g F, 619–3402 µg/g S and 805–1240 µg/g Cl ranges imply strong
764 pressure release from 456 to 35 MPa, corresponding to ~15.7–1.2-km-depth range of magma
765 ascent.

766 2. Significant negative correlations of S with incompatible trace elements, no clear relationships
767 of S with H₂O, CO₂ and Cl but strong positive correlations of S/K₂O with H₂O/K₂O, Cl/K₂O
768 and F/K₂O suggest that later magma degassing and/or contamination by crustal rocks were
769 not the governing processes affecting the amounts of S and probably of the other volatile
770 components preserved in inclusions

771 3. Sulphur isotopes in the studied inclusion and groundmass glasses vary strongly, ranging from
772 -1.6 to +12.3‰ of δ³⁴S, decrease with decreasing S concentrations and show significant

773 positive correlations with H₂O, CO₂ and S, as well as negative correlations with light
774 lithophile (Li, Be and B), and with a number of incompatible trace elements. Our modelling
775 has demonstrated that either open- or close-system magma degassing cannot account for the
776 observed ~14‰ range of $\delta^{34}\text{S}$ variations in the Chikurachki melt inclusions. The linear
777 character of the 1/S vs. $\delta^{34}\text{S}$ relationship suggests mixing of two components possibly
778 represented by melts having similar major and trace element compositions but strongly
779 contrasting volatile contents and S isotopes.

780 4. The $\delta^{11}\text{B}$ values of the studied melt inclusions range from -7.0 to +2.4‰ within the interval of
781 B concentrations of 13–23 $\mu\text{g/g}$. Similarly, the relationships of $\delta^{11}\text{B}$ with B/K₂O and B/Nb,
782 as well as of Cl/K₂O with B/K₂O (and equally, Cl/Nb with B/Nb) cannot be accounted by
783 magma contamination at shallow crustal depths.

784 5. The observed relationships of S/K₂O with K₂O-normalised concentrations of H₂O, Cl and F,
785 as well as the H₂O/K₂O vs. Cl/K₂O and F/Zr vs. Cl/Nb correlations strongly suggest that
786 variations in H₂O, S, Cl and F contents were not primarily affected by degassing or
787 contamination, but likely originated due to the mixing of magmas, which in turn reflect the
788 composition of source components. We contend that subduction slab-derived melt and/or
789 fluid were major agents in controlling chemical and isotopic composition of the mantle
790 wedge and, consequently, of the magmas originated from this hybrid source.

791 6. The behaviour of fluid-mobile vs. fluid-immobile incompatible trace elements points towards
792 strongly varying chemical composition of the subduction component. It ranges from the
793 composition of the pure subducted sediment-derived melt (a lower limit of the range) to that
794 of the sediment melt mixed with up to 60% composite slab-derived fluid, representing in turn
795 a 9:1-mixture of fluid components released from both altered oceanic crust and the sediment
796 of the slab. The ~1–8% admixture of the inferred subduction component to the mantle wedge
797 is required to account for the whole compositional range of the studied Chikurachki magmas,

798 and addition from ~0.4% to ~10% of the subduction component accounts for the broad
799 compositional range of the Kurile arc magmas.

800 7. We conclude that rapid ascent of the volatile-rich basaltic magmas from ~16-km initial depth
801 without their prolonged stagnation and crystallisation in shallower depth magma reservoir
802 but accompanied by near-surface bubble nucleation and growth followed by magma
803 fragmentation was a primary reason caused Plinian character of the Chikurachki eruptions.

804

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814

815

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1311

1312

1313 **Figure captions**

1314 **Fig. 1.** (A) Schematic map of the northern Kurile Islands (Russia) with the locality of the
1315 Chikurachki volcano on Paramushir Island shown in relation to the Kamchatka Peninsula.
1316 Contours show isobars for the top of the Wadati-Benioff zone from [Tatsumi et al. \(1994\)](#). (B)
1317 The Chikurachki volcano, a view from the eastern side ~6 km away.

1318
1319 **Fig. 2.** Isopachs (lines of equal thickness) given in cm of the tephra representing Plinian (A)
1320 1853 and (B) 1986 eruptions of the Chikurachki volcano after [Belousov et al. \(2003\)](#).

1321
1322 **Fig. 3.** Multi-element diagram presenting trace and rare-earth element distribution in olivine-
1323 hosted glass inclusions and groundmass glasses and demonstrating positive H₂O, B, Cl and F
1324 enrichment. The concentrations of trace elements in N-MORB used for normalisation are from
1325 [Hofmann \(1988\)](#), the normalisation values for volatile elements and water are 1350 µg/g H₂O,
1326 0.6 µg/g B, 54.5 µg/g Cl, and 146 µg/g F, which were calculated from the average B/K ≈ 0.001,
1327 H₂O/Ce ≈ 180, K/Cl ≈ 11, and F/Nd ≈ 20, or F/Zr ≈ 2 ratios inferred for MORB using the data of
1328 [Ryan and Langmuir \(1993\)](#), [Jambon et al. \(1995\)](#), [Saal et al. \(2002\)](#), [Kendrick et al. \(2013\)](#), [Le](#)
1329 [Voyer et al. \(2015\)](#) and references therein. The shaded field presents whole-rock data for the
1330 Kurile island arc basalts and andesites (MgO > 2.5 wt.%) from [Bailey et al. \(1987a,b\)](#), [Ishikawa](#)
1331 [and Tera \(1997\)](#), [Ikeda \(1998\)](#), [Ikeda et al. \(2000\)](#), [Takagi et al. \(1999\)](#), [Ishikawa et al. \(2001\)](#).

1332
1333 **Fig. 4.** Concentrations of CO₂ and H₂O dissolved in glass inclusions measured by SIMS. (A)
1334 CO₂ and H₂O corrected for the amount of host mineral crystallised inside melt inclusions
1335 between entrapment and magma eruption and final quenching. (B) CO₂ and H₂O corrected for
1336 the loss of volatiles to the inclusion shrinkage bubble (see text). Isobars of melt compositions in
1337 equilibrium with CO₂-H₂O fluid (*solid lines*) and isopleths of fluid composition (*dashed lines*)

1338 with labels returning molecular fraction of H₂O in the fluid) were calculated using *VolatileCalc*
1339 solution model (Newman and Lowenstern, 2002). The isopleths and isobars were calculated for
1340 basaltic magma composition at 1000°C i.e., the average temperature of the Chikurachki magmas
1341 (Gurenko et al., 2005a). Error bars represent $\pm 2\sigma$ average integral analytical uncertainty, i.e.,
1342 $\pm 18\%$ relative for CO₂ and $\pm 12\%$ relative for H₂O, they are less than the size of a symbol, if not
1343 shown.

1344
1345 **Fig. 5.** Concentrations of S, Cl and F in glass inclusions and lapilli matrix glasses. (A) FeO vs. S
1346 variations. The larger shaded grey symbols denote the compositions of the respective host matrix
1347 glasses. The *MORB and OIB* shaded field presents data for presumably undegassed MORB and
1348 Hawaiian submarine tholeiitic and alkali basaltic glasses from Wallace and Carmichael (1992).
1349 The *S saturation* shaded field represents compositional dependence of sulphur saturation of
1350 MORB-type magmas with immiscible sulfide liquid of pure FeS based on experimental data of
1351 Smythe et al. (2017) and references therein. Legend: *MI* = melt inclusions, *GL* = matrix glasses.
1352 (B) Ce vs. S, (C) H₂O/K₂O vs. S/K₂O, (D) F/K₂O vs. S/K₂O, (E) H₂O/K₂O vs. Cl/K₂O, and (F)
1353 F/Zr vs. Cl/Nb. The observed relationships do not support shallow-depth contamination of the
1354 magma, and rather favour a deep origin of volatiles resulted from slab-derived fluid released
1355 during subduction (see text).

1356
1357 **Fig. 6.** Sulphur isotope composition of glass inclusion and one host matrix glass of the
1358 Chikurachki prehistoric eruption related to (A) S concentrations, (B) H₂O/K₂O and (C) Cl/K₂O
1359 ratios.

1360
1361 **Fig. 7.** Diagrams of (A) H₂O/K₂O vs. Cl/K₂O, (B) H₂O/Ce vs. Cl/Nb, (C) H₂O/K₂O vs. B/K₂O,
1362 and (D) H₂O/Ce vs. B/Nb (given as weight ratios) illustrate the effects of contamination (mixing
1363 lines) of presumably “uncontaminated” arc magma (*UAM*) with different types of contaminants,

1364 i.e., seawater (SW), 15%- and 50%-NaCl saline brines (labelled as *15%-NaCl* and *50%-NaCl*,
1365 respectively), altered oceanic crust (*AOC1* and *AOC2*) and siliceous marine sediment (*SED*) (see
1366 text and **Table 1** for the end-member chemical compositions and further details). Numbers on
1367 the mixing lines refer to wt.% of the contaminant added to the magma. The calculated mixing
1368 trends allow us to conclude that direct contamination of UAM by altered basaltic rocks and
1369 marine sediments at shallow depth and/or by seawater or seawater-derived components (saline
1370 brine) is unable to account for the H₂O, Cl and B enrichment observed in the studied melt
1371 inclusions. Legend: *MI* = melt inclusions, *GL* = matrix glasses.

1372
1373 **Fig. 8.** Boron isotope composition of the studied glass inclusions given in relation to B/K₂O (A)
1374 and B/Nb (B) in context of possible magma contamination. The mixing end-members used (and
1375 their labels) are the same as in **Fig. 7**. It is demonstrated that magma contamination by seawater
1376 or seawater-derived components, altered oceanic crust and marine sediments is unable to account
1377 for B isotopic composition of the studied melt inclusions.

1378
1379 **Fig. 9.** Sulphur isotope fractionation during magma degassing. The $\delta^{34}\text{S}$ values in the melt
1380 inclusions are shown versus fraction of S remaining (*F*). Shifts of $\delta^{34}\text{S}$ were calculated assuming
1381 closed-system (equilibrium, solid and dashed *straight lines*) and open-system (Rayleigh
1382 distillation; solid and dashed *curves*) degassing (see text), the $\alpha_{\text{gas-melt}}$ values of 0.996 and 0.998,
1383 and maximum, undegassed S concentration found in the most S-rich melt inclusions having the
1384 highest $\delta^{34}\text{S}$ values. At the temperature range from 910 to 1180°C and the redox conditions of
1385 NNO+1 to NNO+2 obtained for the studied Chikurachki magmas, the outgassed SO₂ will drive
1386 out the lighter ³²S isotope so that the remaining melt will be progressively enriched in ³⁴S. Thus,
1387 degassing alone cannot explain the observed, ~10‰-S-isotope of the studied melt inclusions.

1388

1389 **Fig. 10.** Diagram Th/Nb vs. Ba/Nb illustrating a possible origin of the Chikurachki magmas as a
1390 result of melting of a three-component magma source. Legend: *MI* = melt inclusions, *GL* =
1391 matrix glasses. The source components are mantle wedge (*MW*) with Ba, Nb and Th
1392 concentrations of the depleted mantle after [Salters and Stracke \(2004\)](#) and hybrid subduction
1393 component (*SUBD*) representing a binary 4:6-mixture of a sediment melt (*SedMelt*) with a
1394 composite slab-derived fluid, which in turn is a 9:1-mixture of a dehydration fluids released from
1395 the altered oceanic crust (*AOCFluid*) and Kurile sediment (*SedFluid*) (see text and **Table 2** for
1396 definition). The compositions of *Kurile lavas* are from [Bailey et al. \(1987a,b\)](#), [Ishikawa and Tera](#)
1397 [\(1997\)](#), [Ikeda \(1998\)](#), [Ikeda et al. \(2000\)](#), [Takagi et al. \(1999\)](#), [Ishikawa et al. \(2001\)](#). *KurileSed*
1398 is a bulk composition of the sediment column subducted at the Kurile trench taken from [Plank](#)
1399 [and Langmuir \(1998\)](#). *AOC* is altered oceanic crust taken from [Staudigel et al. \(1996\)](#), whose
1400 composition was used by [Hochstaedter et al. \(2001\)](#) to calculate *AOCFluid* composition.
1401 *SlabMelt* is a composition of composite hydrous melt released from the slab and contributed to
1402 the origin of magmas erupted in the Tolbachik volcanic field, Kamchatka, which was taken from
1403 [Portnyagin et al. \(2015\)](#) for comparison.

1404
1405 **Fig. 11.** Diagrams of (A) $\delta^{11}\text{B}$ vs. B/Nb and (B) $\delta^{11}\text{B}$ vs. Ba/Nb illustrate the proposed
1406 interpretation to account for B-isotope variations in the Chikurachki mineral-hosted melt
1407 inclusions by addition of slab-derived fluids to the mantle wedge. Mixing lines between the
1408 depleted MORB-type mantle wedge (*MW*) and subduction slab fluids (*SSF1*, *SSF2* and *SSF3*) are
1409 shown (see **Table 1** for chemical composition). Numbers on mixing lines refer to wt% of
1410 component added to MW end-member.

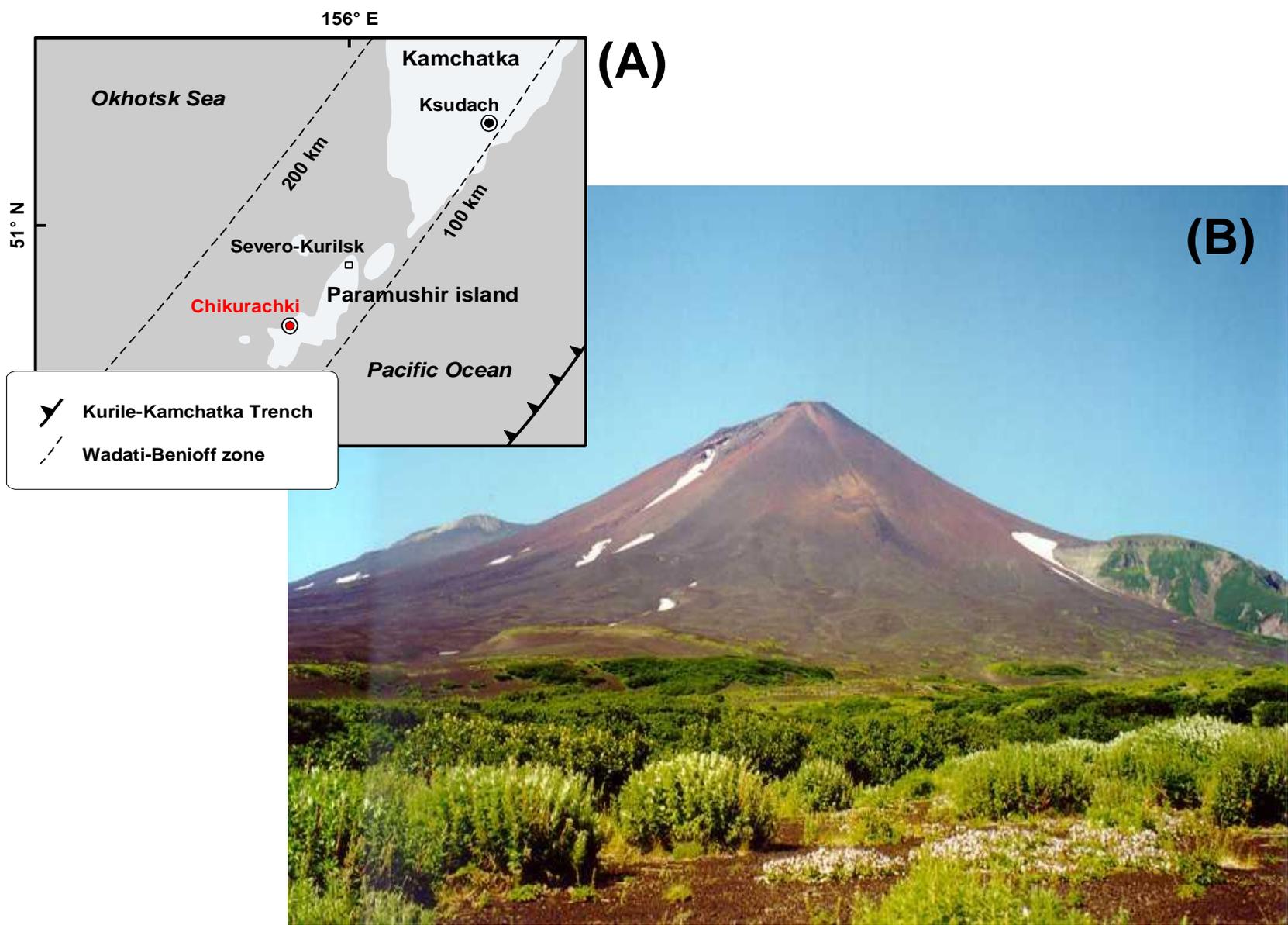
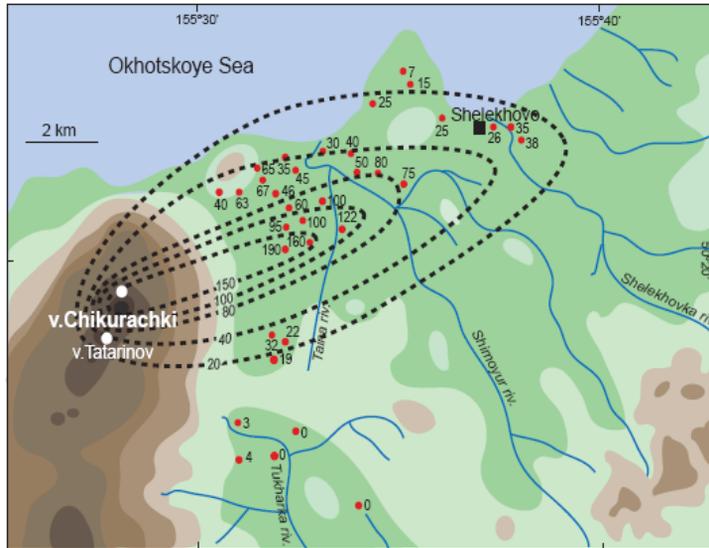


Fig. 1. Gurenko et al.

(A) 1853 eruption



(B) 1986 eruption

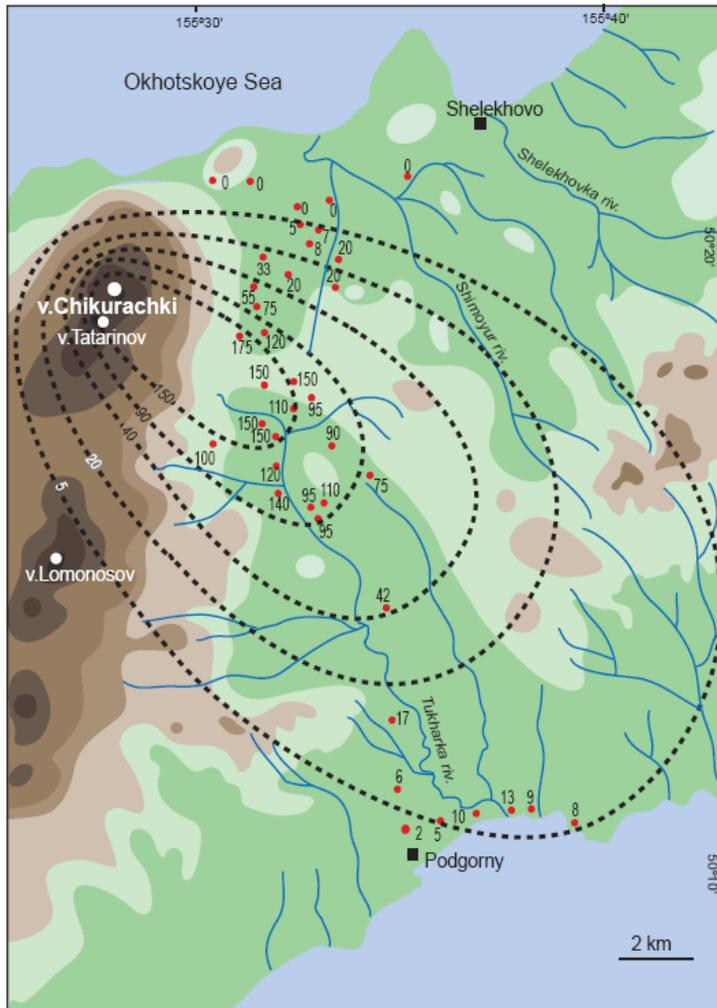


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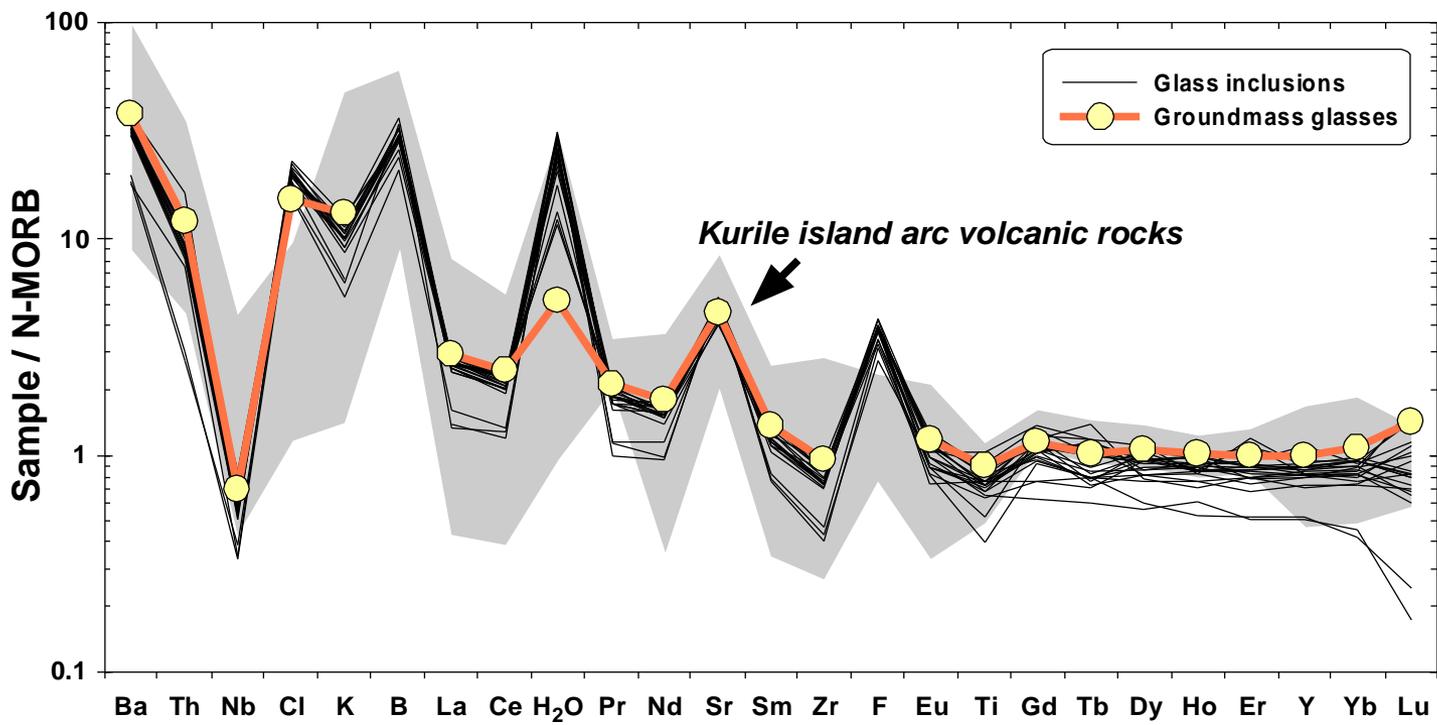


Fig. 3. Gurenko et al.

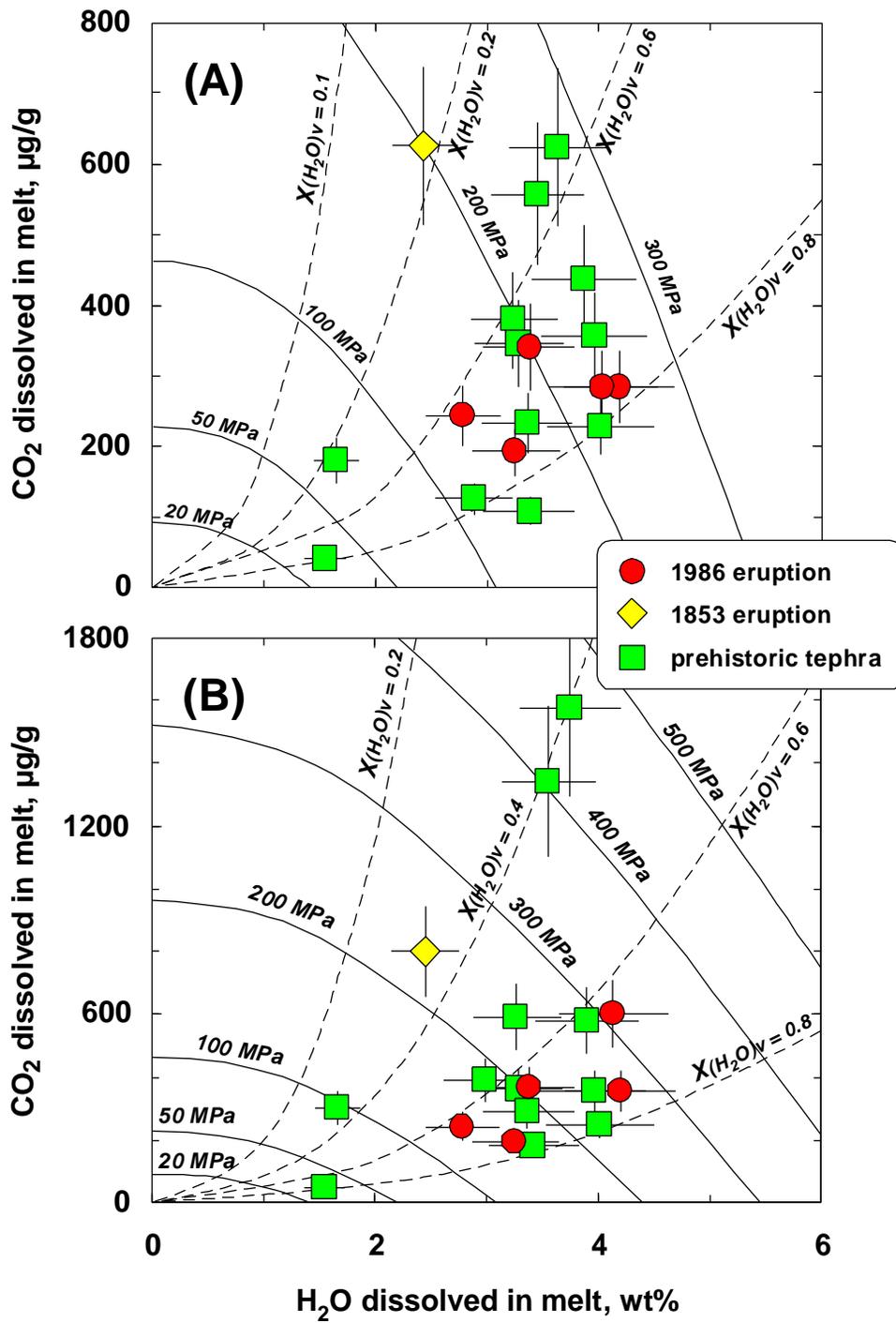


Fig. 4. Gurenko et al.

Figure

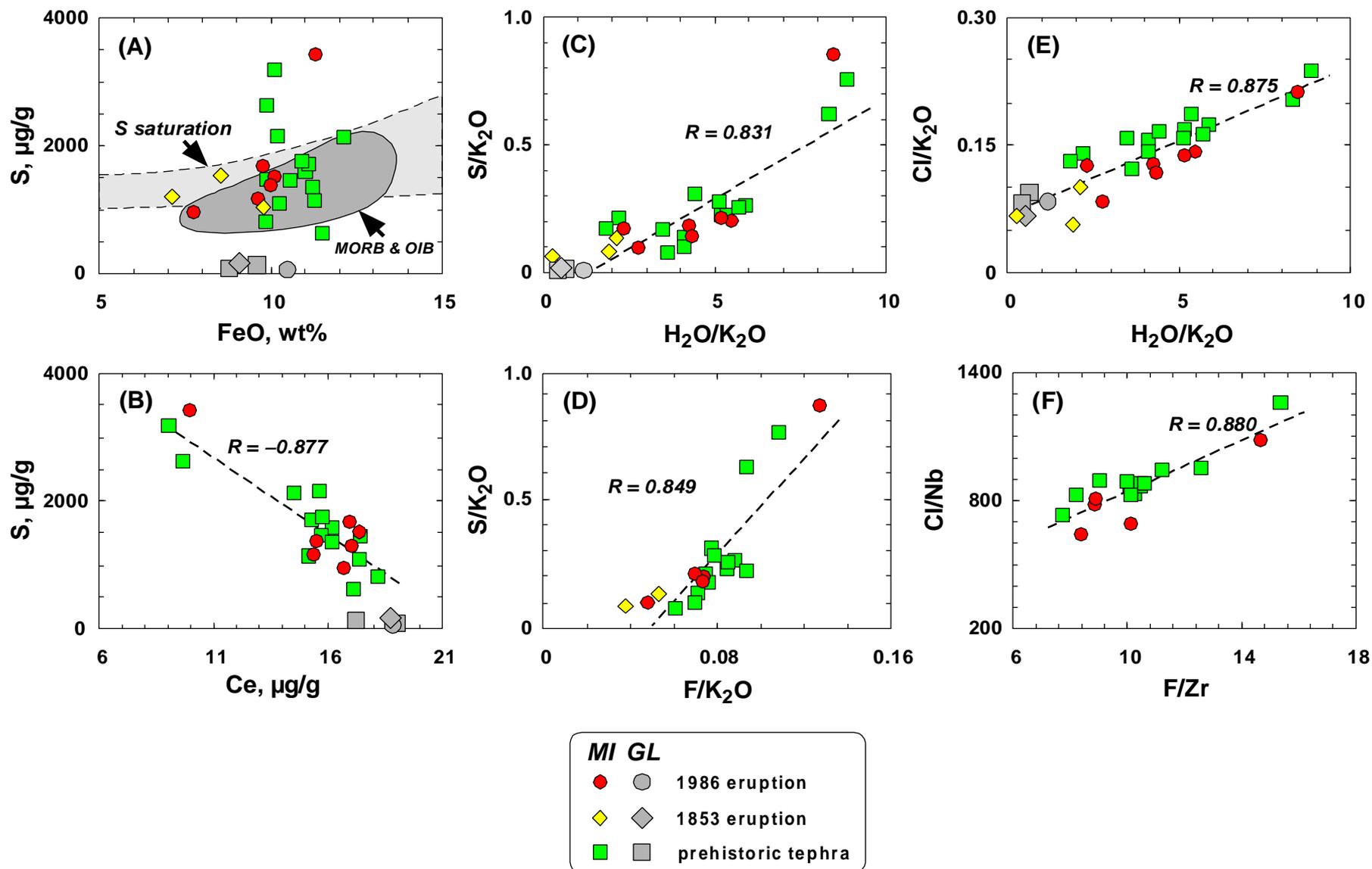


Fig. 5. Gurenko et al.

Figure

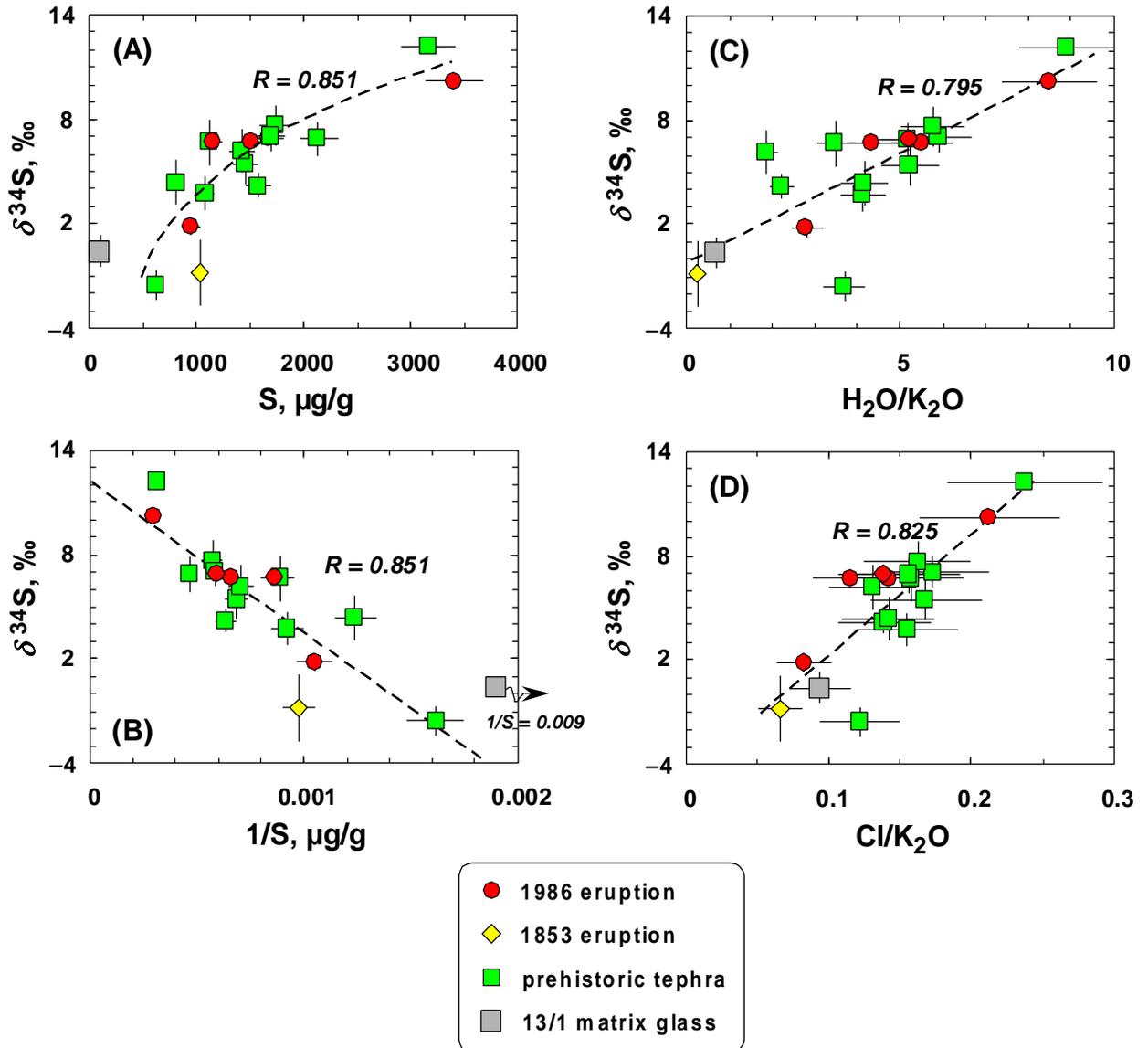


Fig. 6. Gurenko et al.

Figure

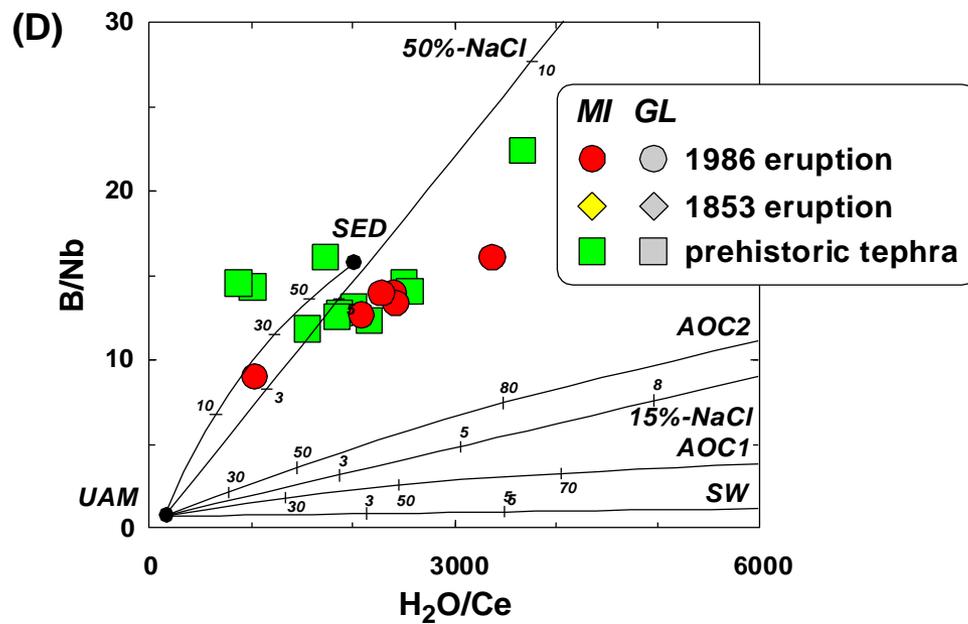
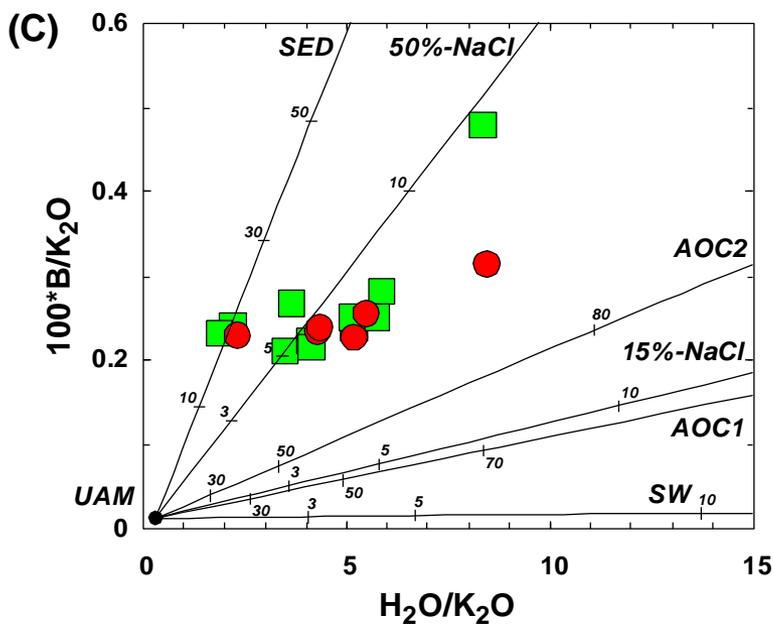
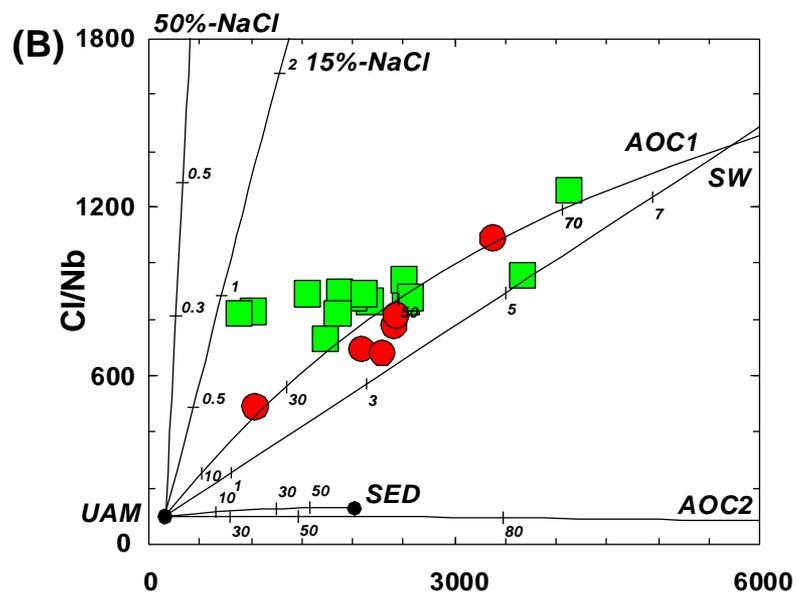
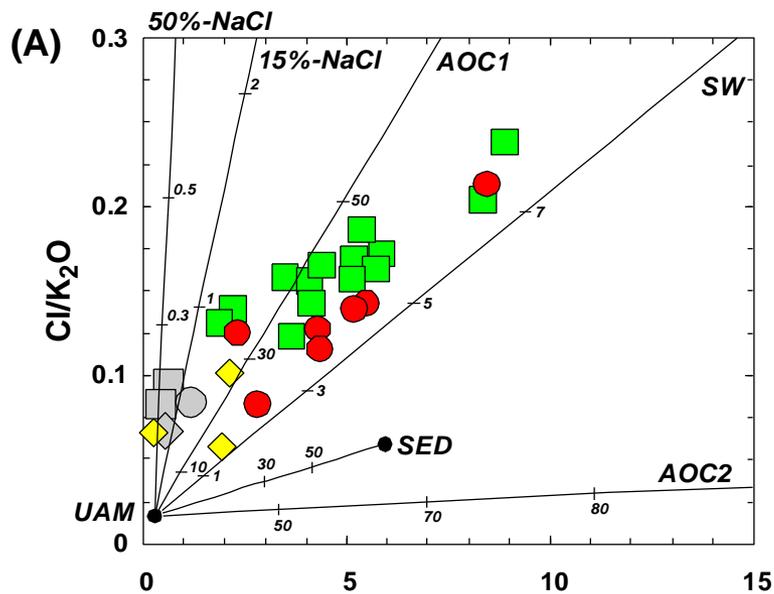


Fig. 7. Gurenko et al.

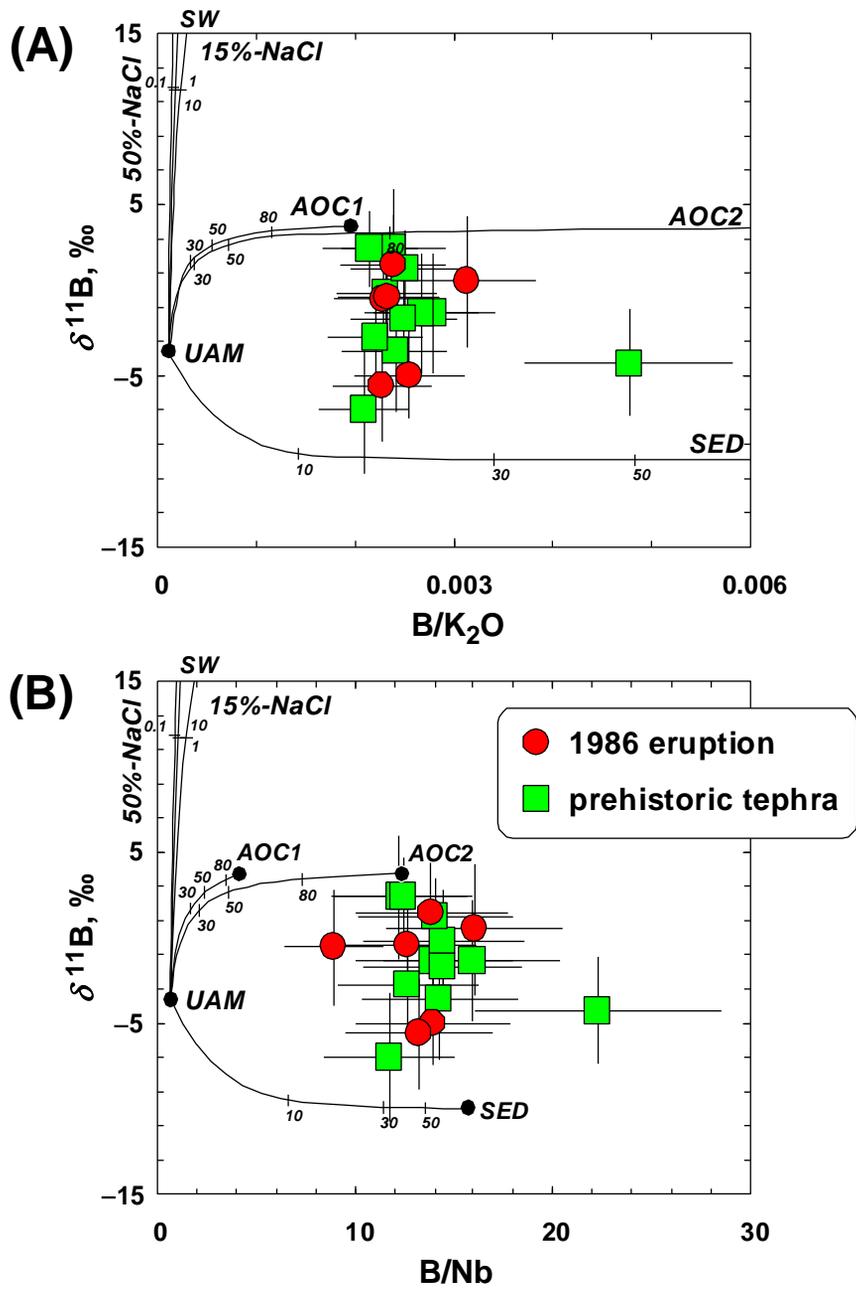


Fig. 8. Gurenko et al.

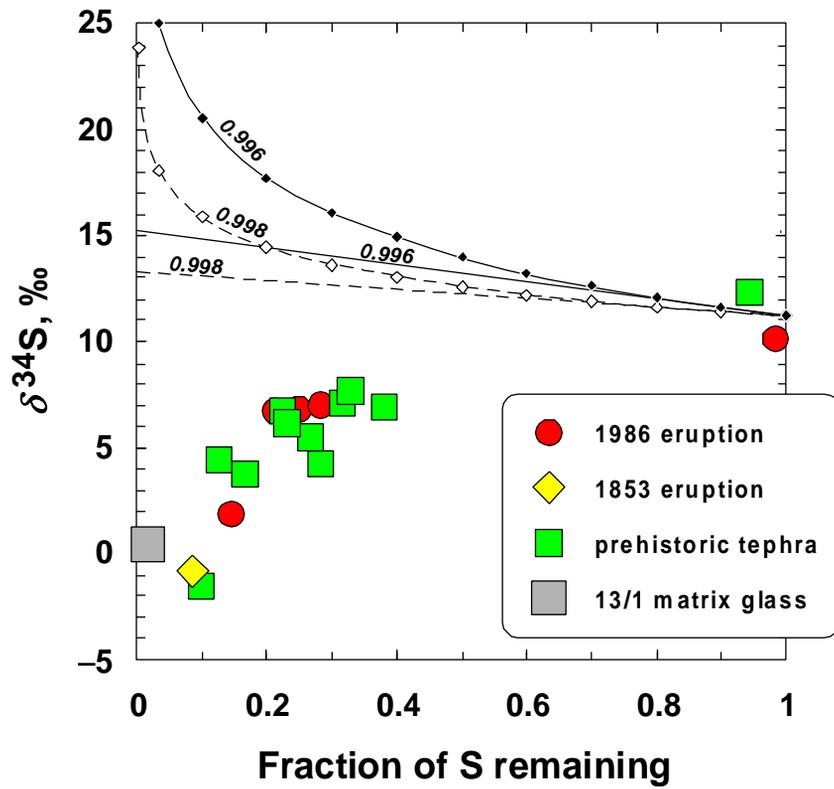


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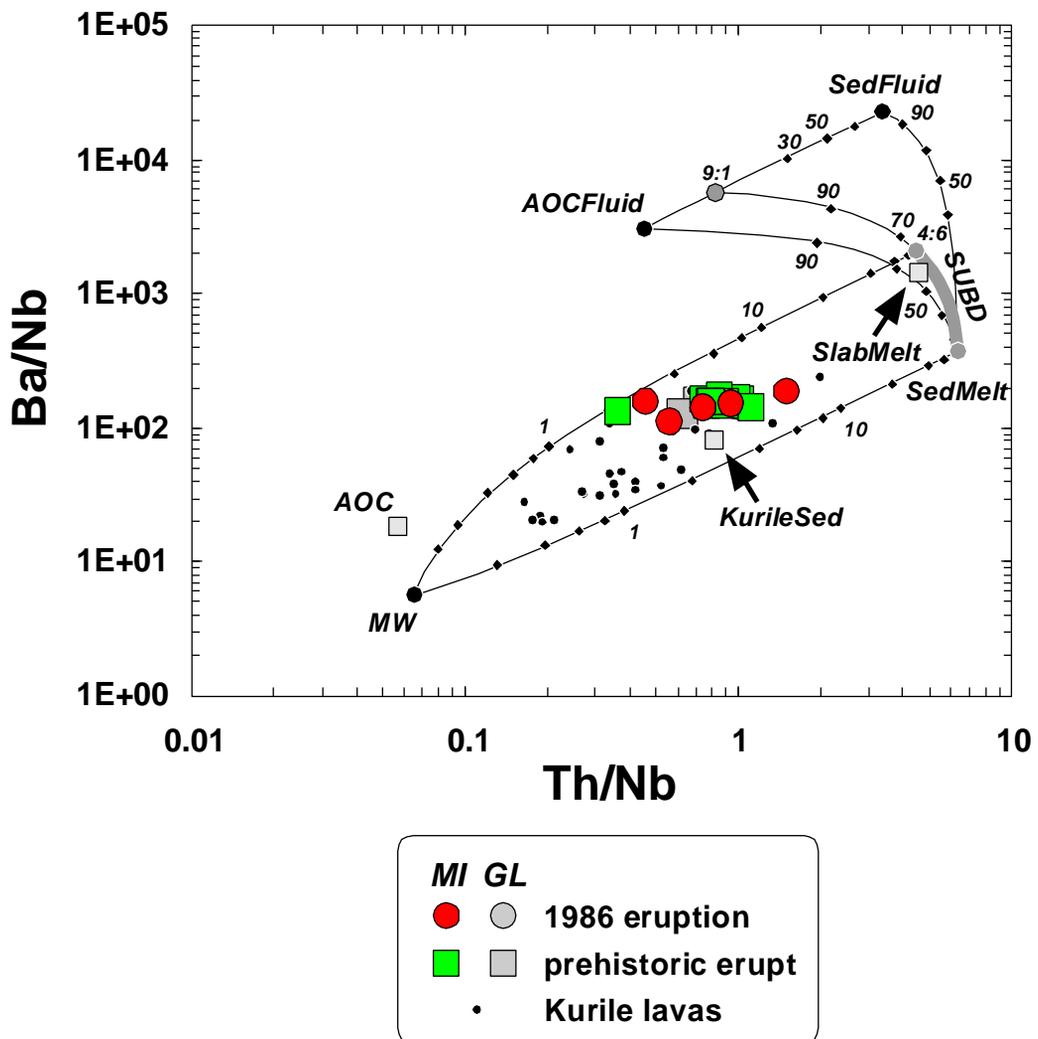


Fig. 10. Gurenko et al.

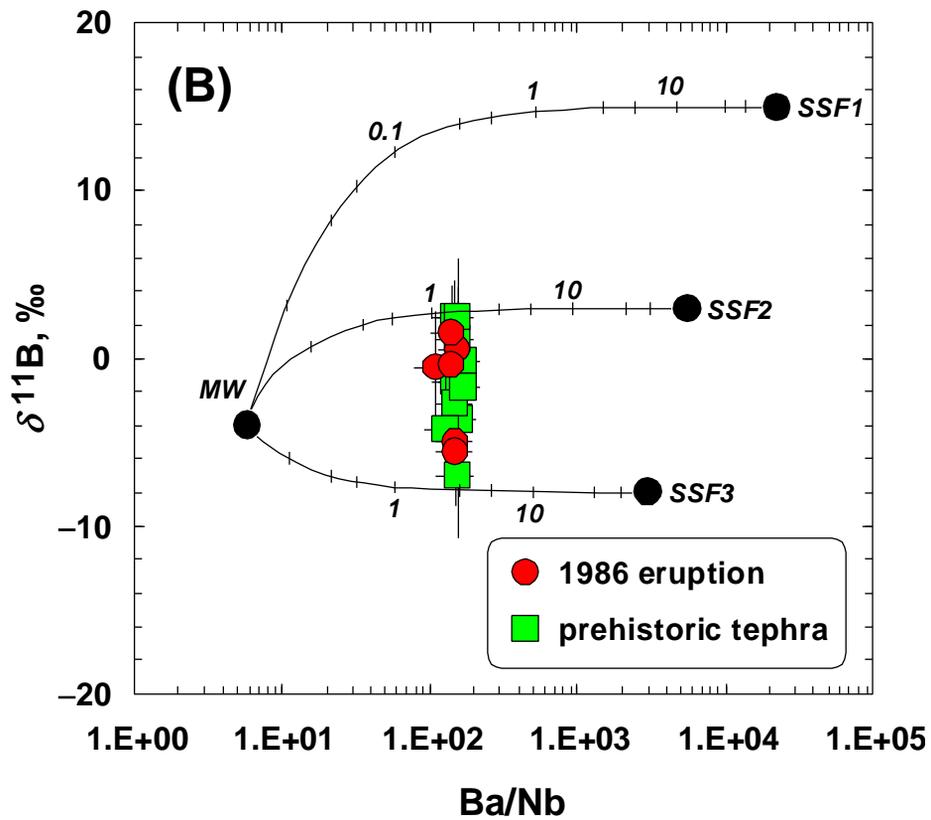
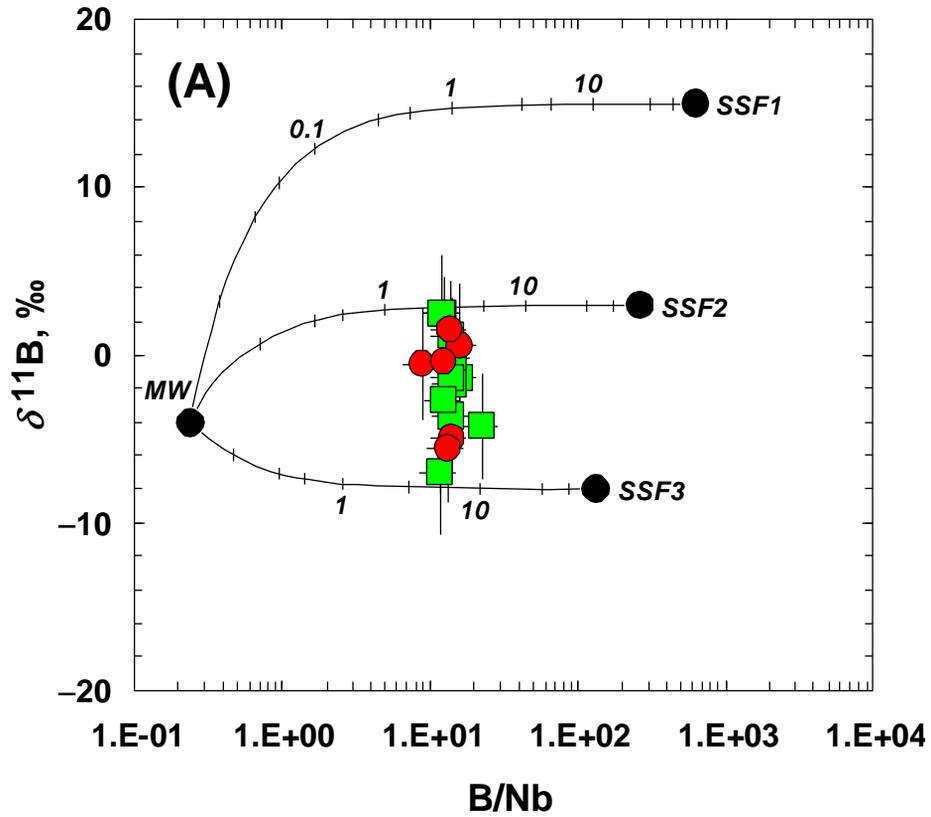


Fig. 11. Gurenko et al.

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