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1 **Tracing of Cl input into the sub-arc mantle through the combined analysis of B, O and**
2 **Cl isotopes in melt inclusions.**

3

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10

11 **Abstract**

12 The effect that recycling crust and sediments have on the composition of the mantle
13 wedge, in particular in terms of volatiles, is still debated. Chlorine, an important fluid mobile
14 element that has stable isotopes with different concentrations in the terrestrial reservoirs, has
15 the potential to be used to trace slab-derived fluids.

16 Olivine-hosted melt inclusions (OHMIs) provide a first order constraint on the $\delta^{37}\text{Cl}$ of
17 primary magmas, since they are unaffected by near surface processes. In this study, $\delta^{37}\text{Cl}$
18 were coupled with $\delta^{11}\text{B}$ and $\delta^{18}\text{O}$ analyses in samples from the Lesser Antilles, Vanuatu,
19 Aeolian, NE Japan and Izu-Bonin arcs. This unique dataset is used to better understand the
20 large $\delta^{37}\text{Cl}$ variation in melt inclusions from a single sample. OHMIs from the Vulcano
21 (Aeolian arc) and Sukumoyama (Izu-Bonin arc) samples have similar $\delta^{37}\text{Cl}$ ($-2.5\pm 0.5\%$ and -
22 $2.6\pm 0.8\%$, respectively). These are different from $\delta^{37}\text{Cl}$ in OHMIs from the other three
23 localities ($\delta^{37}\text{Cl}$ of $-0.7\pm 0.6\%$ for Aoba (Vanuatu arc) and St. Vincent (Lesser Antilles arc), -

24 $1\pm 0.9\%$ for Iwate (NE Japan)). Vulcano OHMIs also have statistically different B and O
25 isotope compositions compared to those from the other locations: average $\delta^{11}\text{B}$ of $-5.1\pm 2.9\%$
26 for Vulcano OHMIs, compared to $2.5\pm 3.7\%$, $5.2\pm 1.4\%$, $7.0\pm 2.2\%$, $3.8\pm 7.5\%$ for
27 Sukumoyama, Iwate, Aoba and St. Vincent OHMIs, respectively. All OHMIs have $\delta^{18}\text{O}$
28 between 4.0 and 7.4‰, except for those from Vulcano, which are significantly different, with
29 $\delta^{18}\text{O}$ from 7.2 to 9.1‰. Combining these three stable isotope systems suggests that the large
30 variation ($>2\%$) of $\delta^{37}\text{Cl}$ in OHMIs from a sample reflects inputs from different sources of Cl
31 rather than heterogeneities in a single main source. Variability between arcs might reflect
32 different major sources of Cl.

33 Comparing OHMIs Cl isotope data from the Aeolian and Izu-Bonin arcs with existing
34 bulk rock Cl isotope data suggest that OHMIs preserve the source signature of Cl input
35 whereas this signal can be lost in whole rocks as a result of Cl isotope diffusive fractionation
36 during Cl degassing. SIMS measurements of Cl isotopes in OHMIs could thus help refine
37 models of Cl cycles in the mantle.

38

39 **Keywords:** melt inclusions; chlorine isotopes; oxygen isotopes; boron isotopes; subduction
40 zones; SIMS

41

42 **1. Introduction**

43 Chlorine has been widely studied as an element in volcanic systems (e.g., Aiuppa et al.,
44 2009; Mather et al., 2012), but to date only a few studies have reported Cl isotopes (noted
45 $\delta^{37}\text{Cl}$) in rocks and minerals and used them to make petrogenetic interpretations (~35 papers
46 since 1995 and a few pioneering works prior to that). After some debate about the Cl isotope
47 values of the terrestrial reservoirs, refinement of bulk rock analytical techniques has brought

48 scientists to a consensus on the relatively narrow range of $\delta^{37}\text{Cl}$ found in terrestrial rocks
49 (Figure 1 and Supplementary material 1). In subduction zones, Cl, a soluble element, could
50 serve as a tracer of different Cl sources that contaminate the mantle wedge. Based on
51 theoretical calculations (Schauble et al., 2003) and experimental work (Liebscher et al., 2006),
52 fractionation of Cl isotopes between silicates and NaCl at $T > 300^\circ\text{C}$ should be limited. This
53 implies that $\delta^{37}\text{Cl}$ should not be (or only slightly) fractionated during slab dehydration
54 (Barnes et al., 2006; Bonifacie et al., 2008; John et al., 2011). The isotopic composition of a
55 metasomatized mantle should thus reflect simple binary mixing between the host rock and the
56 metasomatizing agent. The $\delta^{37}\text{Cl}$ of arcs lavas vary from -2.6 to +3.0‰ (e.g., Barnes et al.,
57 2009; Barnes and Straub, 2010). These studies have been used to estimate the Cl reservoirs
58 and suggested that Cl could be derived from altered oceanic crust (AOC), serpentinites or
59 sediments, depending on the depth of fluid extraction, which leads to a change in $\delta^{37}\text{Cl}$ across
60 an arc (Barnes et al., 2008). Variation along the Central America volcanic arc has also been
61 observed and has been used to suggest different sources of Cl along the arc (Barnes et al.,
62 2009).

63 Recently, Manzini et al. (2017) reported $\delta^{37}\text{Cl}$ in olivine-hosted melt inclusions (OHMIs)
64 from three different arc settings (the Lesser Antilles, Aeolian and Vanuatu arcs). Their study
65 reported large intra-sample $\delta^{37}\text{Cl}$ variations (up to 2.5‰, Figure 1) that are half of the
66 variation exhibited by all the bulk rocks from arc settings measured to date. Two arcs display
67 similar $\delta^{37}\text{Cl}$ (-1.9 to +0.6‰), whereas the third one has significantly different $\delta^{37}\text{Cl}$
68 compositions (-3.4 to -2.0‰). These authors suggested that for the Lesser Antilles and
69 Vanuatu arcs, $\delta^{37}\text{Cl}$ in the OHMIs reflect the imprint of serpentinite (and/or AOC) whereas
70 for the Aeolian arc, $\delta^{37}\text{Cl}$ is influenced by sediments. The difference between the two
71 different sets of compositions might reflect the different slab geometries that the arcs have.

72 As pointed out by Manzini et al. (2017), further work was required to better understand
73 the different $\delta^{37}\text{Cl}$ compositions between the three different arcs, as well as the relatively
74 large variation observed within a sample. Also, new data published for bulk rocks in the
75 Aeolian arc show large $\delta^{37}\text{Cl}$ difference between Stromboli lavas (-0.96 to +0.69‰; Liotta et
76 al., 2017) and Stromboli OHMIs (-3.2 to -1.75‰; Manzini et al., 2017). In order to
77 understand the large variations and assess how representative the $\delta^{37}\text{Cl}$ values recorded in
78 OHMIs are, this study couples $\delta^{37}\text{Cl}$ data obtained by Manzini et al. (2017) with $\delta^{11}\text{B}$ and
79 $\delta^{18}\text{O}$ obtained in the same OHMIs. In addition, new Cl, B and O data from two additional arcs
80 (Izu-Bonin and NE Japan) have been acquired. Oxygen isotopes do not largely fractionate
81 during dehydration at high temperature (e.g., Liebscher et al., 2006; Schauble et al., 2003;
82 Zheng, 1993). Comparison of these two isotopic systems allows sediment vs.
83 AOC/serpentinite influences to be identified. In contrast to O and Cl isotopes, B isotopes
84 largely fractionate during dehydration (e.g., Ishikawa & Nakamura, 1994; Peacock & Hervig,
85 1999), complicating the data interpretation due to the lack of B isotope partitioning data in the
86 different phases involved. However, B isotopes have the potential to distinguish between
87 AOC and serpentinites end-members as their respective bulk rocks are different (Boschi et al.,
88 2013; Chaussidon & Jambon, 1994; Smith et al., 1995; Vils et al., 2009). This unique dataset
89 combining Cl isotopes with two other stable isotope systems in melt inclusions is used to
90 assess if variations of $\delta^{37}\text{Cl}$ in melt inclusions within a sample represent heterogeneities in a
91 single, major, Cl reservoir, or alternatively reflect that Cl is added to the mantle wedge from
92 different sources. Disparities between the whole rocks and OHMIs are also discussed in terms
93 of analytical artefacts and/or fractionation due to diffusion.

94

95 **2. Geological context and sample descriptions**

96 All samples were previously studied and their geological settings are well-known. They
97 were chosen as they contain glassy OHMIs with basaltic compositions, potentially providing
98 access to Cl-undegassed melts. The different arcs have been chosen to represent various
99 amounts of fluids involved in their magma genesis (see section 2.1). They are thus suitable
100 samples to test whether $\delta^{37}\text{Cl}$, coupled with other isotopic systems, could be a useful tracer of
101 Cl sources and the fate of Cl in subduction zones.

102 *2.1. Melt inclusions from previous studies*

103 OHMIs from St. Vincent (Lesser Antilles arc), Vulcano (Aeolian arc) and Aoba (Vanuatu
104 arc) are the same as those reported by Manzini et al. (2017). OHMIs from Iwate Volcano (NE
105 Japan arc) were analyzed for volatiles by Rose-Koga et al. (2014). Nomenclature of each
106 OHMI is identical to their original papers.

107 The intra-oceanic volcanic arc of the Lesser Antilles arc is generated by the subduction of
108 the Atlantic Plate beneath the Caribbean Plate (see Macdonald et al., 2000 for a review).
109 Analyzed OHMIs were separated from a lapilli deposit collected near Troumaka Bay, in St.
110 Vincent, where high-MgO basalts occur. Based on B isotopes, Bouvier et al. (2008) suggested
111 that fluids involved in the magma genesis are derived from serpentinites, sediments and AOC.
112 The Aeolian arc is related to the subduction of the Ionian-Adriatic lithosphere underneath the
113 Calabrian arc. Mantle beneath the Aeolian arc volcanoes has been metasomatised by fluids
114 from the Ionian oceanic crust and the sediments from the Ionian basin in the eastern part of
115 the arc (Peccerillo et al., 2013). The selected OHMIs come from La Sommata scoria cone on
116 Vulcano Island. OHMIs from Stromboli, analyzed for $\delta^{37}\text{Cl}$ by Manzini et al. (2017), were
117 not included in this study as they were too small to undergo further analysis.

118 The Vanuatu arc is generated by the northeastward subduction of the Australian Plate
119 beneath the Pacific Plate. The selected olivine crystals come from three different lapilli layers

120 of Aoba Island (Ao3 from an eruptive fissure on the volcano north flank; Ao15 from Torgil
121 tuff ring; and Ao17 from Red Cliff pyroclastic sequence; Sorbadere et al., 2011). Slab fluids
122 beneath Aoba involved fluids derived from serpentinites (Métrich and Deloule, 2014).

123 NE Japan arc is generated by the subduction of the Pacific Plate beneath the Okhotsk
124 Plate. The sample, coming from arc front Iwate Volcano, was studied by Rose-Koga et al.
125 (2014). These authors showed that fluids from the slab beneath Iwate Volcano are derived
126 from AOC and sediments. The selected OHMIs have already been analyzed for major and
127 volatiles elements, and Pb isotopes, and have been chosen based on their size – they have to
128 be large enough to place a $\delta^{37}\text{Cl}$ SIMS spots in between previous SIMS spots.

129

130 *2.2. New melt inclusions from Izu-Bonin arc*

131 New data for OHMIs from a sample collected from the Sukumoyama scoria cone in the
132 Higashi-Izu Monogenetic Volcano Field (HIMVF), on the northeastern Izu Peninsula, were
133 used in this study. The Izu-Bonin arc is an intraoceanic arc generated by the subduction of the
134 Pacific Plate beneath the Philippine Sea Plate. Since 15 Ma, the Izu-Bonin arc has been
135 colliding with the Honshu Arc in central Japan to form the Izu collision zone. OHMIs from
136 sample IZ27-15 on Sukumoyama were analyzed previously for major, volatile and trace
137 elements (Nichols et al., 2012). Compositional variations were suggested to reflect interstitial
138 melts within the crystal mush of the magma chamber experiencing distinct crystallization
139 histories and variability between contributions from fluid and sediment melt components in
140 the source. For this study, new OHMIs were polished and analyzed from the same sample
141 used by Nichols et al. (2012).

142 **3. Methods**

143 Olivine crystals from the 0.5-1 mm grain size fraction of crushed scoria were hand-picked
144 under a binocular microscope and embedded in epoxy. Olivine crystals containing naturally
145 glassy OHMIs were polished individually in order to expose the OHMI on the surface. Most
146 OHMIs contain a shrinkage bubble, but none contain daughter minerals. Each polished
147 olivine was removed from epoxy and pressed into indium, along with various reference
148 materials for secondary ion mass spectrometry (see below). Each analytical method applies
149 for all OHMIs.

150 *3.1. Electron microprobe (EMPA)*

151 Major element compositions of the MIs and their host olivine were acquired by electron
152 microprobe (EMPA) using a JEOL 8200 Superprobe. For the MIs, analytical conditions were
153 15kV, 10nA current and a 5 μm beam while conditions were 15kV, 15 nA, 1 μm , for the
154 olivine host. Peak counting times were 30 s on all elements, except for K, Na and Ca (20 s).
155 Backgrounds were counted for 15 or 10 s (Si, Fe, Na, Ca, K). Cl was determined by EMPA
156 only in OHMIs analyzed by Manzini et al. (2017); for other OHMIs, Cl content was measured
157 using SIMS. For the MIs, the KL2-G glass standard (Jochum et al., 2006) was used to
158 calibrate SiO_2 and Al_2O_3 . Other elements were calibrated on different minerals. ML3B-G
159 (Jochum et al., 2006) and San Carlos olivine were used as internal standards to check the
160 calibration.

161 *3.2. Secondary Ion Mass Spectrometry (SIMS)*

162 Boron, Cl and O isotope ratios were measured by secondary ion mass spectrometry
163 (SIMS) using the CAMECA IMS 1280-HR at the SwissSIMS laboratory (University of
164 Lausanne, Switzerland). A 1.5-2 nA, 10 kV Cs^+ primary beam was used to analyze Cl and O
165 isotope ratios, over two different sessions. The electron flood gun, with normal incidence, was
166 used to compensate charges. For $\delta^{37}\text{Cl}$, the analytical method was the same as described in

167 Manzini et al. (2017). To summarize, a pre-sputtering of 240 s with a 25 μm raster size was
168 used in order to remove all the possible Cl contamination. Analysis time was 240 s with a 10
169 μm raster. $^{35}\text{Cl}^-$ and $^{37}\text{Cl}^-$ were measured simultaneously on two Faraday cups (FCs), using
170 $10^{11} \Omega$ resistors, with a mass resolving power (MRP) set to ~ 3000 . The internal uncertainty
171 (single measurement) for the samples was 0.15-0.5‰ (two standard errors, 2 s.e.), depending
172 on the Cl content. Reproducibility (point to point) was checked using an in-house Cl-enriched
173 standard UNIL_GI-B7. Reproducibility of UNIL_GI-B7 over eight points at the beginning of
174 each session was $<0.2\%$ (two standard deviations, noted 2 SD hereafter), but up to 0.35‰
175 2SD over a session (24-36h; two measurements of UNIL_GI-B7 every six unknowns).
176 Instrumental mass fractionation (IMF), depending on Si, K, and Al mole content of the
177 glasses was calibrated using six glass standards (Manzini et al., 2017), including UNIL-GI-B7
178 at the beginning of each session (SM 2A). To that purpose, UNIL_GI-B4, UNIL_GI-B6,
179 RMR, PR2 and IB94 were measured four times at the beginning of each session, with two
180 measurements of UNIL_GI-B7 in between each different glasses. To ensure the validity of the
181 calibration over the session and determine the uncertainty of the calibration, UNIL_GI-B6 and
182 UNIL_GI-B4 were measured repeatedly over the session. A reproducibility of 0.3‰ and a
183 maximum uncertainty of 0.4‰ were calculated. The IMF applied to each OHMIs was
184 calculated based on their major element composition, measured by EMPA before the SIMS
185 sessions. $\delta^{37}\text{Cl}$ is referenced to the standard mean ocean chloride (SMOC) $^{37}\text{Cl}/^{35}\text{Cl}$ ratio of
186 0.319592.

187 The Cl content of each OHMI could be estimated based on the ^{35}Cl count per second
188 normalized to the primary beam intensity and compared to the standards. As the estimation by
189 SIMS gives satisfactory results for Cl content <3000 ppm (SM 2B), SIMS was used to
190 estimate the Cl contents of the new Sukumoyama OHMIs, which should have relatively low
191 Cl contents based on those previously analyzed (Nichols et al., 2012).

192 ^{16}O and ^{18}O secondary ions were analyzed at 2400 MRP and collected on two FCs in
193 multi-collection mode using 10^{10} and 10^{11} Ω resistors, respectively. The FCs were calibrated
194 at the beginning of the session, using the calibration routine. Mass calibration was performed
195 at the beginning of each session (<12h). Each analysis takes ~4 minutes, including pre-
196 sputtering (30 s) and automated centering of secondary electrons. Ion mass fractionation was
197 calibrated using several standards with different major element compositions (SM 2C).
198 Reproducibility of the standards is better than 0.3‰. $\delta^{18}\text{O}$ is referenced to the standard mean
199 ocean water (SMOW) $^{18}\text{O}/^{16}\text{O}$ ratio of 2005.2×10^{-6} .

200 To determine $\delta^{11}\text{B}$, ^{10}B and ^{11}B were measured in multicollection mode, using two electron
201 multipliers. The O^- primary beam intensity was 8 nA and mass resolution was set at 2400. A
202 single analysis (60 cycles) took 16 minutes. The instrumental isotopic fractionation was
203 determined by analyzing five standards with different major element compositions (SM 2D).
204 As already reported in the literature, instrumental isotopic fractionation was observed to be
205 independent of major element composition (Rosner et al., 2008). Reproducibility on the
206 standards varies from 2 to 4‰ (2SD), depending on the B content of individual melt
207 inclusions. $\delta^{11}\text{B}$ is referenced to the NBS 951 $^{11}\text{B}/^{10}\text{B}$ ratio of 4.044.

208 Amongst the standards used for $\delta^{11}\text{B}$ and $\delta^{18}\text{O}$ calibrations, BHVO-2G and BCR-2G, with
209 compositions encompassing those of our OHMIs, were also included in the sample mounts, as
210 well as in the standard mount. During the session measuring $\delta^{18}\text{O}$ and $\delta^{11}\text{B}$, several analyses
211 of BHVO-2G and BCR-2G were undertaken before and after a maximum of 18 unknowns to
212 monitor instrument stability (i.e., magnetic field stability). These standards were also treated
213 as unknowns to check the accuracy of the calibration. Accuracies were similar to
214 reproducibility: 0.3‰ for $\delta^{18}\text{O}$ and 3‰ for $\delta^{11}\text{B}$.

215

216 **4. Results**

217 *4.1. Elemental geochemistry of melt inclusions*

218 All major elements, as well as details of the post-entrapment crystallization (PEC)
219 corrections are reported in SMs 3-4. Compared to whole rocks from each locality, OHMIs
220 plot at the primitive end of the differentiation trends (SM 5), and have basanite to basaltic
221 compositions (Figure 2). The OHMIs from the different settings define distinct trends that
222 show variable alkali enrichment, with some of St. Vincent OHMIs being the most alkali-rich,
223 and those from Iwate Volcano, NE Japan arc, the most alkali-poor.

224 Manzini et al. (2017) showed that the highest and most variable Cl contents are in OHMIs
225 from Aoba (0.06 to 0.39 wt%) and Vulcano (0.14 to 0.44wt%) islands, whereas in St. Vincent
226 samples the range is more restricted (0.08 to 0.15 wt%). Rose-Koga et al. (2014) reported
227 0.03 to 0.05 wt% for Iwate OHMIs. The new data for OHMIs from Sukumoyama provide Cl
228 contents from 0.04 to 0.09 wt%, similar to the values published by Nichols et al. (2012).

229 *4.2. Stable isotope compositions*

230 4.2.1. Chlorine isotopes

231 All stable isotope compositions are reported in Table 1. The six new data from Iwate
232 Volcano range from $-2.1 \pm 0.8\text{‰}$ (2 s.e.) to $0.5 \pm 0.8\text{‰}$ (2 s.e.) (average of -1‰), similar to St.
233 Vincent and Aoba OHMIs. The nine data from Sukumoyama OHMIs show distinct values
234 compare to Iwate Volcano OHMIs, ranging from $-4.4 \pm 0.5\text{‰}$ (2 s.e.) to $-1.6 \pm 0.4\text{‰}$ (2 s.e.)
235 (average of -2.3‰), more similar to Vulcano. As for Vulcano OHMIs, Cl isotopes for
236 Sukumoyama OHMIs can be compared to $\delta^{37}\text{Cl}$ bulk rock values. Indeed, lavas from two
237 volcanoes, Oshima and Niijima, located relatively close to Sukumoyama, at the northern end
238 of Izu-Bonin arc have been measured for $\delta^{37}\text{Cl}$ (Barnes et al., 2008). Oshima and Niijima

239 lavas have significantly higher Cl isotope compositions (-0.28‰ and -0.77‰, respectively)
240 compared to Sukumoyama OHMIs.

241 The lowest $\delta^{37}\text{Cl}$ value measured for a Sukumoyama OHMI, $-4.4\pm 0.5\%$ (2 s.e.), is the
242 lowest measured for any OHMI to date and also lower than bulk rock values for solid
243 geological samples (Figure 1). This value has been carefully checked to assess its validity: all
244 SIMS analytical conditions are similar to other MIs measurements (secondary deflectors,
245 primary intensity, topography, etc). Despite the fact that this inclusion also has the lowest Cl
246 content of Sukumoyama MIs (400 ppm), analytical artefact due to low Cl content is
247 discarded: internal error (counting statistic of a single measurement; 0.5‰, 2 s.e.) is similar to
248 the internal error of other OHMIs from this sample. Additionally, some Iwate OHMIs have as
249 low as, or even lower, Cl contents (300-400 ppm) and yet $\delta^{37}\text{Cl}$ for these inclusions is in the
250 range of published values (-1.6 to +0.5‰). Hence the value is considered to be reliable.

251 4.2.2. Boron isotopes

252 The lowest $\delta^{11}\text{B}$ values have been measured in the St. Vincent OHMIs, with values
253 ranging from -18.5 ± 1.9 to $+11.7\pm 1.9\%$ (2 s.e.) (average: +3.6‰). This range, similar to the
254 range previously reported for St. Vincent OHMIs (-25.6 to +11.8‰, average 0.9‰; Bouvier
255 et al., 2008) is by far the largest range of $\delta^{11}\text{B}$ values reported for a group of OHMIs in this
256 study. $\delta^{11}\text{B}$ range from -9.5 ± 1.9 to $-1.0\pm 2.1\%$ (2 s.e.) (average: -5‰) for the Vulcano
257 OHMIs. Aoba OHMIs have positive $\delta^{11}\text{B}$ values (+3.4 to +12.0, average of +7‰), higher than
258 the values reported for MIs from two other Aoba samples (-11.9 to +6.4‰; Métrich and
259 Deloule, 2014). Sukumoyama OHMIs have variable $\delta^{11}\text{B}$ values, ranging from $-4.8\pm 4\%$ to
260 $+5.8\pm 4\%$ (2 s.e.) (average: 1.7‰). Iwate Volcano OHMIs have a restricted range of positive
261 $\delta^{11}\text{B}$ values ($+4.7\pm 1.7\%$ to $+8.1\pm 2\%$; average: 6.3‰).

262 4.2.3. Oxygen isotopes

263 The $\delta^{18}\text{O}$ varies from 4.3 ± 0.4 to $6.9\pm 0.4\%$ (2 s.e.), with an average of 5.8% for the St.
264 Vincent OHMIs, similar to the average (6.0%) $\delta^{18}\text{O}$ reported by Bouvier et al. (2008). Aoba
265 OHMIs have a similar range of $\delta^{18}\text{O}$ composition, from 4.4 ± 0.2 to $7.0\pm 0.2\%$ (2 s.e.)
266 (average: 6.3%); and Sukumoyama OHMIs also have a similar range of $\delta^{18}\text{O}$ (4.8 ± 0.3 to
267 $7.4\pm 0.3\%$, 2 s.e.), but with slightly higher average (6.6%). In contrast, Iwate Volcano OHMIs
268 have slightly lower $\delta^{18}\text{O}$ values of 3.9 ± 0.3 to $6.6\pm 0.3\%$ (2 s.e.), with an average of 5.4% .
269 Vulcano OHMIs have the highest $\delta^{18}\text{O}$ measured in this study. They vary from 6.1 ± 0.2 to
270 $9.1\pm 0.2\%$ (2 s.e.), with an average value of 7.9% .

271

272 **5. Discussion**

273 *5.1. Significance of $\delta^{37}\text{Cl}$ variation in OHMIs within a sample*

274 Manzini et al. (2017) reported the first data of $\delta^{37}\text{Cl}$ in OHMIs from arc settings and
275 showed that Cl isotopes can vary by up to 2.5% within a single sample (St. Vincent). Here,
276 the OHMIs from two new samples from Iwate Volcano and Sukumoyama have variations in
277 $\delta^{37}\text{Cl}$ of 2.6 and 2.8% , respectively, further confirming that relatively large variations ($>2\%$)
278 in Cl isotopes within OHMIs from a single sample might be common. Given the large range
279 of $\delta^{37}\text{Cl}$ in terrestrial Cl reservoirs (Figure 1), the measured variation in OHMIs within a
280 sample could reflect either heterogeneity of a single Cl reservoir, or contributions from
281 different Cl reservoirs. To better understand the variability of $\delta^{37}\text{Cl}$ within a sample, O and B
282 isotopes were measured in the same OHMIs. As mentioned in the introduction, comparison
283 with O isotopes could help to distinguish between the influence of fluids from sediments and
284 the influence of fluids from AOC/serpentinites, whereas B isotopes may differentiate between
285 fluids from AOC and serpentinites.

286 5.1.1. Are the measured $\delta^{37}\text{Cl}$ representative of the source?

287 Before any interpretation of source process(es), it is important to evaluate several potential
288 processes that can disturb the measured $\delta^{37}\text{Cl}$. First, we ensured that the selected OHMIs have
289 not degassed Cl. In a plot of SiO_2 vs. Cl content of the OHMIs (Figure 3), within each sample
290 Cl remains constant over the SiO_2 variation. This suggests that Cl is not degassing from the
291 melts as they were trapped.

292 Analytical artefacts were also investigated. Uncertainty in the calibration for Cl isotopes is
293 0.4‰ (2SD), smaller than the observed variation within a sample ($> 2\%$) or between samples.
294 The absence of correlation between $\delta^{37}\text{Cl}$ and SiO_2 (Figure 4A) and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ (Figure 4B)
295 illustrate that the different $\delta^{37}\text{Cl}$ measured in Vulcano and Sukumoyama OHMIs compared to
296 other OHMIs (Fig. 1) is not an analytical artefact. Indeed, OHMIs from these two samples
297 have different Cl contents (>3000 ppm and <1000 ppm, respectively) and major element
298 compositions (Figure 2, SMs 3 to 5). Since calibrations were made with the same standards
299 for all samples, and that OHMIs are corrected for IMF using their own major element
300 compositions, it cannot be argued that the low $\delta^{37}\text{Cl}$ values in the OHMIs are induced by
301 analytical bias. The absence of correlation between $\delta^{37}\text{Cl}$ and SiO_2 and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ within a
302 sample (Figure 4) also suggests no fractionation of $\delta^{37}\text{Cl}$ during magmatic evolution or due to
303 variable degrees of melting.

304 We have also evaluated the effects of secondary processes (e.g, PEC, shrinkage bubble).
305 Given that Cl is an ultra-trace element (<1 ppm) in magmatic olivine (e.g., Urann et al., 2017),
306 late crystallization of olivine on the wall of OHMIs should not strongly affect the Cl
307 composition and Cl isotopes of OHMIs. This is verified by the absence of any relationship
308 between $\delta^{37}\text{Cl}$ and the extent of PEC. Shrinkage bubbles can contain volatile elements, mostly
309 CO_2 (e.g., Moore et al., 2015). So far, Cl content in such bubbles have not been determined.
310 Most of the OHMIs analyzed here have a shrinkage bubble inside. Several olivines contain

311 two or three OHMIS, but only one olivine contains two OHMIs with one containing a bubble
312 and the other not (Aoba 3-1a and b). The one without bubbles contain 300 ppm less Cl than
313 the one with a bubble, but the two OHMIs have similar $\delta^{37}\text{Cl}$, within error (-0.5 ± 0.2 and -
314 $0.7\pm 0.2\%$; SMs 3-4). Also, within a sample, the range of Cl content and $\delta^{37}\text{Cl}$ are similar for
315 OHMIs with or without a shrinkage bubble. We thus conclude that the presence of a
316 shrinkage bubble does not affect Cl isotopes of OHMIs. This is further confirmed by the
317 absence of a correlation between $\delta^{37}\text{Cl}$ and Cl/K₂O (Figure 5), suggesting no Cl degassing
318 syn- or post-entrapment. Also, Cl is not affected by diffusive re-equilibration through the host
319 olivine (Bucholz et al., 2013). All this information suggests that the measured $\delta^{37}\text{Cl}$ are
320 representative of the melt in which the olivine grew.

321

322 5.1.2. Cl and O isotope systematics

323 In a plot of Cl isotopes compared to O isotopes, AOC and serpentinite fields are distinct
324 from the field for sediments (Figure 6 and references in the caption). Oxygen isotope
325 fractionation between hydrous minerals and fluids at high temperature is relatively small (for
326 example, at 500°C, $\sim -1.5\%$ for serpentinite, amphibole; Zheng, 1993). Also, Cl isotopes in
327 metamorphosed serpentinites and AOC are similar to those in fresh corresponding lithologies,
328 suggesting that $\delta^{37}\text{Cl}$ do not fractionate in fluids during the dehydration of mafic lithologies
329 (Barnes et al., 2006; Bonifacie et al., 2008; John et al., 2011). Thus, the Cl-O isotope
330 systematics in the OHMIs from each location have been compared to these end-members
331 (Figure 6). In all the data taken together, Cl isotopes are negatively correlated with O
332 isotopes, with the lowest $\delta^{37}\text{Cl}$ observed in OHMIs with highest $\delta^{18}\text{O}$ and vice versa. In detail,
333 the OHMIs from St. Vincent and Iwate Volcano display a negative relationship, whereas no
334 systematic could be described for those from Vulcano, Aoba and Sukumoyama. There is

335 greater variation in $\delta^{18}\text{O}$ data at low $\delta^{37}\text{Cl}$ ($< -1.6\text{‰}$). The lowest bulk $\delta^{37}\text{Cl}$ (down to -3‰)
336 and the highest bulk $\delta^{18}\text{O}$ ($> 9\text{‰}$) have been observed in fresh sedimentary rocks, suggesting
337 that the low $\delta^{37}\text{Cl}$ ($< -2\text{‰}$) associated with high $\delta^{18}\text{O}$ ($> 7\text{‰}$) in the OHMIs do probably reflect
338 the influence of fluids derived from sediments. The increased scatter of the OHMIs toward
339 this end-member could be explained by the large range of subducted sediment compositions
340 (carbonates, silicic sediments, shales, e.g., Bindeman, 2008 for a review).

341 High $\delta^{37}\text{Cl}$ ($> 0.5\text{‰}$) associated with low $\delta^{18}\text{O}$ ($< 5.5\text{‰}$) point toward an AOC or
342 serpentinite end-member. In detail, the coupled $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$ values reported for fresh
343 serpentinite rocks formed at more than 100°C suggest that $\delta^{18}\text{O}$ increases with $\delta^{37}\text{Cl}$ in
344 serpentinites (Bonifacie et al., 2008; Boschi et al., 2013). A fluid derived from fresh oceanic
345 serpentinites would have a $\delta^{18}\text{O}$ value 1.8‰ higher than the bulk rock it is derived from
346 (Zheng, 1993) considering serpentinite dehydration at $\sim 680^\circ\text{C}$ (antigorite breakdown, e.g.,
347 Trommsdorff et al., 1998). Thus, a fluid escaping a serpentinite with $\delta^{37}\text{Cl}$ of $\sim 1\text{‰}$ and $\delta^{18}\text{O}$
348 from 4.5 to 7‰ , based on the literature, will have a $\delta^{18}\text{O}$ composition $> 6.3\text{‰}$. Such $\delta^{18}\text{O}$ is
349 too high to explain the highest $\delta^{37}\text{Cl}$ end-member influencing the compositions of three out of
350 four of the OHMIs with $\delta^{37}\text{Cl} > 0\text{‰}$. Subducted serpentinites with higher $\delta^{37}\text{Cl}$ have been
351 reported (up to 2.4‰ , Barnes et al., 2006, 2013, 2014). In subducted serpentinite samples for
352 which $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$ have been determined, the same tendency of $\delta^{37}\text{Cl}$ to increase with $\delta^{18}\text{O}$
353 is observed (Barnes et al., 2014), leading to a similar conclusion as for the fresh oceanic
354 serpentinites: a fluid escaping high $\delta^{37}\text{Cl}$ subducted serpentinites might have a $\delta^{18}\text{O}$ too high
355 to explain the composition of OHMIs with $\delta^{37}\text{Cl} > 0\text{‰}$. AOC, especially high temperature
356 altered portions, have high $\delta^{37}\text{Cl}$ (up to $+1.6\text{‰}$; Barnes and Cisneros, 2012) and could have
357 low $\delta^{18}\text{O}$ (down to 3‰ for the bulk rock (Alt & Bach, 2006); even as low as 0‰ for
358 amphibole veins (Muehlenbachs, 1986)). If we assume a temperature of dehydration for

359 amphibole of ~500°C (blueschist – eclogite transition), a dehydration fluid from amphibole
360 veins would have $\delta^{18}\text{O}$ ~1.7‰ higher than the dehydrating lithology/mineral (Zheng, 1993).
361 Thus, local dehydration fluids from lower AOC could have $\delta^{18}\text{O}$ values as low as 1.7‰,
362 making amphibole-bearing AOC a more suitable candidate for the high $\delta^{37}\text{Cl}$ - low $\delta^{18}\text{O}$ end-
363 member of the correlation. However, in detail, the Aoba OHMIs do not follow the general
364 trend and might also point toward a serpentinite fluid end-member.

365 Following this reasoning, Vulcano and Sukumoyama OHMIs, with lower $\delta^{37}\text{Cl}$ and
366 higher $\delta^{18}\text{O}$ than MORB (Sharp et al., 2007), possibly record the strongest influence from
367 sediment derived fluids. St. Vincent and Iwate Volcano OHMIs, which have $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$
368 both higher and lower compared to DMM, suggest that melts were influenced by a fluid
369 possibly derived from the lower AOC and also some sediments. Aoba OHMIs also have both
370 higher and lower $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$ compared to DMM, suggesting influence from sediment
371 fluids and AOC or serpentinite fluids.

372 It is important to note that contrary to the possible AOC and/or serpentinite end-member,
373 which does not seem to have suffered fractionation of Cl isotopes during dehydration, as
374 previously suggested (Barnes et al., 2006; Bonifacie et al., 2008; John et al., 2011; Schauble
375 et al., 2003), the sediment end-member probably has fractionated at some point, as some
376 OHMIs have $\delta^{37}\text{Cl}$ values lower than the lowest $\delta^{37}\text{Cl}$ reported for bulk sediments. This
377 observation agrees with John et al. (2010), who suggest preferential loss of ^{35}Cl from
378 sediments into pore fluids, even at high temperature, leads to enrichments in $\delta^{37}\text{Cl}$ in recycled
379 subducted marine sediments.

380 5.1.3. Cl and B isotope systematics

381 The distinction between AOC and serpentinite derived fluids is not unique due to their
382 similar $\delta^{18}\text{O}$ and $\delta^{37}\text{Cl}$. Here, we investigate whether they can be distinguished in terms of

383 their Cl-B isotope systematics (Figure 7). To date, Cl isotopes have not been coupled with B
384 isotopes in the same rock samples. Fields for the different lithologies were thus assembled
385 from different samples and different settings. Cl isotope values are given in SM 1. For B
386 isotopes, sediment values are from Smith et al. (1997) and Ishikawa and Nakamura (1993);
387 The AOC values are from Smith et al. (1995), and serpentinite values are from Boschi et al.
388 (2013) and Vils et al. (2009). For reference, the MORB field is also plotted using the data for
389 $\delta^{11}\text{B}$ from Chaussidon and Jambon (1994) and for $\delta^{37}\text{Cl}$ from Sharp et al. (2007).

390 Boron isotopes fractionate strongly during dehydration, with ^{11}B partitioning
391 preferentially into the fluid phase (e.g., Peacock & Hervig, 1999; Ishikawa & Nakamura,
392 1994). Thus, B isotopes of the rock reservoirs cannot be directly compared to MI data. A
393 simple open system Rayleigh distillation is used to estimate the theoretical composition of the
394 dehydration fluids (Bouvier et al., 2010; Rose et al., 2001). For these calculations, B isotope
395 fluid-rock partition coefficients of 3-5 ‰ for serpentinites (Tenthorey and Hermann, 2004);
396 and 5‰ for AOC and sediments (You et al., 1996) were used.

397 There is no simple relationship between Cl and B isotopes for the OHMIs (Figure 7).
398 Instead, for the whole dataset, different end-members are needed to explain the variations of
399 $\delta^{11}\text{B}$ and $\delta^{37}\text{Cl}$ in OHMIs. A first fluid end-member with $\delta^{11}\text{B} > 12\text{‰}$ and $\delta^{37}\text{Cl}$ between -2
400 and -0.5‰ could be described, most probably representing the influence of fluids derived
401 from serpentinite dehydration. Indeed, amongst the three major Cl reservoirs shown in Figure
402 7, serpentinite rocks form the reservoir with the highest $\delta^{11}\text{B}$. Based on the Rayleigh
403 distillation calculation, a fluid derived from the dehydration of serpentinites with an initial
404 average $\delta^{11}\text{B}$ composition of 20‰ (Figure 5) would have $\delta^{11}\text{B}$ down to ~15‰ after 75% of B
405 loss from serpentinite.

406 A second end-member can be described by higher $\delta^{37}\text{Cl}$ (>1‰) and lower $\delta^{11}\text{B}$ (<~4‰).
407 High $\delta^{37}\text{Cl}$ have been reported for AOC with a lithology containing amphiboles (Barnes and

408 Cisneros, 2012) or for metamorphosed serpentinites (Barnes et al., 2014). Based on Figure 6,
409 OHMIs with $\delta^{37}\text{Cl} > 0\text{‰}$ most likely record the influence of fluids released from amphibole
410 bearing- lower AOC. If an influence from an AOC dehydration fluid is assumed, with initial
411 AOC average B isotopes composition of 3‰, $\delta^{11}\text{B}$ of $\sim 4\text{‰}$ would suggest that a fluid
412 escaping from an AOC lithology would have lost $\sim 50\%$ of B.

413 Finally, the last end-members most probably represent fluids from the subducted
414 sediments, as suggested by Figure 6. Indeed, the lowest $\delta^{37}\text{Cl}$ are measured in sedimentary
415 rocks (Figure 1). Likewise, extremely low $\delta^{11}\text{B}$ ($< -15\text{‰}$) measured in OHMIs are generally
416 associated with the influence of fluids lost by dehydrated sediments - be they melts or fluids -
417 derived from such a lithology (e.g., Bouvier et al., 2010; Rose et al., 2001). Interestingly,
418 Sukumoyama and Vulcano OHMIs seem to require two distinct sediment end-members, as in
419 Figure 6 (thus OHMIs with similar $\delta^{37}\text{Cl}$, but different $\delta^{18}\text{O}$ and $\delta^{11}\text{B}$). This distinction could
420 reflect different degrees of dehydration of the sediment lithology. However, due to the
421 relatively small fractionation factor for O isotopes in the fluid at high temperature (650°C , -
422 0.4 and 1.8‰ for quartz and calcite; Zheng et al., 1993, 1999), different degrees of
423 dehydration of similar sediment lithologies would not explain the different $\delta^{18}\text{O}$ of Vulcano
424 and Sukumoyama OHMIs. When compared to sediment bulk rock data, continental sediments
425 have lower $\delta^{11}\text{B}$ than marine sediments (Ishikawa and Nakamura, 1993). Similarly, marine
426 sediments have higher $\delta^{18}\text{O}$ compared to continental sediments (see Bindeman et al., 2008 for
427 a review). Simple Rayleigh distillation of marine sediment with an average initial composition
428 of 5‰ suggest 85% B loss to reach a fluid end-member with an average composition of 0‰.
429 Similarly, an average composition of -8‰ for continental sediments would lead to
430 dehydration fluids with a composition of -14‰ after 90% B loss. Whereas sediments being
431 subducted in the Aeolian arc are mostly continental (dust from Sahara and clastic sediments
432 from river Nile; Klaver et al., 2015), sediments subducted in the Izu-Bonin arc, where

433 Sukumoyama is located, are mainly composed of marine sediments (ODP leg 1149; Plank et
434 al., 2007) or clays (ODP leg 808; Plank and Langmuir, 1998), both of which have higher $\delta^{18}\text{O}$
435 than continental sediments. Oxygen, B and Cl isotopes all point toward two distinct sediment
436 end-members that are coherent with the tectonic settings of Vulcano and Sukumoyama. Boron
437 isotopic variability within each sediment end-member could represent variable degrees of
438 dehydration or variable compositions of the subducted sediments. John et al. (2010) suggested
439 that dehydrated subducted marine sediments could have $\delta^{37}\text{Cl}$ up to +4‰ (2‰ higher than
440 highest measured values for fresh sediments, SM 1) due to Cl isotope fractionation during
441 dehydration. Thus, a fluid derived from the dehydration of sediment with $\delta^{37}\text{Cl}$ as low as -5‰
442 would suggest a similar, but opposite as in fluid and not in solid, fractionation than suggested
443 by John et al. (2010) (2.5‰ lower than lowest measured values for fresh sediments).

444 Combining B, O and Cl isotopes might thus allow better identification of different Cl
445 reservoirs (serpentinites vs. AOC; marine vs continental sediments) involved in magma
446 genesis beneath arcs. Whereas the serpentinite reservoir cannot be easily identified in the O
447 and Cl isotopes system, it can be distinguished from AOC in the B and Cl isotopes system.
448 Similarly, influence of marine vs. terrigenous sediments seems to be more easily tracked in B
449 and Cl isotope systems.

450 5.1.4. Implications for the significance of $\delta^{37}\text{Cl}$ variability

451 Based on Figures 6 and 7, St. Vincent and Aoba mostly vary between AOC and
452 serpentinite dehydration fluid end-members, suggesting a more pronounced influence from
453 AOC and serpentinite fluids, compared to sediment fluids. Sediment fluids for St. Vincent can
454 be marine and/or continental. The influence of three fluid end-members agrees with previous
455 studies (Bouvier et al., 2008, 2010), and the suggested marine and continental sediments
456 agrees with the sediment composition of the Barbados prism (Carpentier et al., 2008). Aoba

457 OHMIs also seem to reflect the mixed influence of AOC and serpentinite fluids, and a marine
458 fluid sediment component. Vulcano and Sukumoyama OHMIs record the strongest sediment
459 influence, with a possible influence from serpentinite fluids to explain the scatter. Iwate
460 Vulcano OHMIs follow the Cl-O isotopes trend (Figure 4) suggesting the influence of both
461 AOC and sediment fluids, in agreement with Pb isotope measurements on Iwate Vulcano
462 OHMIs (Rose-Koga et al., 2014). This is confirmed in Figure 7, with $\delta^{11}\text{B}$ suggesting an
463 influence from marine sediments.

464 Overall, these observations, based on the Cl-O-B isotope systematics, are consistent with
465 the geological settings of the volcanoes that have been sampled and suggest that variability
466 within a sample reflects multiple reservoirs adding Cl to the mantle wedge. Inter-arc
467 variations in $\delta^{37}\text{Cl}$ most probably reflect global differences in the values for the main Cl
468 reservoir (e.g., sediments vs. AOC and/or serpentinites).

469 *5.2. Bulk rock vs. OHMI Cl isotope differences*

470 New low $\delta^{37}\text{Cl}$ ($< -1.5\text{‰}$) are reported here, with Sukumoyama OHMIs having similar
471 $\delta^{37}\text{Cl}$ compositions compared to Vulcano OHMIs. Interestingly, bulk rock values of samples
472 from the same arcs exist and can be compared with OHMI data. Even if bulk rock data are not
473 from the same sample, nor from the same volcanoes, as the OHMIs in this study, nearby
474 volcanoes from the same arc should have similar source(s) of Cl input. For the Aeolian arc,
475 bulk rock data exist for Etna and Stromboli, both having similar $\delta^{37}\text{Cl}$ (-0.96 to 0.69‰ for
476 Stromboli and -0.7 to 0.1 for Etna; Liotta et al., 2017; Rizzo et al., 2013) despite their
477 different magmatic histories (e.g., Tommasini et al., 2007). Also, as described in the
478 introduction, Manzini et al. (2017) reported $\delta^{37}\text{Cl}$ in OHMIs from Stromboli, with values
479 significantly different (-3.2 to -1.75‰) to Stromboli lavas, but similar to Vulcano OHMIs. We

480 thus conclude that bulk rock data from nearby volcanoes (e.g., Stromboli for Vulcano, and
481 Oshima and Niijima for Sukumoyama) could indeed be used to compare to OHMIs.

482 Bulk rock data are clearly different to our OHMI data, with a shift of up to 2‰ and 3.6‰
483 toward lower values for Vulcano and Sukumoyama OHMIs, respectively. As discussed in
484 section 5.1.1., this could not be induced by analytical bias. Rather, the combination of
485 negative $\delta^{37}\text{Cl}$ and $\delta^{11}\text{B}$ associated with elevated $\delta^{18}\text{O}$ suggest that the main source of Cl is
486 from a fluid issued from sediments, as discussed above.

487 Fortin et al. (2017) showed that Cl isotopes could be fractionated by up to 5‰ by Cl
488 diffusion during bubble growth, and potentially more in the case of diffusion not related to
489 bubble growth (depending on time scale). As mentioned by these authors, fractionation by Cl
490 diffusion during the formation of melt inclusions (i.e., via boundary layer entrapment) could
491 not generate lower isotopic compositions, but instead should generate higher $\delta^{37}\text{Cl}$ compared
492 to the initial composition. In section 5.1.1., the migration of Cl into a shrinkage bubble was
493 ruled out. If fractionation due to diffusion of Cl isotopes during shrinkage bubble growth
494 within the OHMIs does occur, it will cause ^{35}Cl to preferentially enter the bubble, leading to
495 $\delta^{37}\text{Cl}$ progressively increasing in the melt (Fortin et al., 2017). In this case, OHMIs should
496 have $\delta^{37}\text{Cl}$ compositions higher than bulk rock, whereas we have observed the opposite. As
497 no correlation has been observed between Cl or Cl/K₂O and $\delta^{37}\text{Cl}$ (Figure 5), the lower $\delta^{37}\text{Cl}$
498 values measured in Vulcano and Sumukoyama OHMIs compared to respective bulk rocks
499 probably do not represent degassing melts. On the contrary, bulk rocks have often suffered
500 some volatile degassing. For example, the Stromboli OHMIs measured for $\delta^{37}\text{Cl}$ have Cl
501 contents from 0.14 to 0.46 wt% (Manzini et al., 2017), whereas bulk rocks only contain 0.03
502 to 0.08 wt% (Liotta et al., 2017). Assuming fractionation due to diffusion of Cl isotopes
503 during bubble growth in the magma (as opposed to shrinkage bubble growth in OHMIs),
504 gases enriched in ^{35}Cl could be created. This will thus create low $\delta^{37}\text{Cl}$ gases and a magma

505 with $\delta^{37}\text{Cl}$ increasing with the increase of degassing. Interestingly, low $\delta^{37}\text{Cl}$ has been
506 measured in Hakone (northern part of Izu-Bonin arc, down to -5.41‰; Barnes et al., 2008)
507 and Stromboli gases (down to -2.2‰; Liotta et al., 2017). OHMIs from Sukumoyama and
508 Vulcano could thus represent relatively primary undegassed melt, whereas the bulk rocks
509 record Cl loss during degassing, enriching the melt in ^{37}Cl due to diffusive fractionation
510 during bubble growth. In that case, the bulk rocks lose the original $\delta^{37}\text{Cl}$ signature of the
511 source of the Cl input.

512 **6. Conclusions**

513 This study expands the dataset of Cl isotopes in OHMIs from arc settings and is the first
514 coupling $\delta^{37}\text{Cl}$ with two other isotopic systems in OHMIs. This dataset suggests that Cl
515 isotopes variation in OHMIs within a single sample most probably record Cl input from
516 different Cl reservoirs, rather than heterogeneity from a single reservoir. Inter-arc variability
517 in $\delta^{37}\text{Cl}$ might reflect differences in the main Cl reservoirs (e.g., larger influences of
518 sediments in some arcs).

519 Indirect comparison of OHMI data from Vulcano and Sukumoyama and bulk rock data
520 from the same arc reveal large (2 to 4‰) differences, with OHMIs having lower $\delta^{37}\text{Cl}$ than
521 bulk rocks. This difference most probably reflects diffusive fractionation of Cl isotopes during
522 degassing of the lavas. OHMIs have relatively primary compositions whereas the bulk lavas
523 have lost the original $\delta^{37}\text{Cl}$ signature during degassing. This conclusion is supported by some
524 low (<0‰) $\delta^{37}\text{Cl}$ gases measured at volcanoes in both arcs.

525 Chlorine isotope measurements by SIMS in MIs could thus provide valuable and unique
526 access to relatively primary (undegassed) $\delta^{37}\text{Cl}$ compositions. Better constraints on the source
527 of Cl is important to better understand the behavior of Cl in different contexts and ultimately,
528 refine the Cl budget.

529

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536

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685

686 **Captions:**

687 Figure 1: Compilation of published $\delta^{37}\text{Cl}$ for terrestrial bulk rocks and olivine-hosted melt inclusions (OHMIs).
688 Sukumoyama and Iwate Volcano OHMIs are new data, the remaining are published data. A summary of the
689 database can be found in SM 1, with all the associated references. OHMIs are plotted using symbols, whereas
690 bulk rocks are represented with bars. Sediments and serpentinite bulk rocks are plotted with dark colors
691 representing fresh rocks, and light colors metamorphic rocks.

692 Figure 2: SiO_2 compared to total alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) (TAS diagram) for OHMIs of St. Vincent (squares),
693 Aeolian islands (triangles), Aoba (diamonds), Sukumoyama (yellow circles) and Iwate (brown circles). The
694 OHMIs have basanitic to basaltic compositions.

695 Figure 3: SiO_2 compared to Cl content in the studied OHMIs. Symbols as in Figure 2. No variation of Cl content
696 with increasing SiO_2 is observed, suggesting Cl is not degassing during OHMIs entrapment.

697 Figure 4: Chlorine isotopes compared to SiO_2 (A) and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ (B) in the OHMIs. No correlation between
698 $\delta^{37}\text{Cl}$ and the major elements are seen, proving that the matrix effect has been corrected. Also, the absence of any
699 correlation suggests that Cl isotopes are not affected by extent of magmatic evolution.

700 Figure 5: Chlorine isotopes compared to Cl/ K_2O ratios. The absence of correlation between $\delta^{37}\text{Cl}$ and Cl/ K_2O
701 supports the absence of Cl degassing at the time of entrapment. Thus, the variation of $\delta^{37}\text{Cl}$ in the OHMIs cannot
702 be linked to degassing.

703 Figure 6: O isotopes compared to Cl isotopes in St. Vincent (squares), Aeolian islands (triangles), Aoba
704 (diamonds), Sukumoyama (yellow circles) and Iwate (brown circles) OHMIs. All OHMIs define a negative
705 relationship between $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$. Sukumoyama and Aeolian OHMIs record the strongest influence from
706 sediment fluids, whereas St. Vincent and Iwate Volcano record fluids derived from the dehydration of both AOC
707 and sediments. Aoba also reflect influences from sediment fluids, and either AOC or serpentinite fluids. Fields
708 for sediments, AOC and serpentinites are based on bulk rock data. Bulk rock O and Cl isotope data were
709 obtained on the same samples only for oceanic serpentinites. Cl isotope data are from the same references as in
710 Figure 1 and SM 1. Oxygen isotope data for AOC are from Alt (2003) and Alt & Bach (2006). Only fresh
711 oceanic serpentinites have been reported here (data for $\delta^{18}\text{O}$ are from Bonifacie et al. (2008) and Boschi et al.
712 (2013)). Fresh sedimentary rock $\delta^{18}\text{O}$ data are from the compilation of Bindeman (2008).

713 Figure 7: B isotopes compared to Cl isotopes. Symbols are as in Figure 5. For comparison, different reservoirs
714 have been plotted (see text for references). As for Figure 4, only fresh sediments and serpentinites have been
715 reported. Reservoirs defined by dashed lines are a compilation of data in which none of the samples have
716 combined $\delta^{11}\text{B}$ and $\delta^{37}\text{Cl}$ measurements. OHMIs suggest the influence of four different fluid end-members, one
717 each for AOC and serpentinites, and two distinct end-members for sediments, one for marine and one for
718 continental sediments.

719

720 Table 1: B, O and Cl isotopes in OHMIs

721

722

723 **Supplementary material**

724 SM1: Database for Cl isotopes in terrestrial bulk rocks and OHMIs

725 SM2: SIMS calibrations

726 SM3: Summary of major element and stable isotopes of OHMIs used in Manzini et al. (2017)

727 SM4: Summary of major elements and stable isotopes of OHMIs from Iwate Volcano and Sukumoyama

728 SM5: Comparison of major element compositions of OHMIs and whole rocks.

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Figure 1
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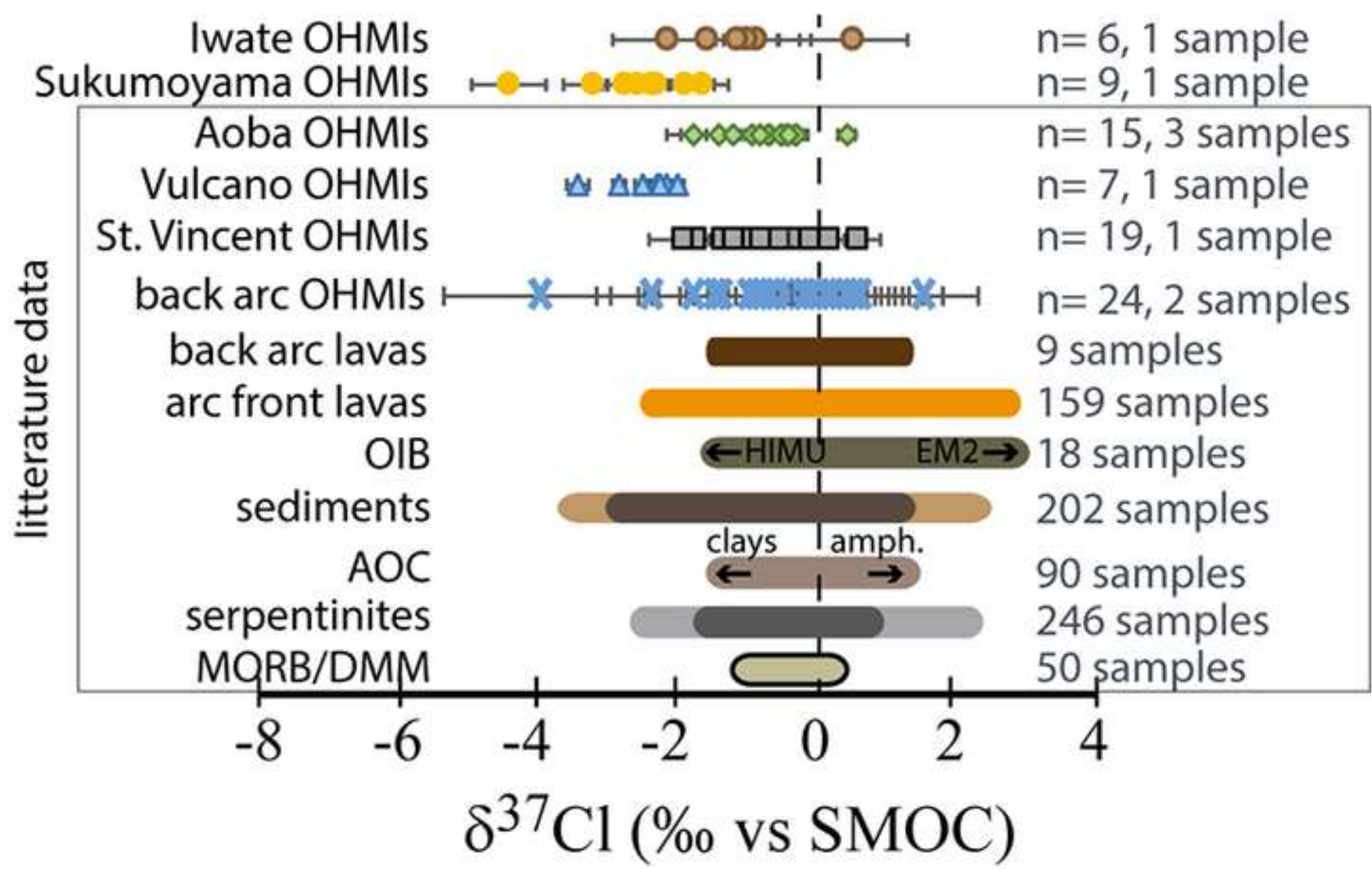


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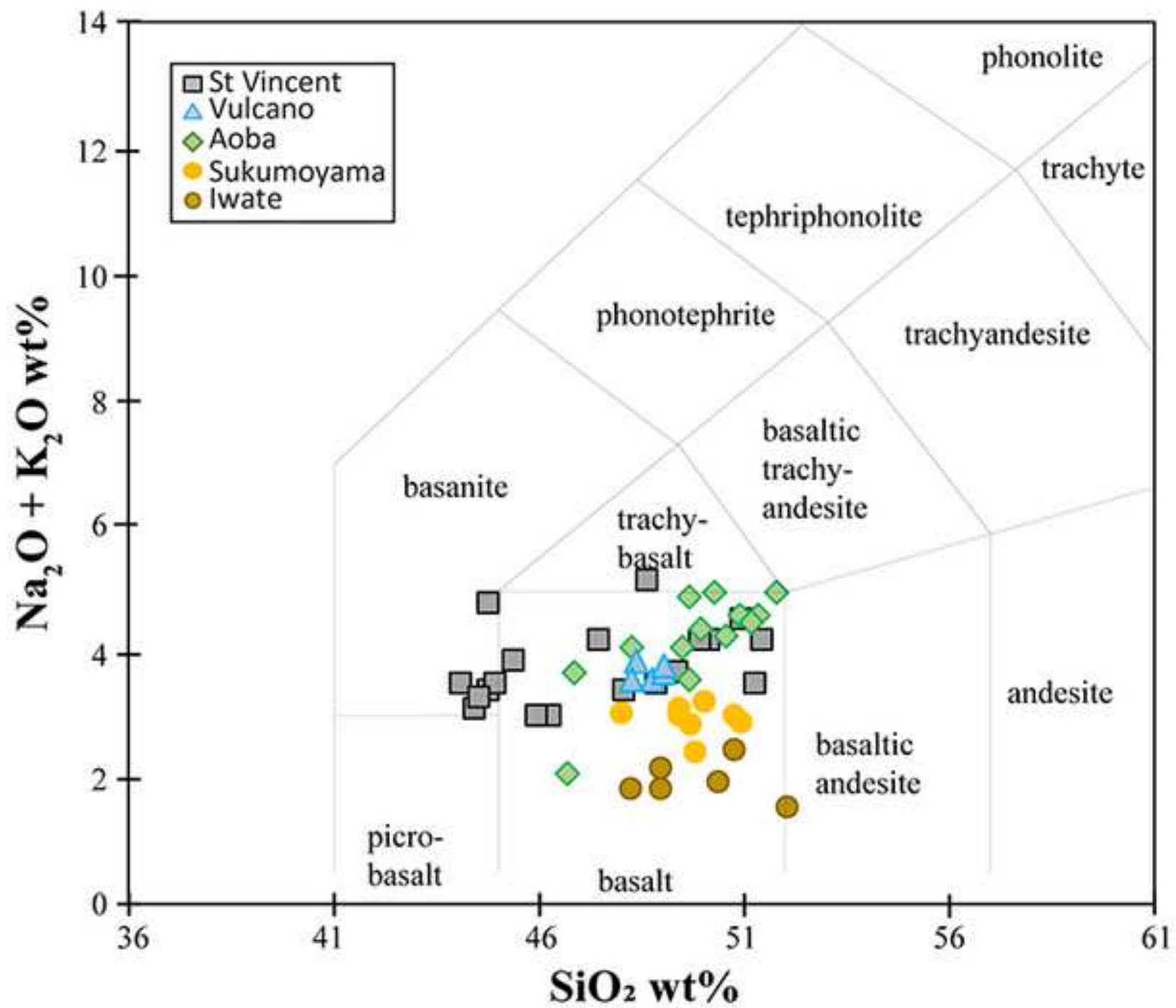


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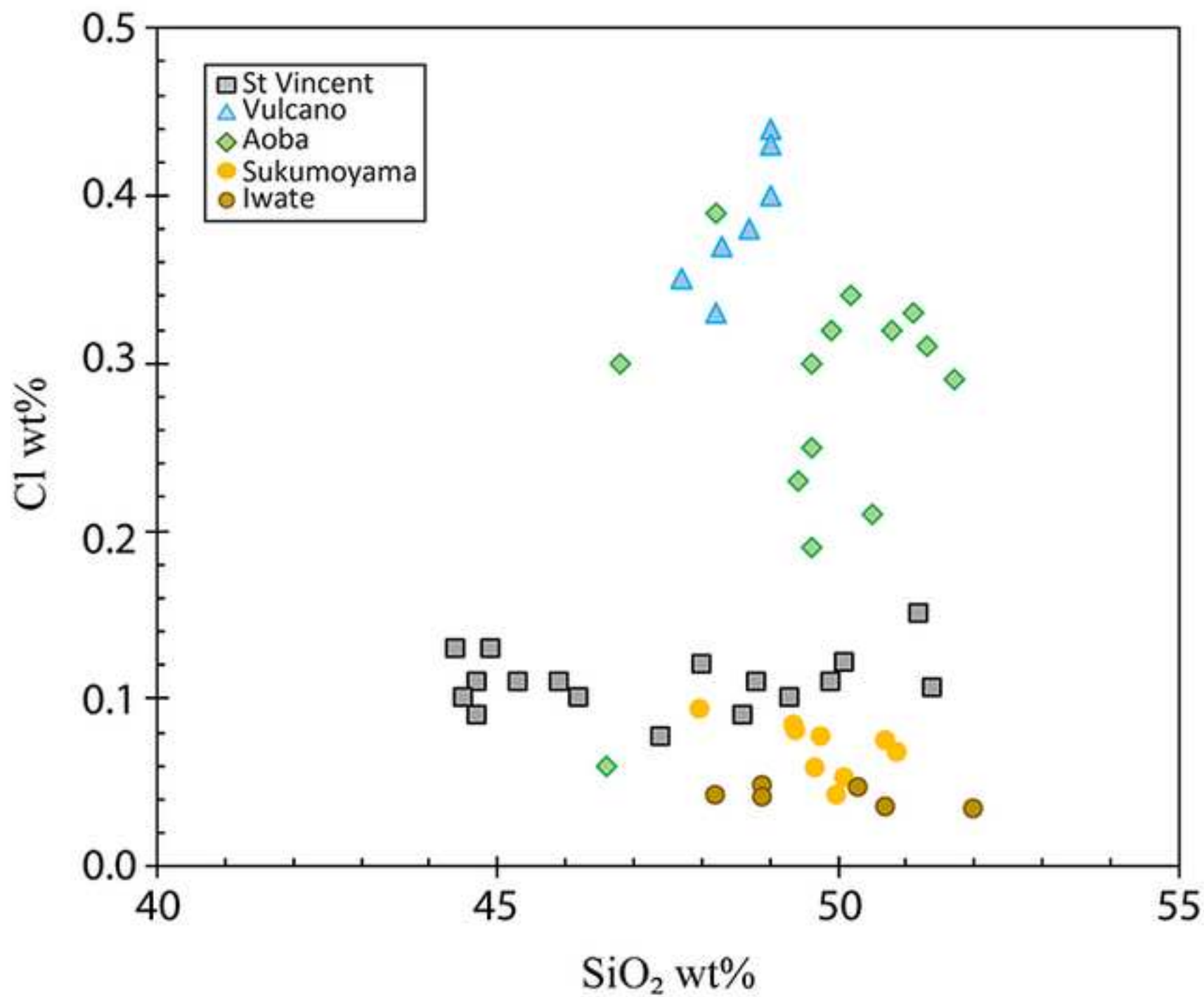


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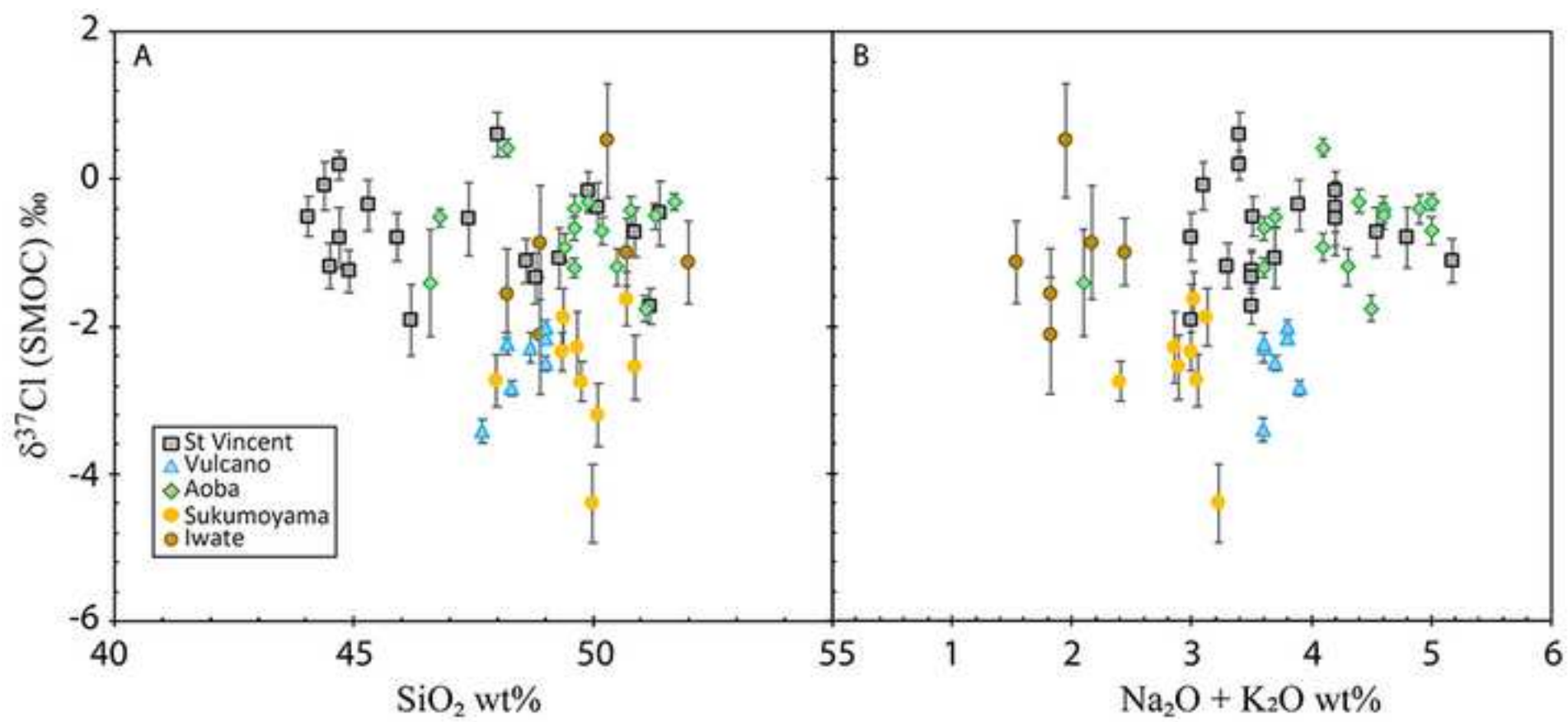


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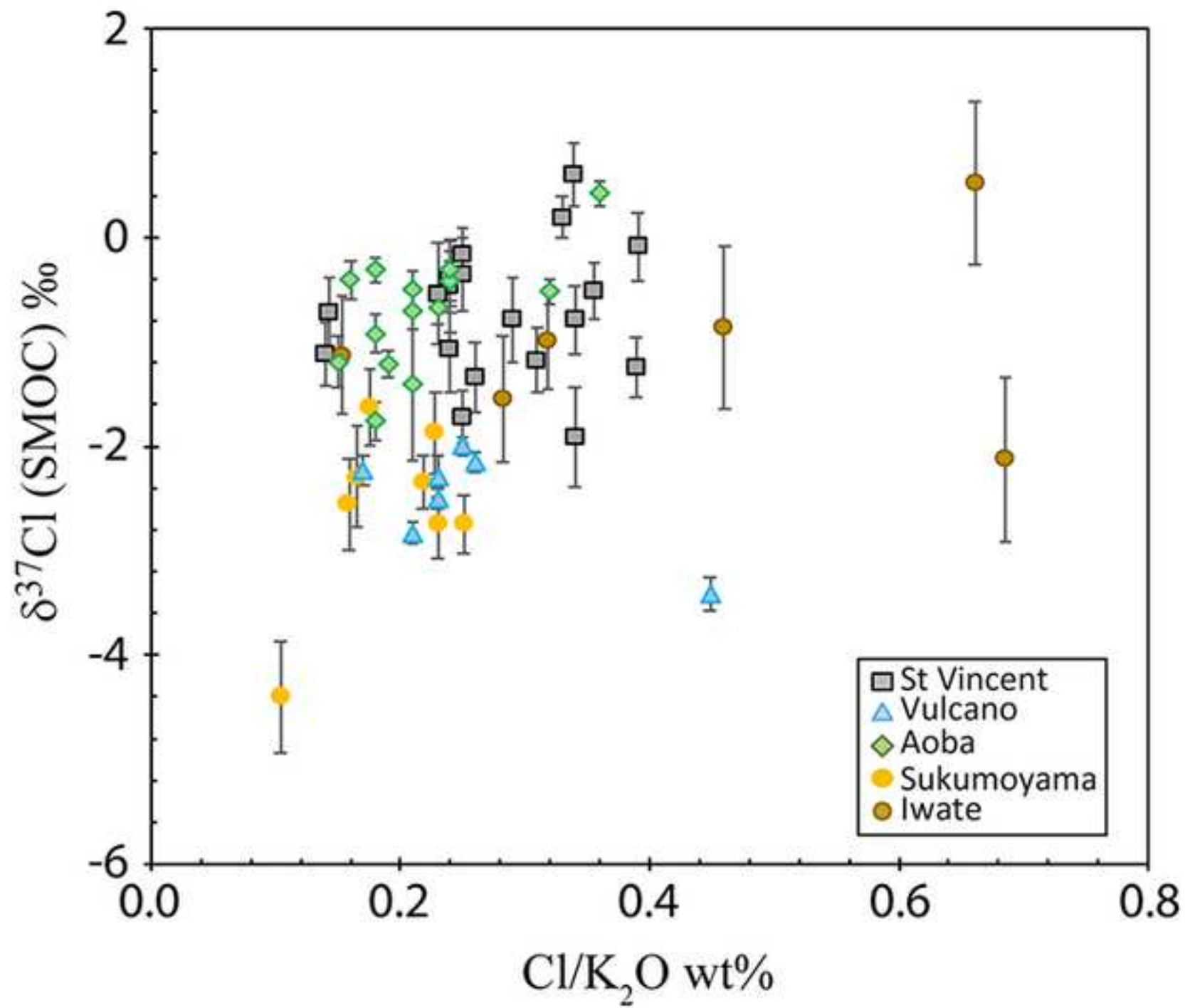


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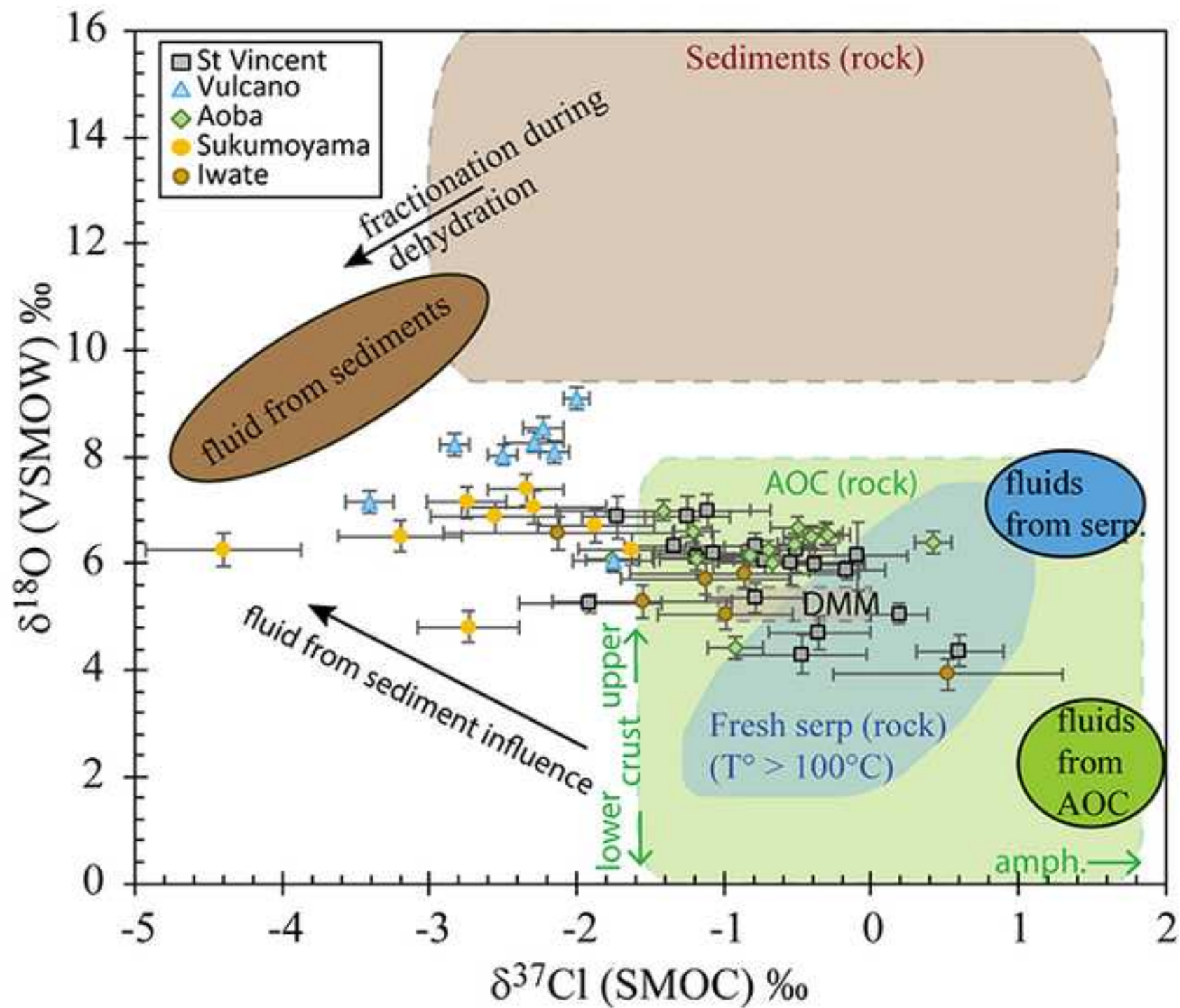


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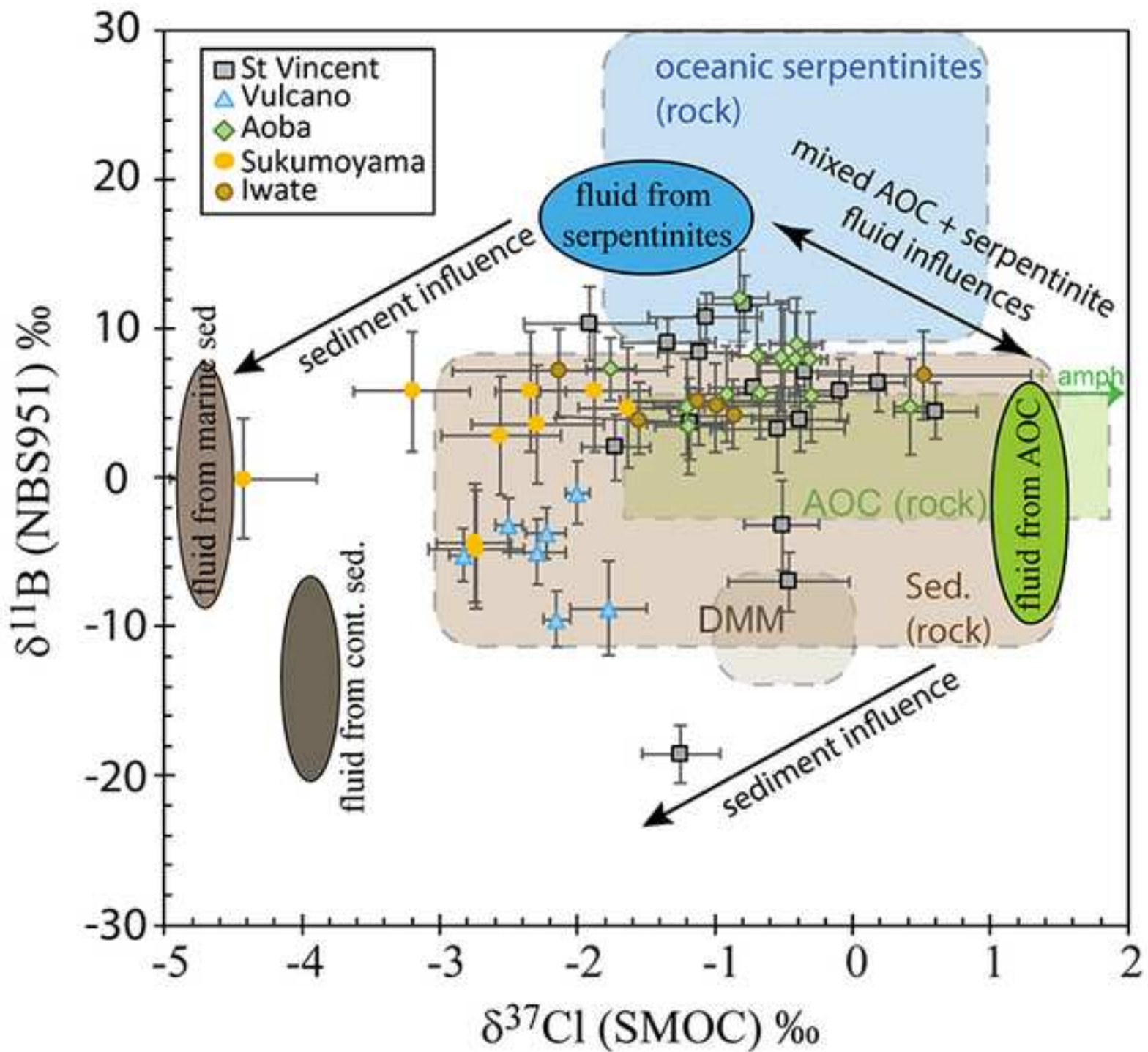


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Figure (high-resolution) 4

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Figure (high-resolution) 5

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Table 1: B, O and Cl isotopes in OHMIs

	$\delta^{37}\text{Cl}$	2σ	$\delta^{18}\text{O}$	2σ	$\delta^{11}\text{B}$	2σ
OHMIs from St. Vincent (Lesser Antilles arc),						
svn4b-24	-0.5	0.4	4.3	0.4	-7.0	2.0
svn4b-36	-0.4	0.3	6.0	0.2	3.9	2.2
svn4b-60	-0.5	0.5	6.0	0.4	3.2	2.9
svn4b-90a	-0.2	0.3	5.9	0.2	n.d.	n.d.
svn4b-90b	-1.1	0.3	7.0	0.3	8.4	2.5
svn4b-90v	-0.7	0.3	6.1	0.3	6.0	n.d.
svn4b-164a	0.2	0.2	5.1	0.2	6.4	2.0
svn4b-171a	-1.2	0.3	6.9	0.4	-18.5	1.9
svn4b-176a	-0.4	0.3	4.7	0.3	7.1	2.0
svn4b-181a	0.6	0.3	4.4	0.3	4.5	1.9
svn4b-181b	-1.7	0.2	6.9	0.4	2.0	2.2
svn4b-184	-0.5	0.3	6.3	0.4	-3.2	3.0
svn4b-186	-0.8	0.4	6.3	0.3	n.d.	n.d.
svn4b-MM1a	-1.3	0.3	6.3	0.1	9.1	1.6
svn4b-MM2	-1.1	0.4	6.2	0.4	10.8	1.6
svn4b-MM3a	-0.1	0.3	6.1	0.7	5.9	2.0
svn4b-MM7	-1.9	0.5	5.3	0.2	10.3	2.4
svn4b-MM15a	-1.2	0.3	6.1	0.4	3.7	2.4
svn4b-MM22	-0.8	0.3	5.4	0.3	11.7	1.9
OHMIs from Aoba (Vanuatu arc)						
17-10-b	-0.4	0.2	n.d.	n.d.	7.9	3.2
17-10-c	-0.3	0.1	6.6	0.2	7.9	3.2
17-16-a	-1.2	0.1	6.6	0.2	4.8	3.2
17-16-b	-0.7	0.2	6.0	0.2	5.8	3.2
3-9	-1.4	0.7	7.0	0.2	n.d.	n.d.
3-10 h3-1-a	-0.9	0.2	4.4	0.2	5.6	3.2
3-1-a	-0.5	0.2	6.7	0.2	7.7	3.6
3-1-b	-0.7	0.2	6.3	0.2	8.2	3.3
3-h1-a	-0.5	0.1	6.4	0.2	8.1	3.7
3-4	-0.82	0.2	6.2	0.2	12.0	3.2
3-5	0.4	0.1	6.4	0.2	4.7	3.2
3-6	-1.8	0.2	6.1	0.2	7.3	2.1
15-1-a	-0.3	0.2	6.5	0.2	5.5	3.2
15-10-a	-1.2	0.3	6.1	0.2	3.4	3.2
15-10-b	-0.4	0.2	6.5	0.2	8.9	3.2
OHMIs from Vulcano (Aeolian arc)						
S1	-2.3	0.2	8.3	0.2	-4.9	2.2
S2	-2.8	0.1	8.2	0.2	-5.1	1.8
S3	-2.5	0.1	8.0	0.2	-3.1	1.8
S7-a	-2.2	0.1	8.1	0.2	-9.5	1.9
S7-b	-2.0	0.1	9.1	0.2	-1.0	2.1
S9	-2.2	0.1	8.5	0.2	-3.7	1.7

SM1 - database

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