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

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Abstract

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

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

1±0.9‰ for Iwate (NE Japan)). Vulcano OHMIs also have statistically different B and O isotope compositions compared to those from the other locations: average $\delta^{11}\text{B}$ of $-5.1\pm2.9\text{‰}$ for Vulcano OHMIs, compared to $2.5\pm3.7\text{‰}$, $5.2\pm1.4\text{‰}$, $7.0\pm2.2\text{‰}$, $3.8\pm7.5\text{‰}$ for Sukumoyama, Iwate, Aoba and St. Vincent OHMIs, respectively. All OHMIs have $\delta^{18}\text{O}$ between 4.0 and 7.4‰, except for those from Vulcano, which are significantly different, with $\delta^{18}\text{O}$ from 7.2 to 9.1‰. Combining these three stable isotope systems suggests that the large variation ($>2\text{‰}$) of $\delta^{37}\text{Cl}$ in OHMIs from a sample reflects inputs from different sources of Cl rather than heterogeneities in a single main source. Variability between arcs might reflect different major sources of Cl.

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

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

1. Introduction

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

58 scientists to a consensus on the relatively narrow range of $\delta^{37}\text{Cl}$ found in terrestrial rocks
59 (Figure 1 and Supplementary material 1). In subduction zones, Cl, a soluble element, could
60 serve as a tracer of different Cl sources that contaminate the mantle wedge. Based on
61 theoretical calculations (Schauble et al., 2003) and experimental work (Liebscher et al., 2006),
62 fractionation of Cl isotopes between silicates and NaCl at $T > 300^\circ\text{C}$ should be limited. This
63 implies that $\delta^{37}\text{Cl}$ should not be (or only slightly) fractionated during slab dehydration
64 (Barnes et al., 2006; Bonifacie et al., 2008; John et al., 2011). The isotopic composition of a
65 metasomatized mantle should thus reflect simple binary mixing between the host rock and the
66 metasomatizing agent. The $\delta^{37}\text{Cl}$ of arcs lavas vary from -2.6 to +3.0‰ (e.g., Barnes et al.,
67 2009; Barnes and Straub, 2010). These studies have been used to estimate the Cl reservoirs
68 and suggested that Cl could be derived from altered oceanic crust (AOC), serpentinites or
69 sediments, depending on the depth of fluid extraction, which leads to a change in $\delta^{37}\text{Cl}$ across
70 an arc (Barnes et al., 2008). Variation along the Central America volcanic arc has also been
71 observed and has been used to suggest different sources of Cl along the arc (Barnes et al.,
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.

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

2. Geological context and sample descriptions

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

2.1. Melt inclusions from previous studies

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

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

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

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

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

2.2. New melt inclusions from Izu-Bonin arc

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

3. Methods

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

3.1. Electron microprobe (EMPA)

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

3.2. Secondary Ion Mass Spectrometry (SIMS)

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

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

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

¹⁶O and ¹⁸O secondary ions were analyzed at 2400 MRP and collected on two FCs in multi-collection mode using 10¹⁰ and 10¹¹ Ω resistors, respectively. The FCs were calibrated at the beginning of the session, using the calibration routine. Mass calibration was performed at the beginning of each session (<12h). Each analysis takes ~4 minutes, including pre-sputtering (30 s) and automated centering of secondary electrons. Ion mass fractionation was calibrated using several standards with different major element compositions (SM 2C). Reproducibility of the standards is better than 0.3‰. δ¹⁸O is referenced to the standard mean ocean water (SMOW) ¹⁸O/¹⁶O ratio of 2005.2×10⁻⁶.

To determine δ¹¹B, ¹⁰B and ¹¹B were measured in multicollection mode, using two electron multipliers. The O⁻ primary beam intensity was 8 nA and mass resolution was set at 2400. A single analysis (60 cycles) took 16 minutes. The instrumental isotopic fractionation was determined by analyzing five standards with different major element compositions (SM 2D). As already reported in the literature, instrumental isotopic fractionation was observed to be independent of major element composition (Rosner et al., 2008). Reproducibility on the standards varies from 2 to 4‰ (2SD), depending on the B content of individual melt inclusions. δ¹¹B is referenced to the NBS 951 ¹¹B/¹⁰B ratio of 4.044.

Amongst the standards used for δ¹¹B and δ¹⁸O calibrations, BHVO-2G and BCR-2G, with compositions encompassing those of our OHMIs, were also included in the sample mounts, as well as in the standard mount. During the session measuring δ¹⁸O and δ¹¹B, several analyses of BHVO-2G and BCR-2G were undertaken before and after a maximum of 18 unknowns to monitor instrument stability (i.e., magnetic field stability). These standards were also treated as unknowns to check the accuracy of the calibration. Accuracies were similar to reproducibility: 0.3‰ for δ¹⁸O and 3‰ for δ¹¹B.

4. Results

4.1. Elemental geochemistry of melt inclusions

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

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

4.2. Stable isotope compositions

4.2.1. Chlorine isotopes

All stable isotope compositions are reported in Table 1. The six new data from Iwate 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. Vincent and Aoba OHMIs. The nine data from Sukumoyama OHMIs show distinct values 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.) (average of -2.3‰), more similar to Vulcano. As for Vulcano OHMIs, Cl isotopes for Sukumoyama OHMIs can be compared to $\delta^{37}\text{Cl}$ bulk rock values. Indeed, lavas from two volcanoes, Oshima and Niijima, located relatively close to Sukumoyama, at the northern end of Izu-Bonin arc have been measured for $\delta^{37}\text{Cl}$ (Barnes et al., 2008). Oshima and Niijima

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

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

4.2.2. Boron isotopes

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

4.2.3. Oxygen isotopes

The $\delta^{18}\text{O}$ varies from 4.3 ± 0.4 to $6.9\pm0.4\text{‰}$ (2 s.e.), with an average of 5.8‰ for the St. Vincent OHMIs, similar to the average (6.0‰) $\delta^{18}\text{O}$ reported by Bouvier et al. (2008). Aoba OHMIs have a similar range of $\delta^{18}\text{O}$ composition, from 4.4 ± 0.2 to $7.0\pm0.2\text{‰}$ (2 s.e.) (average: 6.3‰); and Sukumoyama OHMIs also have a similar range of $\delta^{18}\text{O}$ (4.8 ± 0.3 to $7.4\pm0.3\text{‰}$, 2 s.e.), but with slightly higher average (6.6‰). In contrast, Iwate Volcano OHMIs have slightly lower $\delta^{18}\text{O}$ values of 3.9 ± 0.3 to $6.6\pm0.3\text{‰}$ (2 s.e.), with an average of 5.4‰ . Vulcano OHMIs have the highest $\delta^{18}\text{O}$ measured in this study. They vary from 6.1 ± 0.2 to $9.1\pm0.2\text{‰}$ (2 s.e.), with an average value of 7.9‰ .

5. Discussion

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

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

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

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

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

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

two or three OHMIs, but only one olivine contains two OHMIs with one containing a bubble and the other not (Aoba 3-1a and b). The one without bubbles contain 300 ppm less Cl than the one with a bubble, but the two OHMIs have similar $\delta^{37}\text{Cl}$, within error (-0.5 ± 0.2 and $-0.7\pm0.2\text{‰}$; SMs 3-4). Also, within a sample, the range of Cl content and $\delta^{37}\text{Cl}$ are similar for OHMIs with or without a shrinkage bubble. We thus conclude that the presence of a shrinkage bubble does not affect Cl isotopes of OHMIs. This is further confirmed by the absence of a correlation between $\delta^{37}\text{Cl}$ and Cl/K₂O (Figure 5), suggesting no Cl degassing syn- or post-entrapment. Also, Cl is not affected by diffusive re-equilibration through the host olivine (Bucholz et al., 2013). All this information suggests that the measured $\delta^{37}\text{Cl}$ are representative of the melt in which the olivine grew.

5.1.2. Cl and O isotope systematics

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

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

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

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

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

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

5.1.3. Cl and B isotope systematics

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

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

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

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

A second end-member can be described by higher $\delta^{37}\text{Cl}$ (>1‰) and lower $\delta^{11}\text{B}$ (<~4‰). 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

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

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

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

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

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

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

5.2. Bulk rock vs. OHMI Cl isotope differences

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

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

Bulk rock data are clearly different to our OHMI data, with a shift of up to 2‰ and 3.6‰ toward lower values for Vulcano and Sukumoyama OHMIs, respectively. As discussed in section 5.1.1., this could not be induced by analytical bias. Rather, the combination of 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 from a fluid issued from sediments, as discussed above.

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

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

6. Conclusions

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

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

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

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Captions:

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

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), Aeolian islands (triangles), Aoba (diamonds), Sukumoyama (yellow circles) and Iwate (brown circles). The OHMIs have basanitic to basaltic compositions.

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

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 $\delta^{37}\text{Cl}$ and the major elements are seen, proving that the matrix effect has been corrected. Also, the absence of any correlation suggests that Cl isotopes are not affected by extent of magmatic evolution.

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

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

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

Table 1: B, O and Cl isotopes in OHMIs

Supplementary material

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

SM2: SIMS calibrations

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

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

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

Figure 1
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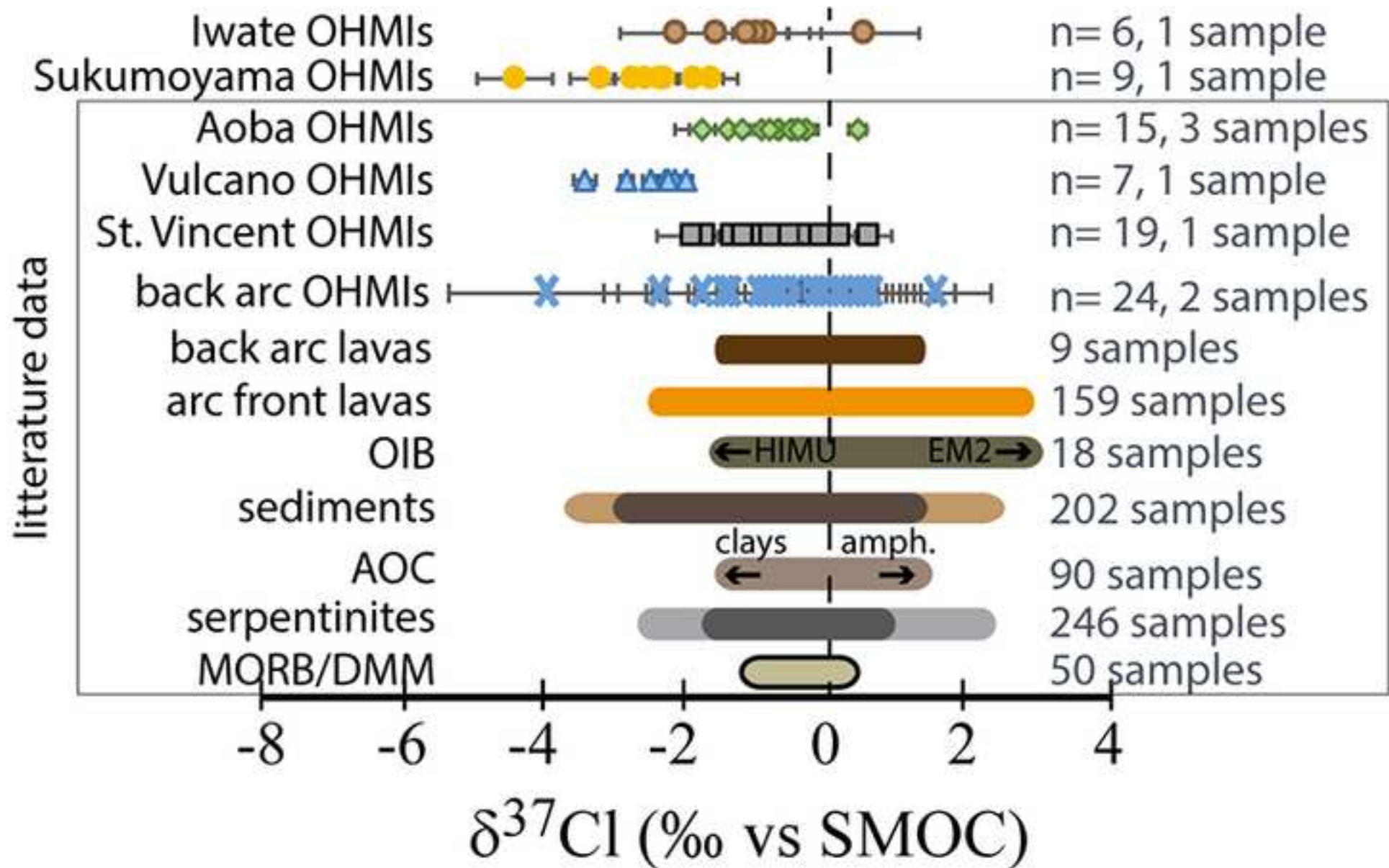


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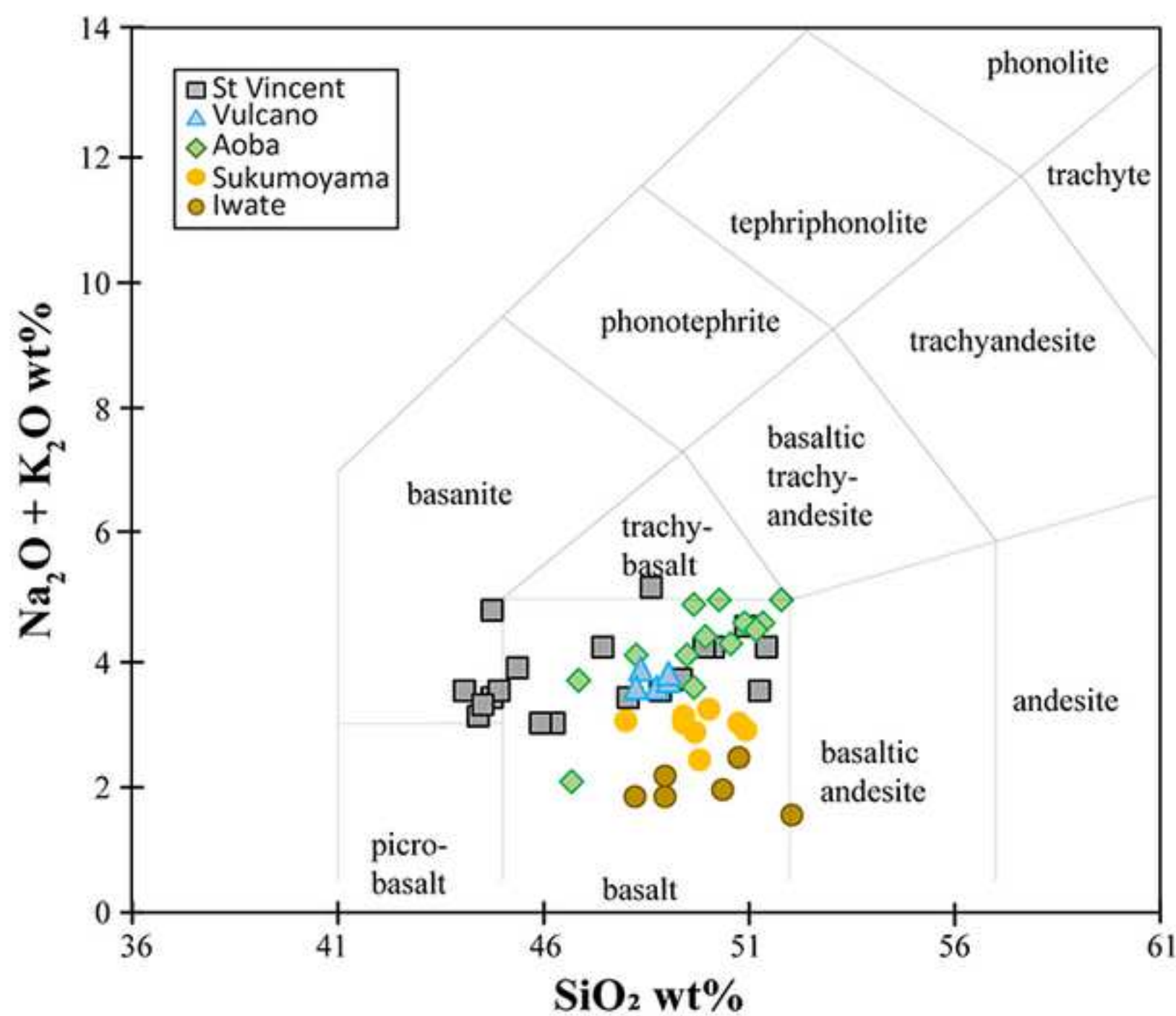


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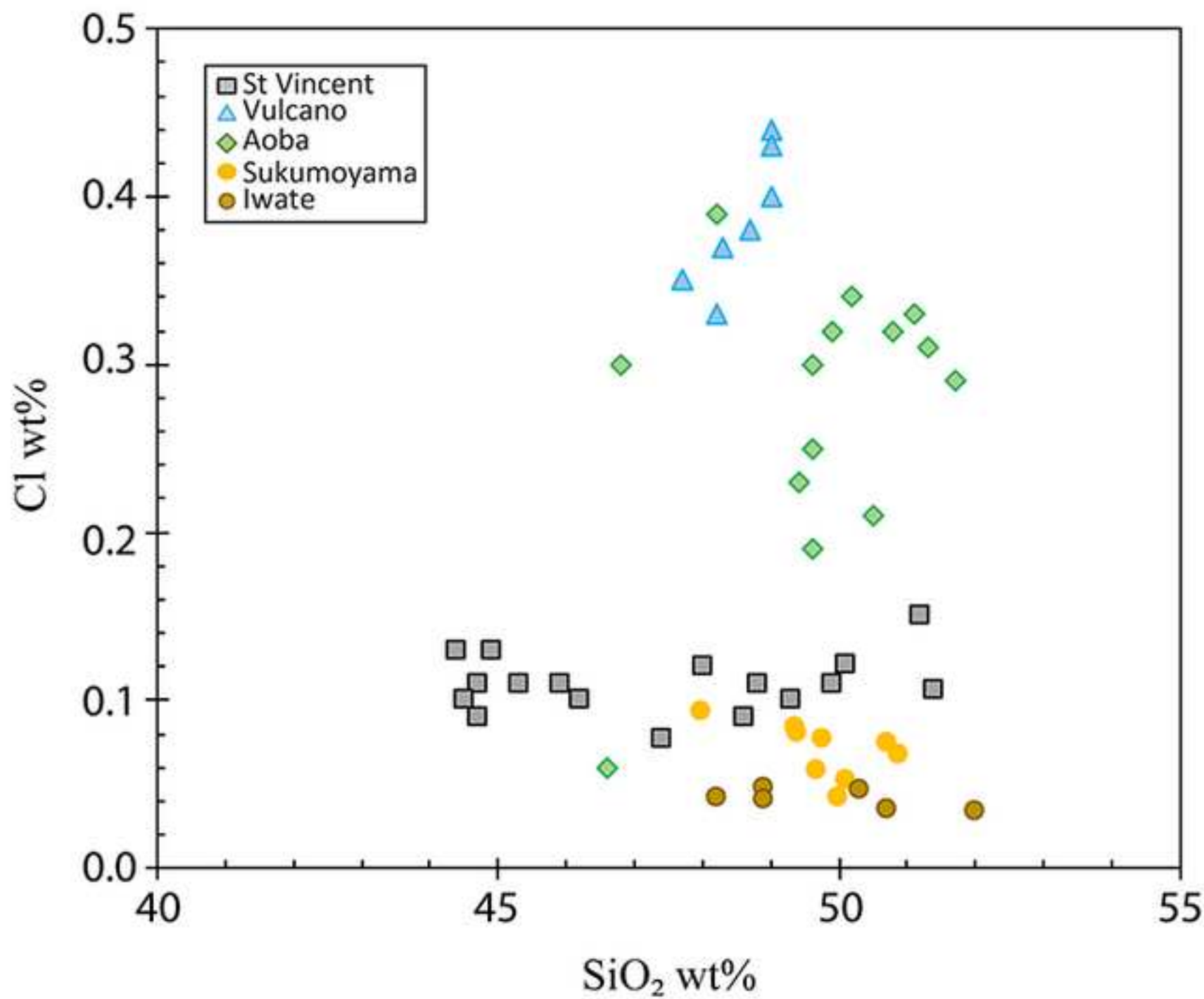


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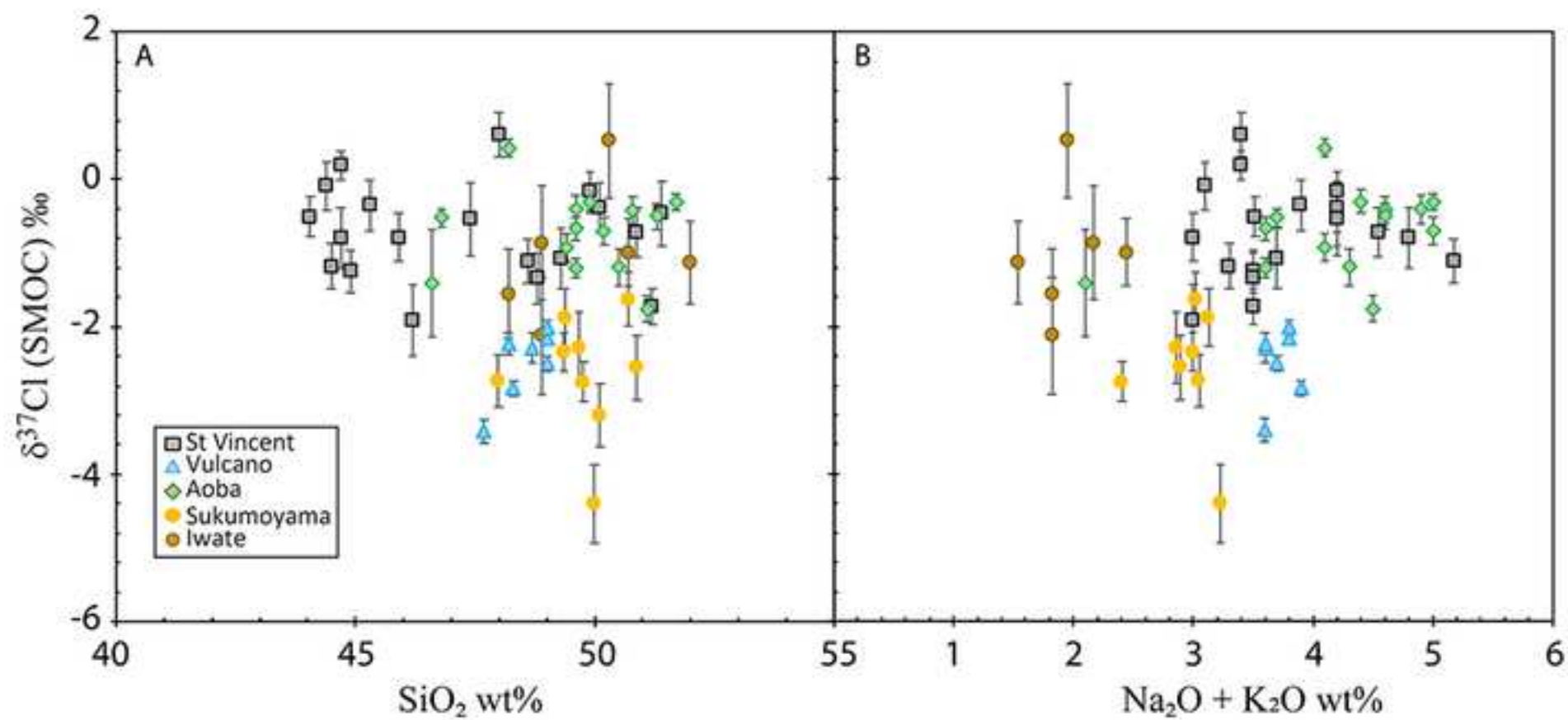


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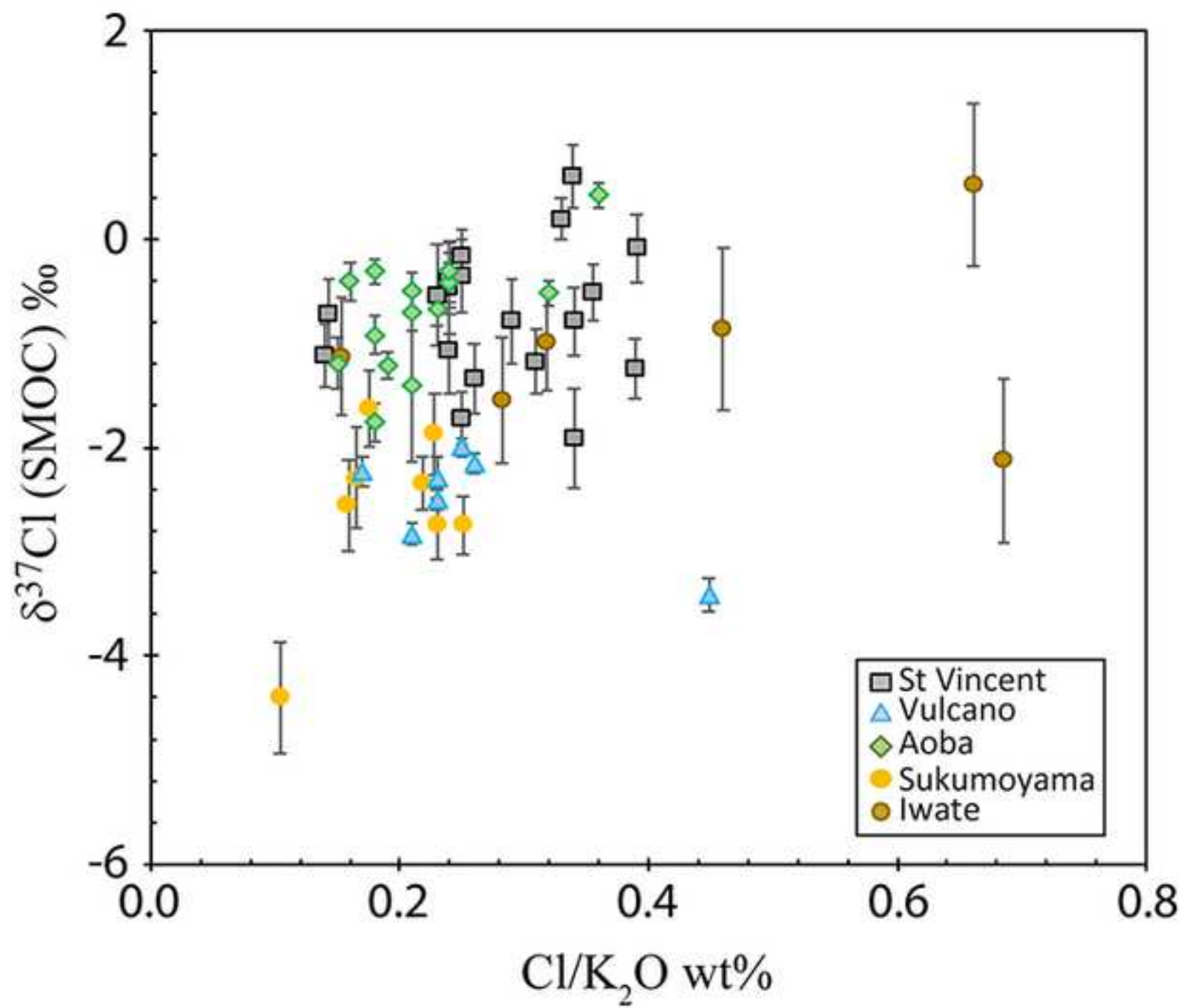


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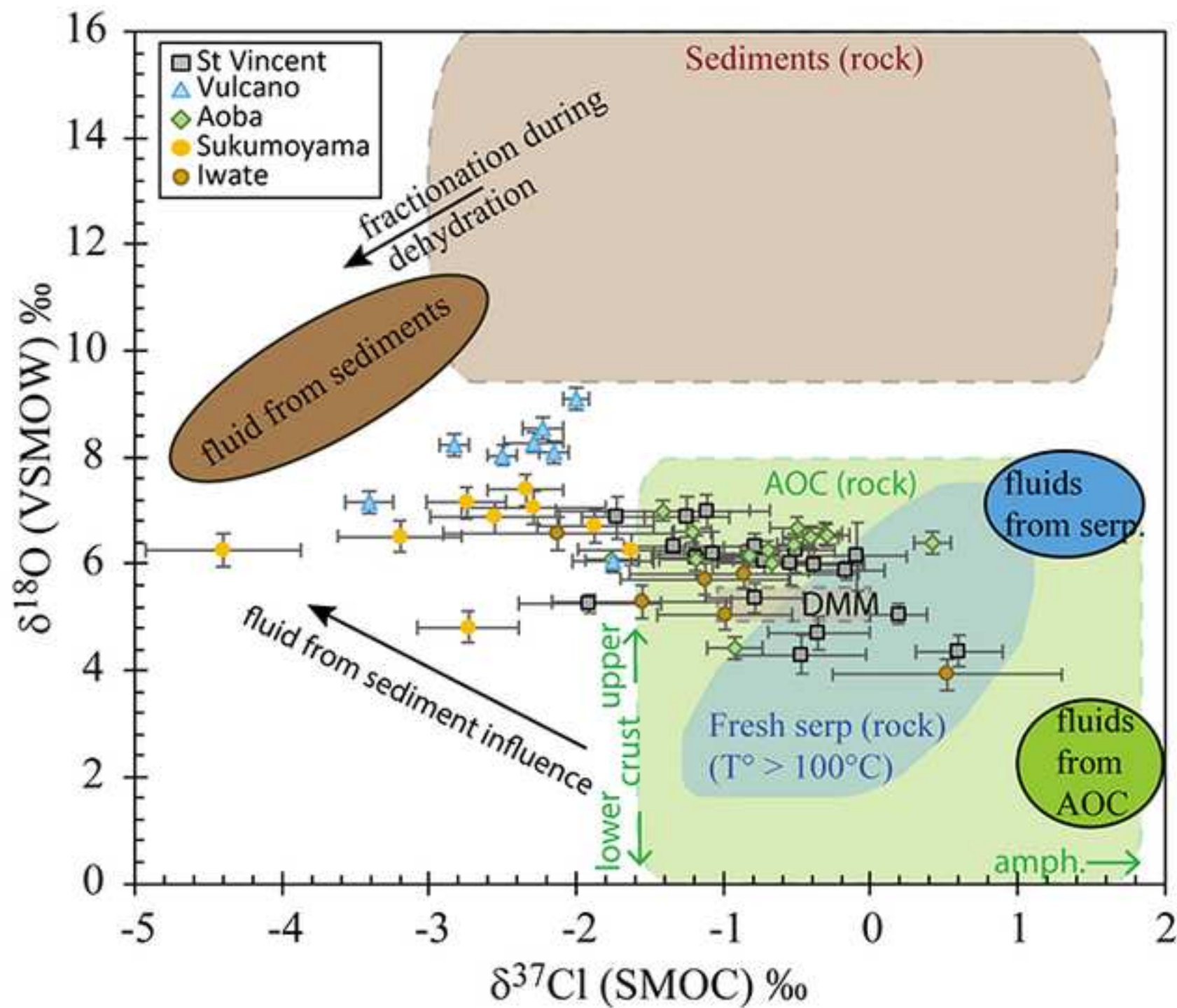


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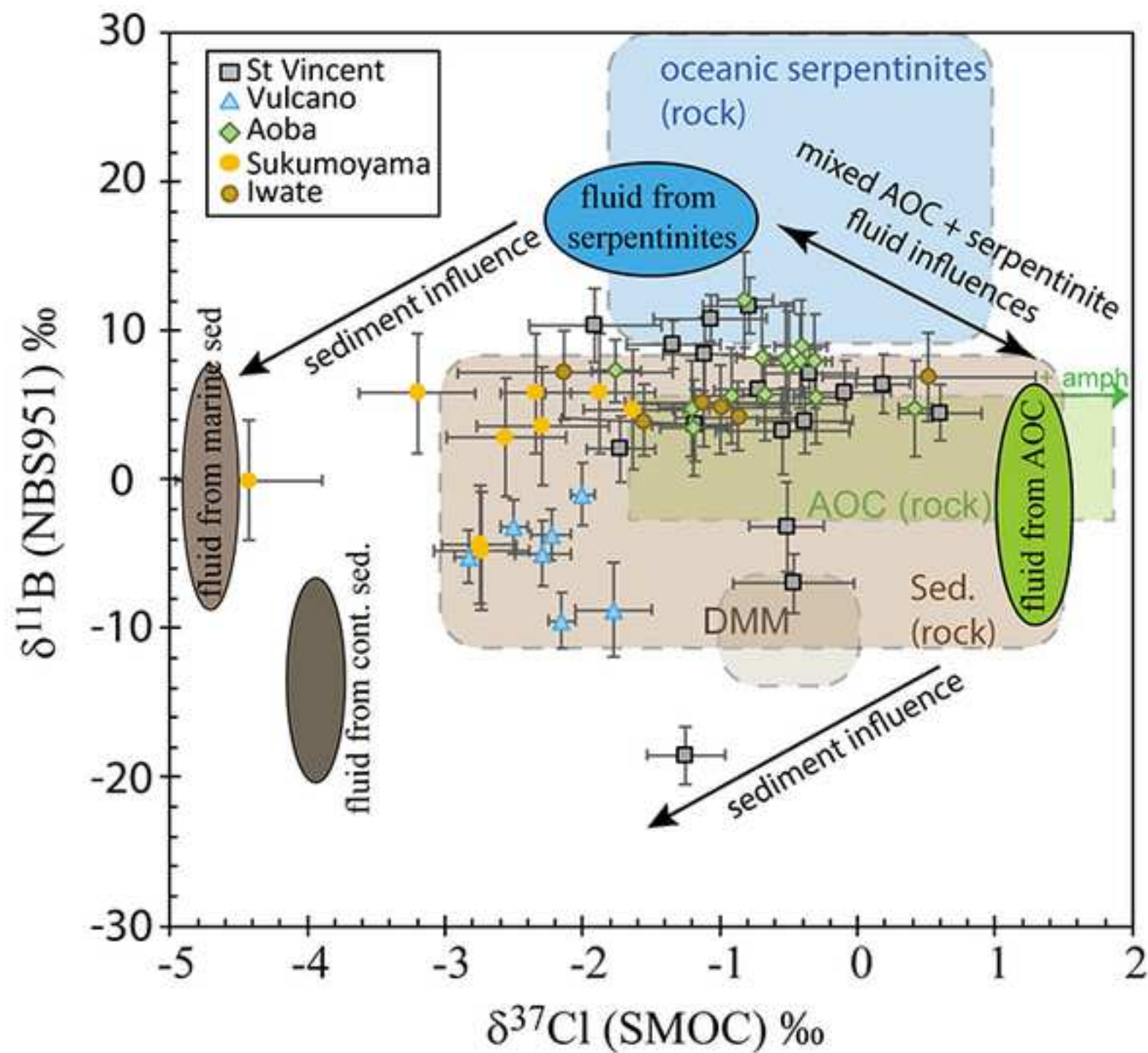


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Figure (high-resolution) 5

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Figure (high-resolution) 7

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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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SM2 - calibrations

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SM4

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