

Supplementary text and figures for: Carbonated mantle peridotites represent a hidden sink for subducted CO₂

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1 Derivation of modelling equations

The following derivation demonstrates that the final halogen composition of a carbonating fluid depends upon the rates at which each halogen is lost from the rock during carbonation, the initial halogen ratios and the initial Cl/CO₂ ratio of the fluid. This can ultimately be expressed as a simple equation which relates the Cl/CO₂ of the fluid to the degree of halogen fractionation observed, fixing the relative abundance of Cl and CO₂ in the carbonating fluid and thereby helping to constrain its origin and associated carbon flux.

It should be noted that the least carbonated ophiocarbonates have been affected by interaction with fractionated low Br/Cl fluids. A key assumption in the following calculations is therefore that compositional gradients of halogens and CO₂ content across the reaction zone (main text Figure 5) were in steady state, such that all samples analysed evolved (or would have evolved) along the same compositional gradient as a transient compositional front. If this is not the case, then the rate of Cl loss during carbonation may be overestimated relative to other halogens, resulting in underestimation of CO₂/Cl through the following calculations. That said, it is reasonable to think that such a steady state should have evolved since low Br/Cl fluids can only be maintained at low fluid/rock ratios, limiting their ability to supply excess Cl to uncarbonated rocks downstream. Conversely, increasing fluid/rock ratios increases the capacity of the fluids to deliver excess Cl downstream rocks but at the same time increases the Br/Cl of those fluids. The existence of low Br/Cl serpentinites affected by a fractionated fluid therefore suggests a balance between these countervailing tendencies. It is also possible that the least carbonated ophiocarbonates are compositionally intermediate between their serpentinite protolith and the evolved

carbonating fluid, since they were most likely serpentinised prior to carbonation¹. The effect of this would tend to cancel out any potential overestimation of Br/Cl_{out} and suggests that these assumptions and the modelling approach which follow are reasonable given the available constraints.

To begin with, we define the change in CO₂ per gram of rock or fluid:

$$\Delta[CO_2]_{rock} = \frac{CO_{2added}}{rock} \quad (1)$$

$$\Delta[CO_2]_{fluid} = \frac{CO_{2lost}}{fluid} \quad (2)$$

Where $\Delta[CO_2]_i$ is the change in the concentration of CO₂ in component i (in g/g), CO_{2 added} and CO_{2 lost} are the mass of CO₂ (in g) added to/lost from the rock or fluid, respectively, and rock and fluid are the mass (in g) of rock and fluid involved in the reaction.

Since the mass of CO₂ added to the rock is the same as that lost from the fluid

$$\Delta[CO_2]_{rock} \cdot rock = \Delta[CO_2]_{fluid} \cdot fluid \quad (3)$$

Rearranging (3) gives:

$$\frac{fluid}{rock} = \frac{\Delta[CO_2]_{rock}}{\Delta[CO_2]_{fluid}} \quad (4)$$

A minimum fluid/rock ratio can be calculated by assuming that all CO₂ from the fluid is consumed by the carbonation reaction:

$$\Delta[CO_2]_{fluid} = [CO_2]_{fluid} \quad (5)$$

$$\frac{fluid}{rock} = \frac{\Delta[CO_2]_{rock}}{[CO_2]_{fluid}} \quad (6)$$

To determine the amount of Cl, Br and I lost from the rock relative to the amount of CO₂ added during the reaction we define the ratios R_{Cl}, R_{Br} and R_I

$$R_{Cl} = \frac{\Delta[Cl]_{rock}}{\Delta[CO_2]_{rock}} \quad (7)$$

$$R_{Br} = \frac{\Delta[Br]_{rock}}{\Delta[CO_2]_{rock}} \quad (8)$$

$$R_I = \frac{\Delta[I]_{rock}}{\Delta[CO_2]_{rock}} \quad (9)$$

R_{Cl}, R_{Br} and R_I are determined by linear regression of bulk halogens and carbon abundance from reaction zone samples. Chlorine shows two distinct parts of the reaction, each with a different slope. There is rapid Cl loss during the early part of the

reaction (bulk CO₂ = 7 to 12%) followed by a shallower slope during the later part of the reaction (CO₂ = 12 to 40%). Alternatively, Cl loss can be fitted by exponential function as:

$$Cl = a \cdot e^{-kCO_2} \quad (10)$$

Where a is 0.1088 wt% and $k = 0.12399$ (with CO₂ in wt%). The rate of Cl loss against CO₂ is then itself dependent on CO₂ and given by:

$$R_{Cl} = \frac{dCl}{dCO_2} = -ka \cdot e^{-kCO_2} \quad (11)$$

$$R_{Cl} = -k \cdot Cl \quad (12)$$

Br and I by contrast appear to be lost more gradually throughout the reaction and are fit with a single linear slope. The result of this is that halogens are highly fractionated during the early part of the reaction, resulting in low Br/Cl and I/Cl ratios fluids expelled from the rock which mix with the carbon-bearing fluids.

The Br/Cl and I/Cl ratios of fluids expelled can be calculated by combining (7) or (10) with (8) and (9) as:

$$\left(\frac{Br}{Cl}\right)_{out} = \frac{R_{Br}}{R_{Cl}} \quad (13)$$

$$\left(\frac{I}{Cl}\right)_{out} = \frac{R_I}{R_{Cl}} \quad (14)$$

Calculated rates of halogen loss (as g halogen/g CO₂ added) are as follows:

	<i>Part 1</i>	-6.43 x 10 ⁻³
	<i>Part 2</i>	-0.78 x 10 ⁻³
R _{Cl} (g/g)	<i>Exponential initial (CO₂ = 0)</i>	-1.35 x 10 ⁻²
	<i>Exp. least carbonated (CO₂ = 7.1%)</i>	-5.62 x 10 ⁻³
R _{Br} (g/g)		-1.38 x 10 ⁻⁶
R _I (g/g)		-0.10 x 10 ⁻⁶

Since calculating an initial rate of Cl loss from the exponential model involves projecting beyond the sample data to zero CO₂, there is a risk this may not accurately reflect the behaviour of the system in the very earliest stage of the reaction (CO₂ = 0–7 wt%). Calculated at the CO₂ content of the least carbonated sample (CO₂ = 7.06 wt%), the exponential model gives a very similar R_{Cl} to part 1 of the two-stage linear model. Given this similarity and in the interests of simplicity, we use only the linear model hereafter. Combining R_{Cl} with R_{Br} and R_I from above gives the following halogen ratios for fluids lost from the rock during carbonation:

Br/Cl (g/g)	Part 1	0.21 x 10 ⁻³
	Part 2	1.77 x 10 ⁻³
I/Cl (g/g)	Part 1	16 x 10 ⁻⁶
	Part 2	130 x 10 ⁻⁶

To determine the effect of this outflux of halogens from the rock we need to calculate the composition of some mixture of this fluid and the original carbon-bearing fluid.

$$\left(\frac{Br}{Cl}\right)_f = \left(\frac{Br}{Cl}\right)_i \cdot X_{Cl} + \left(\frac{Br}{Cl}\right)_{out} \cdot (1 - X_{Cl}) \quad (15)$$

$$\left(\frac{I}{Cl}\right)_f = \left(\frac{I}{Cl}\right)_i \cdot X_{Cl} + \left(\frac{I}{Cl}\right)_{out} \cdot (1 - X_{Cl}) \quad (16)$$

Where Br/Cl and I/Cl are the weight ratio of the respective halogens, X_{Cl} is the weight proportion of Cl contributed by the original fluid and the subscripts *out*, *i* and *f* refer to the outflux from the rock, the initial fluid and the final fluid, respectively.

X_{Cl} can be expressed as:

$$X_{Cl} = \frac{[Cl]_i}{[Cl]_i + \Delta[Cl]_{fluid}} \quad (17)$$

Where $[Cl]_i$ is the initial Cl concentration in the fluid and $\Delta[Cl]_{fluid}$ is the change in concentration due Cl expelled from the rock.

To determine X_{Cl} in terms of the fluid Cl concentration and :

$$\Delta[Cl]_{fluid} = \Delta[Cl]_{rock} \left/ \left(\frac{fluid}{rock} \right) \right. \quad (18)$$

Where $\Delta[Cl]_i$ is the change in concentration of [Cl] (in g/g) in the respective component and

Substituting (6) in (18) (with the assumption of complete consumption of CO₂ from the fluid):

$$\Delta[Cl]_{fluid} = \Delta[Cl]_{rock} \cdot \frac{[CO_2]_{fluid}}{\Delta[CO_2]_{rock}} \quad (19)$$

Dividing by $[Cl]_i$ the initial fluid Cl concentration (in g/g) gives us:

$$\frac{\Delta[Cl]_{fluid}}{[Cl]_i} = \Delta[Cl]_{rock} \cdot \frac{[CO_2]_{fluid}}{\Delta[CO_2]_{rock}} \cdot \frac{1}{[Cl]_i} \quad (20)$$

Rearranging:

$$\frac{\Delta[Cl]_{fluid}}{[Cl]_i} = \frac{[CO_2]_{fluid}}{[Cl]_i} \cdot \frac{\Delta[Cl]_{rock}}{\Delta[CO_2]_{rock}} \quad (21)$$

Substituting definition of R_{Cl} (eq. (7) from above):

$$\frac{\Delta[Cl]_{fluid}}{[Cl]_i} = \frac{[CO_2]_{fluid}}{[Cl]_i} \cdot R_{Cl} \quad (22)$$

To reframe this equation in terms of X_{Cl} we can divide equation (17) by $[Cl]_i$

$$X_{Cl} = \frac{1}{1 + \Delta[Cl]_{fluid}/[Cl]_i} \quad (23)$$

Substituting (22) into (23):

$$X_{Cl} = \frac{1}{1 + \frac{[CO_2]_{fluid}}{[Cl]_i} \cdot R_{Cl}} \quad (24)$$

We can now rearrange to calculate the initial CO_2/Cl ratio of the fluid from X_{Cl} .

$$X_{Cl} \left(1 + \frac{[CO_2]_{fluid}}{[Cl]_i} \cdot R_{Cl} \right) = 1 \quad (25)$$

$$\frac{[CO_2]_{fluid}}{[Cl]_i} \cdot R_{Cl} = \frac{1 - X_{Cl}}{X_{Cl}} \quad (26)$$

$$\frac{[CO_2]_{fluid}}{[Cl]_i} = \frac{1}{R_{Cl}} \left(\frac{1}{X_{Cl}} - 1 \right) \quad (27)$$

Rearranging equation (15) as a level rule type relationship:

$$X_{Cl} = \frac{\left[\left(\frac{Br}{Cl} \right)_f - \left(\frac{Br}{Cl} \right)_{out} \right]}{\left[\left(\frac{Br}{Cl} \right)_i - \left(\frac{Br}{Cl} \right)_{out} \right]} \quad (28)$$

Finally combining equations (27) and (28):

$$\frac{[CO_2]_{fluid}}{[Cl]_i} = \frac{1}{R_{Cl}} \left(\frac{\left[\left(\frac{Br}{Cl} \right)_i - \left(\frac{Br}{Cl} \right)_{out} \right]}{\left[\left(\frac{Br}{Cl} \right)_f - \left(\frac{Br}{Cl} \right)_{out} \right]} - 1 \right) \quad (29)$$

And equivalently:

$$\frac{[CO_2]_{fluid}}{[Cl]_i} = \frac{1}{R_{Cl}} \left(\frac{\left[\left(\frac{I}{Cl} \right)_i - \left(\frac{I}{Cl} \right)_{out} \right]}{\left[\left(\frac{I}{Cl} \right)_f - \left(\frac{I}{Cl} \right)_{out} \right]} - 1 \right) \quad (30)$$

Equations (29) and (30) give the minimum initial CO_2/Cl ratio in the carbonating fluid needed to explain a given final fluid composition (Br/Cl_f or I/Cl_f). Alternatively, equation (24) can be used to calculate the relative proportions of Cl derived outflux from the rock versus the carbonating fluid. This can be input into equations (15) and (16) to calculate the composition of a fractionated fluid.

In either use case these numbers represent an endmember scenario, giving the minimum CO_2/Cl ratio required for a given degree of fractionation or the maximum fractionation for a given CO_2/Cl ratio. This is due to the assumption that all CO_2 present in the fluid is consumed by the reaction, implicitly fixing the fluid/rock ratio to its minimum possible value: that required to supply the amount of carbon present in the rock. In reality, the fluid CO_2 content should trend towards an equilibrium value. However, since X_{CO_2} of fluid in equilibrium with magnesite + talc + quartz is low (~ 0.0032)² it has been assumed that CO_2 is quantitatively removed from the fluid by the reaction. Fluid/rock ratios could be higher than the minimum bound calculated by this method; this would result in a lower degree of fractionation for a given CO_2/Cl ratio and conversely a higher CO_2/Cl ratio required to explain a given degree of fractionation.

Within our sample set we take the mean composition of serpentine in the least carbonated serpentinites 44z1 as representing the maximum degree of fractionation in the fluid. It is assumed that halogen ratios in serpentine reflect those of the fluid from which it formed, following Kendrick et al. (2013). The average composition of serpentine determined by SIMS in sample 44z1 is $\text{Br}/\text{Cl} = (1.07 \pm 0.57) \times 10^{-3}$ and $\text{I}/\text{Cl} = (1.01 \pm 0.55) \times 10^{-4}$ ($n = 31$).

2 Factors favouring forearcs peridotite carbonation

Forearc rocks and fluids may be sampled by dredging and drilling and in some cases, mud volcanism may sample material from the subduction channel at depth (≤ 20 km)^{3,4}. Transit through accretionary prisms of sediment can modify the chemistry of fluids and so the characteristics of slab-derived volatiles and fluid-rock reactions are only easily assessed in non-accretionary subduction zones. The Marianas subduction zone is the type-example of a non-accretionary subduction zone⁵ and is thus among the best-studied forearcs.

Carbonated peridotites have not been recovered from the Marianas or Tonga forearcs through dredging, nor sampled by mud volcanoes (e.g. ref. [3]). Carbonate is present in slab-derived fluids at depth >14 km^[3,6,7] and results in precipitation of calcium carbonate in veins and voids but not bulk replacement of peridotite/serpentinite⁶

The lack of evidence for peridotite carbonation in the Marianas forearc may relate to differences in the thermal structure of the subduction zone and/or the supply of

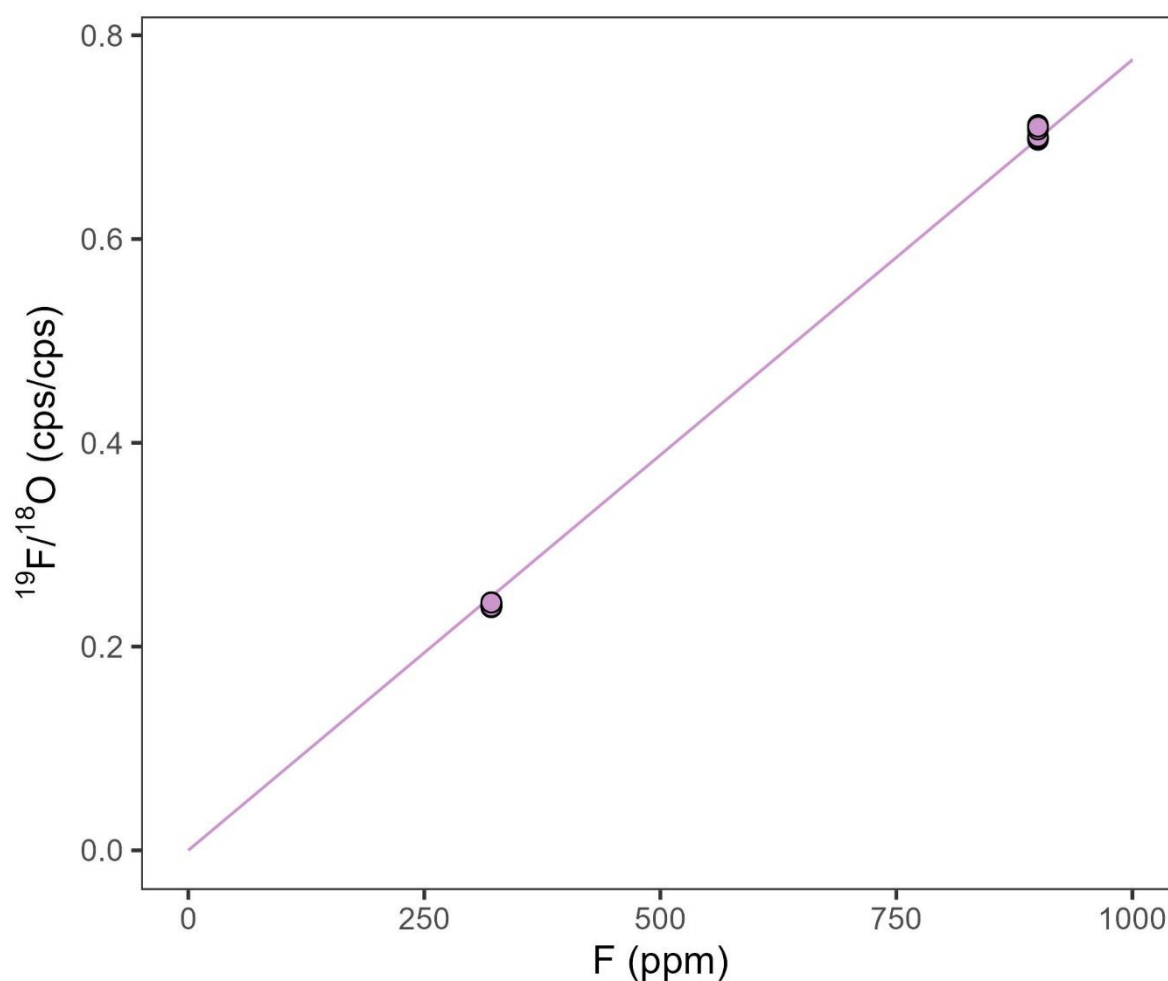
sediment; Marianas is a cold subduction zone characterised by subduction of old crust (>150 Ma ^[8]) with low sediment carbonate contents (2.6% ^[9]). Thermodynamic modelling of decarbonation for the Marianas subduction zone suggest limited decarbonation (<0.5% ^[10]). In contrast, the exhumed metamorphic sole of the Oman Ophiolites shows evidence for high thermal gradients during subduction arising from the overlying hot young proto-ophiolite lithosphere, and resulting in plagiogranites derived from slab melting¹¹. Warmer subduction regimes have been suggested to encourage devolatilisation of both water and carbon in the downgoing plate, resulting in preferential generation of carbon-rich aqueous fluids^{12,13}. Migration of such fluids to shallower levels in the forearc without re-equilibration (e.g. via channelised flow along the slab interface) would be expected to result in significant carbonation.

Moreover, unlike those in the Mariana, subducting allochthonous Oman sediments were carbonate-rich with abundant reef carbonates and calc-siliciclastics in Haybi and Hawasina complexes, respectively^{14,15}. The mean CO₂ content of the latter is 8.6%^[15]. Thus, the composition of subducting sediment may too be an important factor in the generation of carbon-rich fluids and forearc listvenites. Relative to pure siliciclastic/volcanics or carbonates, mixed lithologies with 15-30% CO₂ have been suggested to result in the largest decarbonation fluxes due to the influence of aqueous fluids on carbonate stability¹⁶. It is therefore notable that along the Central American arc where there is perhaps the best evidence of ongoing carbonation at depth in the forearc¹⁷ the subducting sediment is mixed siliciclastic-carbonate with ~25% CO₂ ^[9].

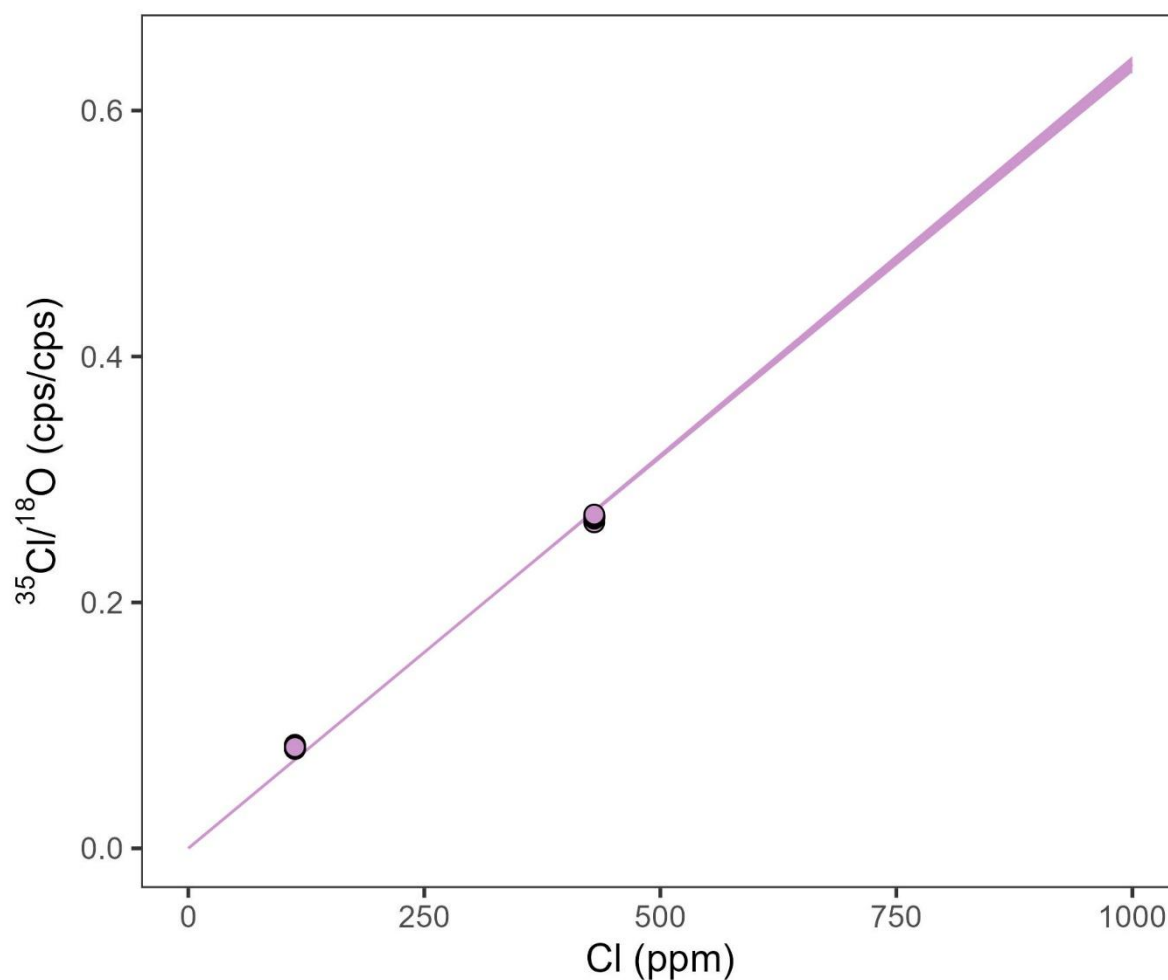
A further factor which has an important bearing on the formation of listvenites is the redox state of the fluid and the relative timing of serpentinisation and carbonation. Serpentinisation results in a reducing fluid and H₂ production and will encourage reduction of carbonate to methane⁶. As a result, listvenite formation is only likely to occur either under relatively oxidising conditions or after serpentinisation has completed. Textural relicts of serpentinite mesh texture within the BT1b listvenites strongly suggest that in Oman carbonation proceeded after serpentinisation¹.

Together these observations suggest that listvenite formation in forearcs may be encouraged by warm subduction, channelisation of deep fluids, subduction of carbonate-rich mixed siliciclastic sediment, oxidising conditions and/or prior serpentinisation of mantle wedge peridotites, although further work is necessary to clarify the relative importance of these factors. This raises the important possibility that the magnitude of the forearc carbon sink may vary spatially and temporally in response to differences in oceanic sedimentation, subduction thermal regime and redox state over geological time. Differences in sedimentation in particular are likely to have a strong influence on the CO₂ input to subduction and the redox state of fluids (e.g., ^{18,19}). Preferential forearc carbonation due to subduction of carbonate-bearing sediments may therefore have an important role in fluctuations in the long-term carbon cycle.

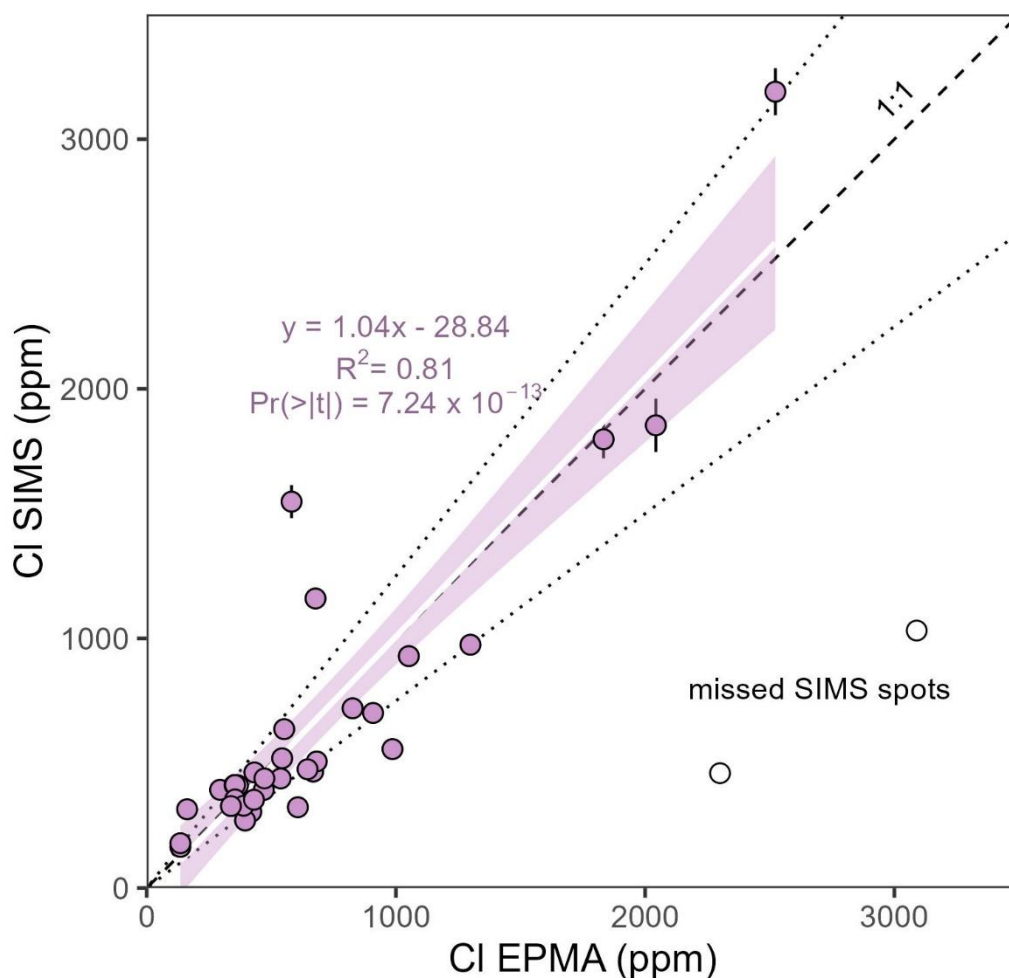
3 Supplementary figures – SIMS calibration and data quality



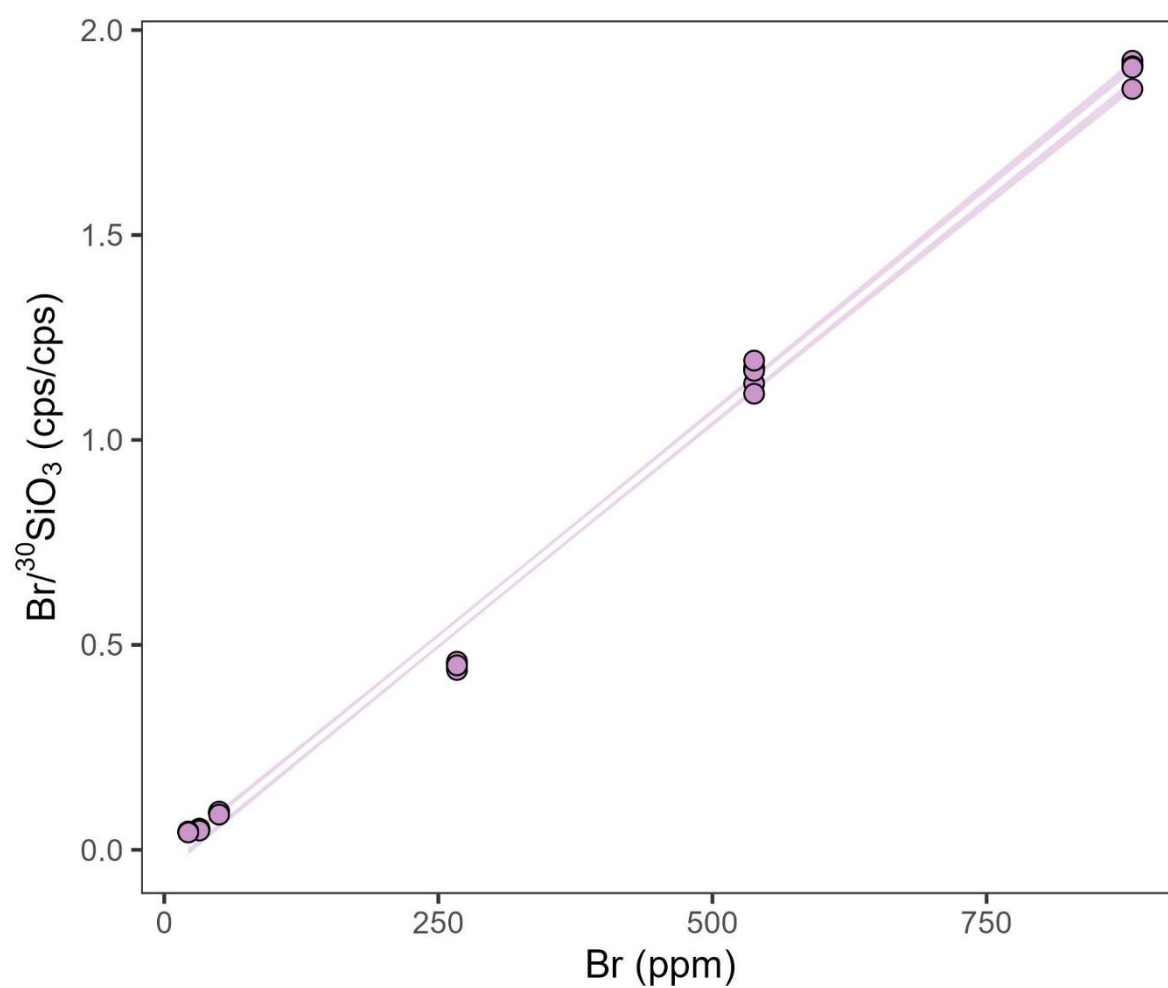
Supplementary Figure 1 – plot of SIMS $^{19}\text{F}/^{18}\text{O}$ signal ratio against certified F contents for two natural glass standards (T1G, ATHO) with widely differing matrices (SiO_2 = 50 and 75 wt%, respectively) and Cl contents (321, 900 ppm, respectively) showing linearity of SIMS response. SIMS standard data are given in Supplementary Data 9.



Supplementary Figure 2 – plot of SIMS $^{35}\text{Cl}/^{18}\text{O}$ signals against certified Cl contents for two natural glass standards (T1G, ATHO) with widely differing matrices ($\text{SiO}_2 = 50$ and 75 wt%, respectively) and Cl contents (100, 400 ppm, respectively) showing linearity of SIMS response and linear increase in uncertainty with Cl content. SIMS standard data are given in Supplementary Data 9.



Supplementary Figure 3 – comparison of Cl data from EPMA and SIMS showing strong correlation ($R^2 = 0.81$) and linearity ($m = 1.04$). EPMA Cl data were derived from averaging of maps around spot locations as described in Methods. Two points with large excesses in Cl measured by EPMA relative to SIMS appear to be due to mistargeting of fine scale Cl-rich features visible on EPMA mapping but difficult to discern in reflected light.



Supplementary Figure 4 – plot of SIMS Br/³⁰Si¹⁶O₃ signal against Br content showing linearity across a range of standard matrices (scapolites BB1, BB2, SY, and synthetic glasses GSD and GSE) and Br contents (10-800 ppm). SIMS standard data are given in Supplementary Data 9.

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