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1 Direct analyses of fluorine in aqueous fluids extracted from 2 1-GPa experiments

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9
10 Declarations of interest: none

11 12 **Abstract:**

13 Fluorine has been proposed as a useful geochemical tracer for tracking the
14 transport of volatile elements in subduction zones as it is the last volatile element to
15 be exsolved during magma ascent and crystallization. Accurate determination of the
16 concentration of fluorine in geological fluids under high *P-T* conditions would greatly
17 further the understanding of its geochemical behavior during aqueous transport and
18 magma genesis in arcs. Mass balance is the most widely used method for calculating
19 fluid compositions in hydrothermal experiments. However, the method is inaccurate
20 for large uncertainties of phase compositions and/or proportions. In the current study,
21 we present an alternative method by directly measuring the concentration of F in
22 fluids by extracting the enclosed liquid within experimental samples, and by
23 performing high-pressure liquid chromatography (HPLC) measurement. We then
24 compared the results of this direct analysis with those obtained by mass-balance
25 calculations. Our experimental data demonstrate that direct analysis yields more
26 accurate concentration values than mass-balance calculation. The direct method is a
27 useful alternative, when i) the phase assemblage is complex, ii) the total F content or

1 28 the fluid proportion is low, or iii) when there is significant presence of hydrous melts.
2
3 29 Caution should be exercised when applying direct analysis to samples that contained
4
5 30 insoluble quench phases and/or were low in fluid. Direct HPLC analysis, combined
6
7 31 with an improved extraction method that ensures the separation of quench phase,
8
9 32 minerals and melts, could be of great utility for studying water-rock reactions.

10
11 33 **Key words:** fluorine; high P - T experiments; aqueous fluid; HPLC
12
13 34

1. Introduction

Primitive melt inclusions are formed by the sequestration of primary lava inside crystallizing minerals during magma ascension. The main volatile species in these melt inclusions, which generally include H₂O, CO₂, S, Cl and F, are subjected to varying degrees of degassing as a result of magmatic ascent. Such partially-degassed magmas tend to retain initial abundance of F and Cl, while H₂O, CO₂, and SO₂ are significantly depleted (e.g., [Villemant and Boudon, 1999](#)). As these volatile elements are exclusively derived from subducting slabs, the retained halogens serve as ideal tracers for investigating the physico-chemical state and the mobility of volatile elements in subduction zones ([Le Voyer et al., 2010](#); [Spilliaert et al., 2006](#); [Straub and Layne, 2003](#); [Van den Bleeken and Koga, 2015](#); [Wu and Koga, 2013](#)). Data on the mineral-melt-fluid partitioning of F and Cl are therefore critical for geologists to deduce the conditions of magma genesis and the nature of slab flux. Although a number of research groups have measured the mineral-melt partition coefficients of F and/or Cl under high *P-T* conditions ([Adam et al., 2016](#); [Bernini et al., 2013](#); [Beyer et al., 2012](#); [Dalou et al., 2012](#); [Dalou et al., 2014](#); [Fabbrizio et al., 2013](#); [Hauri et al., 2006](#); [Joachim et al., 2015](#); [O'Leary et al., 2010](#); [Rosenthal et al., 2015](#); [Van den Bleeken and Koga, 2015](#); [Wu and Koga, 2013](#)), there are significantly fewer studies on the distribution of these elements between aqueous fluids and mineral phases. This disparity is likely attributed to the difficulty in experimentally simulating water-rock reactions and accurately determining the chemical composition of fluid equilibrated under high *P-T* laboratory settings. Accurate quantification of the abundances of F and Cl in aqueous fluids is necessary for experimentally determining their fluid-mineral partition coefficients, which can provide key information on arc magmatism.

Mass balance is the most commonly used method for quantifying F and Cl in unquenchable aqueous fluids (i.e. fluids that undergo compositional changes during rapid cooling to ambient *P-T* conditions). The method assumes a closed system and attributes the mass difference between the bulk and the sum of all solid phases to the

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fluid ([Ayers et al., 1997](#); [Bernini et al., 2013](#); [Brenan et al., 1995](#); [Chevychelov et al., 2008](#)). To measure the mass fractions of F and Cl in minerals, a secondary ion mass spectrometer (SIMS) is used to analyze crystal grains with cross sections greater than 50 μm to ensure sufficient accuracy of measurement. Although mineral seeds are often used to promote crystal growth ([Brenan et al., 1995](#)), they can partially dissolve in aqueous fluid under high P - T conditions, which changes the bulk composition and thus introduces uncertainties to mass-balance calculation. Also, the accuracy of mass balance decreases rapidly as the fluid fraction decreases ([Koga et al., 2005](#)). These drawbacks highlight the need for the development of an analytical methods that can directly determine fluid compositions.

High-pressure liquid chromatography (HPLC) has been used in a number of high P - T geological studies to determine the abundance of various fluid-soluble elements, including halogens, in aqueous systems. For example, [Michel and Villemant \(2003\)](#) quantified F and Cl in 17 reference rocks using digestion and HPLC. A similar strategy was employed to measure the concentrations of ammonium and potassium ions in fluid samples extracted from hydrothermal experiments ([e.g. Pöter et al., 2004](#)). In this study, we determined the F contents in aqueous solutions extracted from piston-cylinder hydrothermal experiments, which equilibrated with hornblende and a humite group mineral, using both direct HPLC analyses and mass-balance calculation. We also estimated the level of F in complex with cations such as Al, Fe and Mg in the extracted solution.

86 **2. Experimental methods**

87 **2.1 Starting materials**

88 Experiments were conducted with a natural mineral specimen composed mainly
89 of Na_2O - FeO - CaO - MgO - Al_2O_3 - SiO_2 with minor amounts of TiO_2 , Cr_2O_3 , and MnO .
90 A total of four solid samples, designated SP1, SP2, SP3, and SP4, were prepared. SP1
91 - SP3 consisted of orthopyroxene (opx), clinopyroxene (cpx) and Al_2O_3 powder in

1 92 ratios that were slightly different but all stoichiometrically equivalent to that in
2 93 hornblende (Hbl). SP4 was composed of SP1, SP3 and MgO. Both opx and cpx were
3 94 handpicked from a coarse granular garnet lherzolite xenolith from Pali Aike, Chile
4 95 ([Stern et al., 1986](#)). SP1 – SP4 were then doped with MgF₂ to the equivalent of 0, 5, 2
5 96 and 0.5 wt% F, respectively ([Wu and Koga, 2013](#)). The exact chemical composition of
6 97 each sample was determined after converting it to homogeneous glass through
7 98 annealing in graphite capsules at 1550 °C and 1 GPa (Table 1). The bulk composition
8 99 of SP4 was determined by mixing it with LiBO₂ (7.28 mg SP4 : 3.80 mg LiBO₂) to
9 100 lower its melting point. As a consequence, the relative uncertainty of the composition
10 101 of SP4 was greater than those of SP1 – SP3. The samples were individually weighed
11 102 and loaded into separate capsules. Each capsule was weighed, followed by the
12 103 addition of Milli-Q water with a micropipette. The capsules were weighed again after
13 104 water loading. The seed-bearing experiment was performed with SP3 as starting
14 105 material. Richterite crystals (amphibolite from the Western Alps) between 100 and
15 106 200 µm in width were added as seeds (Table 1).

107 108 2.2 Experiments

109 High *P–T* experiments were conducted at Laboratoire Magmas et Volcans
110 (LMV), Clermont-Ferrand, France, using piston-cylinder apparatuses that were 3/4 or
111 1/2 inch in diameter. The capsule was designed based on the cold-sealing technique
112 described in [Ayers et al. \(1992\)](#) with minor modifications. The capsule size was
113 reduced in order to minimize temperature gradients and to accelerate thermal
114 equilibration. The outer chamber was manufactured with nickel, titanium or
115 molybdenum, with dimensions as follows: outer diameter (od) = 4.0 (unit: mm,
116 hereinafter), height (h) = 4.0, and a 3.2 long (l) central hole with a 2.1 or 3.1 inner
117 diameter (id). The inner sleeves are gold or Au-Pd alloy tubes (od=2.0 or 3.0,
118 thickness = 0.2, l = 5.0). The frictional pressure loss and temperature gradient
119 associated with the standard assembly were corrected according to [Laporte et al.](#)
120 [\(2004\)](#). Temperature was measured and controlled by a W₅Re₉₅-W₂₆Re₇₄
121 thermocouple. An 0.5 mm-thick aluminum disk was placed between the thermocouple

122 and the capsule to protect the former from contamination.

123 The experimental procedures were described in detail in [Wu and Koga \(2013\)](#).
124 Briefly, the solid sample and Milli-Q water were loaded into the capsule, which was
125 then placed in the piston cylinder. The pressure, temperature and experiment time
126 were set to 1 GPa, 750 - 1057 °C, and 34 - 215 h, respectively (Table 2). After
127 quenching, the capsule was retrieved from the piston cylinder, cleaned of any
128 adhering magnesium oxide, washed in an ultrasonic bath, and pierced with a blade.
129 The punctured capsule was submerged in a beaker containing Milli-Q water and
130 sonicated to extract the fluids within. This procedure was repeated two to four times
131 to ensure the complete extraction of all soluble materials. The extraction solution
132 from each sample was pooled in a volumetric flask and diluted 2,100 to 54,300 fold.
133 The capsule was then oven-dried for one day at 120 °C and weighed. The difference in
134 the weight of the capsule before opening and after drying represented the combined
135 mass of the fluid and the solid materials that were soluble in the extraction solution
136 under ambient *P-T* conditions.

137 Because the formation of quench phases at higher pressure could affect the
138 accuracy of mass-balance calculations, we also performed feasibility studies at 2.0 -
139 2.5 GPa and 877 °C.

140

141 2.3 Determination of fluid composition

142 The fluid composition in each sample was determined by mass balance. The
143 underlying assumption is that the total mass of an element in the bulk should be the
144 sum of its masses in all phases. This can be expressed by the general equation shown
145 below:

$$146 \quad x_{Flu}^i = \frac{100 \cdot x_{bulk}^i - \sum_{s=1}^n (x_s^i \cdot \varphi_s)}{\varphi_{Flu}} \quad (1)$$

147 where x_{bulk}^i and x_s^i represent the mass fractions of oxide *i* in the bulk and in
148 phase *s*, respectively. φ_s and φ_{Flu} denote the proportion of phase *s* and fluid in the
149 bulk, respectively. Because the system is assumed to have no mass exchange with the
150 environment, the proportion of the bulk is set to 100%.

151 To determine the composition of a solid phase, the concentrations of major oxide
152 species were measured by an electron probe microanalyzer (EMPA, CAMECA SX
153 100 at LMV). It is worth mentioning that we chose to measure F with a TAP detector
154 to avoid potential interference with the tail L_{α} -line of Fe (e.g., [Moune et al., 2007](#)).
155 Meanwhile, the mass fractions of water in hydrous minerals and hydrous melts were
156 determined by stoichiometry and charge balance, respectively. To calculate the charge
157 balance in hydrous melts, Fe was assumed to exist exclusively as Fe^{2+} (FeO). With the
158 estimated mass fractions of water in hydrous minerals and melts, normalization was
159 performed and the mass fractions of other elements in these phases were obtained,
160 which were then applied to Equation (1). Detailed description of the mass-balance and
161 charge-balance calculations used in this study can be found in [Wu and Koga \(2013\)](#)
162 (section 2.5).

163 The extracted fluids, without further treatment, were analyzed on a DIONEX
164 DX-120 Ion Chromatograph System at the Institute de Physique du Globe de Paris,
165 France. Free fluoride (F^{-}) was measured by loading 1 mL of the fluid onto an AS9-HC
166 column and eluting with 9 mmol/L Na_2CO_3 at a flow rate of 0.85 mL/min ([Michel and
167 Villemant, 2003](#)). Calibration was performed every four runs by injecting a standard
168 solution of 50 ppb F. All measurements were performed in duplicate. Detection limit
169 was approximately 1 ppb, well below the lowest concentration of fluoride in the
170 extracted solution (6 ppb). At this level, satisfactory reproducibility was still achieved
171 between the duplicate measurements. Other F species, such as various F complexes,
172 could not be detected by the column, which might lower the measurement accuracy
173 by causing the total F content to be underestimated.

174 The quantitation of common cations such as Na^{+} , Mg^{2+} , Ca^{2+} and K^{+} was
175 performed following a similar protocol as described above with the following
176 modifications. The fluid sample was loaded onto a CS12A column (Thermo
177 ScientificTM) and separation was performed by running 20 mmol/L CH_4O_3S as mobile
178 phase at a flow rate of 0.98 mL/min.

179 ICP-MS measurement was conducted at Geosciences Environnement Toulouse.
180 Each extraction solution was pre-mixed with 7-10 g of 5% in volume nitric acid and

181 0.12 g of an internal In/Re standard solution. Calibration was performed using three
182 multi-element standards containing 1, 30 and 60 ppb of Mg, Ca, Al, Si, or Fe.

183

184 **3. Results**

185 Four different F-bearing samples, designated as SP1 (F-free), SP2 (F-rich), SP3
186 (intermediate-F), and SP4 (low-F), were tested under high P – T conditions designed to
187 simulate natural Hbl-bearing systems. The melt-free phase assemblage for each
188 sample at 1 GPa was as follows: SP1 – Hbl; SP2 – Hbl and norbergite (Nrb,
189 $\text{Mg}_2\text{SiO}_4 \cdot \text{Mg}(\text{OH})_2$); SP3 – Hbl and chondrodite (Chn, $\text{Mg}_2\text{SiO}_4 \cdot 2\text{Mg}(\text{OH})_2$); SP4 –
190 augite (Aug), clinohumite (Chu, $\text{Mg}_2\text{SiO}_4 \cdot 4\text{Mg}(\text{OH})_2$), and Hbl or clintonite
191 ($\text{Ca}_2(\text{Mg},\text{Al})_6(\text{Si},\text{Al})_8\text{O}_{20}(\text{OH},\text{F})_4$) (Table 2). The mineral species of the humite group
192 in SP2 changed from Nrb to Chn, then to humite (Hu, $\text{Mg}_2\text{SiO}_4 \cdot 3\text{Mg}(\text{OH})_2$) with
193 increasing temperature. Specifically, the disappearance of Nrb in SP2 was observed at
194 947 °C, whereas the formation of Chn and of Hu occurred at 977 °C and 1057 °C,
195 respectively. In addition, hydrous melt in SP2 appeared at 947 °C and its proportion
196 steadily increased with rising temperature. In comparison, no Hbl was observed in
197 SP2 at 2.5 GPa; instead, the phase assemblage of the sample consisted of
198 hydrogrossular (OH-Grs, a hydrous garnet, with a chemical formula of $(\text{Mg},\text{Ca}^+)_3\text{Al}_2$
199 $(\text{SiO}_4)_{3-x}(\text{F},\text{OH})_{4x}$), Nrb, Aug (Fig. 1a) and quench phase (Fig. 1b).

200 Back-scattered electron imaging indicated that large crystals were concentrated
201 in the top section of the capsule (Fig. 2a). To obtain larger crystals, we increased the
202 experimental time or temperature. However, running longer experiments at the same
203 temperature resulted in greater water loss without notable improvement in crystal size
204 (e.g., 1-SP2-24, which lasted 215 hours at 750 °C). On the other hand, while we
205 successfully generated larger crystals at higher temperatures, we also observed the
206 formation of hydrous melts, which, for instance, occurred above 947 °C in SP2
207 experiments. The melts contained 6.5 to 10.3 wt% of water based on the calculation
208 of charge balance, and could be easily recognized by their vesicular texture that

209 resulted from fluid degassing and exsolution (Fig. 2c). Similar levels of water content
210 have been reported by [Holtz et al. \(1995\)](#) in $\text{SiO}_2\text{-NaAlSi}_3\text{O}_8\text{-KAlSi}_3\text{O}_8$ systems at
211 0.5-8 kbar and 800 °C. Our results was also consistent with [Mitchell et al. \(2017\)](#)'s
212 finding of a water solubility of 20.6 ± 0.9 wt% in basalt melt at 1 GPa and 1200 °C, as
213 the water content of melt generally decreases with a drop in temperature.

214 We further investigated whether seeding could improve the crystal size. In
215 1-SP3-10, we seeded F-bearing Hbl with 10 μm -wide F-free Hbl grains derived from
216 1-SP1-8 (Fig. 2b). The similarity between the chemical composition of SP1 and that
217 of SP3 could minimize the possibility of contamination introduced by seeding.
218 Nevertheless, the seeds failed to induce the formation of sufficiently large Hbl crystals,
219 suggesting that they either had dissolved or were too small. To address this problem,
220 natural richterite seeds with width over 100 μm were used in 1-SP3-11. As illustrated
221 in Fig. 2d, back-scattered electron imaging revealed the formation of a smooth
222 boundary around the seed crystal, suggesting its partial dissolution prior to the
223 precipitation of new crystals. EMPA showed that the overgrowth comprised two zones
224 with slightly different compositions (Fig. 2d). Specifically, the contents of MgO and
225 SiO_2 in Zone 1 were shown to be greater than those in Zone 2 by 1 wt% and 4 wt%,
226 respectively. On the other hand, the levels of CaO, Al_2O_3 and F in Zone 1 were 1 wt%,
227 6 wt% and 0.1 wt% lower than their respective counterparts in Zone 2. These results
228 highlighted the potential impact that seeding might produce on the bulk composition
229 and those of the newly precipitated crystals.

230

231 4. Discussion

232 4.1 Limitations and validation of the mass-balance approach

233 One of the most significant contributing factors to inaccurate mass balance
234 results is the unintended loss of materials by diffusion and/or leakage, as well as the
235 inadvertent introduction of contaminants. Such anomalies have been reported in a
236 number of studies. [Ayers et al. \(1997\)](#) observed that hydrogen generated from the

1 237 thermal decomposition of water could diffuse through gold capsule and contribute to
2 238 the decrease of aqueous fluids. In one of [Brenan and Watson \(1991\)](#)'s experiments,
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4 239 fluid expansion during quenching was suspected to have caused capsule failure and
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6 240 vapor leakage. Absorption of Fe by Pt-based capsules was noted by [Watson \(1991\)](#).
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8 241 This loss could not be completely prevented even by pre-saturating the capsule with
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10 242 Fe-bearing compounds (personal communication with C. Dalou). Based on these
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12 243 findings, we identified four factors that could compromise the accuracy of
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14 244 mass-balance calculations in our current study.

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16 245 First, loss of materials was suspected in some experiments of this study, such as
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18 246 in 1-SP2-14, which had a considerably different phase assemblage (Hbl-Nrb-Chn-Flu)
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20 247 from other SP2 runs (Hbl-Nrb-Flu). The observation of Chn, which contains less F
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22 248 than Nrb, suggested a decreased abundance of the halogen in the bulk of 1-SP2-14.
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24 249 Because missing mass had to be assumed as part of the fluid, this anomaly in bulk
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26 250 composition artificially inflated the calculated level of F in the fluid. Similarly, in
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28 251 1-SP2-23, sonication of the capsule might have led to an inadvertent loss of spinel
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30 252 crystals rich in Al, Mg and Fe, causing the mass-balance method to overestimate the
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32 253 concentration of Al in the fluid. In some cases, low-abundance solid phases could
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34 254 elude detection and thus not be included in the mass-balance calculations. When we
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36 255 compared the data of different SP3 experiments, we noticed that a small proportion of
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38 256 Chn (<6 wt%) was observed in all runs except 1-SP3-1, 10 and 11. Further
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40 257 investigation revealed that the composition of Hbl remained almost constant in these
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42 258 experiments, but the fluid proportion varied significantly. Taken together, these results
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44 259 implied that all SP3 experiments should have reached phase equilibrium at the end,
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46 260 which in turn suggested that the absence of Chn in 1-SP3-1, 10 and 11 was likely due
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48 261 to detection errors. Therefore, in subsequent mass-balance calculations, we corrected
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50 262 the phase assemblage of 1-SP3-1 by assuming that its composition of Chn was
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52 263 identical to that in 1-SP3-3, based on the fact that both runs used the same starting
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54 264 sample and were conducted under similar *P-T* conditions.

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56 265 Second, when determining the chemical composition of a solid phase, the results
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58 266 obtained from the measurement of a few large crystals are often not sufficiently
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1 267 representative due to phase inhomogeneity. A previous study described by [Larocque](#)
2 268 [and Canil \(2010\)](#) showed that the abundances of Al and Si in hornblende varied
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4 269 significantly according to the pressure and temperature at which the phase was formed.
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6 270 Based on this finding, we speculated that the comparatively large uncertainties of the
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8 271 mass fractions of Si and Al in hornblende that we observed in our experiments could
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10 272 also have been caused by the temperature gradient in the lower capsule.

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12 273 Third, the calculation of phase proportions, which are an essential part of the
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14 274 mass-balance equation, involves the selection of conservative elements and the
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16 275 determination of their concentrations. Although the mass-balance method assumes
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18 276 these elements to be completely insoluble, this is generally not true under high *P-T*
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20 277 conditions. In fact, mass balance likely produced incorrect phase proportion results in
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22 278 many experiments that involved SP4 or hydrous melts (Table 2), as the calculation of
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24 279 F content in the fluid yielded zero or negative values in obvious contradiction to direct
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26 280 HPLC analysis. One emerging strategy that could potentially improve the accuracy in
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28 281 the measurement of phase proportion is to directly visualize and quantify mineral
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30 282 distribution by computed tomography (CT) imaging ([Friese et al., 2013](#)). It is worth
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32 283 emphasizing that non-metal capsules or sample removal from metal capsules would
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34 284 be required.

35
36 285 Fourth, the accuracy of mass balance decreases as the proportion of fluid in the
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38 286 sample drops. [Koga et al. \(2005\)](#) argued that having more mineral-compatible
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40 287 elements and less fluids in fluid-bearing experiments would increase the uncertainties
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42 288 of the fluid compositions and partition coefficients via mass-balance approach. In the
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44 289 current study, as F resided mostly in hydrous minerals, decreased fluid proportion in
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46 290 samples would reduce the accuracy of the mass-balance method (Fig. 3). Based on
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48 291 our estimates, the relative uncertainty of F abundance in fluid calculated by mass
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50 292 balance could exceed 100% when its proportion drops below 50 wt%, which is
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52 293 consistent with [Koga et al. \[2005\]](#)'s modeling of error propagation in mass-balance
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54 294 calculations. This would ultimately generate large uncertainties in partition
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56 295 coefficients between fluids and minerals, which can only bring a weak constraint on
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58 296 the geochemical behavior of tracer elements.

297 One way to validate the mass-balance approach is to compare the abundances of
298 Si, Al, Mg and Ca in the extracted fluids calculated by mass balance to their literature
299 values. The normal SiO₂ concentrations in the fluids by mass-balance calculations
300 were in the range of 1.09-5.61 wt%, which was in good agreement with [Newton and](#)
301 [Manning \(2002\)](#)'s study (2.9 wt% SiO₂, equilibrium with enstatite-forsterite-H₂O
302 systems at 1 GPa and 700-900 °C). However, several experiments, such as in
303 1-SP2-23 (11.86 wt%) and 1-SP3-3 (18.82 wt%), exhibited abnormally high levels of
304 SiO₂, presumably due to water loss and/or other compositional changes that
305 invalidated the closed-system assumption. Meanwhile, the concentrations of Al₂O₃ in
306 the aqueous fluid ranged from 0.26 to 1.77 wt%, echoing Manning et al.'s finding that
307 Al is less soluble than Si in the assemblage of albite-paragonite-quartz at 1 GPa and
308 350-620 °C ([Manning et al., 2010](#)). Moreover, our ICP-MS data also indicated that
309 SiO₂ (0.27-7.86 wt%) was more abundant in the fluid than Al₂O₃ (0.009-0.37 wt%) in
310 Hbl-Hu systems. In addition, mass-balance calculations and ICP-MS quantitation
311 found very low levels of MgO (0.016-0.25 wt%) and CaO (0.028-0.373 wt%) in the
312 fluids. Taken together, we conclude that mass-balance results in most of our
313 experiments are consistent with those reported previously. Despite the limitations
314 described above, we argue that mass balance should be particularly useful in
315 experiments with a relatively simple phase assemblage (e.g. certain SP2 and SP3
316 experiments that involved only two to three mineral phases).

317 318 4.2 Quantitation of soluble elements F and Na in fluids

319 We measured the concentration of F in the fluid via both mass balance and direct
320 analysis. As shown in Fig. 4a, the two approaches were largely consistent with each
321 other in most 1-GPa SP2 and SP3 experiments. On the one hand, the mass-balance
322 method showed that the levels of F in the fluids extracted from SP2 and SP3 runs
323 were 0.2-0.8 wt% and 0.06-0.4 wt%, respectively, with uncertainties in the range of
324 0.16 wt% to 2.6 wt% or relative uncertainties of 57% to 370%. In comparison, HPLC
325 quantitation showed that the level of aqueous F ranged between 0.057 wt% and 0.56
326 wt% in SP2 runs, and between 0.029 wt% and 0.106 wt% in SP3, with substantially

1 327 smaller uncertainties (0.001-0.01 wt%) than those of the mass-balance method. On the
2 328 other hand, the levels of F calculated by mass balance greatly exceeded those of direct
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4 329 HPLC analysis in all 2- and 2.5-GPa experiments (2 GPa: mass balance – 1.65 wt%,
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6 330 direct analysis – 0.365 wt%; 2.5 GPa: mass balance – 1.09 wt%, direct analysis –
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8 331 0.055 wt%). This was likely due to the presence of F in the quench phase (Fig. 1b),
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10 332 which sequestered soluble elements, rendering them unextractable and thus
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12 333 inaccessible to HPLC analysis, and to the larger proportion of quench phase at higher
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14 334 pressures. System leakage could also cause mass-balance results to be significantly
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16 335 greater than those of direct analysis for the obvious reason that lost F-bearing
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18 336 materials were not extracted and therefore not measured. Finally, in 1-SP2-21,
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20 337 1-SP4-3 & 4, 1-(SP2+Qtz) and 1-(SP1+MgF₂), mass-balance calculations yielded
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22 338 negative F concentrations, whereas HPLC quantitation was apparently not affected
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24 339 due to its low detection limit. Overall, HPLC results were shown to be reliable when
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26 340 the proportion of quench phase in the bulk was less than 10% in volume of total solid
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28 341 phases (estimated by cross-section image).

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32 342 In comparison, mass balance and direct analysis generated comparable levels of
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34 343 Na (Fig. 4b). One obvious reason for the better consistency was that the solubility of
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36 344 Na in water is much higher than that of F, resulting in lower relative uncertainties. An
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38 345 additional contributing factor is that the quench phase usually contained
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40 346 disproportionate amounts of cations such as Si, Al, Mg and Ca, which could sequester
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42 347 F⁻ and other negatively charged F-bearing species via electrostatic interaction.
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44 348 Consequently, a significant portion of these F species could have been transferred
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46 349 from the fluid to the quench phase and became unextractable. Taken together, the
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48 350 results of mass balance and direct analysis are both acceptable in most experiments;
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50 351 however, there are scenarios in which one method would be more preferred than the
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52 352 other. Mass-balance calculations are prone to yield negative concentration values
53
54 353 when the total F content in the bulk is low, whereas direct analysis is not suitable for
55
56 354 samples that contain significant amounts of unextractable F-bearing quenched solutes.

57
58 355

59
60 356 4.3 Assessing the accuracy of direct HPLC analysis

1 357 The total fluorine in extracted fluid can exist as F^- , HF, and/or fluoride-based
2 358 complexes such as SiF_6^{2-} and AlF_6^{3-} . However, only F^- can be quantified on the
3
4 359 AS9-HC column used in the current study. Therefore, the exact chemical form of
5
6 360 fluorine before and during HPLC analysis plays a crucial role in ensuring accurate
7
8 361 measurement. Nevertheless, we reasoned that the strong alkalinity (pH \sim 12) of the
9
10 362 mobile phase and the dilution of the recovered fluid should ensure the near-complete
11
12 363 conversion of HF to F^- .

14 364 SiF_4 and its derivatives can also be found in various geological fluids and gases.
15
16 365 For example, SiF_4 has been detected in volcanic plume via remote observation
17
18 366 employing FT-IR spectroscopy ([Mori et al., 2002](#)). Although the presence of SiF_4 in
19
20 367 high P - T fluid has not been reported, it is known to be able to form H_2SiF_6 and silica
21
22 368 in aqueous solutions under ambient conditions ([Aigueperse et al., 2000](#)). Mirroring
23
24 369 these findings, our previous mass-balance calculations revealed a positive correlation
25
26 370 between the aqueous concentration of F and the solubility of Si, implying that the two
27
28 371 elements might have reacted and formed soluble species, possibly SiF_6^{2-} , under the
29
30 372 experimental conditions involved in the study ([Wu and Koga, 2013](#)). However, SiF_6^{2-}
31
32 373 has been shown to completely hydrolyze at pH $>$ 4 ([Finney et al., 2006](#)), which would
33
34 374 lead to the release of F^- and its subsequent detection by HPLC. Therefore, SiF_6^{2-} was
35
36 375 unlikely to be a major fluorine species in the fluid during the HPLC analysis.

37 376 The contribution of various metal-fluoride species to measurement uncertainties
38
39 377 can be estimated by calculating the fractions of F in these complexes based on their
40
41 378 association constants ([Lange and Speight, 2005](#)), the concentration of F^- determined
42
43 379 by HPLC, and the total level of each metal measured from ICP-MS measurement
44
45 380 (Table 3). Given that the relative uncertainty of the HPLC method is approximately
46
47 381 1%, we concluded that aluminum, iron and magnesium fluorides together accounted
48
49 382 for less than 0.3% of total aqueous F and thus could be safely ignored. This also
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51 383 suggested that dilution of the extracted fluid also promoted the dissociation of the
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53 384 metal-fluoride species.

54 385 Taken together, the dissociation of various F-bearing complexes and the
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56 386 deprotonation of HF were strongly favored due to the chemical nature of the eluent.

1 387 Consequently, free F⁻ was by far the predominant form of fluorine during HPLC
2 388 analysis and its concentration could be safely used to approximate that of total F in
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4 389 the fluid.
5

6 390

8 391 4.4 Limitation of the direct analysis method

9
10 392 The primary error source of the direct analysis method is the change of fluid
11
12 393 composition during quenching and/or annealing. Rapid cooling of the capsule could
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14 394 result in the crystallization of quench phases and/or the exsolution of fluid from
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16 395 hydrous melts depending on the run conditions. In addition, water loss could lead to
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18 396 the saturation and subsequent precipitation of certain solutes from the fluid.
19

20
21 397 The precipitation of insoluble quench phases greatly affects the accuracy of
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23 398 direct analysis by trapping otherwise extractable elements such as Na and F. As
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25 399 discussed in Section 3.1, we argued that the mass-balance method could be suitable
26
27 400 for estimating the aqueous concentration of F in 3-SP2-1 because the bulk was F-rich
28
29 401 and contained only two solid phases, Hbl and Nrb. The discrepancy between mass
30
31 402 balance and HPLC analysis (2 GPa: mass balance – 1.65 wt%, direct analysis – 0.365
32
33 403 wt%) was probably due to the significant amount of quench phases ([e.g., Ayers et al.,](#)
34
35 404 [1997](#)). One strategy to re-solubilize the trapped elements is through the recovery of
36
37 405 quench phases. For example, [Koga et al. \(2005\)](#) demonstrated that certain types of
38
39 406 quench phase could be re-dissolved by washing with acidic or alkaline reagents,
40
41 407 which would reduce their detrimental impact on direct analysis.
42

43
44 408 The exsolution of water from liquid-rich hydrous melts poses an additional
45
46 409 problem by increasing the mass of the extractable fluid. [Van den Bleeken and Koga](#)
47
48 410 [\(2015\)](#)'s study of water-enriched melts has shown F to be quenchable in silicic glasses,
49
50 411 which echoed the general observation that F is least affected by degassing among all
51
52 412 major volatiles (e.g., [Spilliaert et al., 2006](#); [Villemant and Boudon, 1999](#)). We
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54 413 speculated that the formation of hydrous melts in 1-GPa experiments (>900 °C), as
55
56 414 evidenced by their vesiculated texture, might cause the aqueous level of F to be
57
58 415 underestimated (Fig. 2c). Therefore, it is strongly recommended to run the experiment
59
60 416 at temperatures below the solidus.
61

1 417 The reliability of direct analysis could also vary according to the amount of fluid
2 418 present in the sample. This effect was shown by plotting the fluid proportion against
3 419 the aqueous F content determined by HPLC in each run. As illustrated in Fig. 5, the
4 420 HPLC concentrations were relatively constant and in agreement with those obtained
5 421 by mass-balance calculations (SP2: 0.30 ± 0.10 wt%; SP3: 0.15 ± 0.10 wt%) when the
6 422 fluid proportions were above 30 wt%. In contrast, the levels of F in the fluid were
7 423 apparently overestimated at low fluid proportions, particularly in SP2 experiments.
8 424 One possible explanation is that the decreased amount of fluid in the sample could
9 425 lead to incomplete convective mixing of liquid in different parts of the capsule,
10 426 causing otherwise soluble F-bearing species to become locally saturated and
11 427 precipitate. Such precipitates were often extractable under ambient conditions and
12 428 would therefore artificially boost the aqueous level of F during HPLC analysis. This
13 429 might also have occurred in studies using capsule with diamond trap technique
14 430 ([Stalder et al., 2001](#)). Taken together, the precipitation of otherwise soluble F-bearing
15 431 species in dehydrated samples would cause the level of F in fluid to be overestimated
16 432 by both mass-balance calculations and direct analysis.

17 433 We thus screened our results and identified all experiments that were generally
18 434 unaffected by the abovementioned detrimental factors. The $D_F^{\text{Flu/Hbl}}$ derived from
19 435 HPLC measurements in these runs were highlighted in ***bold italic font*** in Table 2.
20 436 Consistent with our previous study, $D_F^{\text{Flu/Hbl}}$ from SP2 and SP3 experiments is
21 437 independent of temperature. Thus, we used the weighted average of $D_F^{\text{Flu/Hbl}}$ in each
22 438 group. The unpaired Student's t-test gives that $t=8.6824$, and the two-tailed P-value is
23 439 less than 0.0001, which suggests to reject the null hypothesis. Thus, the weighted
24 440 averages of the partition coefficients from HPLC concentrations were found to be
25 441 significantly different between the qualified SP2 (0.042 ± 0.003) and SP3 ($0.029 \pm$
26 442 0.002) experiments at the pressure of 1 GPa. In contrast, no such discrepancy was
27 443 detected between the two groups based on a similar examination of the mass balance
28 444 results using the same test (SP2: 0.14 ± 0.05 ; SP3: 0.10 ± 0.07). This suggested that
29 445 the direct analysis method showed greater precision than mass balance and might be
30 446 suitable for investigating the migration patterns of (volatile) elements in the

1 447 subduction zone.

2 448

3 449 **5. Conclusions**

4 450 The results of our study demonstrated the feasibility of using HPLC analysis to
5 451 directly measure the concentration of F in aqueous fluids at 1 GPa and below solidus.
6 452 The obtained HPLC data suggested that the mass-balance calculation results of
7 453 soluble elements were generally reliable in 1-GPa experiments. Meanwhile, it should
8 454 be noted that the direct analysis method showed considerable depletion of elements
9 455 when the bulk contained a significant proportion of quench phase, e.g., experiments
10 456 above 2 GPa.

11 457 Secondly, both mass balance and direct analysis were shown to have incorrectly
12 458 included the exsolved content of hydrous melt and/or the precipitates from extracted
13 459 fluids caused by local saturation. Therefore, a fluid/solid ratio above 0.4 is
14 460 recommended for HPLC measurement of F or any other analyzable elements. It is
15 461 also necessary to improve the current annealing method in order to promote fluid
16 462 convection (or stirring), such as using rocking high-pressure apparatus ([Schmidt and](#)
17 463 [Ulmer, 2004](#)).

18 464 Lastly, the HPLC method could also be employed to quantify other volatile
19 465 species (e.g., halogens, sulfur, and NH_4^+) and soluble cations (e.g., Li^+) in aqueous
20 466 fluids from high P - T environments. Post-quench treatment might be necessary to
21 467 recover quench phases from experimental capsules to improve the accuracy of HPLC
22 468 analysis (e.g., [Ayers et al., 2012](#); [Koga et al., 2005](#)).

23 469

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1 Fig. 1 Back-scattered electron images of 4-SP2-1 experiment at 2.5 GPa and 877 °C. The
2 dark area surrounding minerals is pore space impregnated by epoxy. This open space indicates
3 the presence of a large volume of fluid during annealing, which benefits large crystals growth.
4 The scale bar at the bottom indicates 200 μm . a) Phase assemblies: hydrogrossular (Hgr),
5 augite (Aug), and chondrodite (Chn). b) The quench phases, which are present next to the
6 wall in the middle portion of the capsule, are too small ($< 5 \mu\text{m}$) to be analyzed by electron
7 microprobe. The presence of significant quench phases reveals that the content of the
8 extracted fluid is depleted in elements that are insoluble at ambient conditions.
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19 Fig. 2 Back-scattered electron images for typical 1-GPa experiments. a) The middle
20 portion of 1-SP3-4 experiment at 837 °C. The scale bar is 500 μm . The elongated minerals are
21 Hbl, and the two grey lumpish crystals in the center are Chd. The bright parts are gold chips. b)
22 The bottom portion of 1-SP1-8 experiment at 807 °C. The scale bar is 500 μm . Hbl is the
23 unique mineral phase in this run. The crystals are all small and are distributed evenly in the
24 bottom of the charge. c) Cross section texture of the hydrous melt in experiment 1-SP2-18.
25 The grey holes in the center of the melt indicate the degassing and exsolution during quench.
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Fig. 3 The standard deviation (2σ , wt%) of F concentration in aqueous fluids versus fluid
proportion (wt%) after quench. All the data are based on 1-GPa experiments. Blue diamond,
red square, and orange triangle symbols represent the starting materials of SP2 (5 wt% F),
SP3 (1.9 wt% F), and SP4 (0.5 wt% F) respectively. In a general tendency, the standard
deviation of F concentration from mass balance calculation (solid symbols) decreases with
fluid proportion increasing in bulk composition. On the contrary, the standard deviation of F
concentration from HPLC analyses (open symbols) is independent with fluid proportion, and
is one magnitude order lower than those from mass balance result.

Fig. 4 The comparisons of a) F and b) Na_2O concentrations in fluids between HPLC and

1 mass balance calculation. Blue diamond, red square, orange triangle and blue crossing
2 symbols represent the starting materials of SP2 (5 wt% F), SP3 (1.9 wt% F), SP4 (0.5 wt% F)
3 and Mix composition, respectively. The experiments mentioned above were conducted at 1
4 GPa. Black open round represents the SP2 experiments under 2 GPa and 2.5 GPa. A black
5 solid line $y=x$ was plotted as a reference.
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12 Fig. 5 F concentrations of aqueous fluids measured by HPLC versus fluid proportion
13 (wt%) in bulk composition after quenching. The data setting is the same with Fig. 3. Each
14 solid line and dashed line of the same color represents the average level of F determined by
15 mass balance and the uncertainty, respectively, in the corresponding experiment run. The
16 corresponding experimental temperature is attached below (blue) and above (red) the symbols
17 of SP2 and SP3 experiments, respectively. F concentration decreases dramatically when fluid
18 proportion increases from 20 to 40 wt%, and then almost constant when fluid proportion is
19 larger than 30 wt%.
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Figure 1a

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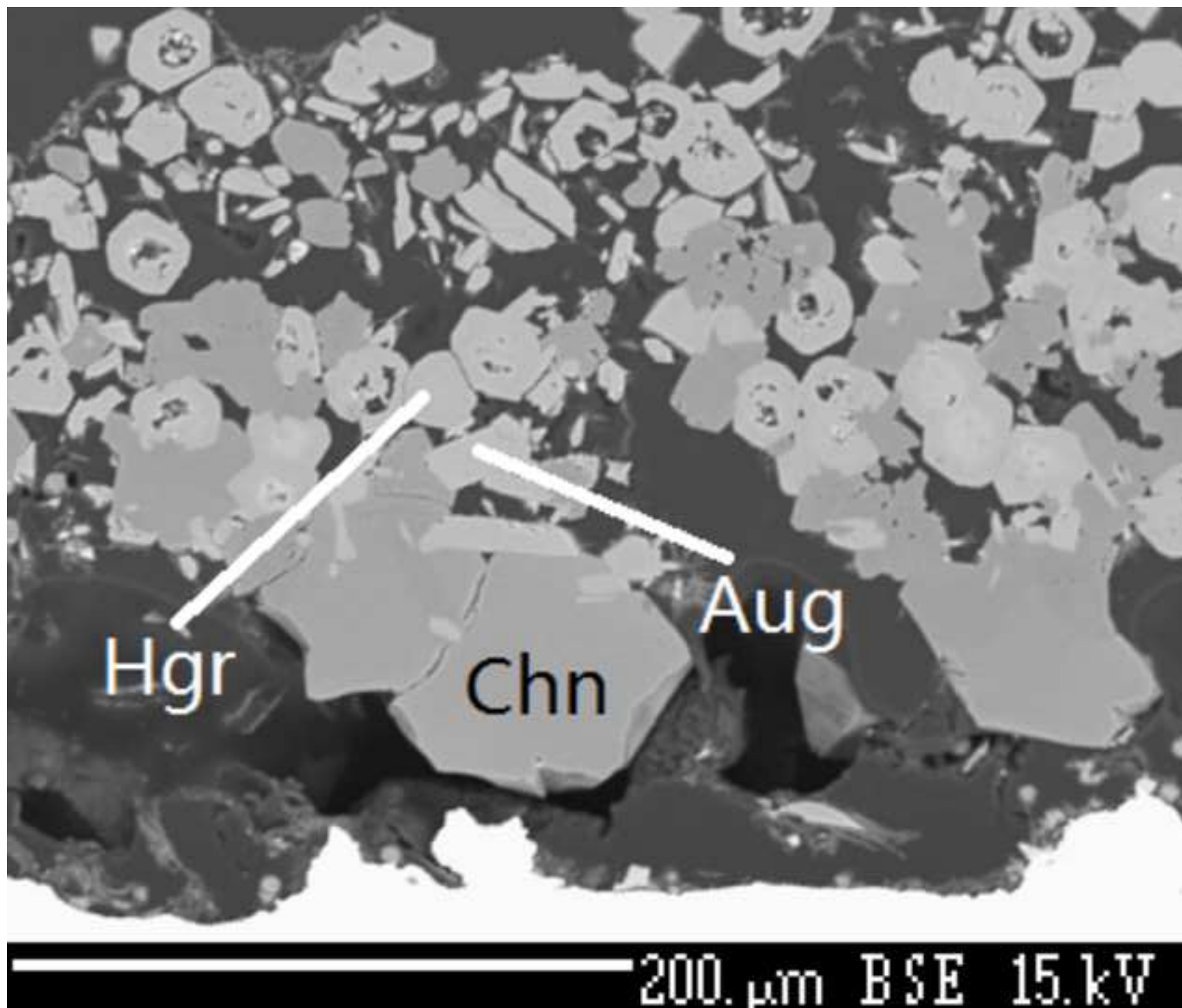


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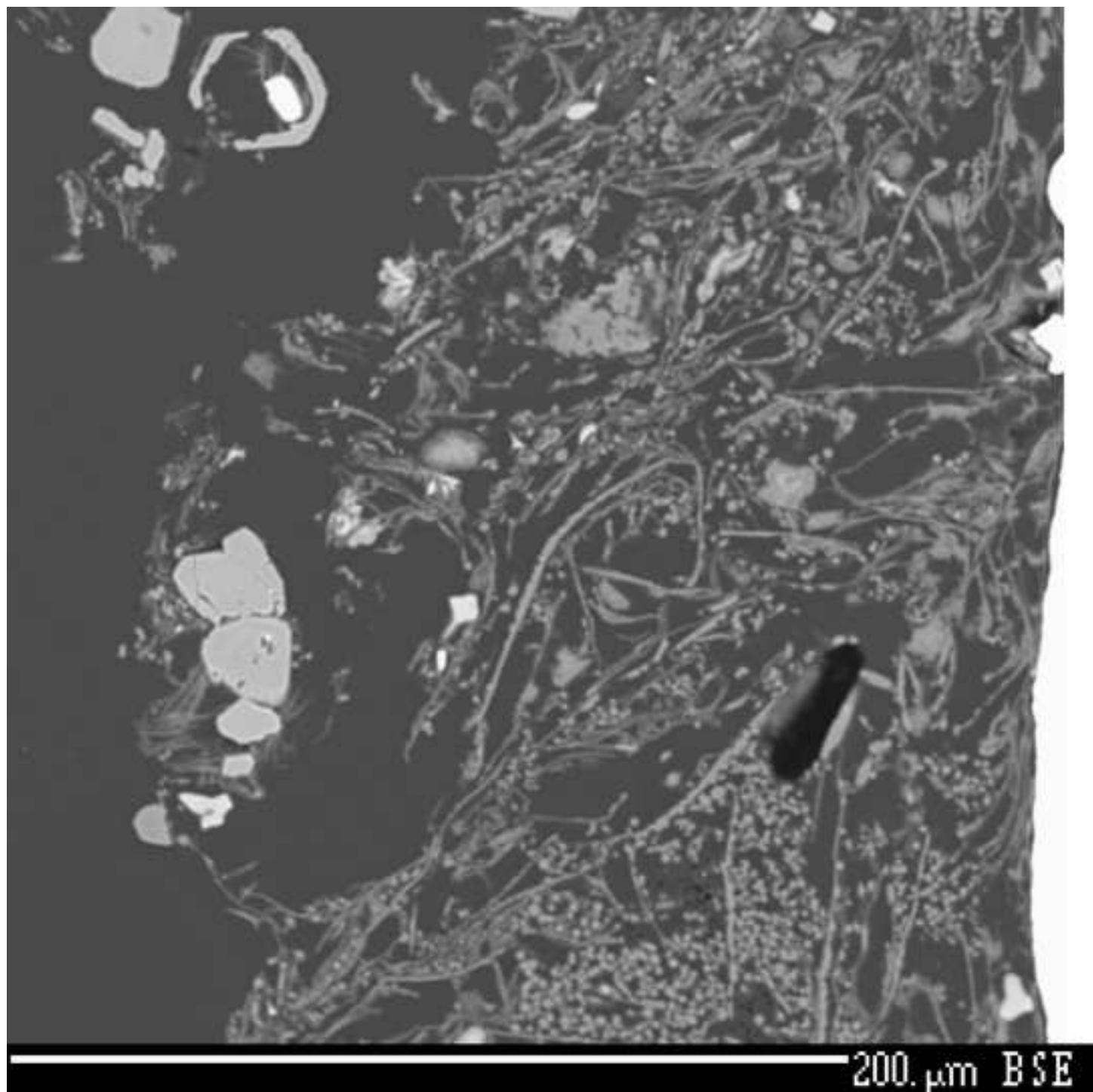


Figure 2a

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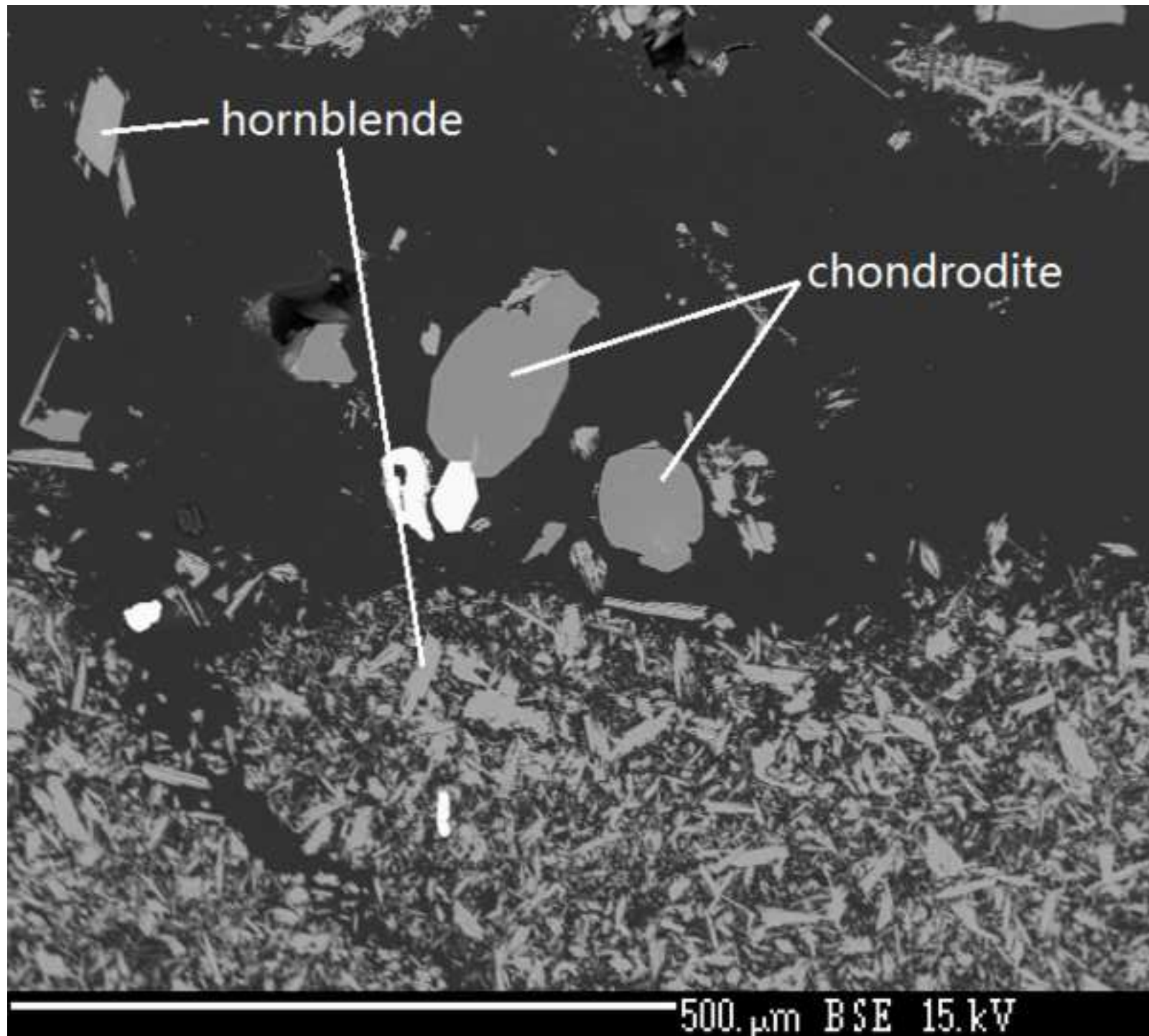


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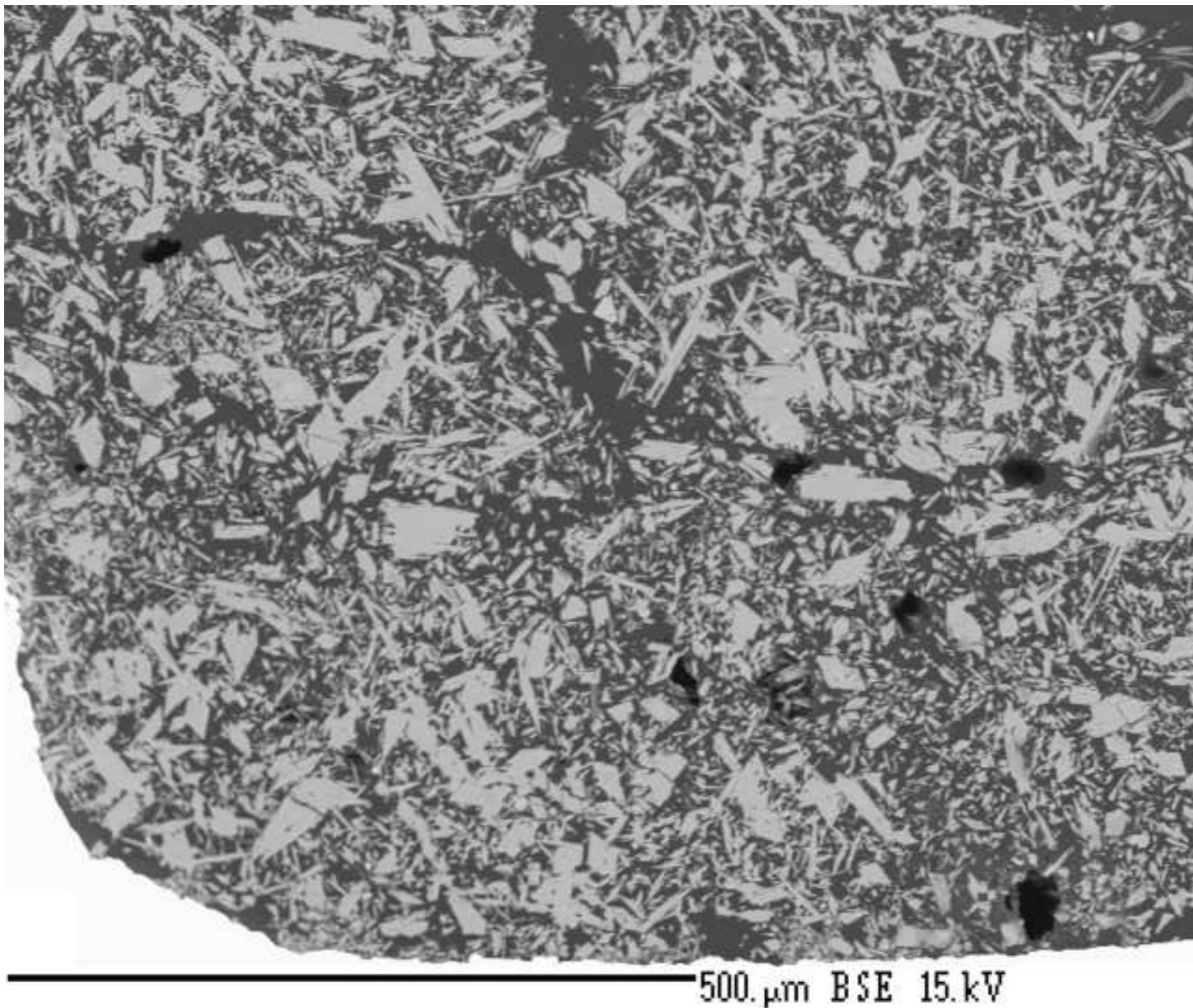


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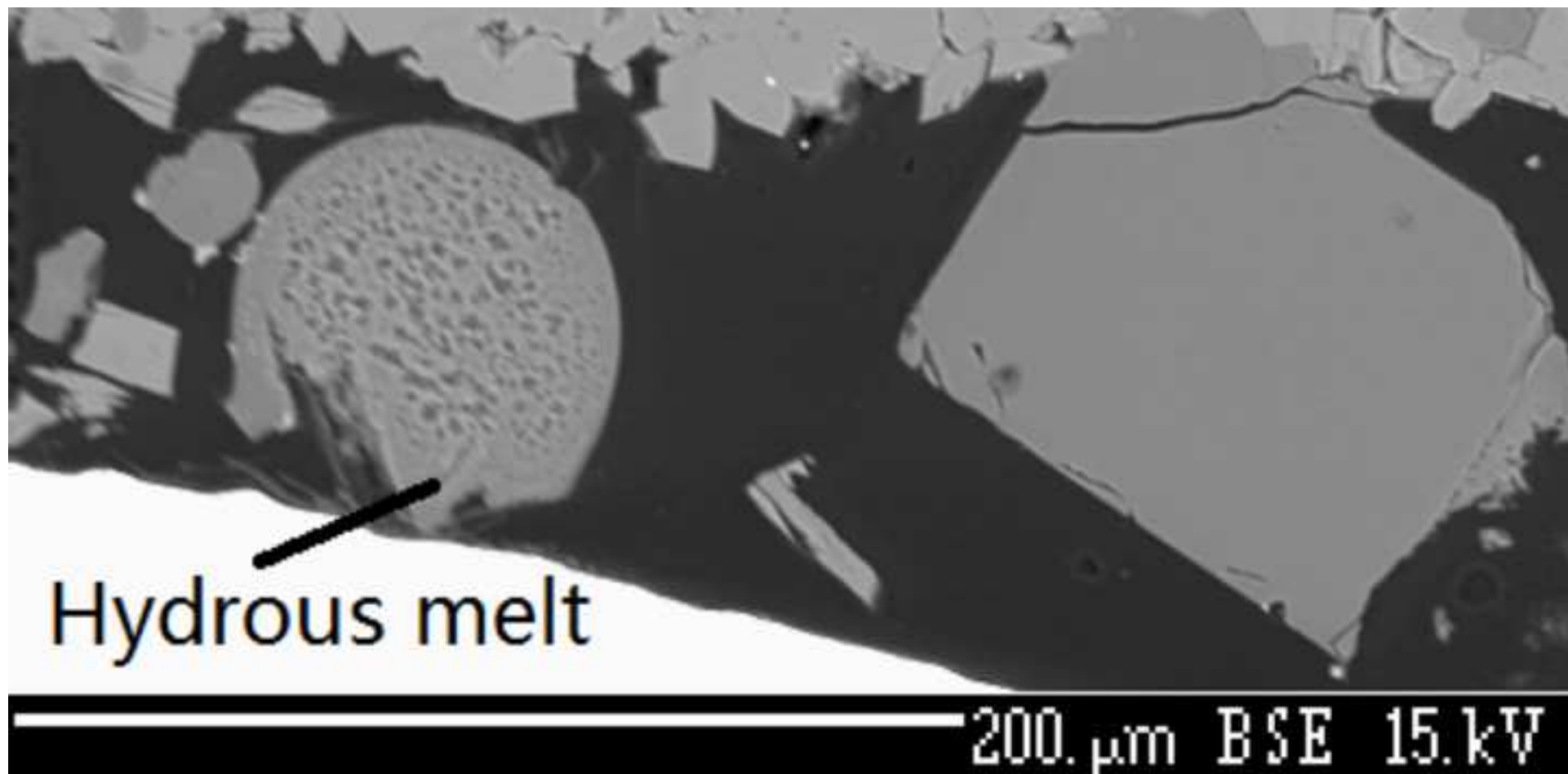


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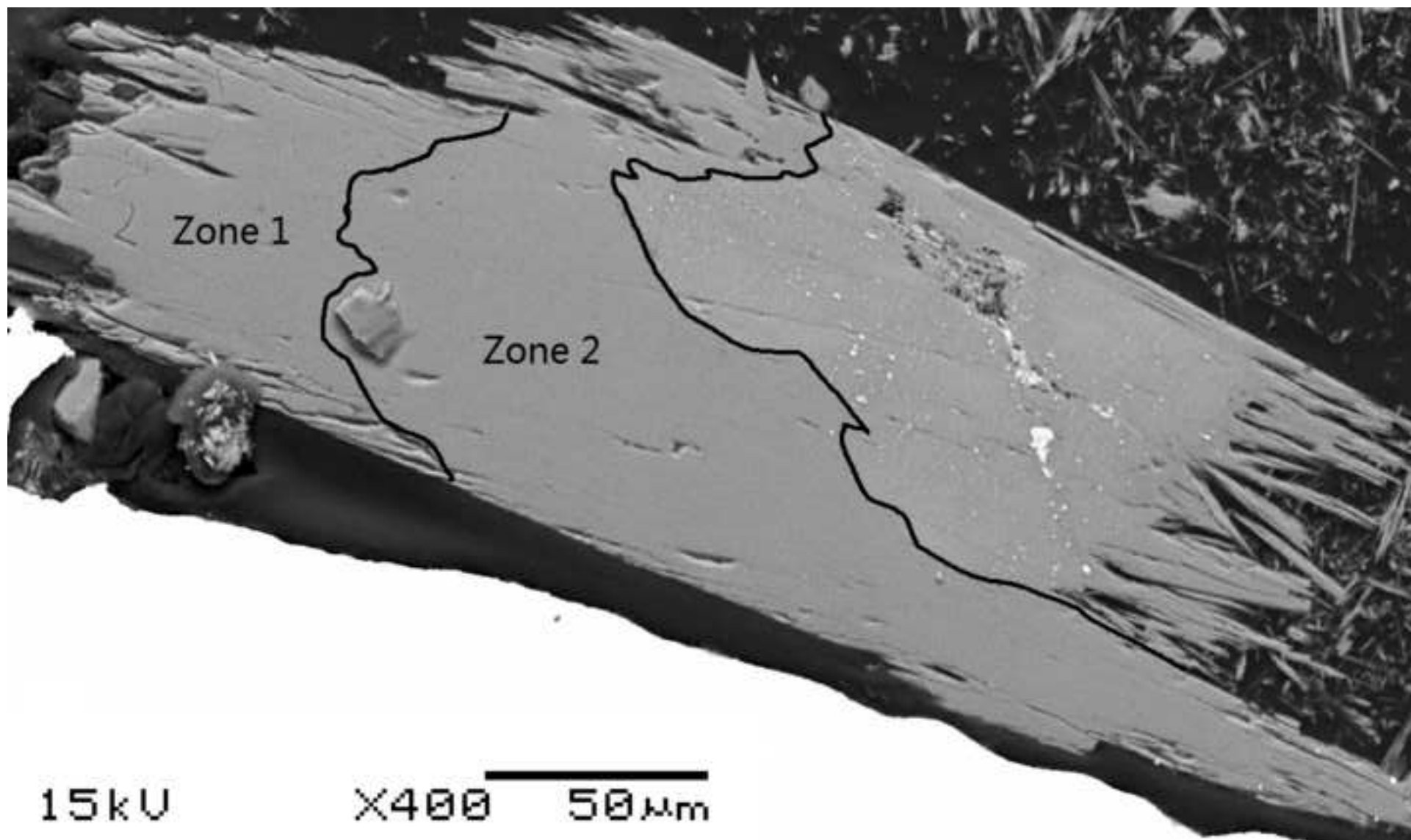


Figure 3
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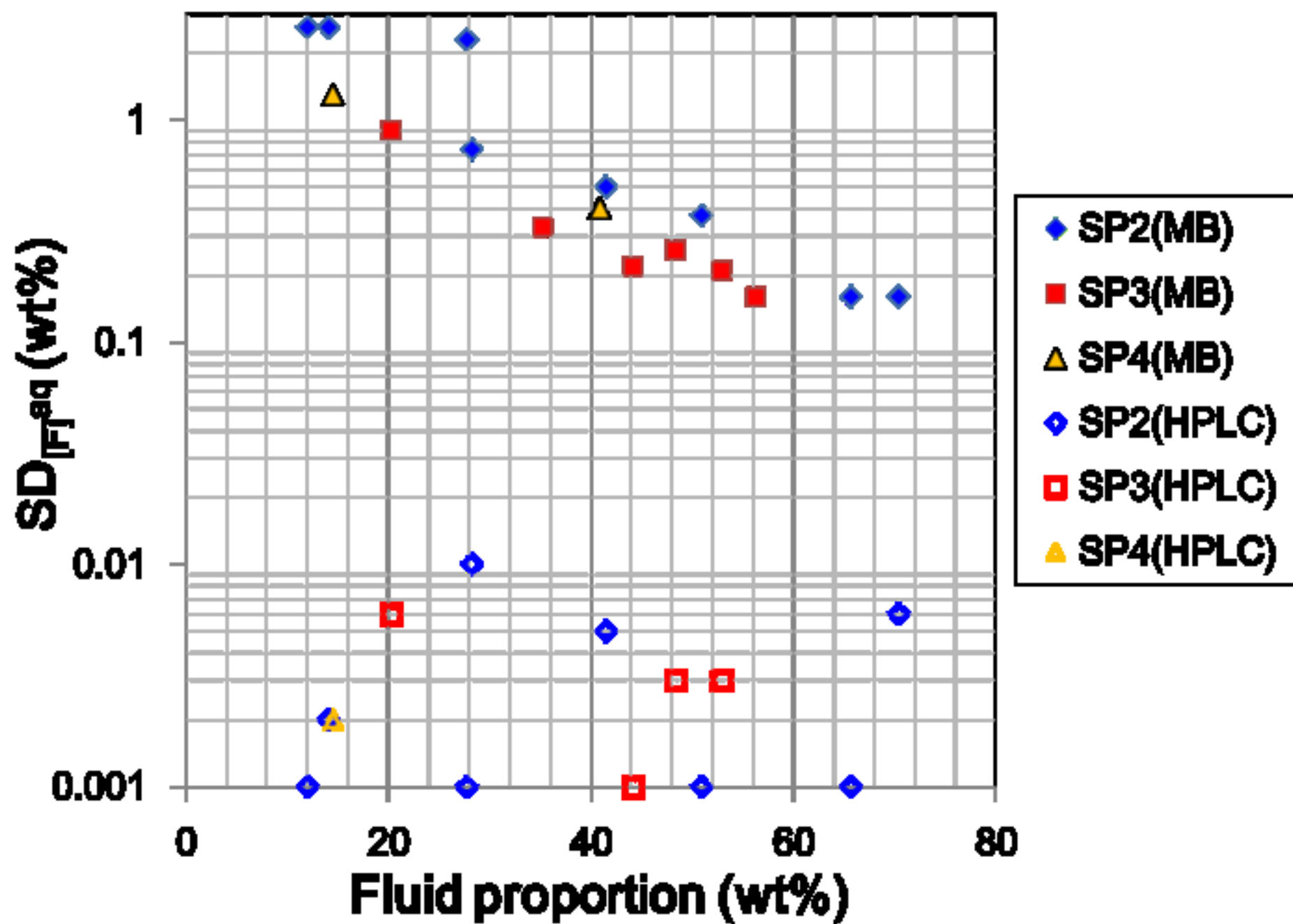


Figure 4a
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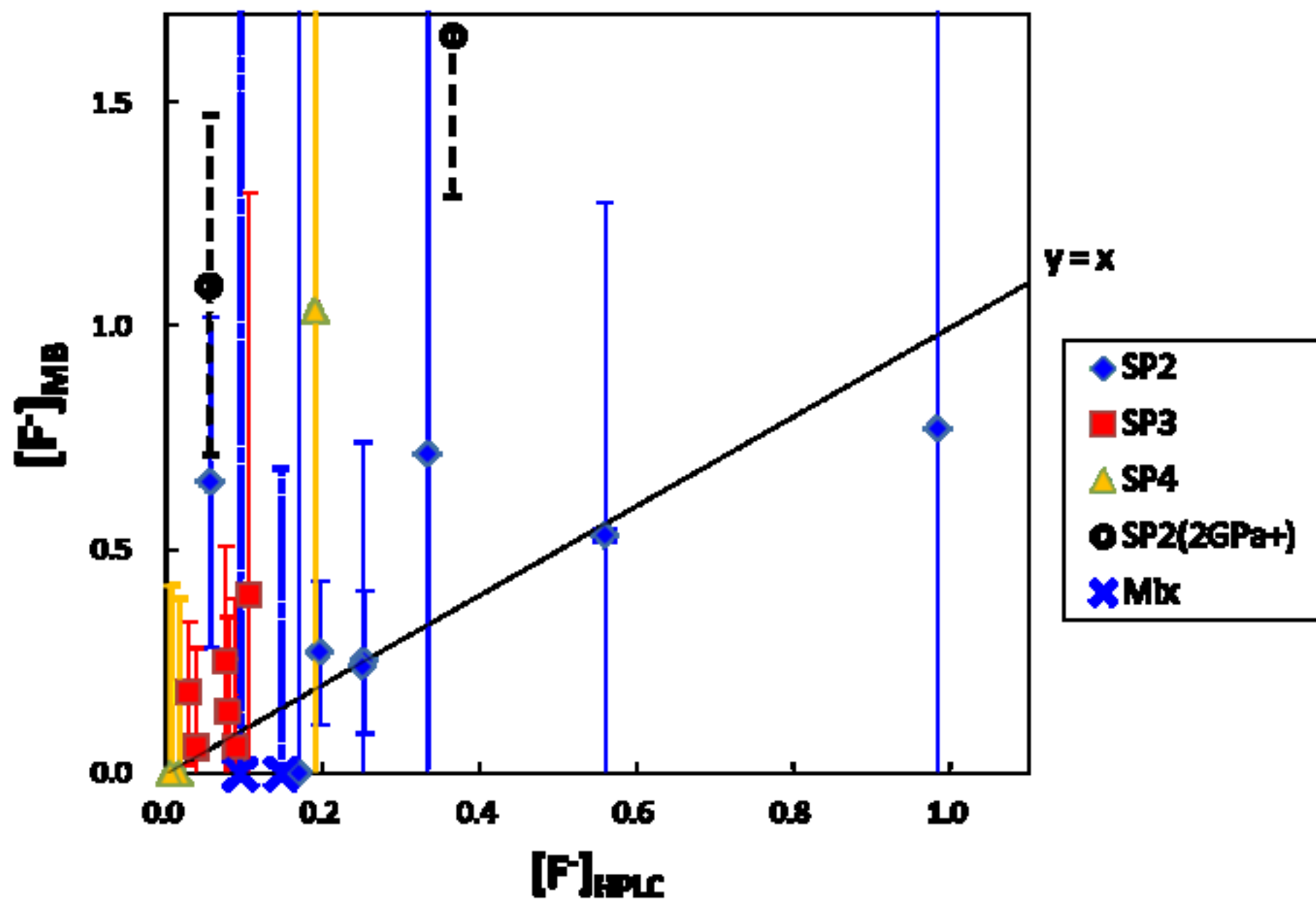


Figure 4b
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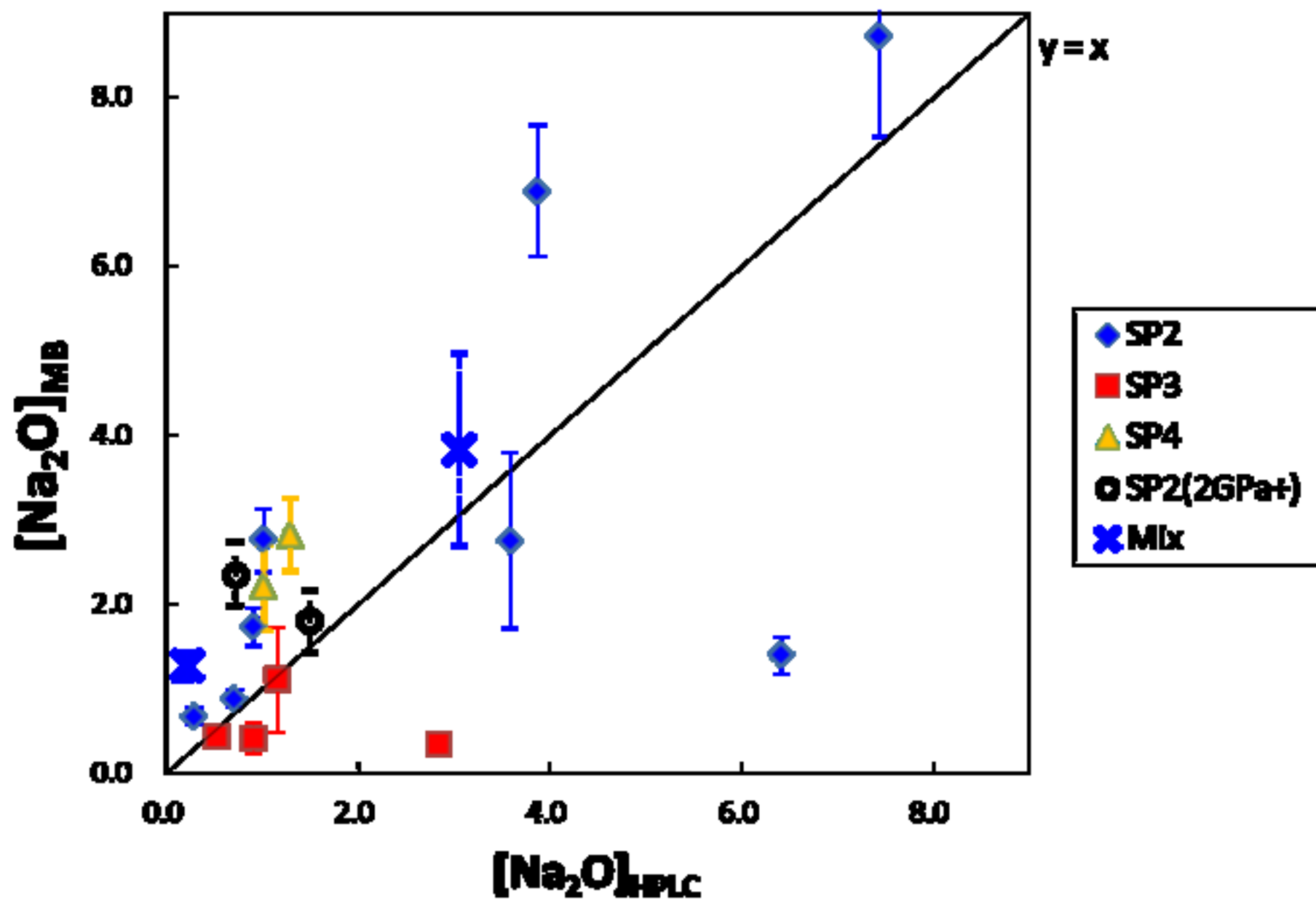


Figure 5
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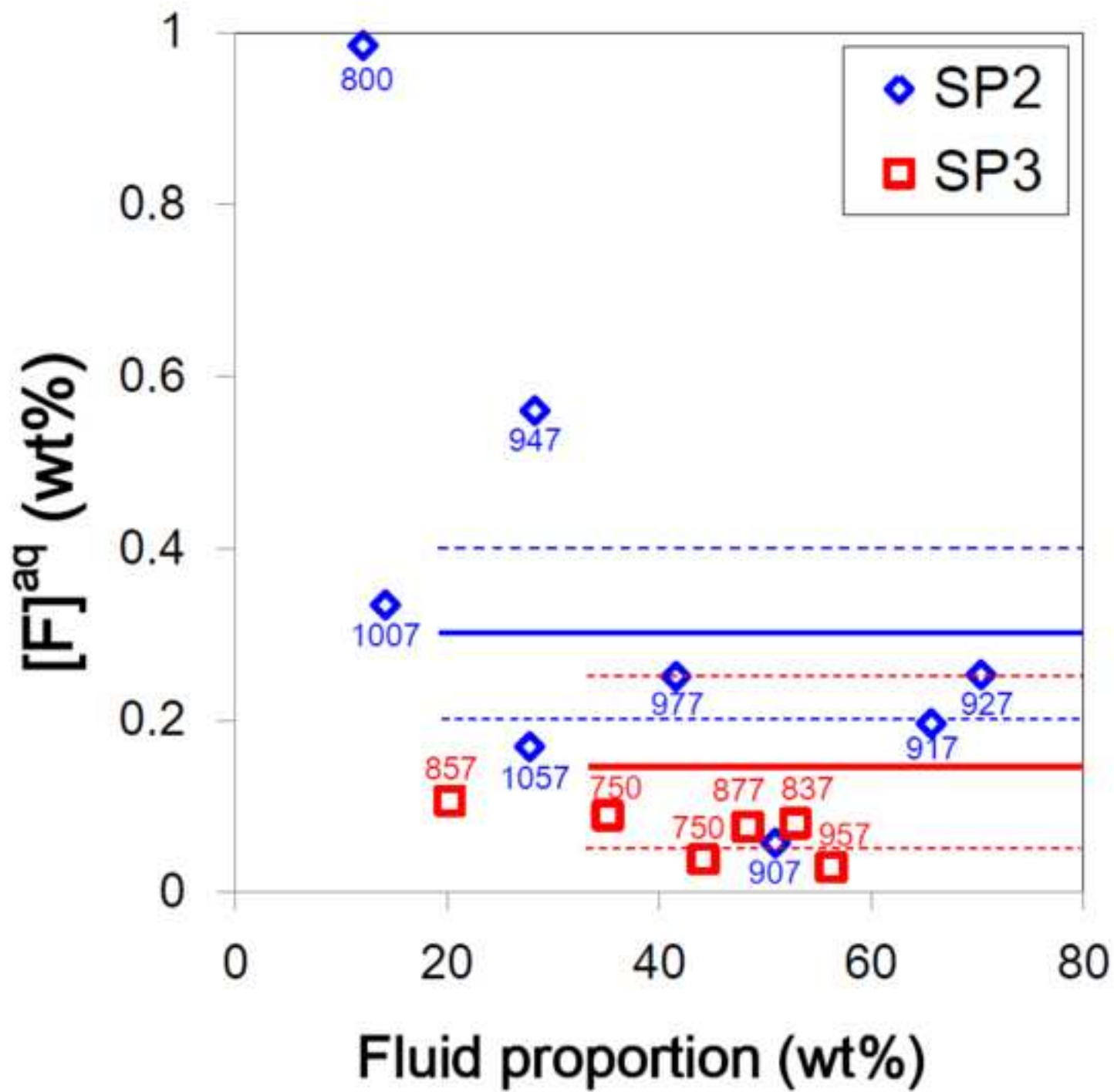


Table 1[Click here to download Table: Table1\(V1.0\).docx](#)**Table 1: Compositions of starting materials (unit: wt%)**

	SP1	SP2	SP3	SP4	Richterite *
SiO ₂	47.5(4)	43.1(6)	47.3(2)	37.5(1.0)	44.2(7)
TiO ₂	0.42(6)	0.36(4)	0.38(3)	0.3(2)	4.3(3)
Al ₂ O ₃	13.4(2)	12.1(2)	12.9(1)	10.1(5)	9.6(3)
Cr ₂ O ₃	0.72(6)	0.67(8)	0.71(5)	0.6(2)	0.04(4)
FeO	3.6(1)	3.1(2)	3.57(8)	2.9(4)	10.9(4)
MgO	20.4(1)	24.0(3)	20.4(2)	37.0(9)	13.8(4)
CaO	11.7(2)	10.6(2)	11.4(1)	9.0(6)	10.2(4)
MnO	0.09(4)	0.09(4)	0.07(3)	0.07(15)	0.05(9)
Na ₂ O	1.44(7)	2.1(1)	1.36(5)	2.1(3)	4.3(3)
F	0.02(2)	4.81(7)	1.88(5)	0.51(24)	n.d
Total	99.3	101.6	100.0	100.0	97.6

Uncertainties given in parentheses apply to the last digit cited. n.d indicates “not determined”.

*the seed mineral composition in 1-SP3-11.

Table 2

[Click here to download Table: Table2\(V2.2\).docx](#)

Table 2: Experimental conditions, product proportions, and fluorine concentrations from mass balance calculations and HPLC measurements

Expt. ID	Conditions		Starting material		Fluid (mg)	Diluted factor	Phase assemblies (wt%)	F concentrations (wt%)		D _F (Flu/Hbl)	
	T (°C)	Duration (h)	Solid (mg)	H ₂ O (mg)				MB	HPLC	MB	HPLC
1-SP1-8	807	114	1.91(1)	2.96(4)	1.21(4)	8074	Hbl(61.2), Flu(38.8)	n.d.	n.d.	n.d.	n.d.
1-SP2-24	750	215	3.27(1)	5.9(1)	0.71(1)	34401	Hbl, Nrb, Flu	n.d.	0.295(1)	n.d.	n.d.
1-SP2-23	800	143	4.78(2)	5.3(1)	0.45(1)	54278	Hbl(73.8), Nrb(14.1), Flu(12.1)	0.8(2.6)	0.985(1)	0.06(97)	0.416(64)
1-SP2-14	877	120	1.5(1)	2.6(1)	0.6(1)	16283	Hbl, Nrb, Chn, Flu	n.d.	0.082(1)	n.d.	0.040(5)
1-SP2-15	907	91	1.4(1)	2.2(1)	1.27(8)	26925	Hbl(40.6), Nrb(8.5), Flu(51.0)	0.65(37)	0.057(1)	0.29(17)	0.026(3)^b
1-SP2-17	917	100	1.64(5)	3.3(1)	2.66(3)	3673	Hbl(27.6), Nrb(6.7), Flu(65.7)	0.27(16)	0.196(1)	0.13(8)	0.093(12)^b
1-SP2-16	927	34	1.31(8)	3.65(5)	2.77(5)	17635	Hbl(23.9), Nrb(5.8), Flu(70.4)	0.25(16)	0.253(6)	0.11(8)	0.114(14)^b
1-SP2-18	947	117	1.80(2)	2.03(2)	0.73(1)	13384	Hbl(52.6), Nrb(10.5), Melt(4.3), Precipitate(4.3), Flu(28.3)	0.53(74)	0.56(1)	0.32(25)	0.251(37)^b
1-SP2-19	977	94	1.35(2)	n.d.	1.00(4)	9770	Hbl(25.5), Chn(11.6), Melt(21.3), Flu(41.6)	0.24(50)	0.251(5)	0.23(12)	0.121(10)^b
1-SP2-20	1007	74	1.53(3)	3.05(1)	0.30(1)	32567	Hbl(32.6), Chn(19.2), Spl(0.7), Melt(33.3), Flu(14.2)	0.7(2.6)	0.334(2)	0.35(1.30)	0.166(18)
1-SP2-21	1057	73	1.86(2)	1.38(5)	0.84(1)	11631	Hu(15.4), Spl(1.2), Melt(55.6), Flu(27.8)	0.0(2.3)	0.169(1)	n.d.	n.d.
3-SP2-1	877	96	1.44(3)	5.15(3)	0.94(3)	10394	Hbl(47.4), Nrb(10.4), Flu(42.3)	1.65(36)	0.365(2)	1.03(27)	0.227(24)
4-SP2-2	877	191	2.04(3)	n.d.	1.62(6)	6031	OH-Grs(29.4), Nrb(13.4), Aug(7.5), Flu(49.7)	1.09(38)	0.055(1)	n.d.	n.d.
1-SP3-10 ^a	750	135	1.89(2)	8.24(2)	1.34(1)	7440	Hbl(51.1), Chn(4.8), Flu(44.2)	0.06(22)	0.038(1)	0.04(16)	0.027(4)^b
1-SP3-11 ^a	750	141	2.60(1)	11.5(1)	1.16(1)	42974	Hbl(59.0), Chn(5.8), Flu(35.2)	0.06(33)	0.089	0.04(23)	0.063(8)^b
1-SP3-4	837	169	1.7(1)	2.3(1)	1.76(4)	11102	Hbl(44.2), Chn(2.9), Flu(52.9)	0.14(21)	0.080(3)	0.10(15)	0.056(9)^b
1-SP3-3	857	119	1.4(1)	1.7(1)	0.28(5)	34893	Hbl(74.8), Chn(5.0), Flu(20.3)	0.40(90)	0.106(6)	0.27(61)	0.071(11)
1-SP3-1	877	160	1.3(1)	2.1(1)	1.09(5)	8963	Hbl(48.6), Chn(3.0), Flu(48.4)	0.25(26)	0.076(3)	0.18(19)	0.054(9)^b
1-SP3-8	957	96	1.64(4)	2.34(6)	1.91(2)	5115	Hbl(41.0), Chn(2.7), Flu(56.3)	0.18(16)	0.029	0.12(11)	0.020(3)^b
1-SP4-4	843	143	1.50(2)	2.59(2)	0.85(2)	11494	Hbl(10.9), Aug(15.9), Chu(32.4), Flu(40.8)	0.0(4)	0.006	0.0(7)	0.011(3)

Expt. ID	Conditions		Starting material		Fluid (mg)	Diluted factor	Phase assemblies (wt%)	F concentrations (wt%)		D _F (Flu/Hbl)	
	T (°C)	Duration (h)	Solid (mg)	H ₂ O (mg)				MB	HPLC	MB	HPLC
1-SP4-3	890	>68	2.13(3)	3.03(5)	1.43(1)	6832	Cln(15.2), Aug(14.0), Chu(30.0), Flu(40.9)	0.0(4)	0.017	n.d.	n.d.
1-SP4-5	950	127	2.51(1)	9.6(1)	0.40(1)	24425	Cln(21.2), Aug(19.0), Ol(45.1), Flu(14.6)	1.0(1.3)	0.190(2)	n.d.	n.d.
1-(SP2 + Qtz)	950	94	4.28(1) [SP2] + 6.63(1) [Qtz]	6.1(1)	4.53(1)	2157	Hbl(10.0), Talc(19.8), Melt(40.8), Flu(29.3)	0.0(7)	0.147(1)	0.00(31)	0.066(11)
1-(SP1 + MgF ₂)	965	118	6.37(2) [SP1] + 0.77(1) [MgF ₂]	8.2(1)	1.25(2)	19540	Chn(25.0), Spl(2.2), Melt(59.7), Flu(13.1)	0.0(8.4)	0.095(2)	n.d.	n.d.

The first numbers of Expt. ID indicate the experimental pressure during annealing: 1, 3, and 4 represents 1.0, 2.0, and 2.5 GPa, respectively.

Concentrations are in wt%. For mass balance results, 2σ errors are reported in parentheses; HPLC analyses generally conducted twice, the errors represent the difference between the results and the average value; The data without uncertainties indicates that the measurement only performed once. Uncertainties given in parentheses apply to the last digit cited.

n.d indicates “not determined”. Abbreviations, Hbl : hornblende ; Nrb : norbergite ; Chn : chondrodite ; Hu : humite; Chu : clinohumite; OH-Grs : hydrogrossular; Cln : clintonite; Aug: augite; Ol:olivine; Spl: spinel; Flu: fluid.

Phase proportions are calculated by mass-balance approach. Uncertainties given in parentheses apply to the last digit cited.

^a The phase proportions are calculated with the chondrodite composition from 1-SP3-3, for SP3 experiments are in equilibrium in the Hbl-Chn-Flu system.

^b The values of D_F(Flu/Hbl) in ***bond italic fonts*** from HPLC measurements indicates that the fluid proportion of experiments from SP2 and SP3 groups are higher than 30 wt%.

Table 3[Click here to download Table: Table3\(V1.1\).docx](#)**Table 3 Relative complexed fluorine concentrations in 1-SP2-16 extracted solution**

Ions	Concentration		lgK ₁	lgK ₂	lgK ₃	relative [F ⁻] _{complexed} (%)
	ppb	10 ⁻⁹ mol/L				
F ⁻	142	7470				
Fe ³⁺	0.264	4.74	5.28	9.30	12.06	0.04
Al ³⁺	4.74	87.8	6.10	11.15	15.00	0.2
Mg ²⁺	0.618	25.4	1.30			<10 ⁻⁵

The cumulative formation constants are derived from Lange's handbook of chemistry.

Appendix: Compositions of solid phases

Expt. ID	T/°C	Phases	Na ₂ O	K ₂ O	FeO	MgO	CaO	MnO	NiO	TiO ₂	SiO ₂	Al ₂ O ₃	Cr ₂ O ₃	F	H ₂ O	Total
1-SP2-23	800	Hbl	1.21(15)	0.03(5)	3.33(25)	19.03(45)	13.39(44)	0.10(8)	0.18(13)	0.43(8)	47.16(81)	11.43(96)	1.03(23)	2.37(37)	1.02(12)	99.69
		Nrb	0.01(5)	0.01(5)	3.10(79)	56.31(97)	0.53(11)	0.17(10)	0.25(21)	0.61(15)	27.85(72)	0.15(11)	0.10(11)	18.1(1.0)	0.11(20)	107.20
1-SP2-18	947	Hbl	1.30(14)	0.03(5)	4.31(30)	18.96(41)	13.44(45)	0.06(9)	n.d.	0.23(11)	43.58(69)	13.30(33)	0.92(16)	2.22(33)	1.07(5)	98.36
		Nrb	0.02(5)	0.00(5)	0.71(13)	57.63(77)	0.23(8)	0.05(8)	n.d.	0.92(15)	29.10(54)	0.03(5)	0.10(9)	15.44(78)	1.47(16)	104.25
		Melt	0.63(21)	0.41(19)	1.61(37)	13.75(99)	6.42(74)	0.06(19)	0.01(15)	0.45(25)	44.5(1.2)	19.32(84)	0.04(21)	6.4(1.2)	9.05(247)	102.71
		Precipitate	0.45(19)	0.05(12)	0.97(30)	9.86(85)	1.56(22)	0.09(17)	0.04(14)	0.22(22)	53.4(1.3)	18.04(68)	0.07(19)	4.6(1.0)	12.61	101.92
1-SP2-19	977	Hbl	1.42(15)	0.02(5)	4.21(28)	19.40(44)	13.54(50)	0.05(9)	0.08(11)	0.20(11)	43.79(82)	12.37(34)	0.97(16)	2.07(16)	1.14(2)	98.13
		Chn	0.00(5)	0.00(5)	1.19(16)	56.56(85)	0.16(7)	0.08(9)	0.13(11)	0.49(12)	34.77(70)	0.03(5)	0.08(10)	7.99(29)	1.41(9)	101.48
		Melt	0.66(16)	0.15(9)	2.63(34)	10.91(47)	13.37(68)	0.06(15)	0.02(11)	0.55(14)	44.4(1.0)	17.42(52)	0.02(16)	5.67(86)	6.51(71)	102.39
1-SP2-20	1007	Hbl	1.07(13)	0.01(5)	4.28(28)	19.26(39)	14.48(48)	0.06(9)	0.12(8)	0.22(11)	43.30(67)	13.40(40)	0.71(15)	2.02(22)	1.20(5)	98.92
		Chn	0.01(5)	0.01(5)	2.19(20)	55.98(64)	0.17(8)	0.11(9)	0.32(8)	0.57(13)	34.76(60)	0.04(5)	0.09(10)	7.51(39)	1.65(9)	101.76
		Spl	0.02(7)	0.01(5)	30.2(1.7)	17.96(41)	0.19(8)	0.28(12)	1.06(12)	0.21(10)	0.08(6)	26.7(1.4)	18.81(57)	n.d.	n.d.	95.55
		Melt1	1.01(26)	0.10(9)	2.99(36)	9.4(1.6)	13.76(70)	0.08(14)	0.03(11)	0.48(13)	41.0(1.3)	17.01(56)	0.05(16)	6.3(1.4)	10.4(3.7)	102.67
		Melt2	1.39(23)	0.10(11)	0.16(16)	0.17(9)	1.93(29)	0.02(13)	0.01(6)	0.04(11)	84.5(1.6)	7.19(34)	0.04(17)	0.88(40)	3.9(1.3)	100.37
1-SP2-21	1057	Hu	0.01(5)	0.01(5)	0.93(14)	56.09(83)	0.13(7)	0.05(8)	0.32(12)	0.31(11)	36.81(64)	0.03(5)	0.16(11)	5.14(36)	1.23(4)	99.98
		Spl	0.01(7)	0.00(6)	24.01(97)	20.48(48)	0.02(6)	0.20(11)	0.71(15)	0.17(10)	0.26(21)	14.63(35)	33.0(1.6)	n.d.	n.d.	93.49
		Melt	1.28(50)	0.12(15)	3.14(52)	13.8(1.1)	12.17(64)	0.11(19)	0.05(16)	0.29(24)	43.0(1.7)	13.80(66)	0.07(24)	5.1(1.1)	9.2(1.6)	102.15
3-SP2-1	877	Hbl	1.11(13)	0.01(5)	3.84(27)	18.23(39)	13.40(48)	0.09(9)	0.59(13)	0.17(10)	44.97(70)	13.39(31)	0.79(15)	1.61(24)	1.37(5)	98.18
		Nrb	0.01(5)	0.01(5)	1.64(18)	56.72(72)	0.19(7)	0.06(8)	0.65(13)	1.07(15)	29.06(54)	0.03(5)	0.06(10)	13.89(61)	2.20(11)	103.39
4-SP2-2	877	OH-Grs	0.01(5)	0.00(2)	5.62(74)	15.3(1.9)	13.9(1.9)	0.19(19)	n.d.	0.19(8)	39.7(1.2)	22.21(40)	1.08(37)	1.19(52)	0.73(41)	99.41
		Nrb	0.01(5)	0.00(2)	1.57(19)	55.82(86)	0.11(3)	0.01(14)	1.51(13)	1.17(7)	28.99(57)	0.04(5)	0.1(4)	13.24(55)	2.46(19)	102.58
		Aug	0.18(7)	0.01(5)	2.1(2)	16.35(41)	23.91(59)	0.04(9)	0.84(11)	0.06(7)	53.27(88)	2.53(18)	0.43(14)	0.09(12)	n.d.	99.81
1-SP3-10	750	Hbl	0.86(16)	0.02(5)	5.20(74)	17.07(69)	13.05(45)	0.10(9)	0.04(10)	0.63(14)	44.8(1.6)	13.7(2.9)	0.19(11)	1.39(18)	1.45(3)	97.06
		Chn ^a	0.00(5)	0.00(5)	0.98(15)	56.34(68)	0.06(6)	0.06(9)	0.60(10)	1.14(16)	34.46(59)	0.03(5)	0.06(10)	7.52(44)	1.63(7)	101.26
1-SP3-11	750	Hbl (zone1)	1.06(14)	0.01(5)	3.99(27)	18.33(40)	13.46(46)	0.09(9)	0.10(11)	0.57(13)	46.18(60)	12.07(97)	0.36(14)	1.42(18)	1.45(5)	97.65
		Hbl (zone2)	0.69(11)	0.00(5)	4.20(28)	16.30(38)	14.39(47)	0.07(9)	0.25(12)	0.81(15)	41.37(57)	17.83(35)	0.03(10)	1.82(21)	1.27(4)	97.76

Expt. ID	T/°C	Phases	Na ₂ O	K ₂ O	FeO	MgO	CaO	MnO	NiO	TiO ₂	SiO ₂	Al ₂ O ₃	Cr ₂ O ₃	F	H ₂ O	Total
1-SP3-8	957	Chn ^a	0.00(5)	0.00(5)	0.98(15)	56.34(68)	0.06(6)	0.06(9)	0.6(1)	1.14(16)	34.46(59)	0.03(5)	0.06(10)	7.52(44)	1.63(7)	101.26
		Hbl	0.92(12)	0.01(5)	3.86(29)	19.26(73)	12.95(45)	0.11(9)	0.07(8)	0.43(12)	44.0(1.6)	14.2(2.3)	0.37(27)	1.44(20)	1.41(6)	97.55
1-SP4-4	843	Chn	0.02(5)	0.01(5)	1.21(18)	55.6(1.1)	0.32(44)	0.07(9)	0.19(8)	1.32(17)	35.0(6)	0.24(34)	0.08(10)	6.62(37)	2.09(4)	100.66
		Hbl	3.16(22)	0.01(2)	4.46(30)	18.43(43)	13.40(22)	0.06(16)	n.d.	0.37(5)	40.63(79)	14.74(96)	0.41(5)	0.59(15)	1.80(4)	96.26
1-SP4-3	890	Aug	0.36(51)	0.00(2)	2.94(34)	15.40(38)	24.1(1.6)	0.08(17)	n.d.	0.69(24)	49.0(1.0)	5.8(1.0)	0.90(26)	0.06(9)	n.d.	99.35
		Chu	0.00(4)	0.00(2)	0.88(16)	56.24(85)	0.22(3)	0.07(17)	n.d.	0.70(6)	38.16(68)	0.01(5)	0.02(4)	2.35(24)	1.75(1)	98.67
		Cln	0.30(8)	0.00(2)	4.11(30)	20.99(45)	12.40(21)	0.00(16)	n.d.	0.15(4)	19.62(45)	34.47(52)	0.50(5)	0.58(14)	3.79(5)	93.14
		Aug	0.05(6)	0.00(2)	3.39(78)	14.84(74)	25.06(32)	0.05(16)	n.d.	0.57(23)	48.4(1.7)	5.9(1.5)	0.52(46)	0.07(9)	n.d.	98.83
1-SP4-5	950	Chu	0.00(5)	0.00(2)	1.29(26)	55.36(84)	0.22(6)	0.09(17)	n.d.	0.74(6)	38.09(69)	0.04(5)	0.06(4)	2.32(24)	1.74(4)	98.21
		Cln	0.01(3)	0.00(5)	3.25(24)	18.42(40)	12.80(45)	0.02(8)	5.43(48)	0.18(10)	18.95(41)	35.03(56)	0.29(12)	0.69(21)	3.75(2)	95.09
		Aug	0.01(5)	0.00(5)	2.8(5)	14.97(69)	25.86(66)	0.03(8)	0.80(11)	0.55(13)	48.3(1.5)	6.6(1.3)	0.20(12)	0.18(14)	n.d.	100.30
1-(SP2 + Qtz)	950	Ol	0.00(5)	0.02(5)	0.36(11)	55.89(74)	0.29(9)	0.09(9)	1.48(33)	0.01(6)	42.45(66)	0.00(5)	0.00(6)	0.19(12)	n.d.	100.80
		Hbl	0.32(8)	0.01(5)	2.90(23)	22.35(50)	11.34(41)	0.03(9)	0.61(10)	0.44(8)	54.18(90)	4.63(18)	1.17(17)	2.21(35)	1.13(17)	100.20
		Talc	0.03(6)	0.03(6)	0.69(13)	19.41(49)	0.05(6)	0.00(8)	16.67(40)	0.07(7)	58.58(98)	0.20(6)	0.21(12)	2.46(36)	3.22(18)	98.39
1-(SP1 + MgF ₂)	965	Melt	0.35(11)	0.01(7)	0.64(19)	1.00(21)	4.26(36)	0.03(11)	0.16(11)	0.17(10)	76.9(1.4)	6.76(29)	0.05(14)	2.04(50)	8.51(74)	100.86
		Chn	0.01(5)	0.02(5)	2.54(25)	55.75(77)	0.19(7)	0.08(8)	0.51(13)	0.34(11)	33.77(53)	0.04(5)	0.14(11)	8.64(94)	1.04(17)	102.04
		Spl	0.01(7)	0.01(5)	27.7(3.3)	15.61(67)	0.57(44)	0.28(12)	1.68(28)	0.17(10)	0.39(65)	17.3(2.4)	31.5(3.0)	n.d.	n.d.	95.28
		Melt	0.91(26)	0.09(13)	2.74(48)	11.53(64)	14.83(95)	0.1(2)	0.08(22)	0.44(26)	38.5(1.1)	16.32(72)	0.02(23)	8.6(2.0)	9.45(153)	103.60

n.d indicates “not determined”. Abbreviations, Hbl : hornblende ; Nrb : norbergite ; Chn : chondrodite ; Hu : humite; Chu : clinohumite; OH-Grs : hydrogrossular; Cln : clintonite; Aug: augite; Ol:olivine; Spl: spinel.

Concentrations are in wt%, 2σ errors are reported in parentheses. Uncertainties given in parentheses apply to the last digit cited.

Water content is calculated by stoichiometry for minerals and charge balance for hydrous melt. Compositions of hydrous melt are normalized to 100%. “Total” values are did not exclude the oxygen substituted by F.

^a Chn composition of 1-SP3-3 was used for 1-SP3-10 & 11 mass balance calculation. SP3 experiments are in equilibrium in the Hbl-Chn-Flu system.