



Originally published as:

Kusebauch, C., John, T., Whitehouse, M. J., Engvik, A. (2015): Apatite as probe for the halogen composition of metamorphic fluids (Bamble Sector, SE Norway). - *Contributions to Mineralogy and Petrology*, 170.

DOI: <http://doi.org/10.1007/s00410-015-1188-6>

1 **Apatite as probe for the halogen composition of metamorphic fluids (Bamble Sector SE**  
2 **Norway)**

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## 22 **Abstract**

23 Halogen composition of replaced apatite formed during a regional metasomatic event  
24 (Bamble Sector SE Norway) reveals information about the composition and evolution of the  
25 hydrothermal fluid. Infiltration and pervasive fluid flow of highly saline fluids into gabbroic  
26 bodies lead to scapolitization and amphibolitization, where magmatic Cl-rich apatite reacts  
27 with the hydrothermal fluid to form OH- and/or F-rich apatite. Apatite from highly altered  
28 samples adjacent to the shear zone has highest F (up to 15000  $\mu\text{g/g}$ ) and lowest Br (4-25  $\mu\text{g/g}$ )  
29 concentrations, whereas apatite from least altered samples has very low F (30-200  $\mu\text{g/g}$ ) and  
30 high Br (30-85  $\mu\text{g/g}$ ). In addition, individual replaced apatite grains show a zonation in F with  
31 high concentrations along rims and cracks and low F in core regions. Iodine concentrations  
32 remain rather constant as low values of 0.18-0.70  $\mu\text{g/g}$ . We interpret all observed  
33 compositional features of replaced apatite to be the result of a continuous evolution of the  
34 fluid during fluid-rock interaction. Due to its high compatibility, F from the infiltrating fluid  
35 is incorporated early into recrystallized apatite (close to shear zone and rims of individual  
36 apatite grains). In contrast, Br as an incompatible halogen becomes enriched in the fluid and is  
37 highest in the most evolved fluid. Using experimental partition data between replaced apatite  
38 and fluid, we calculated F concentrations of the evolving fluid to decrease from 60 to  $<1$   $\mu\text{g/g}$   
39 and Br to increase from  $\sim 1500$  to  $\sim 6500$   $\mu\text{g/g}$ ; I concentrations of the fluid are constant in the  
40 order of 300  $\mu\text{g/g}$ . Although, Cl is expected to show a similar behavior as Br, replaced apatite  
41 has constant Cl concentrations throughout the alteration sequence ( $\sim 1$  wt.%), which is likely  
42 the result of a rather constant Cl activity in the fluid. Chlorine stable isotope values of  
43 individual apatite grains are heterogeneous and range from  $-1.2\text{‰}$  to  $+3.7\text{‰}$ . High  $\delta^{37}\text{Cl}$   
44 values are generally correlated with OH-rich zones of replaced apatite, whereas low  $\delta^{37}\text{Cl}$   
45 values are measured in F-rich zones of replaced apatite and in Cl-apatite of probably  
46 magmatic origin. Though apatite  $\delta^{37}\text{Cl}$  values follow the general bulk trend, the individual  
47  $\delta^{37}\text{Cl}$  signature seems to reflect the highly localized composition of interfacial fluid at the  
48 reaction front.

49 Our observations suggest that apatite can be used as a fluid probe for F, Br and I to detect a  
50 compositional evolution of the fluid, which can be quantified by using experimentally derived  
51 partition coefficients. Partitioning of Cl and Cl stable isotopes between highly saline fluids  
52 and apatite is complex and likely controlled by more unknown factors than just the Cl  
53 concentration.

54

## 55 **Introduction**

56 Halogens (F, Cl, Br and I) are major constituents of all kinds of hydrothermal fluids.  
57 Compared to other anions (e.g. OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>), halogen ions have a major impact on  
58 petro-physical and chemical properties of solid and liquid phases due to their enhanced  
59 complexation capability of dissolved cations (Rapp et al. 2010; Williams-Jones and Heinrich  
60 2005; Tsay et al. 2014). They strongly influence element transport and mobility in fluid media  
61 and play a key role in ore-forming processes (Smith et al. 2013; Williams-Jones et al. 2012).  
62 As shown by experimental studies, saline fluids enhance the solubility of major silicate phases  
63 and lead to a mass transfer of rock forming oxides during metasomatism of crustal and mantle  
64 rocks (Newton and Manning 2006; Newton and Manning 2010; Tropper et al. 2013). Also,  
65 trace elements like high-field-strength-elements (HFSE) or rare earth elements (REE) which  
66 are often considered to be fluid immobile, can be dissolved in halogen-bearing fluids of  
67 different composition (John et al. 2008; John et al. 2004; Tropper et al. 2013; Tsay et al.  
68 2014). Although fluid inclusions reveal a direct sample of hydrothermal fluid at pressure-  
69 temperature conditions of their entrapment and can be used to extract halogen concentrations  
70 of the fluid phase, they can be lacking in some metasomatically altered rock types. Halogen-  
71 bearing minerals formed during fluid-rock interaction can provide a probe of halogen  
72 concentrations if distribution between mineral and fluid is known. Apart from halogen-  
73 bearing amphiboles, mica and scapolite, apatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>[Cl, OH, F]) is a particularly  
74 suitable mineral as it incorporates large amounts of halogens in accordance to the halogen  
75 activity of the fluid (Kusebauch et al. 2015a; Rasmussen and Mortensen 2013; Yardley 1985;  
76 Zhu and Sverjensky 1991; Zhu and Sverjensky 1992). Additionally, apatite reacts sensitively  
77 to changing hydrothermal conditions via a coupled dissolution-precipitation process in  
78 aqueous metasomatic systems (Engvik et al. 2009; Harlov and Forster 2003; Harlov et al.  
79 2002; Jones et al. 2014; Yanagisawa et al. 1999). The newly formed replaced apatite is  
80 assumed to be in local equilibrium with the hydrothermal fluid and should, therefore,  
81 represent the halogen composition of the fluid. A changing composition of the fluid during  
82 apatite replacement will lead to chemical zonation of the replaced apatite with the rim  
83 representing an early fluid as it is replaced first and the core being replaced last and therefore,  
84 representing a later fluid (e.g., Kusebauch et al. 2015a). In addition to compositional aspects,  
85 apatite formed during interaction with aqueous fluid also samples the stable Cl isotopic  
86 composition of the hydrothermal system. The Cl isotopic composition (given in standard  $\delta$   
87 notation, where  $\delta^{37}\text{Cl} = [((^{37}\text{Cl}/^{35}\text{Cl})_{\text{sample}} - (^{37}\text{Cl}/^{35}\text{Cl})_{\text{SMOC}}) / (^{37}\text{Cl}/^{35}\text{Cl})_{\text{SMOC}}] * 1000$  and SMOC  
88 = Standard Mean Ocean Chloride) for most geologically relevant reservoirs varies between -

89 8‰ and +3‰ (Barnes and Sharp 2006; John et al. 2010; Sharp et al. 2013). Fractionation of  
90 Cl isotopes can be related to processes occurring during fluid-rock interaction (Amundson et  
91 al. 2012; Barnes and Cisneros 2012; Kusebauch et al. 2015b; Selverstone and Sharp 2013).  
92 The only existing in situ  $\delta^{37}\text{Cl}$  values of apatite are from studies of Martian and lunar  
93 meteorites and range from -4‰ to +9‰ for Martian (Sharp et al. 2014; Shearer et al. 2014)  
94 and from +5‰ to +20‰ for lunar apatites. Surprisingly, there are little or no data available on  
95 the spatial distribution of halogens and Cl isotopes in apatites from terrestrial samples in  
96 general and samples that underwent metasomatism in particular.

97 To study the behavior of halogens and Cl stable isotopes during interaction of aqueous fluid  
98 and apatite, natural samples of hydrothermally altered gabbros from the Kragerø area of  
99 Bamble Sector in SE Norway (Fig. 1) were investigated. Recently published halogen and  
100 isotope data suggest a local evolution of highly saline fluids during pervasive fluid infiltration  
101 along major fluid pathways leading to scapolitisation and amphibolitisation of the gabbroic  
102 body at mid crustal P-T conditions (Kusebauch et al. 2015b). Additionally, two different  
103 apatite-bearing samples from the well-known Ødegarden verk apatite deposit (Engvik et al.  
104 2009; Harlov et al. 2002), also located in the Bamble Sector, were revisited and analyzed for  
105 halogens and Cl stable isotopes.

106 Here, we compare halogen and Cl stable isotope data of apatite measured in-situ with SIMS  
107 with published ex-situ data of bulk and mineral separates to investigate the use of apatite as a  
108 fluid probe for halogens.

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## 112 **Geological setting and sample description**

113 The Bamble Sector is a gneiss terrane of Mesoproterozoic age of prevailing high-grade  
114 metamorphism at Sveconorwegian age (1200-980 Ma) (Bingen et al. 2008 and references  
115 there in). The Kragerø area of Bamble Sector (Fig. 1) underwent extensive metasomatism by  
116 highly saline aqueous and carbonaceous fluids (Engvik et al. 2014; Touret 1985) effecting  
117 almost all rock types. In particular, gabbroic rocks, intruded at ~1040 Ma, show large-scale  
118 amphibolitisation and scapolitisation caused by the pervasive infiltration of fluids highly  
119 enriched in Cl, CO<sub>2</sub>, Na, K, Mg, P and B (Engvik et al. 2009; Engvik et al. 2011; Kusebauch  
120 et al. 2015b). Mid crustal P-T conditions of 600-700°C and 0.2-0.4 GPa are estimated for this  
121 metasomatic event (Engvik et al. 2011; Nijland and Touret 2001). Gabbroic bodies are cut by  
122 cm- to dm-sized amphibolitic and albitic veins and shear zones into tens of m- to several dm-  
123 sized blocks. Starting from these shear zones, the blocks of pristine gabbro are progressively  
124 altered by pervasive fluid ingress and show different alteration zones. Fluid inclusions  
125 (Nijland and Touret 2001; Touret 1985) and Cl concentrations of amphibole (Kusebauch et al.  
126 2015b) suggest a brinish (~48 wt.% NaCl) composition of the initial fluid, that originates  
127 most likely from mobilization of marine sediments and sedimentary pore fluids during  
128 orogeny (Bast et al. 2014; Engvik et al. 2011; Kusebauch et al. 2015b).

129 Two alteration sequences from two different gabbroic bodies (Langøy and Valberg; Fig. 1)  
130 were sampled to study fluid-rock interaction under crustal conditions. Both sequences are  
131 composed of samples showing different stages of alteration as a function of distance to the  
132 shear zone going from pristine gabbro through zones of amphibolitisation and scapolitisation  
133 to the shear zone itself. They are described in detail by Kusebauch et al. (2015b). The least  
134 altered gabbro of both sequences consists of plagioclase, olivine and clino- and  
135 orthopyroxene, the latter three show coronas of pargasitic amphibole. In the amphibolitisation  
136 zone olivine and pyroxenes are progressively replaced by Cl-bearing pargasitic amphibole  
137 while plagioclase is unaltered. In the scapolitisation zone that follows, plagioclase is replaced  
138 by scapolite. Pargasitic amphibole and Ti-rich biotite are other major alteration phases  
139 (Kusebauch et al. 2015b). The shear zone consists of monomineralic amphibole, also of  
140 pargasitic composition.

141 The sample from Langøy represents a continuous sequence showing all alteration reactions  
142 within a 30x20x10 cm-sized block. In addition to the alteration sequence, a pristine gabbro  
143 from the same complex was sampled. Thin sections from the block were sliced perpendicular  
144 to the shear zone to provide a profile of increasing distance to the shear zone. Although, the

145 profile from Valberg is larger (~140 cm), samples show the same alteration sequence  
146 according to their distances to the shear zone.

147 A third set of samples from the Bamble Sector was analyzed to broaden the findings of local  
148 fluid-rock interaction concentrated in shear zones to the more regional metasomatic event in  
149 the area. For this purpose we reevaluated apatite from samples from the abandoned Apatite  
150 mine 'Ødegardens Verk', which was previously studied by Engvik et al. (2009) and Harlov et  
151 al. (2002), for halogens and Cl stable isotopes with SIMS. Samples from the Ødegardens Verk  
152 include one unaltered gabbro and one scapolitized metagabbro, both of which are described in  
153 detail in Engvik et al. (2009).

154

155

## 156 **Analytical methods**

### 157 **Electron Microprobe Analyses (EMPA)**

158 We used a JEOL super probe 8900 equipped with 4 wavelength-dispersive spectrometers at  
159 the University of Muenster to examine the chemical composition of apatites. Operating  
160 conditions for all apatite measurements were 15 kV, 4 nA and spot sizes varied between 2 and  
161 5  $\mu\text{m}$ . To minimize migration of halogens due to extensive electron beam exposure, halogens  
162 (F and Cl), CaO and  $\text{P}_2\text{O}_5$  were measured in a first run with low counting times of 10s  
163 (Goldoff et al. 2012). All other elements ( $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{Ce}_2\text{O}_3$ ,  $\text{MgO}$ ) were measured  
164 afterwards with counting times ranging from 5-20s. Standardization was done using well  
165 established synthetic and natural mineral standards (CaO,  $\text{P}_2\text{O}_5$ : Durango apatite; F: synthetic  
166 fluoride; Cl: natural tugtupite;  $\text{K}_2\text{O}$ : natural sanidine;  $\text{Na}_2\text{O}$ : natural jadeite,  $\text{Ce}_2\text{O}_3$ : synthetic  
167 Ce-phosphate;  $\text{SiO}_2$ : natural hyperstene;  $\text{MgO}$ : natural olivine). Multiple analyses ( $n>55$ ) of  
168 different apatite standards (including Durango and another F-rich apatite) give a standard  
169 deviation for each standard of 1% for CaO, 2% for  $\text{P}_2\text{O}_5$  and  $\sim 10\%$  for F and Cl, respectively.  
170 Uncertainties for minor elements ( $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{Ce}_2\text{O}_3$ ,  $\text{MgO}$ ) are in the range of 10% to  
171 20%. Theoretical detection limits for F and Cl are 0.1 and 0.02 wt%, respectively, and for all  
172 other elements in the order of 0.02 to 0.06 wt.%. The accuracy of halogen EMPA  
173 measurements was checked by using Durango apatite as an unknown. Mean concentrations  
174 ( $n=28$ ) are  $3.68 \pm 0.27$  wt% for F and  $0.39 \pm 0.05$  wt% for Cl, which is in agreement with  
175 reported literature data ( $3.35 \pm 0.06$  wt% F and  $0.46 \pm 0.04$  wt% Cl; Marks et al. 2012).  
176 Structural formula of apatite was calculated for each analyzed apatite on the basis of 26  
177 cations. The OH component ( $X_{\text{OH}}=\text{OH}/(\text{OH}+\text{Cl}+\text{F})$ ) was afterwards calculated assuming a  
178 perfect solid solution of F, OH and Cl on the anion site and that the difference from the ideal  
179 apatite formula on this site is OH.

180 After finishing quantitative analyses apatite of Langøy samples was mapped for F, Cl, Ca and  
181 P and cathodoluminescence (CL) pictures were taken.

182

### 183 **Secondary Ion Mass Spectroscopy (SIMS)**

184 Halogens (i.e., F, Cl, Br, I) and stable Cl isotopes were measured using a CAMECA ims1280  
185 large geometry SIMS instrument at the NORDSIM facility located at the Swedish Museum of  
186 Natural History, Stockholm. As different routines for different measurements (i.e., halogen  
187 concentrations and Cl stable isotopes) were applied, spots for individual measurements



188 needed to be set on different positions of the same apatite. This procedure makes a direct  
189 comparison of halogen concentrations with Cl isotopic composition of individual spots  
190 unfeasible. Nevertheless, positions of individual spots were set close together (in  $\mu\text{m}$  distance)  
191 and caution was taken to measure in areas with a similar inner structural position and  
192 composition as inferred from BSE images and EMPA element maps. In general we measured  
193 3-5 individual spots on 2-3 individual apatite grains from one sample section for Cl isotopes  
194 as well as halogen concentrations.

#### 195 Halogen concentration

196 Analytical conditions for all measurements closely follow those described by Marks et al.  
197 (2012) and Kusebauch et al., (2015a). These were a critically focused  $\sim 15\mu\text{m}$   $^{133}\text{Cs}^+$  primary  
198 beam with  $\sim 1.8$  nA beam current and 20 kV impact energy (10 kV primary beam, -10 kV  
199 secondary beam), low-energy normal-incidence electron flooding to counteract charge build-  
200 up on insulating targets, and a mass resolving power (MRP) of 5000 ( $M/\Delta M$ ). Prior to  
201 measurement, chosen sites were pre-sputtered for 120s to remove the gold coating over a 25  
202 by 25  $\mu\text{m}$  rastered area and use of a 2500  $\mu\text{m}$  field aperture further minimized surface  
203 contamination by restricting the field of view to ca. 22 by 22  $\mu\text{m}$ . Secondary ions were  
204 measured either on electron multipliers ( $< 10^6$  cps) or Faraday cups ( $> 10^6$  cps) in peak  
205 switching mode. Data were acquired over 5 scans with an overall integration time of 120s. At  
206 the MRP of 5000,  $^{19}\text{F}^-$ ,  $^{37}\text{Cl}^-$  and  $^{127}\text{I}^-$  signals were free of molecular interferences; however,  
207 neither  $^{79}\text{Br}^-$  nor  $^{81}\text{Br}^-$  can be resolved from  $\text{CaCl}^-$  interferences at  $\text{MRP} < 16000$ , which  
208 cannot be achieved on the ims1280 without significant transmission loss. Hence, a combined  
209  $[\text{}^{81}\text{Br} + \text{}^{44}\text{Ca}^{35}\text{Cl} + \text{}^{46}\text{Ca}^{37}\text{Cl}]^-$  peak was measured and corrected using the intensity of the  
210 measured  $^{40}\text{Ca}^{37}\text{Cl}^-$  peak together with the natural isotopic abundances of Ca and Cl. All  
211 measured peaks were normalized to the matrix  $^{40}\text{Ca}^{31}\text{P}^-$  signal and concentrations determined  
212 relative to Durango apatite (Kusebauch et al. 2015a). Detection limits are estimated based on  
213 an average  $^{40}\text{Ca}^{31}\text{P}$  signal of 300,000 cps and a typical ion counter background of 0.05 cps  
214 times three; this yields  $6.6 \cdot 10^{-5}$   $\mu\text{g/g}$  for F,  $1.3 \cdot 10^{-4}$   $\mu\text{g/g}$  for Cl,  $3.8 \cdot 10^{-3}$   $\mu\text{g/g}$  for Br and  
215  $7.9 \cdot 10^{-4}$   $\mu\text{g/g}$  for I. Multiple measurements ( $n=87$ ) of Durango apatite reveal a standard  
216 deviation ( $1\sigma$ ) of 7% for F, 5% for Cl, 16% for Br and 4% for I, respectively. The  
217 uncertainties are in agreement with published data (Marks et al. 2012) for Durango apatite.

218

219

220 Chlorine stable isotope measurements

221  $\delta^{37}\text{Cl}$  measurements were performed using operating conditions similar to these for halogen  
222 measurements (primary beam: 1.3- 2.1 nA, 10 kV, field aperture: 2500, MRP: ~2500, pre  
223 sputtering for 120s of 25x25  $\mu\text{m}$  raster). Secondary ions of the stable isotopes  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$   
224 were measured simultaneously on Faraday cups in multi-collection mode over 40 cycles (4  
225 blocks of 10 integrations) with an overall counting time of 160s. Correction for instrumental  
226 mass fractionation (IMF) was made using two different apatites (natural Durango and  
227 synthetic pure Cl-apatite) of known isotopic composition (measured by stable isotope mass  
228 spectrometry of solution from pyrohydrolyses of Durango ( $\delta^{37}\text{Cl}=0.5\text{‰}$ ) and synthetic Cl-  
229 apatite ( $\delta^{37}\text{Cl}=2\text{‰}$ )). These reference materials (RM) were regularly interspersed with  
230 analyses of the unknown apatites. Multiple measurements of Durango (n=60) and the Cl-  
231 apatite RMs (n=70) apatite reveal a relative reproducibility of  $\delta^{37}\text{Cl}$  of 0.25‰, and 0.15‰,  
232 respectively. Internal precision ranges from 0.09 to 0.28‰ for individual measurements. To  
233 account for matrix dependent IMF (Godon et al. 2004; Layne et al. 2004), a correction to the  
234 measured isotopic ratios was made according to their Cl-concentration assuming a linear  
235 concentration dependency of IMF determined from the two different apatite RMs.

236

237

238 **Results:**

239 **Detailed alteration sequences (Langøy and Valberg)**

240 Apatite is observed in trace abundances in all samples from all localities as anhedral grains  
241 varying from 20-300  $\mu\text{m}$  in size (Fig. 2). Apatite from unaltered Langøy and Valberg gabbro  
242 is generally zoned and has a Cl-rich zone free of pores and a Cl-poor zone with a large  
243 amount of up to  $\mu\text{m}$ -sized pores (Fig. 2a-b). Both zones are separated by a sharp interface.  
244 Apatite from altered samples is Cl-poor, shows pores and lacks Cl-rich zones (Fig. 2d-e).  
245 Although, apatite from altered samples seems to be homogenous when studied by optical  
246 microscope and SEM, detailed chemical mapping by EMPA and CL reveals a zonation in F  
247 (Fig. 2d and 3). In general, F is enriched in the rims and along cracks of individual apatite  
248 grains. These F-rich zones are most prominent in apatite closest to the shear zone and  
249 diminish with increasing distance to the shear zone. Areas of high F concentration in apatite  
250 coincide with areas of a strong cathodoluminescence.

251 Although, apatite from the Ødegardens Verk samples shows a similar pattern with Cl-rich and  
252 Cl-poor zones (Fig. 2c), they are found in different assemblages. Apatite from the unaltered  
253 gabbro sample is a homogenous solid solution of F-apatite and Cl-apatite, whereas apatite  
254 from the altered metagabbro and an apatite-phlogopite vein shows Cl-rich and OH-rich zones  
255 within the same grain, similar to apatite from unaltered gabbro sample of the Langøy section.

256

257 **Cation apatite chemistry (EMPA)**

258 Averaged CaO and  $\text{P}_2\text{O}_5$  concentrations of Cl-rich apatite from pristine gabbro are  $53.5 \pm 0.7$   
259 wt.% and  $40.8 \pm 0.8$  wt.%, respectively (n=36). Cl-poor apatite from altered samples has  
260 higher CaO ( $54.9 \pm 0.7$  wt.%) and  $\text{P}_2\text{O}_5$  ( $41.7 \pm 0.7$  wt.%) concentrations (n=370). Although  
261 major components (Ca and P) for Cl-rich and Cl-poor apatite are statistically invariant within  
262 the given errors, Cl-rich apatite shows systematically lower concentrations. A similar  
263 tendency was found in synthetic Cl-apatite that was replaced by Cl-poor apatite during  
264 interaction with aqueous fluids (Kusebauch et al. 2015a). A possible reason for the different  
265 Ca and P concentrations of Cl-rich and Cl-poor apatite might be a Ca and P deficiency of  
266 pristine magmatic apatite produced during high-temperature crystallization that was erased  
267 during replacement with hydrothermal fluid. Averaged Ca/P ratios for all analyzed apatite are  
268  $1.66 \pm 0.04$  and do not vary with anion composition. Minor cations ( $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{Ce}_2\text{O}_3$ ,

269 MgO) have generally low concentrations (Table S1) for all measured apatite grains and show  
270 no correlation with anion composition or distance to the shear zone.

### 271 **F, Cl and OH concentrations (EMPA) of apatite**

272 Cl-rich apatite from unaltered gabbro of the three locations has Cl concentrations of  $6.4 \pm 0.4$   
273 wt.% for Cl and F concentrations close to or below detection limit ( $<0.1$  wt%) for EMPA. Cl-  
274 rich apatite is almost a pure Cl-apatite end member ( $X_{\text{Cl}} = 0.95 \pm 0.05$ ) with a minor OH  
275 component ( $X_{\text{OH}} < 0.1$ ). Cl-poor zones of the same apatite grains range between 0.1 and 0.2 in  
276  $X_{\text{Cl}}$  (corresponding to 0.5-1.7 wt.% Cl) and show varying F contents depending on the sample  
277 locality. Cl-poor apatite from unaltered gabbro from Langøy has no detectable amounts of F  
278 ( $<0.1$  wt%) and is, therefore, classified mainly as OH-apatite ( $X_{\text{OH}} = 0.8-0.9$ ), whereas Cl-poor  
279 apatite from unaltered Valberg samples has variable F concentrations. Single measurements  
280 show F concentrations up to 1.7 wt.% ( $X_{\text{F}} = 0.49$ ). Other individual measurements fall on a  
281 trend line between the most F-rich apatite and the most F-poor pristine magmatic apatite (Fig.  
282 4b).

283 Apatite from the amphibolitisation zone of the Langøy sequence is mainly F-poor OH-apatite  
284 ( $X_{\text{OH}} = 0.8-0.9$ ,  $X_{\text{Cl}} = 0.1-0.2$ ,  $X_{\text{F}} = 0-0.15$ ). Porous zones of apatite from Valberg of the same  
285 alteration zone show basically the same composition, also pure Cl-apatite is rarely observed in  
286 the amphibolitisation zone (Fig. 4b). With increasing alteration of the gabbro (and decreasing  
287 distance to the shear zone) Cl-apatite disappears and porous apatite is enriched in the F-apatite  
288 component. Apatite from the scapolitisation zone of both localities is strongly heterogeneous  
289 in F and OH components but homogenous in Cl component. Composition ranges from 0 to  
290 0.4 in  $X_{\text{F}}$ , from 0.4 to 0.9 in  $X_{\text{OH}}$  and from 0.1 to 0.2 in  $X_{\text{Cl}}$ . Highest F concentrations of up to  
291 1.7 wt.% were measured close to the rim of individual apatite grains or adjacent to cracks. On  
292 average, apatite from the altered Valberg samples has lower  $X_{\text{Cl}}$  than apatite from altered  
293 Langøy samples.

294

### 295 **Halogen concentrations and Cl stable isotopes (SIMS) in apatite**

296 Concentrations of F, Cl, Br and I as well as  $\delta^{37}\text{Cl}$  of apatite from the Langøy alteration  
297 sequence and from the Ødegardens Verk were measured by SIMS in more detail to compare  
298 apatite with other halogen-bearing major phases (i.e., amphibole, biotite, and scapolite) from  
299 the same sample measured by Kusebauch et al. (2015b). Additionally, SIMS allows the

300 measurement of low concentrations of F. Spots for SIMS analyses were set in a way to  
301 measure the different compositional zones within individual apatite crystals as observed by  
302 EMPA element maps and CL pictures (Fig. 2 and 3). After analysis individual data points of  
303 each sample were grouped into the following zones: 1. Cl-rich and porous free apatite of  
304 unaltered gabbro, 2. OH-rich zones, and 3. F-rich zones of apatite from altered samples. To  
305 distinguish between zones 2 and 3 we used relative differences in F within individual apatite  
306 grains rather than fixed threshold values (see spots in Fig. 3). Although apatites are strongly  
307 zoned in halogen composition on a  $\mu\text{m}$ -scale and comparison of EMPA and SIMS  
308 measurements for F and Cl of the exact same spots is impossible to obtain, halogen  
309 concentrations measured with both techniques are in good agreement with each other (Fig. 5).  
310 Only Cl concentrations of almost pure Cl-apatite (pore free zones) seem to be overestimated  
311 by SIMS as the measured values are higher than the theoretical maximum for pure Cl-apatite  
312 (6.8 wt.%) and EMPA measurements. The overestimation might be caused by deviation from  
313 an assumed linearity in the concentration working curve, especially considering that Durango  
314 apatite used as reference has an order of magnitude lower Cl-concentrations.

#### 315 *Halogens (F, Cl, Br, I)*

316 Fluorine concentrations of Cl-rich apatite from pristine Langøy gabbro samples range  
317 between 450 and 915  $\mu\text{g/g}$  (Fig. 6a). In Cl-poor zones of the same apatite grains F is slightly  
318 higher and varies from 875 to 1660  $\mu\text{g/g}$ . Bromine values are highest in pore-free apatite  
319 (350-1480  $\mu\text{g/g}$ ) and lower (117-380 $\mu\text{g/g}$ ) in the porous zones. A clear trend for I is not  
320 observed and concentrations range between 0.2 and 0.5  $\mu\text{g/g}$  for both zones.

321 Although, individual apatite grains from hydrothermally altered Langøy samples are generally  
322 heterogeneous, compositional trends can be observed (Fig. 6). As already shown by EMPA  
323 measurements, the concentrations of F increase with decreasing distance to the shear zone.  
324 Apatite from least-altered samples of the amphibolitization zone has F concentrations of 30-  
325 200  $\mu\text{g/g}$ , whereas apatite from highest altered samples has 1000-15000  $\mu\text{g/g}$  (i.e., 0.1-1.5  
326 wt.%). When individual spots were grouped according to their relative F contents (i.e., OH-  
327 rich apatite and F-rich apatite zone), the trends of increasing concentrations can be observed  
328 for the two compositional zones (Fig. 7). Contrastingly, Br shows decreases from 30-85  $\mu\text{g/g}$   
329 in apatite from the least altered samples to 4-25  $\mu\text{g/g}$  in apatite from highly altered samples.  
330 Cl concentrations range from 0.4 to 1.8 wt.% without a distinct correlation with distance to  
331 the shear zone. Iodine is generally low in all measured apatites and concentrations range from  
332 0.15 to 1.2  $\mu\text{g/g}$ .

333 Apatite from unaltered Ødegardens Verk gabbro is homogeneous and average halogen  
334 concentrations are  $2.40 \pm 0.05$  wt% for F,  $2.06 \pm 0.21$  wt.% for Cl,  $290 \pm 66$   $\mu\text{g/g}$  for Br and  
335  $0.72 \pm 0.03$   $\mu\text{g/g}$  for I, respectively, and are in agreement with microprobe data (Engvik et al.  
336 2009). Cl-rich zones of apatite from the metagabbro are also homogenous and have average  
337 concentrations of  $88 \pm 12$   $\mu\text{g/g}$  F,  $22.9 \pm 1.3$   $\mu\text{g/g}$  Br and  $0.23 \pm 0.02$   $\mu\text{g/g}$  I. Similar to Cl-rich  
338 zones of other Bamble samples, Cl concentrations of pure Cl-apatite are again likely to be  
339 overestimated by SIMS measurements. OH-rich zones of the same apatite grain are  
340 heterogeneous and values vary between 0.25 and 1.1 wt.% for F, 1.0 and 2.1 wt.% for Cl, 20  
341 and 28  $\mu\text{g/g}$  for Br and 0.25 and 0.48 for I, respectively.

#### 342 $\delta^{37}\text{Cl}$ of apatite

343 Cl-rich zones of three individual apatite grains from the unaltered Langøy gabbro sample  
344 reveal  $\delta^{37}\text{Cl}$  values in the range of -1.2 to +1.0 ‰ (Fig. 8). Although measurements of Cl-rich  
345 zones within individual grains show a homogeneous distribution of  $\delta^{37}\text{Cl}$  values for each  
346 grain (Fig. 8), the grains itself differ from each other by 1-2 ‰. Cl-poor apatite of the same  
347 samples is heterogeneous and  $\delta^{37}\text{Cl}$  values range from +0.8 to +2.8‰. Cl-poor zones are  
348 always higher in  $\delta^{37}\text{Cl}$  than Cl-rich zones of the same grain. Apatite from Langøy samples  
349 reflecting different degrees of alteration shows highly variable  $\delta^{37}\text{Cl}$  values that range from -  
350 0.7 to +3.7‰ with a slight tendency of higher  $\delta^{37}\text{Cl}$  values towards the shear zone (Fig. 8).  
351 Although a simultaneous analysis of  $\delta^{37}\text{Cl}$  values and halogens was not possible, individual  
352 spots of  $\delta^{37}\text{Cl}$  can be linked to halogen composition due to their position within the apatite  
353 grain determined by elemental mappings (Fig. 3; i.e. OH-rich or F-rich zone). Zones having  
354 elevated F concentrations reveal low  $\delta^{37}\text{Cl}$  values and more OH-rich zones show high  $\delta^{37}\text{Cl}$   
355 values (Fig. 8).

356 Apatite from the unaltered Ødegardens Verk gabbro has  $\delta^{37}\text{Cl}$  value of  $-0.8 \pm 0.2$  ‰ based on  
357 multiple measurement spots on one apatite (n=14). Patchy apatite from the metagabbro  
358 sample reveals different  $\delta^{37}\text{Cl}$  values for different zones. Cl-rich apatite has a  $\delta^{37}\text{Cl}$  value of  
359  $+0.8 \pm 0.1$ ‰ on average, whereas OH-rich zones of the same apatite show slightly higher  
360 values of  $+1.3 \pm 0.2$  ‰.

## 361 **Discussion**

### 362 *Apatite replacement reactions*

363 Apatite is known to react to changes of its surrounding fluid environment via a coupled  
364 dissolution-reprecipitation process (Engvik et al. 2009; Kusebauch et al. 2015a; Yanagisawa  
365 et al. 1999). In particular, Cl-apatite is affected by replacement as it is the least stable apatite  
366 phase in a hydrothermal environment. It has been shown experimentally that Cl-apatite reacts  
367 to OH-apatite in the presence of a variety of different geological relevant fluids ranging from  
368 high pH fluids (like KOH and NaOH) to neutral NaCl solutions to low pH fluids (HCl-sol)  
369 (Kusebauch et al. 2015a; Rendon-Angeles et al. 2000; Yanagisawa et al. 1999). Reaction rates  
370 of Cl-apatite replacement are fast (hours to days) and depend mainly on the chemistry of the  
371 fluid. In general, replaced apatite (OH- or F- rich) has smaller lattice parameters compared to  
372 pristine Cl-apatite and pseudomorphic replacement will lead to the production of pores  
373 (Putnis 2002). In turn these pores will affect transport properties as they provide new  
374 pathways for the fluid. As the newly formed apatite is precipitating from the fluid during  
375 recrystallisation, it is assumed to be in local equilibrium with this fluid and the replaced  
376 apatite should, therefore, represent the chemical composition of the fluid. If F is present in the  
377 hydrothermal fluid, it will preferentially fractionate into the newly formed apatite (Doherty et  
378 al. 2014; Kusebauch et al. 2015a; Zhu and Sverjensky 1991). Once F-rich apatite is formed, it  
379 is kinetically hindered from re-equilibrating with a fluid of slightly different composition.

380 Although metasomatism of the Bamble Sector affected both mafic and felsic rock units and  
381 mineral phases therein (e.g., biotite, amphibole, scapolite and feldspars), apatite plays an  
382 exceptional role in recording fluid-rock interaction. The different composition of natural  
383 apatite from the Bamble area can be explained by the interaction of magmatic apatite with a  
384 hydrothermal fluid of changing composition via a coupled dissolution-reprecipitation process.  
385 Cl-rich apatite from the unaltered and least altered rock samples of the Langøy and Valberg  
386 sequence is interpreted to be of primary magmatic origin (i.e. gabbro) as it shows no pores  
387 and individual grains are homogeneous in their halogen composition. Cl-poor zones of the  
388 same apatite grains are the result of replacement leading to the production of pores and a  
389 sharp interface between Cl-rich and Cl-poor apatite. As the amount of alteration increases  
390 towards the shear zone, interaction of pristine apatite with the hydrothermal fluid increases,  
391 leading to a complete replacement of magmatic apatite in the altered samples.

392 Apatite from Ødegardens Verk suggests another possible origin of zoned apatite. Here,  
393 magmatic apatite from the most pristine sample is a homogenous solid solution of F- and Cl-  
394 apatite (Engvik et al. 2009). Patchy apatite from the metagabbro is then interpreted to  
395 originate from interaction of the pristine F-Cl apatite with a high salinity fluid producing a  
396 pure Cl-apatite, which in a second process is replaced by OH-rich apatite. Similar to apatite  
397 from other shear zone samples from Langøy and Valberg, apatite from Ødegardens Verk is  
398 high in F, which suggests a replacement with a fluid similar in composition.

### 399 *Apatite as a monitor for halogens in the fluid*

#### 400 The fluorine case

401 Fluorine is highly compatible in the apatite structure and experiments reveal distribution  
402 coefficients ( $D$ ) between apatite and NaF-bearing aqueous fluid in the order of 70-300  
403 depending on F concentration in the fluid (Doherty et al. 2014; Kusebauch et al. 2015a). This  
404 is one order of magnitude higher than partition coefficients between apatite and melt (Doherty  
405 et al. 2014; Mathez and Webster 2005; Webster et al. 2009). The high affinity of F towards  
406 apatite will result in a preferred incorporation of F over OH during replacement of precursor  
407 apatite. Fluorine-containing fluid that reacts with dry gabbro containing Cl-apatite will  
408 become depleted in F during metasomatism due to apatite replacement if sufficient apatite is  
409 present. Hereby, F-rich apatite will form first along rims and cracks of precursor Cl-apatite as  
410 these are the first parts to react with the fluid (Kusebauch et al. 2015a). Replaced apatite that  
411 forms later is in equilibrium with a fluid already depleted in F and is, therefore, relatively OH-  
412 rich. This behavior of F during apatite replacement can explain the observed trends in apatite  
413 composition with distance to the shear zone (Fig. 6). F-rich zones of individual apatite grains  
414 show highest F concentrations close to the shear zone and represent the first replacement  
415 product of interaction with the hydrothermal fluid. At this stage, the infiltrating fluid has its  
416 highest F concentration. During ongoing pervasive fluid ingress into the reacting rock the  
417 fluid gets depleted in F due to ongoing replacement and F partitioning into newly formed  
418 apatite. Apatite that is replaced later (i.e., cores of pristine Cl-apatite or apatite far away from  
419 the shear zone) has lower F as it is in local equilibrium with an already F-depleted fluid. The  
420 evolution of the fluid is in this case recorded by two different observations: 1. by the internal  
421 zonation in F of individual apatite grains from different parts of the alteration sequence  
422 showing high F at rims and along cracks (Fig. 3) and 2. by the overall higher F concentrations  
423 in apatite rims closer the shear zone (Fig. 6).



424 Another possibility to explain the different zones in F concentration is that two individual  
425 fluid pulses of different composition infiltrated the gabbro. The first pulse was characterized  
426 by a low F concentration causing the formation of OH-apatite from Cl-apatite, whereas the  
427 second pulse was higher in F and formed the F-rich zones of already replaced OH-apatite.  
428 Nevertheless, both different pulses would also show an evolution of F concentration of the  
429 fluid during ongoing fluid-rock interaction (Fig. 7).

430 Measured F concentrations of apatite can be used to estimate F concentrations of the  
431 hydrothermal fluid that was coexisting with the replaced apatite. Although the partitioning of  
432 F between apatite and fluid does not follow Henry's law behavior as it is a major component  
433 in apatite but only a tracer in the fluid, experimental results allow an estimation of the  
434 distribution of F between replaced apatite and F bearing fluid (Boyce et al. 2014; Kusebauch  
435 et al. 2015a). The distribution can be described as:

$$436 \quad c_{fluid}^F = c_{apatite}^F / D_{ap/fl}^F \quad (1)$$

437 with  $D_{ap/fl}^F$  being the estimated partition coefficient of F between apatite and fluid and  $c$  the  
438 concentration of F in fluid and apatite. As pointed out by Boyce et al. (2014) the use of  
439 halogen partition coefficients in the system melt-apatite is critical and D should be replaced  
440 by equilibrium constants ( $K_D$ ) for defined exchange reactions including the activities of all  
441 components (i.e., different apatite, OH, F and Cl). Unfortunately, the required activity data do  
442 not exist for all components and also their interaction within aqueous solution is poorly  
443 constrained and cannot be measured directly from experiments. Therefore, we use partition  
444 coefficients derived from experiments as a simplification.

445 Following empirical correlations from experiments done at the pressure and temperature  
446 range of the Bamble metasomatic event (400-700°C and 0.2 GPa; Kusebauch et al. 2015a)  
447 with aqueous NaF solutions, replaced apatite with a F concentration of 1.5 wt% (F-rich zones  
448 of Langøy apatite) has a D value of 250 and is, therefore, in equilibrium with a fluid having  
449 60 µg/g F. OH-rich apatite with the lowest F concentrations (30-200 µg/g) reveals a F  
450 concentration in the replacing fluid of about <1 µg/g. The observed trends of apatite F  
451 concentration with distance can be linked to an evolving fluid that had an initial F  
452 concentration of ~60 µg/g when it first interacted with the pristine apatite and was depleted to  
453 F concentration of less than 1 µg/g due to this interaction. This observation implies that the  
454 cores of apatite close the shear zone were replaced at the same time with a fluid of the same  
455 composition as the rims of apatite in 15-20 cm distance to the shear zone (Fig. 3).

456 The bromine case

457 Although, replaced apatite is heterogeneous in Br and concentrations can vary over almost an  
458 order of magnitude within a single grain, averaged concentrations show decreasing Br  
459 towards the shear zone (Fig. 6). If a constant partition of Br between fluid and apatite is  
460 assumed, the observed trend implies an evolution of the fluid in its Br concentration. In this  
461 case, the Br concentrations of the hydrothermal fluid were highest in the least-altered samples  
462 located far away from the shear zone, whereas those close to the shear zone the fluid had less  
463 Br. Concentrations of Br in the fluid can be estimated using partition coefficients derived in  
464 the same pressure and temperature range estimated for the Bamble metasomatic event  
465 (Kusebauch et al. 2015a) by applying following equation:

$$466 \quad c_{fluid}^{Br} = c_{apatite}^{Br} / D_{ap/fl}^{Br} \quad (2)$$

467 with  $D_{ap/fl}^{Br}$  being the experimentally derived partition coefficient between apatite and fluid,  
468  $c_{fluid}^{Br}$  the resulting concentration of Br in the fluid and  $c_{apatite}^{Br}$  the measured concentration of Br  
469 in apatite. The use of partition coefficients in the case of Br is justified as Br is a trace element  
470 in both, replaced apatite and fluid. By using an experimentally derived partition coefficient  
471 (D) of 0.01 for a high salinity fluid (Kusebauch et al. 2015a), Br concentrations of fluid  
472 increase from ~1600  $\mu\text{g/g}$  close to the shear zone to ~6500  $\mu\text{g/g}$  in least altered samples. OH-  
473 rich apatite from the most pristine sample (metagabbro) was replaced by a fluid with even  
474 higher Br concentrations (~15000  $\mu\text{g/g}$ ). This fluid is likely to be the last fraction of fluid  
475 infiltrating the metagabbro unit and it displayed, therefore, the most evolved fluid.

476 The iodine case

477 Iodine shows fairly constant concentrations throughout the whole alteration sequence and also  
478 in magmatic apatite. Although, experiments have shown that I behaves in a similar way to Br  
479 during replacement of apatite, a similar trend is not observed in our sample sequence.  
480 Nevertheless, using measurements far away from cracks and experimentally derived partition  
481 data ( $D_{ap/fl}^I = 0.001$ ) (Kusebauch et al. 2015a) in the same way as for F and Br, I  
482 concentrations for the fluid are calculated to be on the order of ~300  $\mu\text{g/g}$ .

483 The chlorine case

484 The calculation of Cl of the hydrothermal fluid in a purely fluid-apatite system is more  
485 complex. Based on results of partition experiments in the system apatite-melt-fluid (Doherty  
486 et al. 2014; Mathez and Webster 2005; Webster et al. 2009), a linear correlation can be

487 facilitated to estimate melt Cl concentrations from Cl concentrations of coexisting apatite  
488 (Boyce et al. 2014; McCubbin et al. 2011). Doherty et al. (2014) show that Cl partitioning  
489 between apatite and fluid (in an apatite-fluid-melt system) is depends strongly on melt  
490 composition and pressure. Partition coefficients for Cl in such a system vary between 0.1 and  
491 1.3. In a reduced system, where only fluid and apatite are present, a simple correlation of  
492 apatite composition with fluid composition is not found (Kusebauch et al. 2015a) and apatite  
493 composition seems to be a complex function of temperature, pressure, pH, amount and  
494 composition of fluid rather than only reliant on its Cl concentration. A reliable estimation of  
495 Cl contents in the fluid from an apatite composition alone is, therefore, presently impossible  
496 as too many controlling factors are unknown. It is the object of ongoing research.  
497 Nevertheless, assuming that halogen partitioning in the apatite-fluid system follows a lattice  
498 strain formulation, the partition coefficient for Cl between apatite and fluid is ~2.3  
499 (Kusebauch et al. 2015a) and, therefore slightly higher than D values in the apatite-fluid-melt  
500 system (Doherty et al. 2014). A calculated Cl concentration for the fluid based on this D value  
501 would be in the range of 0.5 wt.%, which is one to two orders of magnitude lower than  
502 calculations based on Cl in amphibole suggests (Kusebauch et al. 2015b). The complex  
503 partitioning of Cl between fluid and apatite might also explain the large range in Cl  
504 composition (0.4-1.8 wt.% by SIMS measurements, Fig. 6) of replaced apatite within a single  
505 grain without a distinct correlation with other halogens. Although, a quantification of Cl in the  
506 fluid is not possible, the absence of a correlation with distance to the shear zone indicates  
507 either a fairly constant fluid composition during its migration through the rocks or a  
508 counterbalance of different factors controlling the incorporation of Cl into apatite, e.g. a  
509 simultaneous increase of Cl concentration and pH of the fluid will lead to a constant apatite  
510 composition.

511

#### 512 *Distribution of chlorine stable isotopes during replacement*

513 The Cl stable isotope system provides a powerful tool to trace interaction of rock with Cl  
514 bearing fluids. During fluid-rock interaction, Cl isotopes can be fractionated either by  
515 Rayleigh-type or kinetic processes.

516  $\delta^{37}\text{Cl}$  values of apatite from the Langøy alteration sequence are highly variable and range over  
517 almost 4‰. Magmatic Cl-rich apatite precursor zones and replaced F-rich apatite zones have  
518 on average 2‰ lower  $\delta^{37}\text{Cl}$  values than those of replaced OH-rich apatite of the same apatite

519 grain (Fig. 8). Additionally, different apatite grains from unaltered gabbro vary between -  
520 1.2‰ and +1.0‰ indicating an already existing  $\delta^{37}\text{Cl}$  variation within the different magmatic  
521 Cl-rich apatite grains. This might result from different conditions during their crystallization  
522 in a magma chamber. The distribution of Cl stable isotopes can be affected by equilibrium  
523 fractionation even at high temperatures (Kusebauch et al. 2015b; Schauble et al. 2003)  
524 allowing a Rayleigh fractionation of Cl isotopes in a magma chamber system. This would  
525 imply that apatite incorporating Cl early during crystallization would have relatively higher  
526 (heavier)  $\delta^{37}\text{Cl}$  values, whereas apatite forming later has lower (lighter)  $\delta^{37}\text{Cl}$  values. In the  
527 presented sample suite the magmatic apatite with lowest  $\delta^{37}\text{Cl}$  values also has the lowest F  
528 concentration. This argues for either compositional heterogeneity in the magma chamber or a  
529 different crystallization time as F is preferentially incorporated in apatite leading to an early  
530 relatively F-rich apatite whereas F-poor apatite forms towards the end of crystallization  
531 (Boyce, 2014). The different composition of magmatic Cl-rich apatite probably influences the  
532 composition of replaced apatite formed from these precursor grains due to its interaction with  
533 hydrothermal fluid.

534 F-rich zones of replaced apatite vary between 0 and +2.2‰ in  $\delta^{37}\text{Cl}$  without a clear trend with  
535 distance to the shear zone and values are similar to  $\delta^{37}\text{Cl}$  values of Cl-rich precursor apatite.  
536 As discussed above, the F-rich zones most likely originated early during fluid-rock interaction  
537 from a fluid still enriched in F and represent the early alteration products. Assuming a  
538 pervasive fluid flow, the amount of fluid present at the beginning of fluid-rock interaction is  
539 low. The Cl budget is, therefore, controlled by Cl-bearing minerals (i.e., apatite, amphibole)  
540 and their  $\delta^{37}\text{Cl}$  values. In this case, the  $\delta^{37}\text{Cl}$  values of F-rich zones of replaced apatite reflect  
541 the  $\delta^{37}\text{Cl}$  values of a rock-dominated system at the beginning of metasomatism: the  $\delta^{37}\text{Cl}$   
542 values are controlled by the magmatic apatite. Due to ongoing fluid infiltration of highly  
543 saline fluid (i.e., NaCl/KCl brine), the fluid to rock ratio increases and the Cl budget of the  
544 alteration unit is strongly dominated by the infiltrating fluid. Consequently, the higher  $\delta^{37}\text{Cl}$   
545 values of replaced OH-rich apatite represent the  $\delta^{37}\text{Cl}$  value of the hydrothermal fluid.

546 The observed trend of slightly decreasing  $\delta^{37}\text{Cl}$  values with increasing distance to the shear  
547 zone of OH-rich apatite (Fig. 8) might result either from a decreased fluid to rock ratio far  
548 away from the shear zone and, therefore, an increased influence of the lower  $\delta^{37}\text{Cl}$  of the rock,  
549 or an evolution of the Cl isotope ratios of the fluid towards lower values. Kusebauch et al.  
550 (2015b) interpret decreasing  $\delta^{37}\text{Cl}$  values of amphiboles and bulk samples from the same  
551 alteration sequence to be the result of Rayleigh fractionation of Cl isotopes due to the

552 consumption of heavier Cl and incorporation into rock-forming Cl bearing phases (i.e.,  
553 amphibole, biotite and scapolite). This results in an evolving fluid which changes its  $\delta^{37}\text{Cl}$   
554 value during pervasive fluid flow and interaction with unaltered gabbro.

555 A second possible explanation would be the influence of different fluids leading to different  
556 replacement events. Assuming two different fluid pulses or events, the different  $\delta^{37}\text{Cl}$  values  
557 of F-rich and F-poor zones (Fig. 8b) would represent the Cl isotope composition of individual  
558 fluids. In this case the F-poor fluid (first fluid) will have a high  $\delta^{37}\text{Cl}$  value of  $\sim +3.5\%$  and  
559 the F-rich fluid (second fluid) will have a lower  $\delta^{37}\text{Cl}$  value of  $\sim +1\%$ . In this case all other  
560  $\delta^{37}\text{Cl}$  values would result from mixing between the different fluids and the magmatic values.  
561 Apart from apatite, no other mineral present in the alteration sequence shows indications of  
562 two fluid events. All isotopic and compositional features of amphibole and bulk can be  
563 explained by evolution of the fluid phase of a single event (Kusebauch et al. 2015b).  
564 Therefore, we interpret the different zones observed in F concentration and  $\delta^{37}\text{Cl}$  of replaced  
565 apatite as the result of the same fluid event and related evolution due to fluid-rock interaction.

566 Although absolute  $\delta^{37}\text{Cl}$  values of apatite from the Ødegardens Verk are different from values  
567 of Langøy apatite, they display a similar pattern in  $\delta^{37}\text{Cl}$  during replacement. Magmatic  
568 apatite, in this case a solid solution of F-apatite and Cl-apatite, has the lowest  $\delta^{37}\text{Cl}$  value of -  
569  $0.8 \pm 0.2\%$ , which is similar to the lowest  $\delta^{37}\text{Cl}$  values of magmatic apatite from Langøy. If  
570 almost pure Cl-apatite is already a product of fluid-rock interaction, as suggested by Engvik et  
571 al. (2009), their  $\delta^{37}\text{Cl}$  value of  $+0.8 \pm 0.1\%$  represents the influence of Cl from an extremely  
572 saline hydrothermal fluid. OH-rich apatite with a  $\delta^{37}\text{Cl}$  value of  $+1.3 \pm 0.2\%$  is most  
573 representative for the fluid as it originates from replacement of Cl-rich apatite and should,  
574 therefore, be in equilibrium with fluid. The observations made in the Ødegardens Verk  
575 samples suggest interaction of a fluid with high  $\delta^{37}\text{Cl}$  and magmatic apatite with low  $\delta^{37}\text{Cl}$  for  
576 the whole area.

577 Although spatially resolved SIMS measurements provide an additional tool to study stable Cl  
578 isotopes, the interpretation of the data is complicated. It seems that single apatite grains are  
579 very heterogeneous and incorporation of different Cl isotopes into apatite is probably affected  
580 by various competing fractionation and mixing processes. Non-spatially resolved methods to  
581 measure Cl stable isotopes will not suffer from these very local heterogeneities and will show  
582 processes on a larger scale.

583 *Correlations of halogen data from apatite with bulk and silicate mineral separates*

584 Fluid-rock interaction in the Bamble Sector leads not only to replacement of apatite but also  
585 replacement of primary magmatic halogen-free olivine, pyroxene and plagioclase by halogen-  
586 bearing alteration minerals amphibole, biotite and scapolite. Halogens of mineral separates as  
587 well as bulk samples from the same alteration sequence were measured by ion  
588 chromatography (for F) and ICP-MS of pyrohydrolysis solutions (for Cl, Br and I)  
589 (Kusebauch et al. 2015b). Halogen concentrations of alteration silicates and bulk samples  
590 reveal following major results: 1. generally low F concentrations (< 300 µg/g) in bulk samples  
591 and minerals; 2. very high Cl and Br bulk concentrations (up to 1.1 wt.% Cl and ~30 µg/g Br)  
592 close to the shear zone and decreasing but relatively high concentrations (0.4-0.5 wt.% Cl and  
593 ~10 µg/g Br) towards unaltered gabbro; 3. constant I for all bulk rock and mineral separates;  
594 4. increasing Cl and Br concentrations of amphibole with increasing distance to the shear  
595 zone; and 5. decreasing  $\delta^{37}\text{Cl}$  values towards unaltered gabbro. These findings suggest an  
596 intensive interaction of gabbro with a pervasive infiltrating highly saline fluid of evolving  
597 halogen composition (Engvik et al. 2011; Kusebauch et al. 2015b). In this context apatite  
598 provides an additional probe for halogens as it replaces in accordance to an evolving fluid.

#### 599 Fluorine

600 Apart from apatite biotite, which is stable close to the shear zone but not throughout the whole  
601 alteration sequence, is another potential host for F. However, F concentrations of biotite are  
602 low (130-340 µg/g) indicating low F concentrations of the hydrothermal fluid also during the  
603 formation of biotite (Kusebauch et al. 2015b). Amphibole and scapolite that formed during  
604 fluid-rock interaction incorporates F in a range of 100-350 µg/g and 40-100 µg/g, respectively  
605 and show highest F concentrations close to the shear zone similar to apatite.

#### 606 Chlorine

607 Although, Cl in amphibole shows an increasing concentration trend with decreasing  
608 alteration, which is related to an increase in Cl concentration of the infiltrating fluid due to  
609 desiccation as it reacts with unaltered rock, Cl contents in apatite are constant throughout the  
610 same section. Nevertheless, apatite should record significant changes of Cl concentration in  
611 the fluid similar to amphibole if partitioning controlling factors (i.e., pH, T, P, cation  
612 concentration) are constant for all samples. The absence of a compositional trend is, therefore,  
613 either the result of simultaneously changing factors that work opposite to each other (e.g., pH  
614 and cation concentration) or the changes of Cl concentration in the fluid are too small to be  
615 reflected in the apatite composition. The latter explanation seems to be more likely as the

616 calculated composition of the fluid based on Cl in amphibole (see Kusebauch et al. 2015a for  
617 calculation) changes during infiltration from 48 wt.% NaCl ( $X_{\text{NaCl}}=0.22$ ) close to the shear  
618 zone to 73 wt.% ( $X_{\text{NaCl}}=0.45$ ) in the least altered samples. Additionally, apatite seems to be  
619 replaced faster than silicates and might be formed prior to the desiccation-related Cl  
620 concentration changes of the fluid.

## 621 Bromine and Iodine

622 Bromine behaves differently as it is a trace element in the fluid as well as in alteration  
623 minerals. The trend of increasing Br with decreasing alteration produced by a desiccated fluid  
624 is observed in apatite as well as in amphibole. Combination of Br, I and F data for the fluid  
625 from this study with Cl data from Kusebauch et al. (2015b) enables the calculation of  
626 representative halogen ratios for the infiltrating fluid. The Cl concentration of the unevolved  
627 fluid is 29.1 wt.% (based on a salinity of 48 wt.%) as calculated from amphibole data, Br  
628 concentration of the same fluid is about 1600  $\mu\text{g/g}$ . I is about 300 $\mu\text{g/g}$  and F concentration is  
629 around 60  $\mu\text{g/g}$  as calculated from apatite composition. Therefore, the Br/Cl, I/Cl and F/Cl are  
630  $5.5 \cdot 10^{-3}$ ,  $1 \cdot 10^{-3}$  and  $0.2 \cdot 10^{-3}$ , respectively. The calculated Br/Cl and I/Cl ratios for the initial  
631 fluid are in good agreement with the estimated ratios by Kusebauch et al. (2015b) of  $>3 \cdot 10^{-3}$   
632 for Br/Cl and  $>0.025 \cdot 10^{-3}$  for I/Cl and supports their interpretation of the fluid being derived  
633 from marine pore fluids and marine sediments rather than from remobilization of evaporites.  
634 Also, the low F/Cl ratio argues for an origin related to a marine environment of the Bamble  
635 fluids as other fluid reservoirs (i.e., magmatic fluids, altered crust, mantle) have orders of  
636 magnitude higher F/Cl ratios (John et al. 2011).

## 637 Cl isotopes

638 The Cl isotopic values of bulk-rock and mineral separates (i.e., amphibole, biotite and  
639 scapolite) of the Langøy and Valberg alteration sequence vary between -0.7 and +1.0‰, and -  
640 1.8 and +1.2‰, respectively. In general, low  $\delta^{37}\text{Cl}$  values are found in less altered samples,  
641 whereas higher  $\delta^{37}\text{Cl}$  values are mainly observed in highly altered samples. It is important to  
642 state that  $\delta^{37}\text{Cl}$  of bulk and silicates were measured by isotope ratio mass spectrometer  
643 analysis of a pyrohydrolyses solution containing extracted Cl from powdered samples (Barnes  
644 and Sharp 2006; Kusebauch et al. 2015b). For this method a certain amount of either bulk  
645 rock powder or powder of mineral separates needs to be prepared. Consequently, all local  
646 heterogeneities in  $\delta^{37}\text{Cl}$  within individual grains are removed and an average  $\delta^{37}\text{Cl}$  value is  
647 measured. Spatially resolved analysis of apatite  $\delta^{37}\text{Cl}$  by SIMS reveals strong heterogeneities

648 within individual grains as well as between different grains of the same sample. Although,  
649 lowest  $\delta^{37}\text{Cl}$  values for apatite of each sample fall in the range of values measured for bulk  
650 rock and mineral separates, the majority of  $\delta^{37}\text{Cl}$  values are 1-2‰ higher.

651 As discussed before, one possible process that might produce heterogeneities is a variable  
652 mixing of Cl from the different reservoirs, i.e., fluids and pristine magmatic apatite, during the  
653 replacement of apatite. Isotope fractionation processes can also lead to a locally  
654 heterogeneous distribution of Cl isotopes in replaced apatite. Diffusion experiments  
655 (Eggenkamp and Coleman 2009) show that kinetic fractionation is a potential process to  
656 change the Cl isotopic signal by 3-4‰ due to different diffusion coefficients of the two  
657 isotopes. Also, equilibrium fractionation of Cl isotopes due different bonding of Cl in  
658 molecules and crystals can cause variations of  $\delta^{37}\text{Cl}$  values between different Cl species  
659 (Gleeson and Smith 2009; Kusebauch et al. 2015b; Schauble et al. 2003; Sharp et al. 2010). If  
660 Cl atoms are exchanged between different types of species on a larger scale (i.e.,  
661 incorporation of Cl into minerals from a fluid, changing from solid state to aqueous to  
662 gaseous) Rayleigh fractionation will become an additional factor to influence the Cl isotopic  
663 composition of a system. Unfortunately, equilibrium fractionation data are lacking, but  
664 calculations based on ab-initio and lattice dynamics modelling (Schauble et al. 2003) suggest  
665 a fractionation in the order of 1.5‰ between Cl-metal complexes and non-bonding Cl even at  
666 temperatures of 300°C. This implies that apatite crystallizing from a hydrothermal fluid is  
667 likely to have a 1.5‰ higher  $\delta^{37}\text{Cl}$  value than the fluid, which might account for some of the  
668 observed variation. Replacement via a coupled dissolution-reprecipitation process always  
669 requires an interfacial fluid, which can be highly variable on a  $\mu\text{m}$  scale in composition but  
670 also in its physico-chemical properties and heterogeneities of this fluid might be imprinted in  
671 the replacement product.

672

### 673 **Conclusions: Ability of applying apatite as a halogen probe**

674 Apatite reacts via a coupled dissolution-reprecipitation process during fluid-rock interaction  
675 and incorporates halogens as a function of fluid chemistry. Halogen composition of apatite  
676 from metagabbros of the Bamble Sector (SE Norway) reveals information about the  
677 composition and history of hydrothermal fluid processes during a regional metasomatic event.  
678 Although, replaced apatite is heterogeneous in halogen and Cl isotope composition,  
679 distinctive trends can be observed suggesting a compositional evolution of fluid during fluid-



680 rock interaction. Halogen concentrations of the fluid were estimated using experimentally  
681 derived partition data between fluid and apatite at the P-T conditions of the Bamble  
682 metasomatic event. Relatively high F concentrations of replaced apatite adjacent to the shear  
683 zone indicate an infiltration of fluid having ~60 µg/g dissolved F. During pervasive fluid flow  
684 and ongoing apatite replacement, F is preferentially incorporated into apatite and depleted in  
685 the fluid to very low concentrations (>1 µg/g). Conversely, calculated Br concentrations of  
686 the fluid increase from ~1600 µg/g to ~6500 µg/g during evolution of the fluid, which is in  
687 agreement with observations of amphibole compositions of the same samples. Calculated I  
688 concentrations of the fluid are constant in the order of 300 µg/g. Using apatite to probe Cl  
689 concentrations and Cl stable isotopes has limitations. Cl concentrations of replaced apatite  
690 cannot be directly related to the Cl concentrations of the fluid and trends in Cl composition of  
691 amphibole (Kusebauch et al. 2015b) are not confirmed by the apatite composition, which  
692 might be related to the high Cl concentrations of the brine-like fluids. Apart from Cl, apatite  
693 can be used as a probe for halogens. In particular, spatially resolved F, Br and I data of  
694 replaced apatite helps to understand the compositional evolution of a hydrothermal fluid  
695 during interaction with unaltered gabbro by pervasive fluid flow.

696 Although,  $\delta^{37}\text{Cl}$  values of different apatites from the Bamble Sector are heterogeneous and  
697 vary between individual grains from the same sample as well as within a single apatite grain  
698 in the order of 1-3‰, they show some patterns in their halogen composition. The most  
699 pristine magmatic Cl-rich apatite has lowest  $\delta^{37}\text{Cl}$  values (-1.2 to +1.0‰), replaced F-rich  
700 apatite has slightly higher  $\delta^{37}\text{Cl}$  values (-0.7 to 1.5‰) and replaced OH-rich apatite shows  
701  $\delta^{37}\text{Cl}$  values of +0.6 to +3.7‰. It seems that this increase reflects the compositional change of  
702 the progressively infiltrating fluid reacting locally with apatite. However, interpreting  $\delta^{37}\text{Cl}$   
703 values in the context of fluid history and evolution, especially from apatite alone, is  
704 complicated as only little is known about mixing and fractionation processes of the Cl  
705 isotopic system during incorporation of Cl from a fluid into minerals.

706

707

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850 Figures:

851 Fig. 1: Geological map of the Kragerø area in the north eastern part of the Bamble Sector  
852 showing the sample sites (stars) near Kragerø (Valberg), at Langøy and Ødegardens Verk  
853 (from Geological Survey of Norway bedrock database).

854 Fig. 2: Back scatter electron (BSE) and cathodoluminescence (CL) images of apatite from  
855 Bamble: a) patchy Cl-rich and OH-rich apatite from Langøy gabbro, b) apatite from slightly  
856 altered Valberg metagabbro showing a pore-free Cl-rich apatite core surrounded by porous  
857 OH-rich apatite rim, c) patchy apatite from Ødegardens Verk metagabbro (picture from  
858 Engvik et al. 2009), d) OH-rich apatite from amphibolitized metagabbro, e) OH-rich apatite  
859 from scapolitized Langøy metagabbro, f) CL image of same apatite showing CL active zones  
860 along cracks.

861 Fig. 3: Langøy alteration sequence (~30 cm in size) going from the shear zone (upper part)  
862 down to the pristine gabbro (PG) sample (lower part). Alteration is strongest close to the shear  
863 zone and decreases towards PG; a) thin sections scans; b) Fluorine and Cl maps of different  
864 apatite grains in accordance to their position within the alteration sequence (spots mark  
865 individual SIMS measurements of halogen concentrations (green) and  $\delta^{37}\text{Cl}$  (red)).

866 Fig. 4: Ternary representation (i.e.,  $X_{\text{F}}$ ,  $X_{\text{OH}}$ ,  $X_{\text{Cl}}$ ) of apatite composition for Langøy (left) and  
867 Valberg (right) sample sequence calculated on the base of EMPA measurements.

868 Fig. 5: Comparison of Cl (a) and F (b) concentrations measured by EMPA and SIMS of  
869 individual apatite grains, error bars: S.D. values of multiple spots in identical zones within a  
870 single grain.

871 Fig. 6: Halogen concentrations (by SIMS) of apatite in accordance to the distance to the shear  
872 zone; each point represents an individual analytical spot; same color = individual grain of the  
873 same sample, analytical uncertainty is smaller or equal to symbol size.

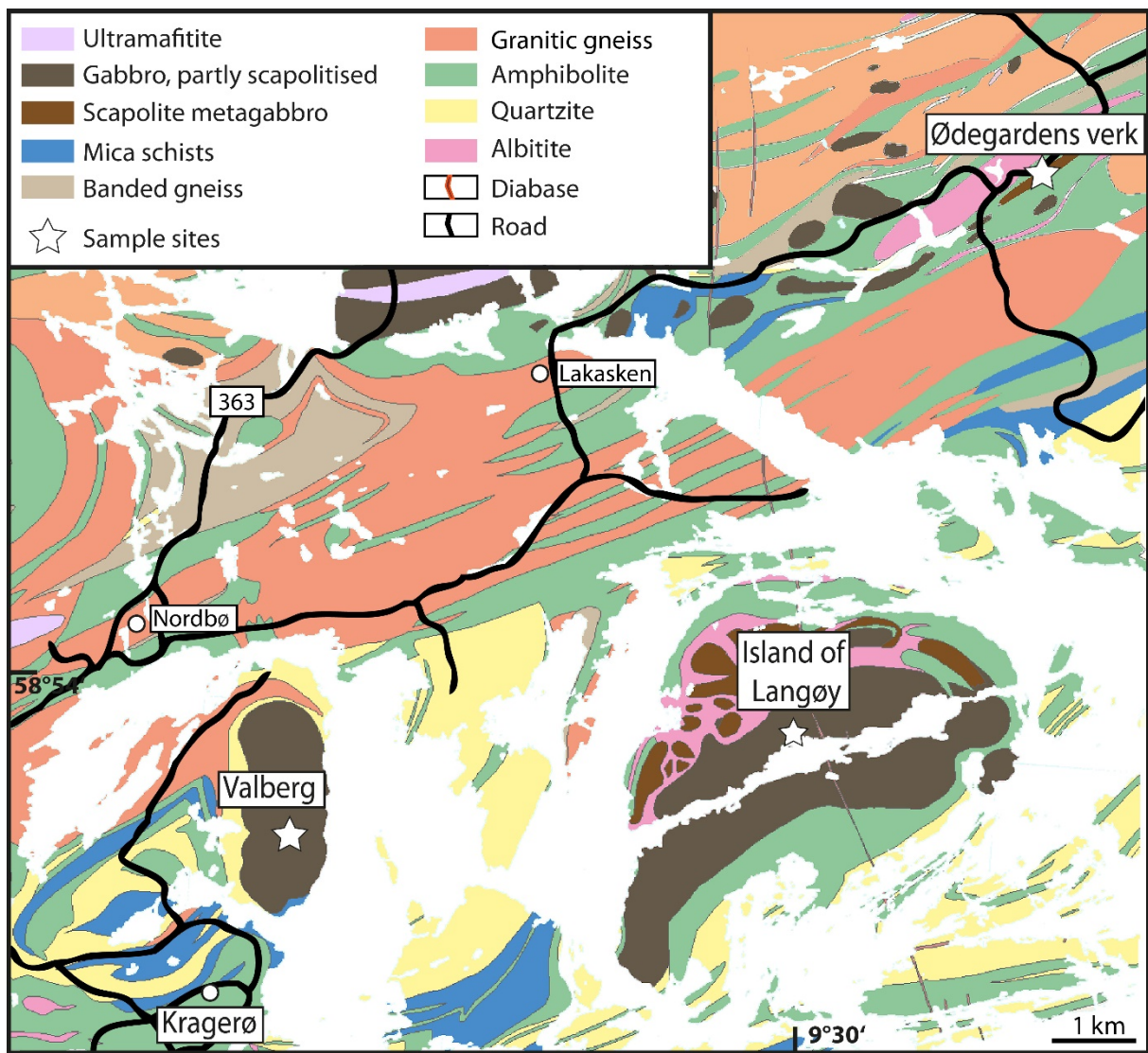
874 Fig. 7: Boxplots of halogen concentration for each sample; blue: Cl-rich apatite of unaltered  
875 gabbro sample, red: F-rich zone of replaced apatite, green: OH-rich zone of replaced apatite.

876 Fig. 8:  $\delta^{37}\text{Cl}$  values of individual apatite grains as a function of their distance to the shear  
877 zone; same color coding as in Fig. 6 and Fig. 7.

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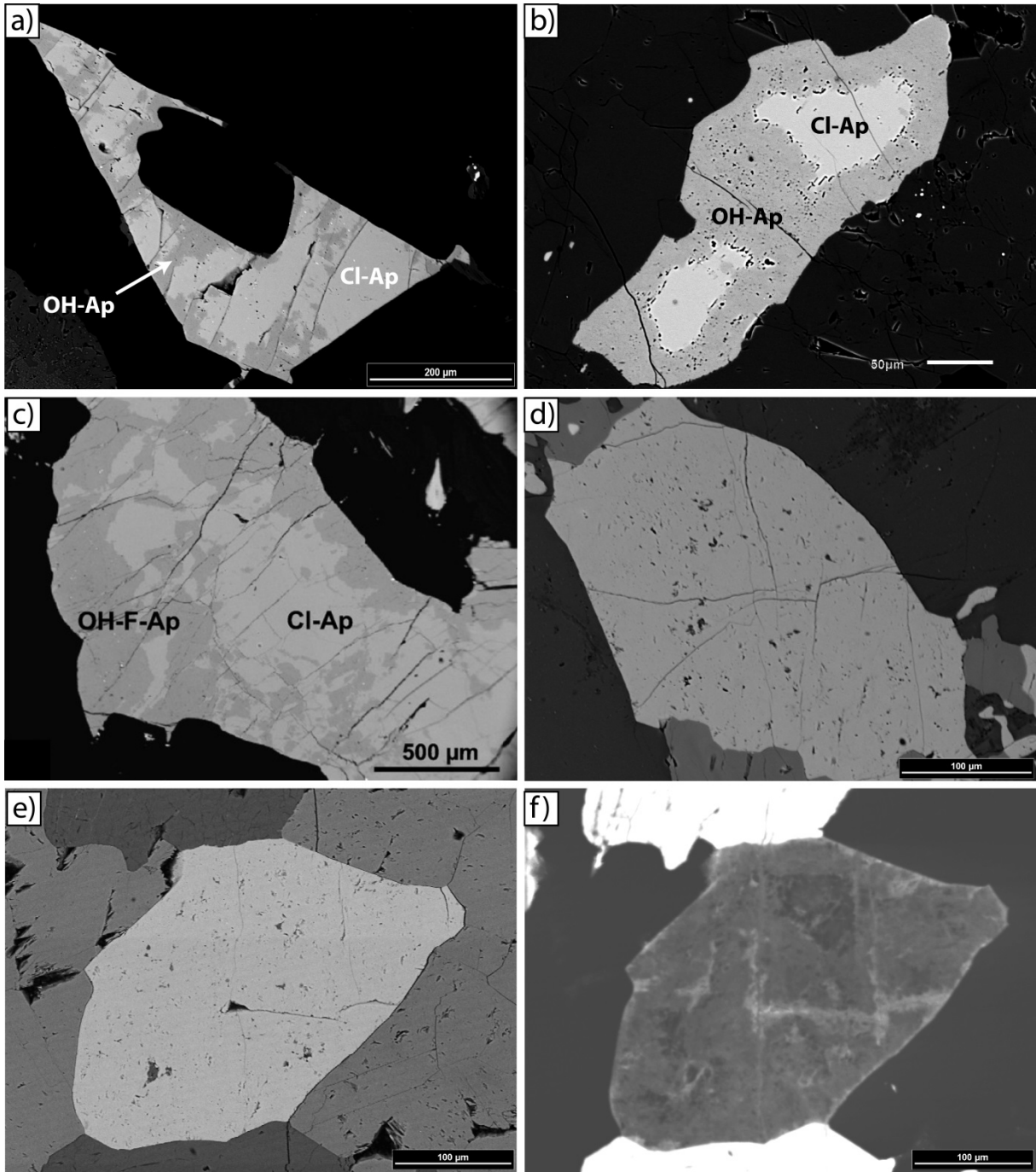
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882 Fig. 1

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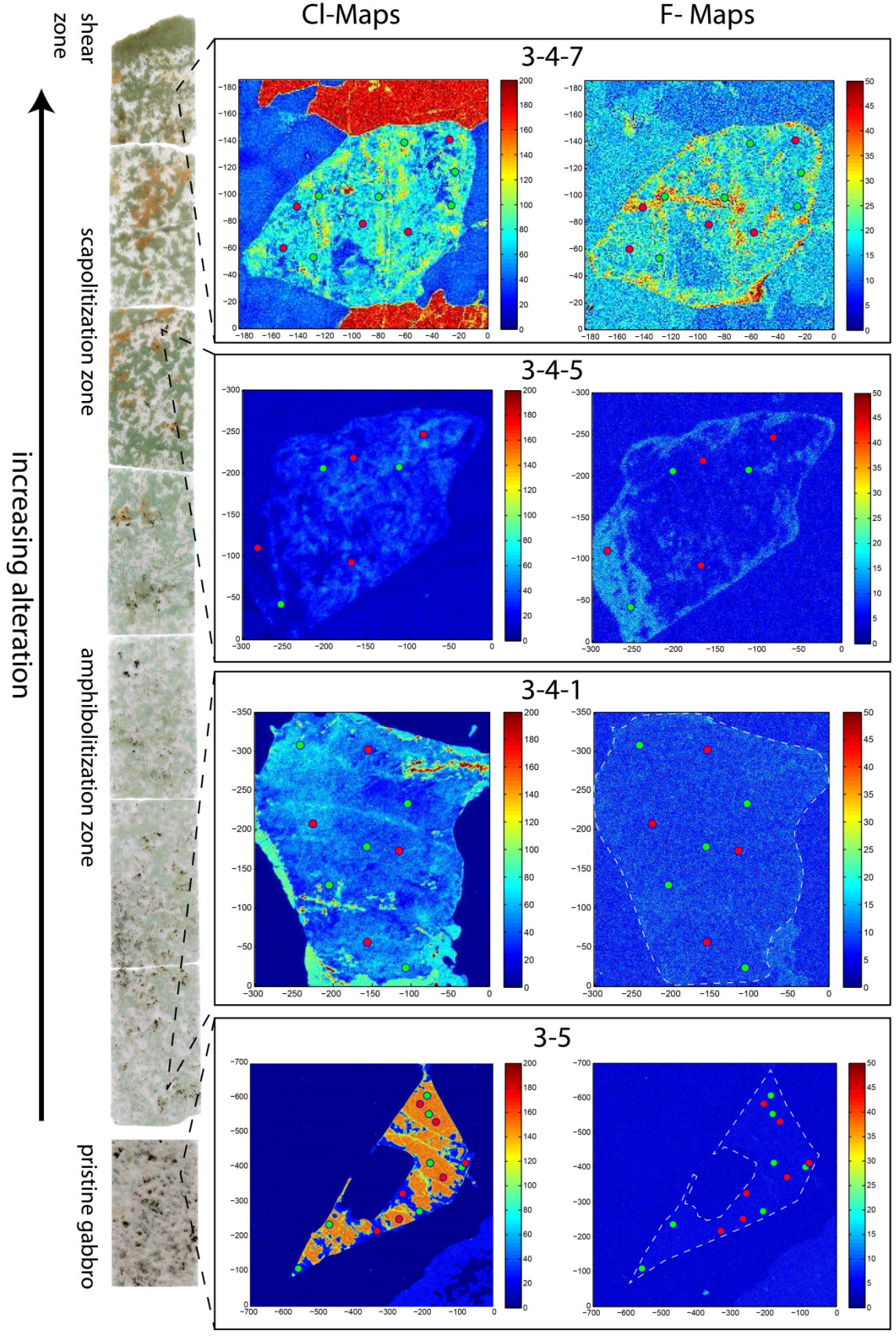
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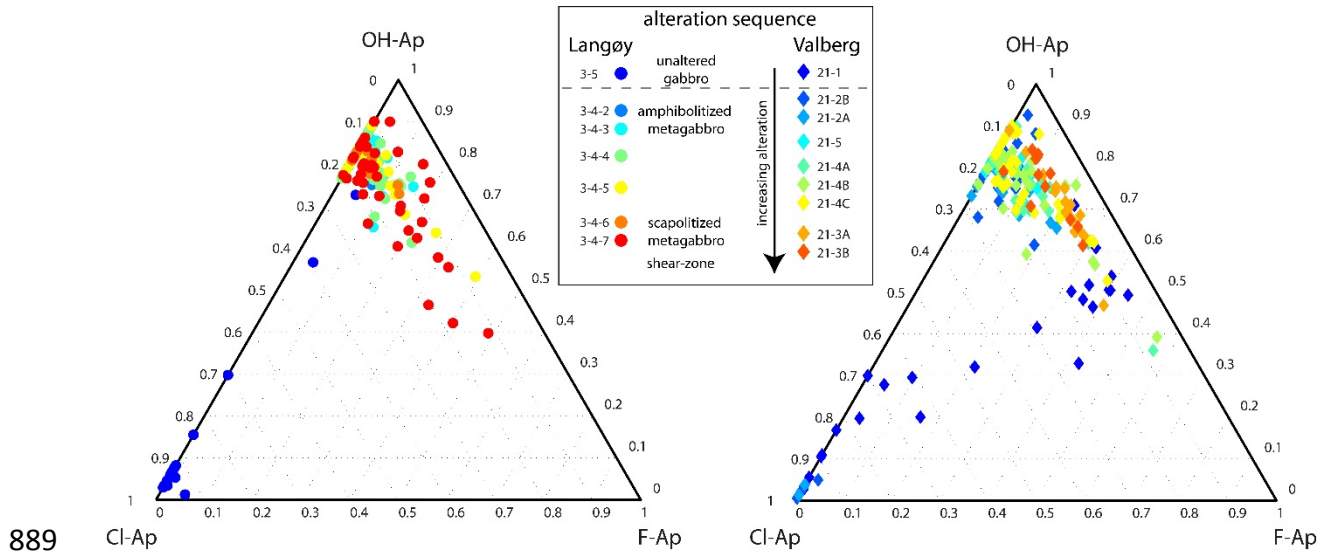
885 Fig. 2

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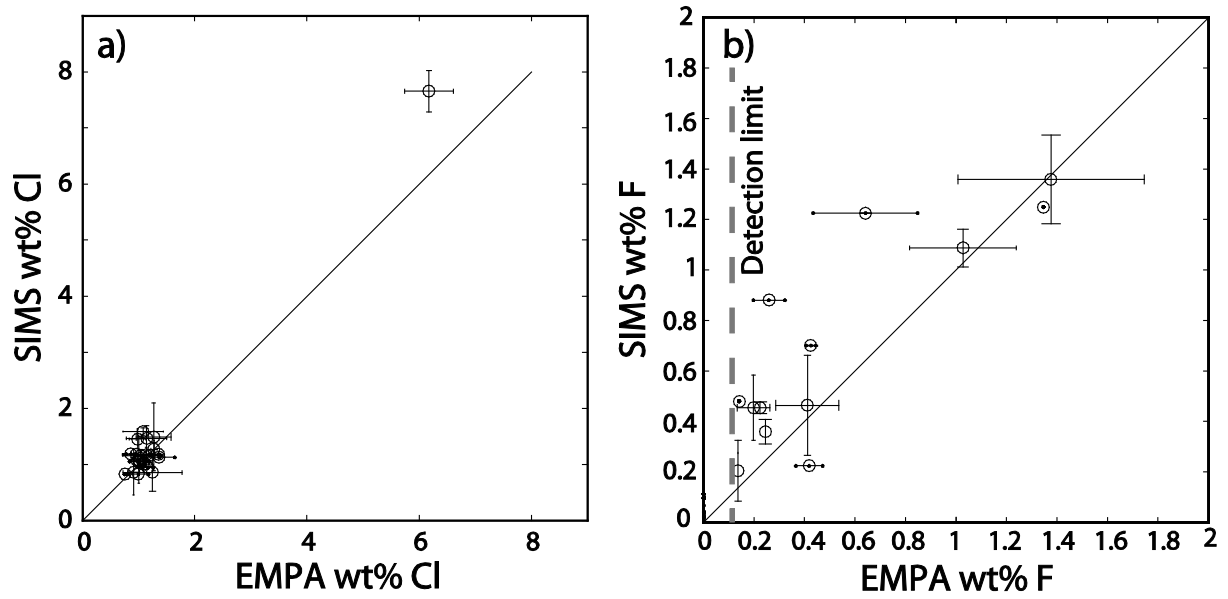




890 Fig. 4

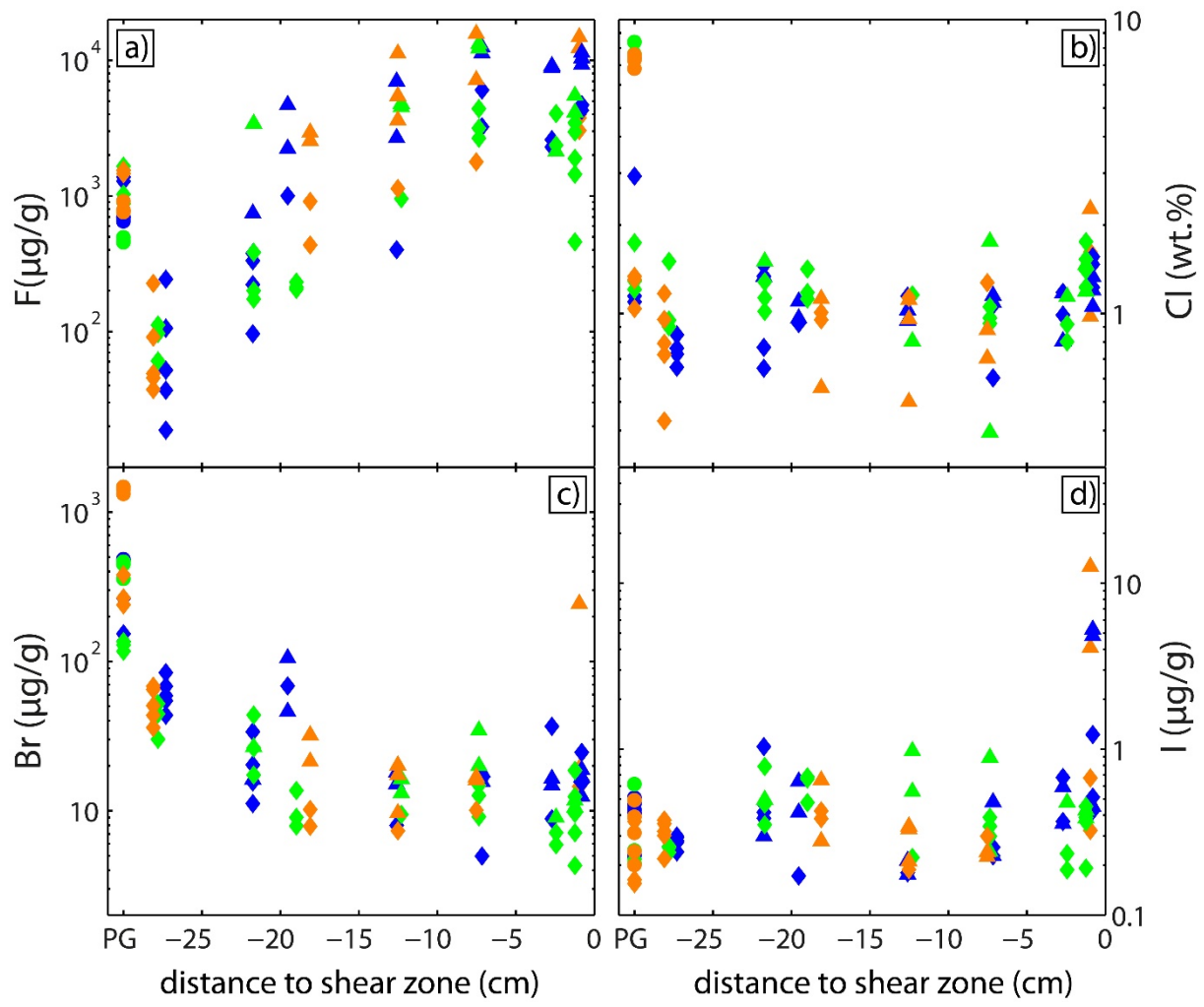
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894 Fig. 5

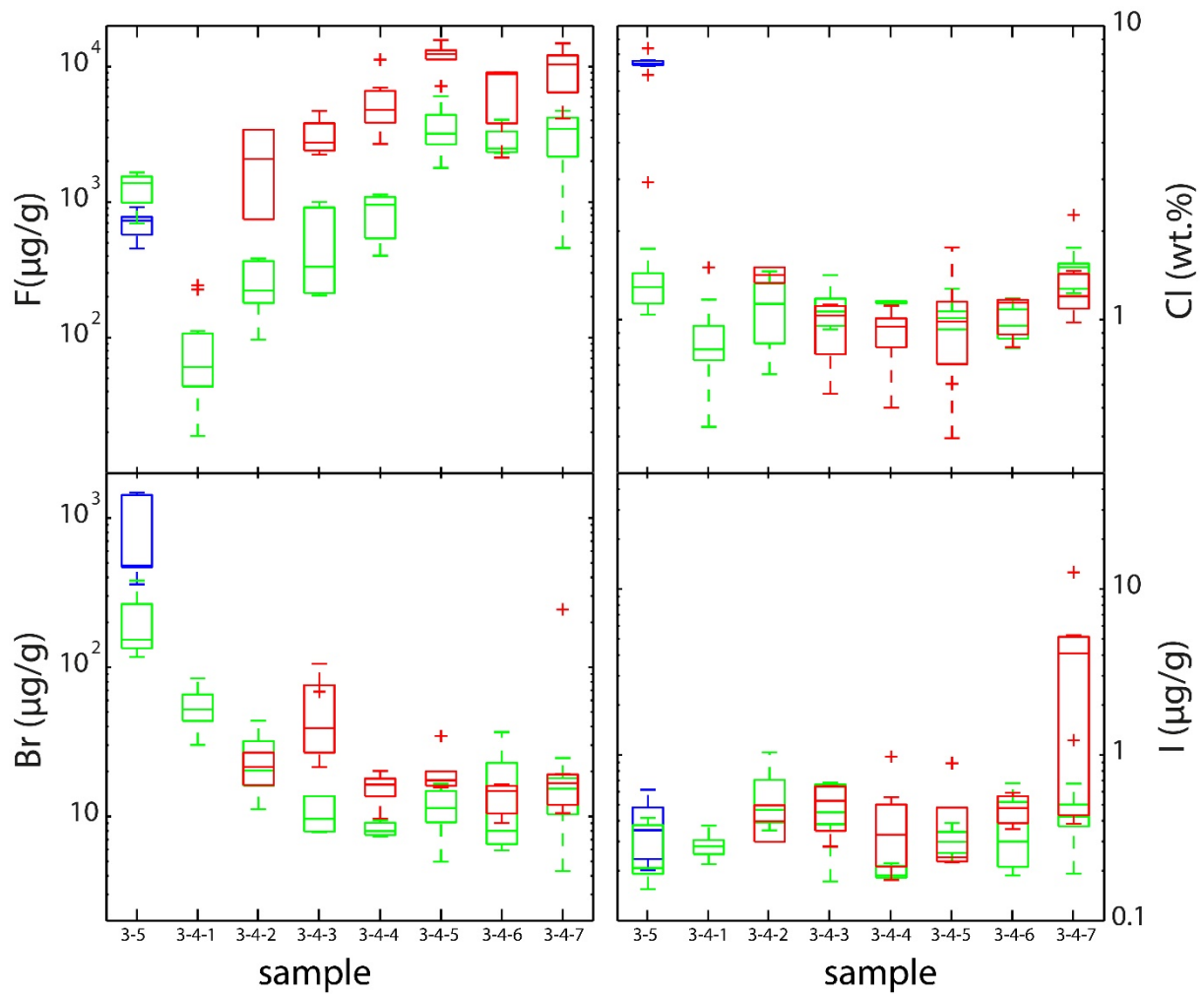
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897 Fig. 6

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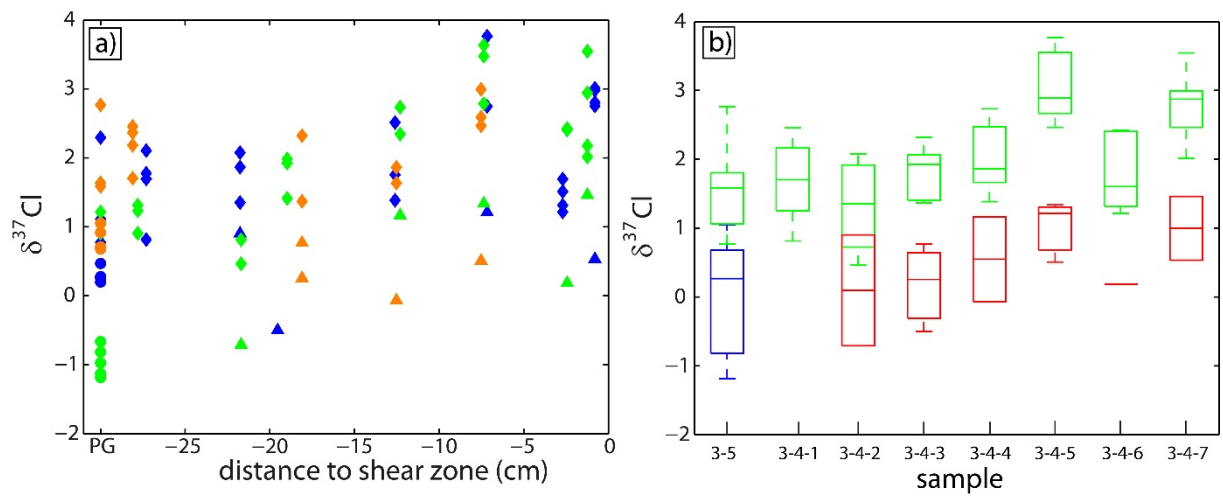


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900 Fig. 7

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904 Fig. 8

905 Table 1: SIMS measurements of halogen concentrations and Cl stable isotopes

906 907	Locality	sample	distance cm	Apatite	F ( $\mu\text{g/g}$ )	Cl ( $\mu\text{g/g}$ )	Br ( $\mu\text{g/g}$ )	I ( $\mu\text{g/g}$ )	Apatite	$\delta^{37}\text{Cl}$ ‰	error
908	Bamble	BAM3-5_ap12_hal@1	-30	Cl-ap	652	76380	482.7	0.23	Cl-ap	0.5	0.14
909	Bamble	BAM3-5_ap12_hal@2	-30	Cl-ap	678	76039	478.9	0.43	Cl-ap	0.3	0.14
910	Bamble	BAM3-5_ap12_hal@3	-30	Cl-ap	701	75406	473.0	0.51	Cl-ap	0.3	0.14
911	Bamble	BAM3-5_ap12_hal@4	-30	Cl-ap	776	75239	478.1	0.47	Cl-ap	0.2	0.14
912	Bamble	BAM3-5_ap12_hal@5	-30	OH-ap	1380	11233	153.1	0.20	OH-ap	0.8	0.15
913	Bamble	BAM3-5_ap12_hal@6	-30	OH-ap	696	30063	264.6	0.41	OH-ap	2.3	0.16
914	Bamble	BAM3-5_ap12_hal@7	-30	OH-ap	1285	11738	136.0	0.42	OH-ap	1.1	0.16
915	Bamble	BAM3-5_ap8_hal@1	-30	Cl-ap	496	75573	359.5	0.20	Cl-ap	-1.2	0.14
916	Bamble	BAM3-5_ap8_hal@2	-30	Cl-ap	465	78140	465.8	0.62	Cl-ap	-1.1	0.14
917	Bamble	BAM3-5_ap8_hal@3	-30	Cl-ap	454	85867	447.2	0.24	Cl-ap	-1.0	0.14
918	Bamble	BAM3-5-ap8-iso-cl@4	-30						Cl-ap	-0.8	0.14
919	Bamble	BAM3-5_ap8_hal@4	-30	OH-ap	1659	17833	117.0	0.22	OH-ap	1.6	0.16
920	Bamble	BAM3-5_ap8_hal@5	-30	OH-ap	1028	12371	135.7	0.20	OH-ap	1.2	0.16
921	Bamble	BAM3-5_ap8_hal@6	-30	OH-ap	876	13204	129.0	0.21	Cl-ap	-0.7	0.15
922	Bamble	BAM3-5-ap8-iso-oh@4	-30						OH-ap	0.9	0.15
923	Bamble	BAM3-5_ap1_hal@1	-30	Cl-ap	916	74698	1410.2	0.31	Cl-ap	0.7	0.14
924	Bamble	BAM3-5_ap1_hal@2	-30	Cl-ap	779	77594	1483.1	0.49	Cl-ap	0.7	0.14
925	Bamble	BAM3-5_ap1_hal@3	-30	Cl-ap	774	76098	1445.1	0.20	Cl-ap	0.7	0.14
926	Bamble	BAM3-5_ap1_hal@4	-30	Cl-ap	757	77806	1480.6	0.24	Cl-ap	1.1	0.14
927	Bamble	BAM3-5_ap1_hal@5	-30	OH-ap	1546	13351	239.7	0.37	OH-ap	2.8	0.15
928	Bamble	BAM3-5_ap1_hal@6	-30	OH-ap	1461	13696	380.2	0.15	Cl-ap	0.9	0.15
929	Bamble	BAM3-5_ap1_hal@7	-30	Cl-ap	783	69678	1327.4	0.39	OH-ap	1.6	0.15
930	Bamble	BAM3-5_ap1_hal@8	-30	OH-ap	1544	10645	266.3	0.16	OH-ap	1.6	0.15
931	Bamble	BAM3-4-1_ap1_hal@1	-27.3	OH-ap	19	7812	43.7	0.24	OH-ap	0.8	0.09
932	Bamble	BAM3-4-1_ap1_hal@2	-27.3	OH-ap	37	7809	84.1	0.28	OH-ap	1.7	0.09
933	Bamble	BAM3-4-1_ap1_hal@3	-27.3	OH-ap	106	7450	54.6	0.30	OH-ap	2.1	0.09
934	Bamble	BAM3-4-1_ap1_hal@4	-27.3	OH-ap	52	8668	59.1	0.29	OH-ap	1.8	0.09
935	Bamble	BAM3-4-1_ap1_hal@5	-27.3	OH-ap	243	6729	68.2	0.27			
936	Bamble	BAM3-4-1_ap2_hal@1	-27.8	OH-ap	97	9232	44.5	0.26	OH-ap	1.3	0.09
937	Bamble	BAM3-4-1_ap2_hal@2	-27.8	OH-ap	112	9721	52.1	0.26	OH-ap	0.9	0.09
938	Bamble	BAM3-4-1_ap2_hal@3	-27.8	OH-ap	61	15409	30.1	0.24	OH-ap	1.2	0.09
939	Bamble	BAM3-4-1_ap6_hal@1	-28.1	OH-ap	49	4416	50.5	0.37	OH-ap	1.7	0.09
940	Bamble	BAM3-4-1_ap6_hal@2	-28.1	OH-ap	37	7427	43.6	0.22	OH-ap	2.2	0.09
941	Bamble	BAM3-4-1_ap6_hal@3	-28.1	OH-ap	227	9784	64.7	0.30	OH-ap	2.4	0.09
942	Bamble	BAM3-4-1_ap6_hal@4	-28.1	OH-ap	46	11988	68.2	0.36	OH-ap	2.5	0.10
943	Bamble	BAM3-4-1_ap6_hal@5	-28.1	OH-ap	91	8110	36.1	0.32			
944	Bamble	BAM3-4-2_ap2_hal@1	-21.76	OH-ap	333	6673	33.8	0.47	OH-ap	2.1	0.20
945	Bamble	BAM3-4-2_ap2_hal@2	-21.76	OH-ap	96	14948	20.3	0.42	OH-ap	1.9	0.20
946	Bamble	BAM3-4-2_ap2_hal@3	-21.76	OH-ap	222	7858	11.2	0.38	OH-ap	1.4	0.20
947	Bamble	BAM3-4-2_ap2_hal@4	-21.76	F-ap	744	13645	16.2	0.30	F-ap	0.9	0.20
948	Bamble	BAM3-4-2_ap2_hal@5	-21.76	OH-ap	378	13727	15.6	1.04			
949	Bamble	BAM3-4-2_ap1_hal@1	-21.7	OH-ap	383	10407	43.7	0.79	OH-ap	0.5	0.20
950	Bamble	BAM3-4-2_ap1_hal@2	-21.7	OH-ap	174	11580	26.3	0.47	F-ap	-0.7	0.20
951	Bamble	BAM3-4-2_ap1_hal@3	-21.7	OH-ap	200	13132	17.3	0.35	OH-ap	0.8	0.20
952	Bamble	BAM3-4-2_ap1_hal@4	-21.7	F-ap	3420	15421	26.8	0.50			
953	Bamble	BAM3-4-3_ap1_hal@1	-19.54	OH-ap	1001	9476	68.5	0.17		-3.1	0.19
954	Bamble	BAM3-4-3_ap1_hal@2	-19.54	F-ap	2244	11277	46.1	0.64	F-ap	-0.5	0.20
955	Bamble	BAM3-4-3_ap1_hal@3	-19.54	F-ap	4696	9878	105.4	0.42			
956	Bamble	BAM3-4-3_ap4_hal@1	-18.98	OH-ap	205	11490	7.9	0.68	OH-ap	2.0	0.20
957	Bamble	BAM3-4-3_ap4_hal@2	-18.98	OH-ap	213	14509	13.6	0.66	OH-ap	1.4	0.20
958	Bamble	BAM3-4-3_ap4_hal@3	-18.98	OH-ap	232	12071	9.0	0.48	OH-ap	1.9	0.20

959	Bamble	BAM3-4-3_ap6_hal@1	-18.1	OH-ap	912	9751	7.9	0.38	OH-ap	1.4	0.24
960	Bamble	BAM3-4-3_ap6_hal@2	-18.1	F-ap	2551	5726	32.1	0.28	F-ap	0.8	0.24
961	Bamble	BAM3-4-3_ap6_hal@3	-18.1	F-ap	2944	11500	21.4	0.65	F-ap	0.3	0.24
962	Bamble	BAM3-4-3_ap6_hal@4	-18.1	OH-ap	435	10324	10.2	0.42	OH-ap	2.3	0.24
963											
964	Locality	sample	distance	Apatite	F	Cl	Br	I	Apatite	$\delta^{37}\text{Cl}$	error
965			cm		( $\mu\text{g/g}$ )	( $\mu\text{g/g}$ )	( $\mu\text{g/g}$ )	( $\mu\text{g/g}$ )		‰	
966	Bamble	BAM3-4-4_ap4_hal@1	-12.6	OH-ap	401	11744	8.0	0.18	OH-ap	1.4	0.20
967	Bamble	BAM3-4-4_ap4_hal@2	-12.6	F-ap	7013	10516	18.1	0.21	OH-ap	1.8	0.20
968	Bamble	BAM3-4-4_ap4_hal@3	-12.6	F-ap	2685	9706	15.1	0.18	OH-ap	2.5	0.20
969	Bamble	BAM3-4-4_ap6_hal@1	-12.3	F-ap	4790	8248	16.4	0.98	OH-ap	2.7	0.20
970	Bamble	BAM3-4-4_ap6_hal@2	-12.3	OH-ap	954	11861	9.5	0.22	OH-ap	2.3	0.20
971	Bamble	BAM3-4-4_ap6_hal@3	-12.3	F-ap	4538	8251	13.2	0.55	F-ap	1.2	0.20
972	Bamble	BAM3-4-4_ap5_hal@1	-12.52	OH-ap	1133	11601	7.3	0.19	OH-ap	1.9	0.20
973	Bamble	BAM3-4-4_ap5_hal@2	-12.52	F-ap	3625	9812	9.7	0.21	OH-ap	1.6	0.20
974	Bamble	BAM3-4-4_ap5_hal@3	-12.52	F-ap	5458	11430	17.4	0.33	F-ap	-0.1	0.20
975	Bamble	BAM3-4-4_ap5_hal@4	-12.52	F-ap	11237	5134	20.2	0.34		0.3	0.20
976	Bamble	BAM3-4-5_ap6_hal@1	-7.16	OH-ap	3233	10927	5.0	0.23	OH-ap	3.8	0.09
977	Bamble	BAM3-4-5_ap6_hal@2	-7.16	OH-ap	6035	6189	16.5	0.26	F-ap	1.2	0.09
978	Bamble	BAM3-4-5_ap6_hal@3	-7.16	F-ap	12492	11795	15.7	0.48	OH-ap	2.7	0.09
979	Bamble	BAM3-4-5_ap6_hal@4	-7.16	F-ap	11291	11173	18.1	0.23			
980	Bamble	BAM3-4-5_ap5_hal@1	-7.36	OH-ap	4405	9905	9.1	0.30	OH-ap	3.5	0.09
981	Bamble	BAM3-4-5_ap5_hal@2	-7.36	OH-ap	3155	9481	12.7	0.39	OH-ap	3.6	0.09
982	Bamble	BAM3-4-5_ap5_hal@3	-7.36	OH-ap	2669	10809	14.8	0.34	OH-ap	2.8	0.09
983	Bamble	BAM3-4-5_ap5_hal@4	-7.36	F-ap	12247	18041	20.0	0.89	F-ap	1.3	0.11
984	Bamble	BAM3-4-5_ap5_hal@5	-7.36	F-ap	13204	4040	34.6	0.24			
985	Bamble	BAM3-4-5_ap4_hal@1	-7.52	OH-ap	1783	13038	10.1	0.30	OH-ap	2.6	0.09
986	Bamble	BAM3-4-5_ap4_hal@2	-7.52	F-ap	7180	9023	16.0	0.24	OH-ap	3.0	0.09
987	Bamble	BAM3-4-5_ap4_hal@3	-7.52	F-ap	15728	7218	16.8	0.22	F-ap	0.5	0.11
988	Bamble	BAM3-4-5_ap4_hal@4	-7.52						OH-ap	2.5	0.09
989	Bamble	BAM3-4-6_ap4_hal@1	-2.7	F-ap	8805	8258	14.8	0.36	OH-ap	1.5	0.20
990	Bamble	BAM3-4-6_ap4_hal@2	-2.7	OH-ap	2298	10125	8.8	0.37	OH-ap	1.7	0.20
991	Bamble	BAM3-4-6_ap4_hal@3	-2.7	OH-ap	2601	12090	36.8	0.67	OH-ap	1.3	0.20
992	Bamble	BAM3-4-6_ap4_hal@4	-2.7	F-ap	9096	12039	16.4	0.59	OH-ap	1.2	0.20
993	Bamble	BAM3-4-6_ap10_hal@1	-2.44	OH-ap	2374	8207	5.9	0.19	F-ap	0.2	0.20
994	Bamble	BAM3-4-6_ap10_hal@2	-2.44	OH-ap	4050	9415	7.1	0.23	OH-ap	2.4	0.20
995	Bamble	BAM3-4-6_ap10_hal@3	-2.44	F-ap	2134	11695	9.0	0.48	OH-ap	2.4	0.20
996	Bamble	BAM3-4-7_ap5_hal@1	-0.96	OH-ap	3044	15458	14.5	0.32			
997	Bamble	BAM3-4-7_ap5_hal@2	-0.96	OH-ap	3965	15531	18.3	0.67			
998	Bamble	BAM3-4-7_ap5_hal@3	-0.96	F-ap	12347	10013	19.2	4.10			
999	Bamble	BAM3-4-7_ap5_hal@4	-0.96	F-ap	14834	23251	244.0	12.62			
1000	Bamble	BAM3-4-7_ap5_hal@5	-0.96	OH-ap	3761	16598	17.3	0.46			
1001	Bamble	BAM3-4-7_ap1_hal@1	-0.8	OH-ap	4645	12569	15.3	1.22	OH-ap	2.8	0.16
1002	Bamble	BAM3-4-7_ap1_hal@2	-0.8	OH-ap	4713	15063	16.2	0.51	OH-ap	3.0	0.16
1003	Bamble	BAM3-4-7_ap1_hal@3	-0.8	OH-ap	4282	15986	24.6	0.43	OH-ap	3.0	0.16
1004	Bamble	BAM3-4-7_ap1_hal@4	-0.8	F-ap	10340	10817	16.7	4.81	F-ap	0.5	0.16
1005	Bamble	BAM3-4-7_ap1_hal@5	-0.8	F-ap	11401	12308	18.8	5.27	OH-ap	2.8	0.16
1006	Bamble	BAM3-4-7_ap1_hal@6	-0.8	F-ap	9298	13663	12.5	0.45			
1007	Bamble	BAM3-4-7_ap2_hal@1	-1.24	OH-ap	459	14383	4.3	0.19	OH-ap	2.0	0.17
1008	Bamble	BAM3-4-7_ap2_hal@2	-1.24	OH-ap	3463	17981	12.4	0.45	OH-ap	3.5	0.16
1009	Bamble	BAM3-4-7_ap2_hal@3	-1.24	OH-ap	1894	12593	7.1	0.37	OH-ap	2.2	0.17
1010	Bamble	BAM3-4-7_ap2_hal@4	-1.24	OH-ap	2970	15655	18.6	0.39	OH-ap	2.9	0.19
1011	Bamble	BAM3-4-7_ap2_hal@5	-1.24	F-ap	4133	14985	11.7	0.38	F-ap	1.5	0.16

