1 REVISION 1

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3 **Assimilation of xenocrystic apatite in peraluminous granitic magmas**

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34   **ABSTRACT**

35   Apatite is a ubiquitous phase in granite plutons and in most adjacent country rocks, thus

36   contamination of a granite magma with wall-rock material results in two genetic types of apatite

37   in the magma: cognate and foreign. These two textural and chemical varieties of apatite undergo

38   textural and compositional changes to reach physical and chemical equilibrium (perfect

39   assimilation) in the melt. Our experiments replicate the conditions in such contaminated granites.

40   The starting materials consist of a peraluminous synthetic SiO_2-Al_2O_3-Na_2O-K_2O (SANK 1.3)

41   granite gel with A/NK of 1.3, synthetic F-apatite, synthetic Cl-apatite, and natural Durango

42   apatite. Initial experiments in cold-seal hydrothermal pressure vessels at magmatically realistic

43   temperatures of 750 °C and pressures of 200 MPa produced negligible reactions, even after run

44   times of 2000 h. Instead, we used an argon-pressurized internally heated pressure vessel with a

45   rapid-quench setup at temperatures of 1200 °C, pressures of 200 MPa, and run durations of 192

46   h. An advantage of this high temperature is that it exceeds the liquidus for quartz and feldspar;

47   therefore, apatite is the only solid phase in the run products. The starting composition of each run

48   was 90 wt.% SANK 1.3 granite gel and 10 wt.% crushed apatite (consisting of one, two, or three

49   varieties), with and without 4 wt.% added H_2O. Run products were examined by SEM for texture

50   and by EMPA and LA-ICP-MS for composition. The starting synthetic granite composition

51   contains no Ca, F, Cl, or REEs thus, in every run, apatite was initially undersaturated in the melt.

52   In all experiments, most large apatite grains consisted of anhedral shards with rounded corners,

53   most small apatite grains were round, and a small proportion of apatite grains developed one or

54   more crystal faces. In experiments with two or three apatite compositions, the run-product apatite

55   grains had compositions intermediate between those of the starting-material grains, and they

56   were homogeneous with respect to Cl, and probably F, but not with respect to REEs. The

57   processes to reach textural equilibrium consist of dissolution until the melt is saturated in apatite,

58   followed by Ostwald ripening to eliminate small grains and to develop crystal faces on larger

59   ones. The processes to reach chemical equilibrium consist of dissolution of apatite, diffusion of

60   cations (Ca, P, REE) and anions (F, Cl, OH) through the silicate melt, and solid-state diffusion in

61   the undissolved apatite grains. The halogens approached chemical equilibrium in all

62   experiments, but in the experiments containing Durango apatite, the REEs have not. Models

63   involving radial diffusion into spherical apatite grains at the temperatures of the experiments

64   show complete re-equilibration of the halogens, but changes in the REE concentrations affecting

65   only the outer few micrometers. We conclude that the rate of chemical equilibrium for the

66   halogens is greater than the rate of physical equilibrium for texture, which in turn is greater the

67   rate of chemical equilibrium for REEs. We illustrate these processes with a natural example of

68   contaminated granite from the South Mountain Batholith in Nova Scotia. Given that all granites

69   are contaminated rocks, we propose that future petrogenetic studies focus on developing

70   techniques for a minerals-based quantitative estimation of contamination (QEC).

71

72   **Keywords:** apatite, granite, chlorine, fluorine, REE, diffusion, equilibration, South Mountain

73   Batholith

74   Running Title: Assimilation of xenocrystic apatite in peraluminous granitic magmas

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INTRODUCTION

76

77   In forensic science, Locard's Principle states that any physical contact between two

78   objects necessitates a transfer of material between them. In geological science, all granites are in

79   physical contact with their wall rocks, *ergo* all granites must have exchanged material with the

80   wall rocks, to varying extents. Country-rock xenoliths, country-rock xenocrysts, and new

81   peritectic phases in the granites all represent physical manifestations of this contamination. If

82   these physically distinct contaminants are included in whole-rock chemical analyses, there

83   clearly must be a country-rock component in those measured compositions. If the contaminants

84   have been completely assimilated, with no physical evidence remaining, again the whole-rock

85   chemical composition will contain a country-rock component.

86   The uniformly peraluminous South Mountain Batholith (~375 Ma) of southwestern Nova

87   Scotia (MacDonald, 2001; Clarke, 2019) is a perfect natural laboratory in which to study the

88   effects of contamination. It is enveloped along more than 95% of its surface by 10-km thick

89   metagreywackes and metapelites of the Cambro-Ordovician Meguma Supergroup. The 15 most

90   abundant mineral species in the country rocks are identical to the 15 most abundant mineral

91   species in the batholith, but the proportions, compositions, and textures of these minerals are, of

92   course, significantly different. When mineral phase X from the country rock joins mineral phase

93   X in the granite magma, the two varieties of X undergo physical and chemical changes to reach

94   physical and chemical equilibrium by chemical exchange through the medium of the silicate melt

95   (Clarke, 2007). Ideally, to fully understand the contamination history of a granite, it is preferable

96   that the system has *not* reached equilibrium so that the contaminants are still physically and

97   chemically recognizable.

98   Over the last two decades, we have systematically studied the contamination in the South

99   Mountain Batholith from a mineralogical standpoint, one phase at a time, including garnet

100   (Lackey et al., 2011), cordierite (Erdmann et al., 2004), andalusite (Clarke et al., 2005), rutile

101   (Carruzzo et al., 2006), ilmenite (Clarke and Carruzzo, 2007), sulphides (Clarke et al., 2009), and

102   apatite (Jähkel, 2010).

103   The dual purposes of this study are to conduct experiments that simulate the

104   contamination of an apatite-bearing granite magma with foreign apatite, and to illustrate the

105   contamination and assimilation processes with an example from the South Mountain Batholith.

106   We demonstrate that a detailed assessment of the role of contamination, as revealed through a

107   careful examination of the mineralogy of individual phases, is essential to understand the

108   petrogenesis of granites.

109

110   **EXPERIMENTAL AND ANALYTICAL PROCEDURES**

111   **Apatite – peraluminous granite melt experiments**

112   We prepared a synthetic peraluminous SiO_2-Al_2O_3-Na_2O-K_2O (SANK 1.3) granite gel

113   using tetra-ethyl orthosilicate (TEOS) and Al-Na-K nitrates (Hamilton and Henderson, 1968;

114   Rizkalla et al., 1991). In this gel, the nominal K_2O/Na_2O ratio is 1.2, and the nominal

115   peraluminosity A/NK ≈ 1.3. Of special note is that this unfused starting gel contains none of the

116   chemical components of apatite (Ca-P-F-Cl-REE), similar to the apatite dissolution experiments

117   of Wolf and London (1994). The unfused SANK 1.3 gel was stored permanently in a drying

118   oven at 110 °C, but it may initially have contained some H_2O, considering that it is extremely

119   hygroscopic, and it could have gained more H_2O from the atmosphere during weighing, grinding,

120   and loading.

121   The apatite used in the experimental runs consisted of grains of synthetic fluorapatite

122   APS-64 (F-Ap), synthetic chlorapatite APS-65 (Cl-Ap), and natural Durango apatite (D-Ap).

123   The synthetic apatite compositions were synthesized using a variation of the molten flux method

124   outlined by Schettler et al. (2011) (see also Cherniak, 2000). Xu et al. (2020) reported the mean

125   major-element composition of the Durango apatite as (wt%): CaO 54.19; P_2O_5 40.78; SiO_2 0.43;

126   FeO 0.04; Na_2O 0.25; F 3.09; Cl 0.42; SO_3 0.33.

127   We conducted two types of experiments (Table 1). The 'dry' experimental runs contained

128   90% SANK 1.3 gel, and equal amounts of two or three different apatite types ground together in

129   an agate mortar before loading into either 1 cm long, 3 mm wide Au capsules (low temperature

130   experiments) or Pt capsules (high temperature experiments), which were arc-welded shut. The

131   'wet' experimental runs were identical to the 'dry experiments' except for containing an

132   additional 4 wt% H_2O (Table 1). The H_2O was loaded first before the solids. The Au or Pt

133   capsules were checked for leaks by weighing, heating in a 105 °C oven overnight, and then

134   weighed again. Any capsule that showed weight loss was discarded.

135   Trial experiments at natural granite magma conditions were first run in standard, cold

136   seal, 6 mm bore autoclaves on a hydrothermal line at 750 °C and 200 MPa for 2000 hours with

137   H_2O as the pressure medium.   These experiments were buffered at approximately the Ni-NiO

138   oxygen buffer resulting from the presence of Ni metal filler rods, which occupied the bore of the

139   autoclave not occupied by the Pt capsules. Temperatures were measured externally by a

140   thermocouple tip inserted into the end of autoclave near the Pt capsules. Thermocouples are

141   accurate to within ±3 °C. No variation in temperature was observed during each run. The

142   maximum temperature gradient along the length of a capsule was approximately 5 °C. Pressure

143   on the hydrothermal line was calibrated against a pressure transducer calibrated against a Heise

144   gauge manometer for which the quoted pressure is accurate to ±5 MPa. The autoclaves were

145   quenched after the run using compressed air, reaching temperatures of ca. 100 °C within 1

146   minute.

147   These experiments produced little or no detectable physical or chemical changes in the

148   apatite compositions. After some further trials, experiments at 1200 °C, 200 MPa, 192 h were

149   run in an internally heated gas pressure vessel (IHPV) at the GeoForschungsZentrum (GFZ) in

150   Potsdam, Germany. The two advantages of these run conditions are that apatite is the only solid

151   phase, and that physical-chemical equilibration is still only partial. The IHPV used is a Harwood

152   argon-pressurized vessel at the GeoForschungsZentrum (GFZ) in Potsdam, Germany, which can

153   reach a maximum pressure and temperature of 1 GPa and 1250 °C, respectively. Holloway

154   (1971) and Berndt et al. (2002) provided general descriptions of IHPVs and rapid quench sample

155   holder setups. The pressure vessel consists of several components: an autoclave, an intensifier, a

156   pre-pressure pump, and an electrical switchboard. The GFZ autoclave is a tool-steel cylinder

157   surrounded by H_2O-cooled copper-tube windings, where a resistance furnace together with a

158   sample holder is inserted from the bottom and fixed onto a closure head sealing the vessel. The

159   thermal gradient inside the sample holder is controlled by two internal S-type (Pt-Pt90Rh10)

160   thermocouples connected to two separate heating loops (molybdenum wires), which are hooked

161   up to a EUROTHERM program controller. Temperature variations along the length of the

162   capsules are less than 5 °C. Pressure is measured *in-situ* with a pressure gauge (measurement

163 accuracy: 1 MPa), while pressure variations were less than 5 MPa, being automatically adjusted

164 throughout the experimental run duration.

165   Experimental run-conditions were kept constant at 1200 °C and 200 MPa for 192 h

166 utilizing two middle thermocouples in contact with the samples (Table 1). Each run consisted of

167 a Pt basket suspended by a Pt wire holding up to six Pt capsules (maximum length 30 mm).

168 Isobaric, rapid quench (~150 °C/sec) was achieved by melting the Pt wire such that the Pt basket

169 dropped into the lower ceramic falling tube part of the sample holder which was kept at room

170 temperature (Berndt et al., 2002).

171   After quench, the capsules were extracted, carefully examined, cleaned, weighed, and

172 opened. The capsules were then dried at 105 °C overnight. A portion of the extracted experiment

173 was mounted in epoxy and polished for back scattered electron (BSE) imaging and electron

174 microprobe (EMP) analysis.

175

176 **Scanning electron microscope observation**

177   The backscattered electron (BSE) images and preliminary chemical analyses were

178 performed on TESCAN Mira3 LMU field emission scanning electron microscope (FE-SEM) at

179 St. Mary's University. It is equipped with an Oxford Instrument X-Max 80 mm^2 large-area

180 silicon drift detector energy-dispersive X-ray spectrometer. Operating conditions were 20 kV

181 with an electron beam spot size of about 5 nm.

182

Electron microprobe (EMP) analysis

Chemical analyses of apatite crystals were performed using the JEOL Hyperprobe JXA-8500F and 8530F+ microprobes at GFZ Potsdam with five wavelength dispersive spectrometers. The samples were coated with a 20 nm thick carbon film and analysed for major and trace elements using an accelerating voltage of 15 kV and a spot size of 10 µm. Standards and operating conditions for EMP analysis of the three apatite types and the peraluminous granite glasses are contained in Tables 2 and 3, respectively. To increase the count statistics for trace elements, but minimize volatile (F, Cl) diffusion (Stormer et al., 1993; Goldoff et al., 2012), a current of 20 nA was applied. Volatiles were measured first.

Problems in measurement of F in apatite grains include: (i) count rates are low for low atomic number elements; (ii) concentrations of F are low (maximum F = 3.77 wt% in fluorapatite); (iii) volatilization of F can occur under the electron beam, resulting in decreasing count rates with time; (iv) the count rate on F, and thus apparent concentration of F, varies as a function of the orientation of the apatite grain (Stock et al., 2015; Stormer et al., 1993; Wudarska et al., 2021); and (v) secondary fluorescence effects. Because of these problems, the error bars for F are large, and we report only the means in the subsequent tables and figures. This error in F measurement translates over to the estimation of OH on the halogen site for an assumed apatite formula of $Ca_5(PO_4)_3(F,Cl,OH)$, because it is a calculated value based on the assumption that the halogen site is fully occupied by F, Cl, and OH, and that the total charge on the halogen site is -1.

For quantitative chemical analyses of the peraluminous granite glasses, a 15 kV, 20 nA, 20 µm diameter electron beam was applied to achieve an acceptable current density of 0.06 nA/mm^2 (Morgan and London, 2005). Under such conditions, the Na loss could be 5%, which is on average 0.18 wt% Na_2O. Further specifications regarding the calibration material and

206   counting times are given in Table 3. Volatiles such as F and Na were measured first, using the L-

207   type variants of necessary crystals to achieve the maximum count rate within the shortest

208   measurement time. Although peaks are narrow, L-type crystals show much higher counting rates

209   than former J-type crystals and are therefore more suitable for trace element concentrations.

210   Minimum detection limits at 3-sigma above mean background are in the range of 0.01 to 0.06

211   wt% for all analysed elements except for REE_2O_3 (0.09 wt%) and F (0.12 wt%).

212   Qualitative line scans were done using the JXA 8500F with 15kV and 5nA. For grains larger

213   than 10 µm the stage scan was used. For smaller grains the beam scan was used. Dwell times

214   varied from 0.5-2s and probe size from ~0.5 to 1µm.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

216   Trace-element concentrations in the Durango apatite starting material and run-product

217   glasses were determined using the laser ablation inductively coupled plasma mass spectrometry

218   (LA-ICP-MS) facility located in the Health and Environments Research Centre (HERC)

219   Laboratory at Dalhousie University. The system employs a frequency quintupled Nd:YAG laser

220   operating at 213 nm, coupled to a Thermo Scientific iCAP Q ICPMS quadrupole mass

221   spectrometer with He flushing the ablation cell to enhance sensitivity (Eggins et al., 1998a,b).

222   Samples were analysed using a laser repetition rate of 10 Hz, spot size of 25 µm, and laser output

223   of ~5 J/cm^2. All samples were analysed by rastering the beam across the sample surface. Factory

224   supplied time resolved software (Qtegra) was utilized for the acquisition of individual analyses.

225   A typical analysis involved 20 seconds of background acquisition with the ablation cell being

226   flushed with He, followed by laser ablation for 60 seconds, then 40 to 60 seconds of cell

227   washout. Analyses were collected in a sequence in which two analyses were done on the NIST

228   610 standard reference material at the start of the acquisition cycle, then after every 20 analyses

229   on the unknowns. All LA-ICP-MS data reduction was done off-line using the Iolite version 4.0

230   software package (Paton et al., 2011). Ablation yields were corrected by referencing to the

231   EPMA-measured concentration of Ca in the apatite and the glass.

232

233   <div align="center">**RESULTS AND DISCUSSION**</div>

234   In this section, we present the results, and discuss, sequentially, all our observations on

235   the chemical compositions of the run-product apatite grains, the glass compositions, the diffusion

236   rates, the textural appearance of the run-product apatite grains, and an example of apatite

237   contamination from the South Mountain Batholith. In our analysis of the results, we consider

238   only stoichiometric $Ca_5(PO_4)_3(F,Cl,OH)$, with no consideration of a possible oxyapatite

239   component.

240

241   **Chemical Composition of Run-Product Apatite Grains**

242   **Preliminary experiments at 750 °C, 200 MPa, and 2000 h.** To determine the rate of chemical

243   and textural equilibration of the fluorapatite and Durango apatite in a peraluminous granitic melt,

244   a set of experiments containing these two apatites plus SANK 1.3 gel experiments plus water

245   were first conducted at geologically reasonable operating conditions, i.e., 750 °C, 200 MPa, and

246   2000 h. Both of the starting apatite compositions showed little textural change, except for slight

247   rounding of the corners of the shards. The Durango fluorapatite appears to show some evidence

248   of diffusion of Cl out of the solid grain with presumably some exactly reciprocal diffusion of OH

249   into the apatite grain (Figure 1).

250   After a set of additional experiments at 1000 °C, 200 MPa, and 72 h, in the IHPV, utilizing Pt

251   capsules, produced results similar to the 750 °C experiments, we then decided to run the

252   experiments at 1200 °C, 200 MPa, and 192 h as a final attempt to obtain an approach to chemical

253   equilibrium between some of the components in the melt and apatites, as well as an approach to

254   textural equilibrium.

255

256   **Experiments at 1200 °C, 200 MPa, and 192 h with two starting apatite compositions.** Here

257   the two starting apatites consisted of the three possible pairs of synthetic fluorapatite (F-Ap),

258   synthetic chlorapatite (Cl-Ap), and natural Durango apatite (D-Ap) (Table 1). The principal

259   chemical differences between the apatite starting materials are in the halogens and the REEs. The

260   starting synthetic fluorapatite has 3.77 wt% F, but no Cl or REEs; the starting synthetic

261   chlorapatite has 6.81 wt% Cl, but no F or REEs; and our measured starting Durango apatite has

262   means of 3.39 wt% F, 0.43 wt% Cl, and 0.91 wt% ΣREEs ($La_2O_3 + Ce_2O_3$). Table 4 shows the

263   mean halogen compositions for the apatite run products in the six experimental runs, including

264   the starting compositions. Figure 2 shows a mol proportion F-Cl plot of those apatite grains. The

265   composition of the run product apatite should be the average of the two starting material apatites,

266   minus the amounts of F and Cl variously taken up in the melt and separate fluid phase (if

267   present).

268   Run-product apatite grains in AA-11 and AA-14 have low F/Cl, as in the Cl-Ap + D-Ap

269   starting material (Table 4). Run-product apatite grains in AA-10 and AA-13 have high F/Cl, as in

270   the F-Ap + D-Ap starting material. Run-product apatite grains in AA-9 and AA-12 have

271   inexplicably high F/Cl, unrelated to the F-Ap + Cl-Ap starting material. The only difference is

272   the absence of Durango apatite and REEs. The question then arises as to whether the REEs

273   somehow stabilize the F/Cl ratio in the run products.

274   Calculating by difference from Figure 2, apatite grains in the AA-9 'dry' run have 13

275   mol% OH, whereas those in the AA-12 'wet' run have 19 mol% OH, an increase of 1.46 times.

276   Similarly, apatite grains in the AA-10 'dry' run have 9 mol% OH, whereas those in the AA-12

277   'wet' run have 16 mol% OH, an increase of 1.78 times. Finally, apatite grains in the AA-11 'dry'

278   run have 24 mol% OH, whereas those in the AA-14 'wet' run have 46 mol% OH, an increase of

279   1.91 times. Apparently, the higher the concentration of Cl in the starting materials, the greater is

280   the loss and replacement by OH (Kusebauch et al., 2015).

281   Only runs AA-10, AA-11, AA-13, and AA-14 contain the Durango apatite, and therefore

282   REEs, in the starting materials (Table 1). If the run-product apatite grains had reached

283   equilibrium for the rare-earth elements, their compositions should be the average of the two

284   starting material apatites, minus the (minor) amounts of La_2O_3 and Ce_2O_3 taken up in the melt.

285   Figure 3 shows that the ΣREE contents in the run-product apatites span the entire range from the

286   Durango apatite to each of the synthetic apatites, suggesting that the system had not yet reached

287   chemical equilibrium for ΣREEs at these run conditions. Instead, the spread in ΣREE

288   concentrations in the run-product apatite grains is a combination of Durango losing ΣREE and

289   the synthetic fluorapatite or chlorapatite gaining ΣREE, but in no case has the system reached

290   chemical equilibrium for the ΣREEs.

291

292

293 **Experiments at 1200 °C, 200 MPa, and 192 h with three starting apatite compositions.** Runs

294 AA-15 to AA-18 contain all three apatites (synthetic fluorapatite, synthetic chlorapatite, natural

295 Durango apatite) as starting materials (Table 1). As in the experiments with two apatite starting

296 materials, the ratio of apatite/(apatite + SANK 1.3) = 0.10. Table 5 shows the mean halogen

297 compositions for the apatite run products, and Figure 4 shows a mol proportion F-Cl plot of these

298 grains. As above, the composition of the run-product apatite grains should be the average of the

299 three starting material apatites, minus the amounts of F and Cl taken up in the melt and separate

300 fluid phase (if present).

301 Unlike the runs containing two apatite compositions, the presence of Durango apatite in

302 these four runs does not appear to stabilize F/Cl in the starting materials and run products. The

303 'dry' runs (AA-15, AA-17) have a low (OH) component; the 'wet' runs (AA-16, AA-18) have a

304 high (OH) content, but the run apatite grains in these experiments did not acquire as much (OH)

305 as in the two-apatite experiments.

306 As in the runs with two apatite starting compositions, if the run-product apatite had

307 reached equilibrium for the REE, their compositions should be the average of the three starting

308 material apatites, minus the (minor) amount of La_2O_3 and Ce_2O_3 taken up in the melt and

309 separate fluid phase (if present). Figure 5 shows that the ΣREE ($La_2O_3 + Ce_2O_3$) contents in the

310 run-product apatites span almost the entire range from the Durango apatite to each of the

311 synthetic apatites, suggesting again that the system had not reached chemical equilibrium for

312 ΣREEs at the chosen run conditions. Also, relative to the results involving two-apatite starting

313 compositions, the compositions of analysed grains in the three-apatite runs are skewed towards

314 low concentration of REEs. This skewness possibly reflects a combination of the 2:1 ratio of

315   REE-free to REE-bearing apatite in the starting materials and the coarser grain sizes in runs AA-

316   17 and AA-18 that inhibit equilibration by chemical diffusion.

317

318   **Chemical composition of run-product glasses**

319   London et al. (2012) cautioned that finely-ground starting materials absorb atmospheric

320   H_2O onto their surfaces, and that it remains there under desiccation. The starting SANK 1.3 gel,

321   was kept dry in a drying oven at 105 °C. However, in an experiment where a sample of the gel

322   was placed in a crimped platinum capsule and heated it to 1000^oC for 2 hours, the weight loss

323   was 3.6%. Thus, the starting material for the 'dry' runs may contain approximately 4% H_2O, and

324   the starting material for the 'wet' runs, with 4% added H_2O, may contain approximately 8%

325   H_2O. To facilitate comparison of the compositions of the glasses, we report their compositions as

326   anhydrous (Table 6).

327

328   **Major Elements in Runs AA-9 and AA-12.** Runs AA-9 and AA-12 contained F-Ap and Cl-Ap

329   and were 'dry' and 'wet', respectively. Glass AA-9 contained some small bubbles, whereas glass

330   AA-12 contained many larger bubbles (Figure 6); thus, both melts appear to have been saturated

331   with H_2O vapor.

332   Table 6 reports the compositions of the starting gel and the glasses in runs AA-9 and AA-

333   12. The starting gel, SANK 1.3, contains no components other than SiO_2-Al_2O_3-Na_2O-K_2O. Any

334   other component in the run glasses has come from dissolution of apatite, namely CaO, P_2O_5, F

335   and Cl; however, the concentration of F is below the EMP lower limit of detection, because it

336   has been strongly partitioned into apatite (Webster et al., 2009; Li and Hermann, 2017). Also, the

337   REEs are absent because there was no Durango apatite in the starting materials. There are several

338   implications arising from the compositions of the glasses in runs AA-9 and AA-12.

339   First, the CaO/P$_2$O$_5$ wt% ratio in stoichiometric apatite is 1.34, but this ratio is 2.47 ±

340   0.10 in the 'dry' AA-9 glass and 3.36 ± 0.15 in the 'wet' AA-12 glass. If apatite had simply

341   dissolved congruently in the SANK 1.3 melt, the CaO/P$_2$O$_5$ ratio in the glass should be 1.34.

342   Alternatively, if the apatite had dissolved incongruently, there should be a new solid phase in the

343   run products (e.g., Wolf and London 1995), but apatite is the only solid present. The remaining

344   explanation for the 'missing' P$_2$O$_5$ is that it partitioned into the fluid as either H$_3$PO$_4$ or as one or

345   more sodium phosphate complexes (London et al., 1993; Keppler, 1994). For run AA-12, which

346   contains more water, these additional fluids could have extracted more P$_2$O$_5$ from the glass

347   (resulting in a higher CaO/P$_2$O$_5$ ratio in the glass) than in run AA-9. Assuming that, in our

348   experiments, CaO is a more reliable indicator of apatite solubility than P$_2$O$_5$, we can use our

349   measured CaO and P$_2$O$_{5\ meas}$ concentrations in the glasses to calculate adjusted values of P$_2$O$_{5\ adj}$

350   (Table 6) so that the CaO/P$_2$O$_5$ ratio in the glass is also 1.34.

351   Second, except for the appearance of the dissolved apatite components, the glass

352   compositions in the two runs are similar to that of the starting gel (Table 6); however, the

353   peraluminosity (A/CNK) is significantly different. Clearly, apatite dissolution has introduced

354   CaO into the melt and has lowered its A/CNK from an initial value of 1.3 to ≈ 1.0.

355   Solubility of apatite is always expressed in terms of some function of P$_2$O$_5$ content. We

356   can compare our apatite solubility data, as indicated by P$_2$O$_{5\ meas}$ or P$_2$O$_{5\ adj}$, at 1200 °C, 200

357   MPa, and 75% SiO$_2$, with other determinations, as follows:

358 (a) No agreement with the dependence of apatite solubility, as determined by P_2O_5 in the melt,

359 on peraluminosity using the empirical relationship

360 $$P_2O_{5melt} = -3.4 + 3.1*(A/CNK)_{melt} \qquad (1)$$

361 of Wolf and London (1994). However, their experiments were done at the much lower

362 temperature of 750 °C, and apatite solubility is strongly dependent on temperature (Harrison and

363 Watson 1984).

364 (b) Potential agreement with the dependence of apatite solubility on peraluminosity, as

365 determined by P_2O_5 in the melt (Pichavant et al. 1992; Fig. 2), but requiring an extrapolation

366 well beyond their experiments at 1000 °C.

367 (c) Good fit with the dependence of the apatite solubility parameter, as determined by

368 $\ln((P_2O_5)^{1.5}*(CaO)^5)$, on melt SiO_2 [$P_2O_{5\ meas} = 2.40$ and $P_2O_{5\ adj} = 3.66$ are within the range

369 reported by Tollari et al. (2006; Fig. 10) for 80.57 and 82.40 mol% SiO_2, respectively].

370 (d) Reasonable fit with the dependence of apatite solubility on melt SiO_2, as determined by

371 $\ln D_P^{\ apatite/melt}$ [= 4.2 for $P_2O_{5\ meas}$ and 3.4 $P_2O_{5\ adj}$ compared with 4.0 for (Harrison and Watson

372 1984; Fig. 3) at 1200°C.

373 (e) Better fit for mean $P_2O_{5\ meas}$ (0.66 wt %) than for mean $P_2O_{5\ adj}$ (1.40 wt %) for the

374 dependence of apatite solubility on temperature (Green and Watson (1982; Fig. 2), who report

375 P_2O_5 concentrations of 0.5 to 1.0 wt % in melts with 75 wt% SiO_2 at temperatures between 1080

376 and 1165 °C.

377 In summary, given the differences in temperature-pressure-composition conditions, the solubility

378 of apatite in our experiments is broadly compatible with a wide range of previous work.

379   Third, the concentration of CaO in the 'wet' glass of AA-12 is slightly higher than in the

380   'dry' glass of AA-9 (Table 6), suggesting that H_2O might have some positive effect on apatite

381   solubility.

382   Fourth, in our experiments, the starting melt has A/CNK=1.3, but as apatite begins to

383   dissolve, the A/CNK of the melt decreases, and apatite solubility contrarily decreases (Wolf and

384   London 1994; Pichavant et al. 1992). Ultimately, apatite dissolution stops because the melt

385   becomes saturated. In our runs, the apatite grains stopped dissolving when the A/CNK of the

386   melt reached approximately 1.0 (i.e., neither peraluminous nor metaluminous). Further

387   dissolution of apatite would take the composition of the melt into the metaluminous (A/CNK <

388   1) domain where apatite solubilities are less well documented.

389   Fifth, our experimental run products consist solely of apatite + glass ± vapor ± saline

390   fluid. The concentration of Cl in the 'dry' and 'wet' glasses is identical, meaning that

391   equilibrium had been reached between the melt and apatite, regardless of the existence or

392   proportion of a separate fluid phase. From Tables 4 and 6, the apatite in 'dry' run AA-9 has 1.34

393   ± 0.04 wt% Cl and the glass has 0.21 ± 0.01 wt% Cl. The apatite in 'wet' run AA-12 has 0.59 ±

394   0.05 wt% Cl and the glass has 0.21 ± 0.01 wt% Cl. Thus, in the 'dry' run, AA-9, the average

395   Cl_{ap}/Cl_{gl} = 6.38 ± 0.36, i.e., Cl is strongly partitioned into the apatite and the minor fluid phase.

396   In the 'wet' run, AA-12, the average Cl_{ap}/Cl_{gl} = 2.81 ± 0.27, i.e., Cl is less strongly partitioned

397   into the apatite, presumably preferring the more abundant free fluid phase, and OH must replace

398   the Cl leaving the apatite. As evidence of the partitioning of Cl into the fluid phase, small

399   crystals of NaCl occur in some of the bubbles in the glasses.

400 Finally, Webster (1992, Fig. 5) and Webster et al. (2015) used the concentration of Cl in

401 haplogranitic melts to estimate the concentration of Cl in coexisting fluid phases. By this simple

402 metric, our glasses with 0.21 wt% Cl would coexist with a fluid containing ~10 wt% Cl.

403 Alternatively, Webster and Piccoli (2015, Fig. 4) used the partitioning of Cl between apatite and

404 glass to infer the concentration of Cl in a coexisting aqueous fluid phase. By this more complex

405 metric, the fluid phase in 'dry' run AA-9 should have contained ~68 wt% Cl, and the coexisting

406 fluid in 'wet' run AA-12 should have contained ~23 wt% Cl. Given these uncertainties in the Cl

407 concentration in the fluids, and the unknown proportions of the run products (apatite-glass-fluid),

408 calculating a mass balance for Cl between starting materials and run products is not possible.

409 **Rare-Earth Elements in Runs AA-10 and AA-13.** Runs AA-10 and AA-13 contained synthetic

410 fluorapatite and natural Durango apatite and were 'dry' and 'wet', respectively. As above, the

411 starting granite gel contained only SiO_2-Al_2O_3-Na_2O-K_2O, so all other elements must have come

412 from the dissolution of apatite, including REEs from the Durango apatite. Table 7 shows the

413 concentrations of the REEs in the glasses and the Durango apatite. The first generalization is that

414 the concentrations of REEs in the 'dry' AA-10 glass and 'wet' AA-13 glass are very similar,

415 suggesting that system H_2O content, at least for concentrations under 10%, is not important in

416 the dissolution of these trace elements. The second generalization is that, for the REEs, the

417 homogeneous glasses contain about 1% of the REE concentrations present in the heterogeneous

418 Durango apatite.

419 **Modeling diffusive re-equilibration of Cl and REE**

420 Measured elemental abundances in apatite from the series of experiments done at 1200

421 °C for 192 hours reveal generally homogeneous levels of Cl, but a significant range for the REE

422 (i.e., Figures 3 and 5). The exception to this homogeneity is the variation in Cl concentrations in

423   apatite from experiment AA-17 (and to a lesser extent AA-18), which show a level of variation

424   of up to 30%, exceeding the typical analytical uncertainty of <10%. In each experiment, large

425   compositional gradients in Cl and the REEs were induced using apatite starting materials that

426   have initial concentration levels that are higher or lower than equilibrium values. Whereas

427   wholesale dissolution and reprecipitation would serve to homogenize both the halogens and REE

428   (which likely occurred on a limited scale as evidenced by crystal faceting), differences in the

429   volume diffusion properties of these elements could result in the variable degrees of

430   homogeneity. As summarized by Cherniak (2010), diffusion coefficients in apatite for the

431   anions (OH, F, Cl and O) all show directional anisotropy (faster parallel to c) and are 1-3 orders

432   of magnitude more rapid than the fastest diffusion trace element cations (Sr and Pb) at geological

433   temperatures. In contrast to the cation sites, the anion columns in apatite therefore represent

434   highly directional, rapid transport pathways through the apatite structure.

435   Cherniak (2000) documented several diffusion mechanisms for the REE in apatite,

436   depending on the substitution mechanism involved. Diffusion coefficients are similar to other

437   divalent cations if simple isovalent REE exchange is involved (e.g., Ce diffusion into apatite that

438   already contains Ce and other LREEs), but more than 10 times slower if a coupled exchange of

439   either $REE^{+3} + Si^{+4} \rightarrow Ca^{+2} + P^{+5}$ or $REE^{+3} + Na^{+1} \rightarrow 2Ca^{+2}$ is involved to maintain charge

440   balance in the lattice (Pan and Fleet, 2002). Thus, if the REE move by solid state diffusion in the

441   lattice they must couple with a Na or a Si ion as well. This constraint dramatically reduces the

442   diffusion rate, even at high temperatures (cf. Cherniak, 2010). The most efficient means by

443   which REE can be moved in or out of the apatite would be via a coupled dissolution-

444   reprecipitation process where REE movement would be facilitated by fluids in an interconnected

445   porosity in the metasomatized areas of the apatite and the possible formation of monazite

446   inclusions or rim grains (see Harlov et al., 2002, 2005; Harlov and Förster, 2003). Such a

447   dissolution-reprecipitation process was apparently not the case here because no apatites from the

448   experiments show metasomatized textures nor the formation of monazite inclusions or rim

449   grains. Instead, the granitic melt interacted with the apatite in such a manner that promoted the

450   exchange of REE between the melt and apatite, based solely on solid state diffusion of REE in

451   the apatite and REE diffusion in the melt. This deduction indicates that the granitic melt was not

452   chemically reactive with either the fluorapatite (synthetic or Durango) or chlorapatite. Rather,

453   each of the three apatite types experienced only some dissolution in, and partial recrystallization

454   from, the melt.

455   To test the hypothesis that highly variable diffusion rates explain the differences in

456   halogen and REE equilibration in the apatite grains, we calculated model diffusion profiles to

457   simulate re-equilibration of spherical apatite grains using halogen and REE diffusion parameters

458   reported in previous studies (Table 8). The choice of a spherical grain model is a simplification,

459   but given the wide variability in the shape of grains introduced as powders (Figures 1, 8, and 9),

460   it serves as a useful approximation for a radial diffusive flux. The solution to Fick's Second law

461   for diffusion into a sphere of radius, a, having an initial solute concentration, C_l, and a

462   concentration at r = a (the crystal-melt interface) fixed at C_o is (Crank, 1975; equation 6.18):

$$\frac{C - C_l}{C_o - C_l} = 1 + \frac{2a}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{a} \exp \left(-\frac{D n^2 \pi^2 t}{a^2} \right) \qquad (2)$$

464   where D is the diffusion coefficient in m^2/second, t is time in seconds, and r is the radial distance

465   (r = 0 is the centre of the sphere, r=a is the outer margin). With the corresponding solution at

466   short times as (Crank, 1975; equation 6.21):

467
$$\frac{C - C_l}{C_o - C_l} = \frac{a}{r} \sum_{n=0}^{\infty} \left\{ erfc \frac{(2n+1)a - r}{2\sqrt{(Dt)}} - erfc \frac{(2n+1)a + r}{2\sqrt{(Dt)}} \right\}$$ (3)

468   in which erfc is 1-erf, and erf is the error function. Values of the diffusion coefficient at a

469   particular temperature were calculated using the Arrhenius equation:

470
$$D = D_o \exp(-Ea/RT)$$ (4)

471   in which D_o is the pre-exponential factor (m^2/s), Ea is the activation energy (kJ/mol), and R is the

472   gas constant (J/K/mol). Each of the apatite re-equilibration experiments involved apatite starting

473   materials having different initial concentrations of the halogens and REE, in turn imposing

474   differences in C_l. Values of C_o are dictated by the equilibrium apatite/melt partition coefficient

475   and would, therefore, be the same for each apatite grain, regardless of the initial internal

476   composition. The direction of the diffusive flux is variable as well; Cl will diffuse out and F

477   diffuse in for the Cl-apatite starting material, with the opposite sense for the F-apatite starting

478   material. In terms of the REE, both Cl-apatite and F-apatite are REE-free, requiring uptake of

479   REEs to approach equilibrium. The situation is less clear for the Durango apatite starting

480   material, which contains elevated, but somewhat variable levels of the REE (~0.6 to 1.7 wt%

481   La_2O_3+Ce_2O_3; Figure 5). A value for the equilibrium C_o for the REE can be estimated using the

482   apatite/melt partitioning data of Watson and Green (1981) who measured $D_{Sm}^{apatite/melt}$, the

483   apatite/melt partition coefficient for Sm, as a function of the melt SiO_2 concentration, yielding an

484   interpolated value of ~15 at the SiO_2 concentration of the melt used in this study. The REE

485   content of the melts from experiments AA-10 and AA-13, both containing Durango apatite, is

486   ~0.013 wt% La_2O_3+Ce_2O_3, yielding an equilibrium C_o of ~0.20 wt% for those experiments.

487   Other experiments with Durango apatite are assumed to have similar levels of REE in the melt,

488   and therefore C_o. Estimating values of C_o for the halogens is complicated by differences in the

489 proportions of the different apatite types, as well as melt water content, and the fact that apatite-

490 melt partitioning cannot be modeled by a simple Nernst-type partition coefficient, but instead

491 requires the full mass balance involving F-OH, Cl-OH and Cl-F exchange (e.g. McCubbin et al.

492 2015; Li and Costa 2020; Piccoli and Candela, 1992; Webster et al., 2017). Alternatively, a

493 value of C_o can be estimated by the concentration of the halogens in the run-product apatites, as

494 their homogeneity likely represents melt-crystal equilibrium achieved over the entire grain-scale,

495 an assumption that is borne out by the diffusion models.

496   Model diffusion profiles for Cl at 1200 °C used the diffusion parameters for F-OH-Cl

497 exchange reported by Brenan (1994; listed in Table 8) for diffusion parallel to the c-axis. Brenan

498 (1994) also report diffusion coefficients measured parallel to the a-axis that are ~100 times

499 slower, therefore the predominant diffusive flux for re-equilibration will be along the c-axis

500 (anisotropy in the diffusion of the REE has not, to our knowledge, been measured or reported

501 (Cherniak, 2010). Diffusion profiles are calculated for durations of 2, 10, and 50 hours, thus less

502 than the 192 hour run-times of the experiments. The profiles presented in Figure 7a were

503 calculated with equation 2. The model simulates diffusion in a 50 μm radius grain of Durango

504 apatite with a value for C_1 of 0.43 wt% Cl (average reported in Table 4), with C_o pinned at the

505 value corresponding to experiment AA-14 (concentrations from other experiments would yield

506 the same overall result in terms of extent of equilibration). As is clear from Figure 7a, complete

507 homogenization of the grain at 1200 °C is essentially complete after 50 hours. For this grain

508 size, employing the diffusion coefficient for Cl measured by Li et al (2020) would yield a similar

509 result, but requiring 100 hours for complete homogenization. The Cl diffusivity reported in Li et

510 al. (2020) corresponds to a "tracer diffusivity", meaning that it applies to diffusion in the absence

511 of OH or F counter fluxes and is, therefore, expected to be larger than the value applicable to F-

512   Cl-OH apatite solutions, thus the re-equilibration time modeled using the Li et al (2020) data is

513   probably a minimum time. Inspection of Figures 1, 8, and 9 show that most apatite grain sizes

514   are generally less than 50 µm, indicating that an experiment duration of 192 hours at 1200 °C is

515   sufficient to completely homogenize the initial gradients in halogen concentration, consistent

516   with the experimental results. However, some larger (> 100 µm) grains are also evident, as

517   shown in Figure 9 for experiment AA-17. Diffusion model results for grains with radii greater

518   than 150 µm indicate homogenization timescales of more than 200 hours. Therefore, analysis of

519   the central portions of these larger grains, such as in AA-17, would yield Cl concentrations either

520   above or below the equilibrium concentration, depending on the identity of the original apatite

521   precursor.

522   Model curves for the diffusive loss of the REE simulated for a grain of assumed Durango

523   apatite initial composition are shown in Figure 7b. In this case, equation 2 is unstable for such

524   small values of the diffusion coefficient for the durations considered, and equation 3 was

525   employed instead. Unlike the case for Cl, the diffusion profiles for the REE show only limited

526   penetration into the apatite grain, extending to only ~3 µm after 200 hours. Random microprobe

527   analyses of initial Durango apatite grains resulting from experiments subject to these conditions

528   would therefore yield total $La_2O_3+Ce_2O_3$ concentrations ranging from C_1 (~0.6 to 1.7 wt%) to C_o

529   (~0.2 wt%). Cl-apatite and F-apatite grains that were initially REE-free would yield

530   concentrations ranging from a C_o of ~0.2 wt% to undetectable. This range of concentrations is

531   indeed observed in the analyses of run-product apatite, consistent with the limited extent of

532   diffusive re-equilibration predicted by the diffusion model. We conclude that the large

533   difference in the level of homogeneity exhibited by Cl and the REE is a product of diffusion-

534   controlled re-equilibration.

535

Textural Modifications of Run-Product Apatite Grains

537   Figure 8 shows the apatite grain sizes and shapes in each of the six runs containing two

starting apatite compositions. All grains began as angular shards, but after the runs, they are all

rounded, and some show development of crystal faces. Theoretically, from the standpoint of the

surface/volume ratio, the many small irregular apatite shards in the starting materials should be

the first to become rounded as they all dissolve in the silicate melt, or disappear entirely

depending on the grain size, until the melt is saturated with apatite. With longer run times, the

remaining apatite grains should gradually develop crystal faces until all the grains become

euhedral as a continuation of the Ostwald ripening effect. Measurement of the attainment of

textural equilibrium are only qualitative, nevertheless we can make some statements about the

progress in this direction based on the development of crystal faces.

547   Figure 9 shows the apatite grain sizes and shapes in the four runs containing three starting

apatite compositions. The run-product apatite grains appear to retain more of their initial angular

shapes than in the two-apatite experiments above, and there are fewer grains developing crystal

faces. Figure 10 shows a schematic representation of what these experiments have shown

regarding how chemical and textural equilibrium is approached in a granitic melt. The physical

appearances of the grains can be deceptive. Euhedral grains of apatite, and all other minerals, can

be purely magmatic, peritectic, or of overgrown xenocrystic in origin. The default origin for a

euhedral grain is magmatic, because we expect that a mineral growing unrestrictedly in a silicate

melt, especially an early-saturated phase such as apatite, would develop unimpeded crystal faces,

at least up to the point where crystals interfere with each other. Peritectic grains are particularly

problematic, because they appear to be magmatic (e.g., andalusite - Clarke et al. (2005);

558   cordierite - Erdmann et al. (2009); K-feldspar - MacDonald and Clarke (2017)), despite their

559   constituent chemical components being foreign. Some euhedral grains are suspect magmatic,

560   because they are not common minerals in granites (andalusite, cordierite), and others are

561   particularly deceptive because they are also common as purely magmatic phases (K-feldspar).

562   Furthermore, two adjacent euhedral grains of the same mineral in the same rock can have

563   completely different origins. Only some combination of physical and chemical parameters can

564   reveal the correct interpretation of their origins.

565

A Natural Example of Apatite Assimilation

566

Apatite mineralogy and compositions

567

568   Jähkel (2010) investigated phosphate mineral relations along both sides of the contact of

569   the contaminated, post-tectonic, peraluminous South Mountain Batholith (MacDonald, 2001;

570   MacDonald and Clarke, 2017) with metasedimentary rocks of the Meguma Supergroup. One

571   granite sample (P7G3) contains a chain of apatite grains extending in both directions from a

572   small xenolith into the enclosing granite (sample P7G3, Figures 11a,b,c), representing a

573   microcosm of the contamination process discussed in this paper. In simple terms, this natural

574   sample contains two distinct types of apatite, analogous to our synthetic experiments. The apatite

575   grains in the xenolith are small and anhedral; the apatite grains in the granite are large and

576   subhedral to euhedral. In the same granite sample, remote from the xenolith, are many other

577   apatite grains (Figure 11d), and in the adjacent country rocks, apatite occurs as ultra-fine-grained

578   bands (Figure 11e). Table 9 shows the chemical compositions for these apatite grains in granite

579   sample P7G3, and Figure 12 shows chemical variation diagrams for Ce-Y and Fe-Mn.

F-Cl Relations

580   All apatite grains (Table 10), regardless of their occurrence in the xenolith or in the

582 granite, and regardless of whether core or rim, have identical halogen compositions, within

583 analytical error. These results suggest that the halogens have reached chemical equilibrium in

584 this contaminated granite. We can deduce from our trial experiments at 750 °C, 200 MPa, and

585 2000 h, where halogen equilibrium was not reached, that this P7G3 natural system, at ca. 750 °C

586 and 300 MPa, clearly must have taken much longer than 2000 h (~ 3 months) to achieve its

587 chemical equilibrium for F-Cl. Our diffusion modeling shows that, at 750 °C, it would take 80

588 years to homogenize Cl in a 50 μm radius apatite grain, and 6000 years in a 500 μm radius

589 apatite grain.

590

Ce_2O_3-Y_2O_3 and FeO-MnO Relations

592   In the P7G3 natural apatite system, the concentrations of La are below our EMP

593 analytical lower limit of detection, but the Ce and Y concentrations are measurable. Thus, we use

594 Ce-Y in the natural system as a proxy for comparing with the La-Ce results in the synthetic

595 system. Also, except for minor Fe and Mn in the Durango apatite, our synthetic system contained

596 no first transition series elements, but almost all natural systems do, so we can examine them as

597 well (Figure 12). We make the following observations:

598 (i) The apatite grains show an extremely wide range of concentrations of Ce_2O_3 (0.03–0.26

599 wt%), Y_2O_3 (0.05–0.39 wt%), FeO (0.05–0.81 wt%), and MnO (0.28–0.97 wt%) in a single thin

600 section; (ii) the green ellipses enclose the tight element distribution in the apatite cores (grains A-

601 4, A-5, A-6, A-7) in the xenolith; and (iii) every apatite grain is zoned, but the core-rim vectors

602 do not point to a single composition.

603

Interpretation

605   In general, accessory minerals (apatite, monazite, zircon, magnetite, ilmenite, rutile,

606   allanite, titanite) in granites contain a wealth of petrogenetic information about age, temperature,

607   F/Cl ratios in the melt and coexisting fluid (if any), contamination, magma differentiation and

608   evolution as captured in zoning, etc. (Stokes et al., 2019; Wolf and London, 1994; Lux et al.,

609   2006; Webster and Piccoli, 2015; Kusebauch et al., 2015; Wones, 1989; Anderson, 1996;

610   Hoshino et al., 2007; Carruzzo et al., 2006; Jung et al., 2000). In addition, textural evidence

611   (Clarke et al., 2021), supported by experimental work (Wolf and London, 1994), shows that

612   apatite may saturate early in peraluminous granite magmas such as the South Mountain

613   Batholith. If so, under such conditions of high T and low crystallinity, these early-formed apatite

614   grains might be expected to be homogeneous in composition, but apparently this is not the case.

615   Granite sample P7G3 is contaminated, clearly containing xenoliths of country rock.

616   Locard's Principle applied to this sample, namely the exchange of materials after physical

617   contact, indicates that the dual processes of attaining chemical and textural equilibrium

618   (assimilation) were still under way when this assemblage of cognate and foreign materials

619   reached its thermodynamic solidus temperature (Clarke, 2007). All the apatite grains in P7G3

620   have equilibrated, i.e., assimilated, with respect to F and Cl, but not for Ce-Y or Fe-Mn in the

621   granite magma that crystallized this rock. The wide chemical variation for Ce-Y and Fe-Mn in all

622   the apatite grains indicates that the rates of cooling above, and perhaps also below, the solidus,

623   were too rapid to achieve chemical equilibrium by diffusion. Likewise, the textural assimilation

624   is, at best, only partial. We deduce that, on the centimeter scale of the thin section, and even on

625   the micrometer scale of the single grains, the apatite grains in granite sample P7G3 have

626   probably had more than the two obvious sources (foreign from the one visible xenolith, and

627   cognate from the granite magma), as observed in other granites (Lux et al., 2006; Sun et al.,

628   2021, and references therein).

629   It is possible that the streaks of ultra-fine-grained apatites in country rock sample P6C1

630   (Figure 11e) were the precursors for the coarsened apatite chain in granite sample P7G3.

631   Specifically, however, any apatite grain in the xenolith almost certainly has a metamorphic

632   origin, but any apatite grain in the granite can be purely magmatic or modified xenocrystic in

633   origin, and those xenocrysts may be different from those in the one xenolithic source observable

634   in granite sample P7G3. The physical and chemical processes that may have been operating in

635   granite sample P7G3 include:

636   (i) fractional crystallization, to explain some of Ce-Y and Fe-Mn zoning in single crystals,

637   however zoning directions are not uniform, suggesting additional disequilibrium processes such

638   as magma recharge, magma mixing, and a wide range of xenocrystic apatite compositions, all

639   recorded by the apatite grains;

640   (ii) local conditions, e.g. apatite is included in, or proximal to, biotite, and an ability to exchange

641   with nearby, but much rarer, monazite or xenotime;

642   (iii) Ostwald ripening, including dissolution of small grains and overgrowth on large grains, to

643   explain some of the cases of reverse zoning of Ce-Y and Fe-Mn, as well as the textural changes

644   in apatite from small and anhedral to large and euhedral; and

645   (iv) diffusion of F-Cl through the silicate melt, including melt along grain boundaries in the

646   small xenolith, and through all the solid apatite grains to achieve chemical equilibrium for the

647   halogens.

648   Because the halogens have reached chemical equilibrium in granite sample P7G3, we

649   deduce that the time the natural system remained active for F-Cl exchange was on the order of

650   the modeled 80-6000 years noted above. Bea (2010) showed that the cooling rates of batholiths

651   to their solidus temperatures are on the order of thousands to tens of thousands of years. The

652   implication would then be that, however long the natural system took to crystallize, in this case

653   of the South Mountain Batholith, it was insufficient to equilibrate Ce-Y, or even Fe-Mn between

654   the melt and the apatite.

655

IMPLICATIONS

657   Contrary to the elementary textbook tripartite classification of rocks, granites are not

658   strictly igneous rocks, but rather hybrids. Granted, their principal component was a siliceous

659   silicate melt, but that melt had been in contact with foreign rocks from the time of its ascent out

660   of the source region to the time of its emplacement. Those foreign components can variously join

661   the initial silicate melt as xenoliths, xenocrysts (including restites), peritectic grains, and melt.

662   The more physically and chemically anomalous the solid foreign material is to the magmatic

663   crystallization products, the easier it is to identify as foreign (e.g., staurolite). The more

664   physically and chemically similar the solid foreign material is to the magmatic crystallization

665   products, the harder it is to identify as foreign (e.g., quartz). Between these extremes are

666   minerals, such as our natural apatite grains in sample P7G3, that show attainment of chemical

667   equilibrium for F and Cl, but not for Fe, Mn, Ce, and Y, and only some indication of attainment

668   of textural equilibrium. Granitic rocks would be much less revealing about their origins if they

669   had always reached physical and chemical equilibrium. In such a scenario, there would be no

670 textural or chemical information preserved about the past histories of their constituent minerals.

671 Consequently, *every mineral grain* in a granite must be interrogated about its origin.

672 As our experiments on, and natural example of, apatite have shown, foreign material will

673 undergo various degrees of physical and chemical equilibration with cognate material. In the rare

674 event of perfect physical and chemical equilibration of cognate and foreign material, only whole-

675 rock geochemistry can detect the former contamination. Otherwise, physically and/or chemically

676 identifiable relics of contamination remain, and this must be the case for most granites.

677 For 50 years, traditional whole-rock geochemistry (majors, traces, isotopes) and

678 application of assimilation-fractional crystallization (AFC) models have reached a petrogenetic

679 limit, and new approaches are needed. Given that all granites are contaminated rocks, we

680 propose that future petrogenetic work should begin to focus instead on a minerals-based

681 quantitative estimate of contamination (QEC). Such work would begin with a detailed inventory

682 and characterization of the minerals in the country rocks to establish the physical and chemical

683 properties of the contaminants, and continue the same characterization in the minerals of the

684 granite. Then apply a range of discriminant techniques, ranging from simple histograms to

685 multivariate statistics, for each quantifiable physical and chemical parameter in minerals of the

686 granite and country rock to arrive at independent quantifiable estimates of contamination (QEC)

687 for each phase.

688 Much of the otherwise tedious data collection can be automated. For example, Clarke et

689 al. (2021) examined the spatial association of >15,000 accessory mineral grains in three granite

690 samples, except that limited study needs to go further to assess the cognate or foreign origin for

691 every grain in the granite sample to get a minimum estimate for the extent of contamination,

32

692   given that some foreign grains may have completely equilibrated by dissolution, melting, or

693   diffusive ion exchange (Clarke, 2007).

694   **ACKNOWLEDGEMENTS**

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874 **Figure Captions**

875 **Figure 1:** Preliminary experiments at 750 °C, 200 MPa, and 2000 h. (a) large grain of Durango

876 apatite showing Cl diffusion gradient over a distance of 20 μm toward its margin. The apatite

877 grain boundary with the silicate melt is not detectable on the Cl line scan. The apatite appears to

878 be losing Cl to the silicate melt and is presumably gaining OH because the F profile appears

879 unchanged. (b) Even this small apparently detached satellite apatite grain is not homogenized

880 with respect to Cl. White lines in both images highlight the microprobe line scan.

881

882 **Figure 2:** Plot of apatite run products as a function of F and Cl for experimental runs with two

883 starting apatite compositions. Apatite compositions in 'wet' runs have lower Cl and higher OH

884 concentrations than those in the corresponding 'dry' runs. Stoichiometric Cl-Ap has 0.192 mol

885 Cl, stoichiometric F-Ap has 0.198 mol F, and stoichiometric OH-Ap has 0.195 mol OH. For

886 representational simplicity, all these mol fractions are rounded to 0.200 in Figures 2 and 4.

887

888 **Figure 3:** REE concentrations in 30 run-product apatite grains from each experiment containing

889 two starting apatite compositions, including the Durango apatite. The wide range of ΣREE in the

890 Durango apatite is a measure of its inhomogeneity; the wider range of ΣREE in the experimental

891 run apatites is a measure of the failure of the system to attain chemical equilibrium with respect

892 to the REE.

893

894   **Figure 4:** Plot of apatite run products as a function of F and Cl for experimental runs containing

895   three starting apatite compositions. Apatite compositions in the 'wet' runs have lower Cl

896   concentrations than those in the corresponding 'dry' runs. The effect of added H_2O is to increase

897   the concentration of OH in the apatite and to lower the Cl/F ratio in the apatite run products,

898   suggesting that Cl is preferentially partitioned into a separate fluid phase.

899

900   **Figure 5:** REE concentrations in 30 run-product apatite grains for all experiments containing

901   three starting apatite compositions. The wide range of ΣREE in the Durango apatite is a measure

902   of its inhomogeneity; the wider range of ΣREE in the experimental run apatites is a measure of

903   the failure of the system to attain chemical equilibrium with respect to the REE. The greater

904   scatter in Cl concentrations for apatites from the 'dry' runs than from the 'wet' runs suggests that

905   a separate fluid phase may be responsible for increasing the rate of anion exchange.

906

907   **Figure 6:** Images of experimental glasses. (a) 'Dry' run AA-9 with some small bubbles.

908   (b) 'Wet' run AA-12 with abundant large bubbles. The only solid phase is apatite.

909

910   **Figure 7.** Diffusion Profiles. (a) Calculated concentration as a function of distance for the

911   diffusive uptake of Cl into a spherical grain of apatite with a radius of 50 μm. Model curves are

912   calculated for a temperature of 1200 °C using the diffusion parameters (D_o, E_a) measured by

913   Brenan (1994) assuming an initial Cl concentration of 0.43 wt% and an equilibrium

914   concentration of 2.2 wt%. The initial value corresponds to the average Durango apatite starting

915   material, and the equilibrium concentration is assumed to be the final concentration of apatite in

916   experiment AA-14. Curves are labelled according to the time in hours. (b) Calculated

917   concentration as a function of distance for the diffusive uptake of REE (sum of La_2O_3 + Ce_2O_3)

918   into a spherical grain of apatite with a radius of 50 µm (note the change of x-axis scale compared

919   to Figure 7a (above). Model curves are calculated for a temperature of 1200 °C using the

920   diffusion parameters (D_o, E_a) reported by Cherniak (2000) assuming an initial La_2O_3+Ce_2O_3

921   concentration of 0.998 wt% and an equilibrium concentration of 0.2 wt%. The initial value

922   corresponds to the average Durango apatite starting material and the equilibrium value at the

923   crystal margin is calculated assuming a $D^{apatite/melt}$ of 15 and a melt La_2O_3 + Ce_2O_3 concentration

924   of 0.013 wt%. Curves are labeled according to the time in hours.

925

926   **Figure 8:** BSE images of experimental run products from experiments AA-9 through AA-14

927   involving two starting apatite compositions. Apatite grains in each of the six runs show

928   significant rounding of their original shard shapes, presumably caused by chemical dissolution.

929   Some of the apatite grains show the development of crystal faces (white arrows), probably as

930   epitaxial overgrowths on the original anhedral grains, which serves as evidence of their approach

931   to textural equilibrium. In addition, many grains show slightly lighter-colored rims that may

932   indicate diffusion-controlled compositional differences prior to reaching either chemical or

933   textural equilibrium.

934

935   **Figure 9:** BSE images of run products from experiments AA-15 though AA-18 involving three

936   starting apatite compositions. Runs AA-15 and AA-16 are 'dry' and 'wet', respectively, and all

937   starting materials were finely ground. Runs AA-17 and AA-18 are 'dry' and 'wet', respectively,

938 and the SANK 1.3 gel was the only finely ground starting material. Run AA-18 contains rare

939 euhedral grains (white arrow), and some clusters of either skeletal/quench apatite grains or

940 apatite grains that have undergone differential dissolution, outlining a rough apatite shape (white

941 arrows with question marks).

942

943 **Figure 10:** Schematic representation of the physical and chemical approaches to equilibrium. In

944 the experiments, and in nature, the processes behind the attainment of chemical equilibrium

945 involve dissolution into the silicate melt, diffusion through the silicate melt, followed by

946 chemical exchange and solid-state diffusion in the apatite grains. Physical/textural equilibrium is

947 attained by changes in shape from shards to round to euhedral, from many to few by Ostwald

948 ripening, and from anhedral to euhedral by epitaxial overgrowth.

949

950 **Figure 11:** Naturally occurring apatite grains in granite sample P7G3 representing a microcosm

951 of the contamination process. (a-c) Chain of apatite grains extending in both directions from

952 within a small xenolith (dashed outline) into the enclosing granite. Apatite grains in the xenolith

953 are small and anhedral. Apatite grains in the granite are large and more euhedral. (d) Four large,

954 subhedral to euhedral, and texturally apparently magmatic, apatite grains in granite sample P7G3

955 outside the chain. (e) CCL image of country-rock sample P6C1 showing a band of ultra-fine-

956 grained apatite. PPL – plane polarized light; BSE – backscattered electrons; CCL – color

957 cathodoluminescence.

958

959   **Figure 12:** Apatite grain compositions in granite sample P7G3, showing cores and rims (joined

960   by arrows) with respect to Ce_2O_3 vs. Y_2O_3 (**a**), and FeO vs. MnO (b). The dashed green ellipses

961   contain the cores of the smallest and most anhedral metamorphic apatite grains (A-4 to A-7) in

962   the xenolith (as in Figures 11a,b,**c**). Boxes summarize core-rim vector quadrants: UL – up left;

963   UR – up right; DL – down left; DR – down right.

Table 1. Experimental conditions

Run	T (°C)	P (MPa)	t (hours)	SANK1.3 (mg)	F-Ap (mg)[a]	Cl-Ap (mg)[b]
AA-9	1200	2	192	21.82	1.09	1.09
AA-10	1200	2	192	21.82	1.09	
AA-11	1200	2	192	21.82		1.09
AA-12	1200	2	192	20.94	1.05	1.05
AA-13	1200	2	192	20.94	1.05	
AA-14	1200	2	192	20.94		1.05
AA-15	1200	2	192	21.82	0.73	0.73
AA-16	1200	2	192	20.91	0.71	0.71
AA-17	1200	2	192	18.50	0.53	0.62
AA-18	1200	2	192	17.46	0.54	0.59

a - synthetic fluorapatite APS-64; b - synthetic chlorapatite APS-65; c - Durango fluorapatit
* - ratio of amount of apatite relative to starting granitic gel by mass.

D-Ap (mg)[c]	Added H_2O (mg)	Ap/Gel*
	0.00	0.10
1.09	0.00	0.10
1.09	0.00	0.10
	0.96	0.10
1.05	0.96	0.10
1.05	0.96	0.10
0.73	0.00	0.10
0.71	0.96	0.10
0.57	0.00	0.10
0.5	0.80	0.10

:e.

Table 2. Operating conditions for electron microprobe analysis of apatite

Element	Calibration Material	Source	Spectral Line/Diffracting Crystal
Ca, P	Apatite, natural	Durango	Kα/PETJ
F	Fluorite, natural	Astimex	Kα/LDE1
Cl	Tugtupite, natural		Kα/PETH
La	LaPO$_4$, synthetic	Smithsonian	Lα/LIF
Ce	CePO$_4$. synthetic		

Counting Time (s) Peak/Background
10/10
10/10
40/60

Table 3. Operating conditions for electron microprobe analysis of peraluminous granite g

Element	Calibration Material	Source	Spectral Line/Diffracting Crystal
Ca, P	Apatite, natural	Durango	Kα / PETL/ PETH
Cl	Tugtupite, natural		Kα / PETH
Mn	Rhodonite, natural		Kα / LIFL
Si	Quartz, natural	Astimex	Kα / TAP
Na	Albite, natural		Kα / TAPL
F	Fluorite, natural		Kα / LDE1L
Al, K	Orthoclase, natural	GeoMK	Kα / TAP/ PETL
Fe	Hematite, natural		Kα / LIFL
Ce	$CePO_4$, artificial	Smithsonian	Lα / LIF
La	$LaPO_4$, artificial		

lasses

Counting Time (s) Peak/Background
20 / 20, 30/ 30 20 / 20
10/10
30 / 30

Table 4. Mean compositions of run-product apatite grains in experiments with two starting apatite comp

Run	Start	n	F (wt%)	1σ	Cl (wt%)	1σ	F (mol)	Cl (mol)
AA-9	F-Ap + Cl-Ap	36	2.49	0.15	1.34	0.04	0.131	0.038
AA-10	F-Ap + D-Ap	30	3.33	0.13	0.09	0.01	0.175	0.003
AA-11	Cl-Ap+ D-Ap	31	1.08	0.13	3.23	0.06	0.057	0.091
AA-12	F-Ap + Cl-Ap	32	2.70	0.22	0.59	0.05	0.142	0.017
AA-13	F-Ap + D-Ap	31	3.09	0.14	0.05	0.01	0.162	0.001
AA-14	Cl-Ap+ D-Ap	32	0.84	0.11	2.17	0.07	0.044	0.061
Stoich F-Ap	*	*	3.77	*	0.00	*	0.198	0.000
Stoich Cl-Ap	*	*	0.00	*	6.81	*	0.000	0.192
D-Ap	*	13	3.39	0.15	0.43	0.04	0.178	0.012
Initial 9-12	F-Ap + Cl-Ap	*	1.89	*	3.41	*	0.099	0.096
Initial 10-13	F-Ap + D-Ap	*	3.58	*	0.22	*	0.188	0.006
Initial 11-14	Cl-Ap+ D-Ap	*	1.70	*	3.62	*	0.089	0.102

Apatite analyses are of randomly oriented grains in the experimental run. Part of the spread in F concent
orientation (Stormer et al. 1993). The most reliable halogen parameter is Cl. F-Ap – synthetic F-apatite;

compositions

OH Diff (mol)	F (mol %)	Cl (mol %)	OH (mol %)
0.026	67.24	19.40	13.36
0.017	89.77	1.35	8.87
0.047	29.16	46.77	24.07
0.036	72.77	8.58	18.65
0.031	83.29	0.71	16.00
0.089	22.77	31.37	45.86
-0.003	101.77	0.00	-1.77
0.003	0.00	98.51	1.49
0.004	91.51	6.22	2.27
0.000	50.88	49.25	-0.14
0.000	96.64	3.11	0.25
0.004	45.75	52.36	1.88

trations is EMPA analytical error, and another part is apatite
Cl-Ap – synthetic Cl-apatite; D-Ap – natural Durango apatite

Table 5. Average compositions of initial and run-product apatite grains in experiments with three start

Run	n	F (wt%)	1σ	Cl (wt%)	1σ	F (mol)	Cl (mol)	OH Diff (mol)
AA-15	31	2.72	0.16	1.20	0.06	0.143	0.034	0.018
AA-16	31	2.16	0.12	0.96	0.04	0.114	0.027	0.054
AA-17	31	2.53	0.17	1.37	0.14	0.133	0.039	0.023
AA-18	34	2.54	0.13	0.72	0.03	0.134	0.020	0.041
F-Ap	11	3.77	0.29	0.00	0.01	0.198	0.000	-0.003
Cl-Ap	9	0.00	0.00	6.81	0.11	0.000	0.192	0.003
D-Ap	13	3.39	0.15	0.43	0.04	0.178	0.012	0.004
Initial Bulk		2.39		2.41		0.13	0.07	0.00

ting apatite compositions

F (mol %)	Cl (mol %)	OH (mol %)
73.42	17.40	9.18
58.43	13.87	27.70
68.29	19.77	11.93
68.46	10.46	21.08
101.77	0.00	-1.77
0.00	98.51	1.49
91.51	6.22	2.27
64.42	34.91	0.67

Table 6. Mean major-element compositions of glasses from runs AA-9 'dry' and AA-12 'wet'

	SANK 1.3* (wt%)	AA-9** (wt%)	1σ	AA-12** (wt%)	1σ
n		10		10	
SiO_2	77.56	74.25	0.95	74.25	1.33
Al_2O_3	14.25	14.49	0.11	14.47	0.19
CaO	0.00	1.83	0.04	1.93	0.01
Na_2O	3.72	4.00	0.11	3.89	
K_2O	4.47	4.47	0.04	4.65	0.04
$P_2O_{5\ meas}$	0.00	0.74	0.03	0.57	0.02
$P_2O_{5\ adj}$***		1.37		1.44	
F	0.00	0.00		0.00	
Cl	0.00	0.23	0.01	0.23	0.01
Total	100.00	101.38		101.43	
A/CNK****	1.30	0.98		0.97	

*Nominal.
**Normalized to anhydrous.
*** $P_2O_{5\ adj}$ = CaO/1.34. Explanation in text.
**** A/CNK = mol (Al_2O_3/(CaO+Na_2O+K_2O)).

Table 7. Rare earth element concentration in run-product glasses and Durango apatite (mg/g)

Experiment	n	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
AA-10	4	48.03	66.18	3.69	9.63	1.18	0.19	1.18	0.12	0.80	0.19	0.44	0.067	0.48	0.059
1σ		8.32	6.33	0.75	2.36	0.37	0.04	0.29	0.05	0.23	0.06	0.22	0.015	0.12	0.009
AA-13	3	48.61	67.06	4.03	10.76	1.51	0.15	1.32	0.13	0.83	0.21	0.63	0.08	0.58	0.05
1σ		2.11	3.94	0.12	0.77	0.49	0.03	0.06	0.02	0.13	0.07	0.14	0.00	0.10	0.00
Durango	7	3658.45	4772.30	346.93	1107.07	158.08	15.92	151.99	18.05	105.35	20.82	57.75	7.02	38.75	4.75
1σ		184.16	269.08	14.62	55.23	8.21	1.26	9.54	1.26	7.21	1.22	4.15	0.54	2.60	0.26

Table 8. Model parameters

Species	Do (m^2/s)	Ea (kJ/mol)	apatite/melt partition coefficient	D 1200°C (m^2/s)	references
REE	2.60E-07	-324	15	8.44E-19	a,b
Cl-F-OH	1.60E-04	-284	---	1.36E-14	c
Cl	7.00E-05	-294	---	2.63E-15	d

Notes:

a: Values are for La diffusion reported by Cherniak (2000).

b: Partition coefficient for Sm estimated from the variation in apatite/melt partitioning with melt SiO_2 concentration from Watson and Green (1981).

c: Values parallel to c-axis from Brenan (1994).

d: Values for Cl self diffusion reported by Li et al (2020).

Table 9. Compositions (wt %) for cores and rims of the apatite grains from granite sample P7G3

Apatite	Core/Rim	SO_3	P_2O_5	SiO_2	Y_2O_3	La_2O_3	Ce_2O_3	Pr_2O_3
A1	Core	0.01	42.26	0.12	0.35	0.02	0.26	0.00
A2	Core	0.00	42.58	0.01	0.17	0.01	0.06	0.06
A3	Core	0.31	39.89	0.10	0.30	0.02	0.09	0.00
A4	Core	0.01	42.06	0.16	0.28	0.07	0.15	0.00
A5	Core	0.00	41.97	0.10	0.30	0.00	0.15	0.01
A6	Core	0.00	42.18	0.09	0.34	0.02	0.14	0.08
A7	Core	0.00	42.12	0.14	0.33	0.00	0.15	0.06
A8	Core	0.00	41.98	0.15	0.39	0.07	0.17	0.13
A9	Core	0.01	42.65	0.15	0.34	0.00	0.15	0.00
A10	Core	0.01	42.08	0.10	0.36	0.06	0.07	0.02
A12	Core	0.00	42.04	0.14	0.32	0.06	0.11	0.00
A11R	Core	0.13	41.65	0.28	0.29	0.05	0.13	0.02
G1	Core	0.00	42.53	0.02	0.08	0.02	0.04	0.00
C1	Core	0.00	42.05	0.07	0.34	0.01	0.13	0.01
C2	Core	0.00	41.90	0.14	0.27	0.02	0.10	0.09
D1	Core	0.00	42.82	0.10	0.32	0.02	0.11	0.00
Mean	Core	0.03	42.05	0.12	0.30	0.03	0.13	0.03
1σ		0.08	0.65	0.06	0.08	0.03	0.05	0.04
A1	Rim	0.01	42.25	0.06	0.29	0.04	0.18	0.00
A2	Rim	0.00	42.47	0.04	0.09	0.00	0.08	0.00
A3	Rim	0.25	40.03	0.13	0.17	0.00	0.04	0.16
A4	Rim	0.01	42.00	0.11	0.24	0.06	0.06	0.00
A5	Rim	0.00	42.22	0.11	0.27	0.00	0.04	0.07
A6	Rim	0.00	41.99	0.10	0.33	0.06	0.13	0.00
A7	Rim	0.01	42.02	0.14	0.32	0.00	0.12	0.20
A8	Rim	0.00	42.19	0.06	0.23	0.02	0.12	0.03
A9	Rim	0.00	42.43	0.08	0.33	0.00	0.13	0.00
A10	Rim	0.01	41.93	0.15	0.29	0.09	0.13	0.02
A12	Rim	0.02	42.04	0.10	0.24	0.05	0.08	0.00
G1	Rim	0.01	42.38	0.04	0.05	0.01	0.03	0.09
C1	Rim	0.01	42.15	0.03	0.29	0.06	0.11	0.04
C2	Rim	0.00	42.06	0.13	0.30	0.00	0.13	0.02
D1	Rim	0.00	42.34	0.11	0.25	0.04	0.11	0.00
Mean	Rim	0.02	42.01	0.09	0.25	0.03	0.10	0.05

| 1σ | | 0.07 | 0.60 | 0.04 | 0.09 | 0.03 | 0.04 | 0.07 |

* - estimated by charge balance on the halogen site.

Nd$_2$O$_3$	MgO	CaO	MnO	FeO	Na$_2$O	F	Cl	H$_2$O*
0.19	0.10	53.59	0.92	0.63	0.22	3.36	0.14	0.33
0.01	0.06	54.48	0.84	0.45	0.11	3.40	0.12	0.32
0.14	0.04	50.66	0.70	0.53	0.53	2.84	0.11	0.67
0.11	0.04	54.50	0.82	0.42	0.18	3.40	0.11	0.31
0.07	0.04	54.44	0.82	0.46	0.26	3.46	0.08	0.26
0.12	0.05	54.04	0.93	0.42	0.20	3.40	0.13	0.30
0.06	0.06	54.44	0.84	0.43	0.19	3.56	0.10	0.16
0.18	0.06	53.72	0.94	0.67	0.16	3.42	0.15	0.26
0.18	0.05	53.87	0.97	0.38	0.22	3.26	0.09	0.48
0.07	0.03	54.28	0.86	0.43	0.21	3.32	0.09	0.39
0.08	0.05	54.34	0.76	0.55	0.15	3.51	0.10	0.20
0.04	0.04	54.20	0.71	0.81	0.16	3.63	0.06	0.10
0.00	0.01	55.86	0.28	0.05	0.05	3.92	0.02	
0.10	0.05	54.08	0.94	0.43	0.22	3.51	0.13	0.18
0.07	0.05	54.35	0.74	0.52	0.10	3.49	0.07	0.23
0.07	0.01	54.98	0.69	0.26	0.21	3.55	0.09	0.22
0.09	0.05	54.11	0.80	0.46	0.20	3.44	0.10	0.27
0.06	0.02	1.06	0.17	0.17	0.10	0.22	0.03	
0.08	0.07	53.78	0.87	0.48	0.22	3.24	0.12	0.46
0.10	0.05	54.88	0.68	0.42	0.05	3.40	0.11	0.33
0.08	0.04	51.82	0.69	0.63	0.21	3.04	0.12	0.50
0.04	0.04	54.68	0.72	0.48	0.17	3.56	0.11	0.15
0.03	0.05	54.69	0.72	0.44	0.18	3.66	0.06	0.09
0.08	0.04	54.25	0.86	0.45	0.21	3.54	0.09	0.17
0.10	0.06	54.29	0.77	0.55	0.20	3.53	0.07	0.20
0.06	0.08	54.15	0.94	0.61	0.21	3.46	0.15	0.23
0.09	0.06	54.01	0.88	0.42	0.11	3.45	0.10	0.27
0.12	0.08	54.23	0.77	0.51	0.22	3.46	0.08	0.26
0.09	0.05	54.66	0.74	0.55	0.06	3.61	0.09	0.11
0.04	0.00	55.86	0.28	0.04	0.00	3.82	0.02	
0.08	0.05	53.99	0.84	0.46	0.08	3.47	0.10	0.23
0.11	0.04	54.29	0.74	0.61	0.18	3.42	0.06	0.31
0.11	0.05	54.93	0.64	0.26	0.20	3.73	0.06	0.03
0.08	0.05	54.26	0.75	0.48	0.15	3.48	0.09	0.23

0.03   0.02   0.87   0.16   0.14   0.08   0.18   0.03

Sum	F=O	Cl=O	Total
102.49	1.41	0.03	101.04
102.69	1.43	0.03	101.23
96.62	1.20	0.02	95.40
102.63	1.43	0.02	101.17
102.43	1.46	0.02	100.95
102.43	1.43	0.03	100.97
102.64	1.50	0.02	101.12
102.44	1.44	0.03	100.97
102.80	1.37	0.02	101.41
102.37	1.40	0.02	100.95
102.42	1.48	0.02	100.92
102.17	1.53	0.01	100.62
102.88	1.65	0.01	101.23
102.24	1.48	0.03	100.73
102.14	1.47	0.02	100.66
103.44	1.49	0.02	101.92
102.17	1.45	0.02	100.70
102.13	1.36	0.03	100.74
102.71	1.43	0.02	101.25
97.68	1.28	0.03	96.37
102.43	1.50	0.03	100.91
102.64	1.54	0.01	101.09
102.28	1.49	0.02	100.77
102.58	1.49	0.02	101.07
102.54	1.46	0.03	101.05
102.36	1.45	0.02	100.88
102.33	1.46	0.02	100.86
102.47	1.52	0.02	100.93
102.65	1.61	0.00	101.04
102.00	1.46	0.02	100.51
102.40	1.44	0.01	100.95
102.87	1.57	0.01	101.29
102.08	1.46	0.02	100.60

Table 10. Average halogen concentrations (wt %) in all apatite grains in granite P7G3, regardless of apparent origin (magmatic or xenocrystic)

	n	Core	1σ	Rim	1σ
F	16	3.44	0.22	3.53	0.22
Cl	15	0.10	0.03	0.09	0.03
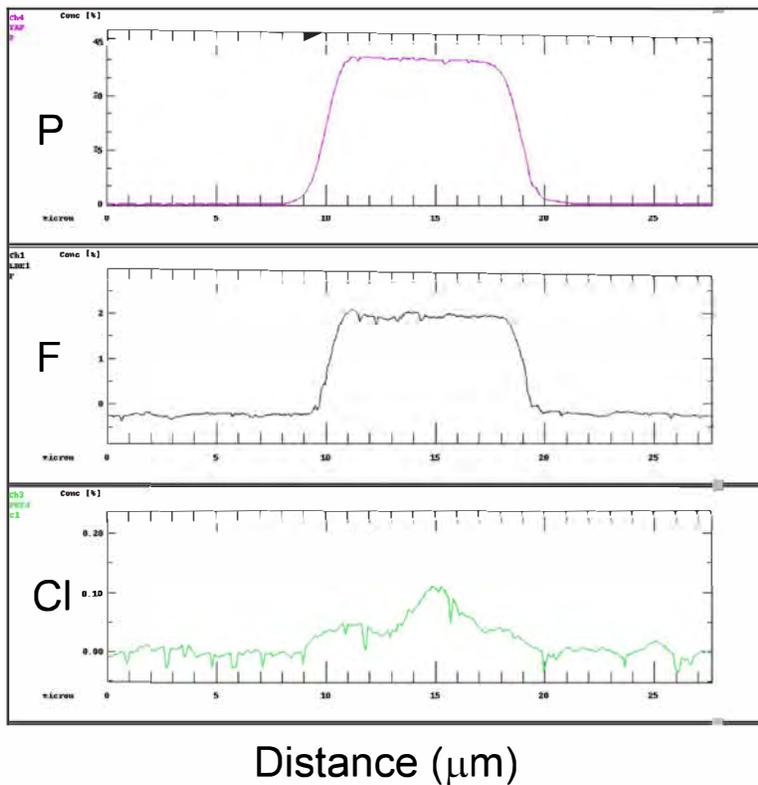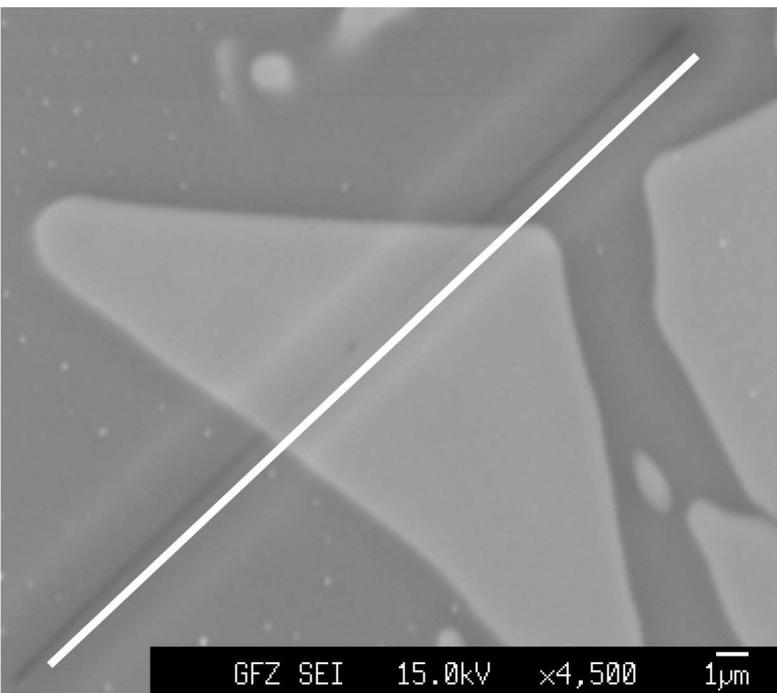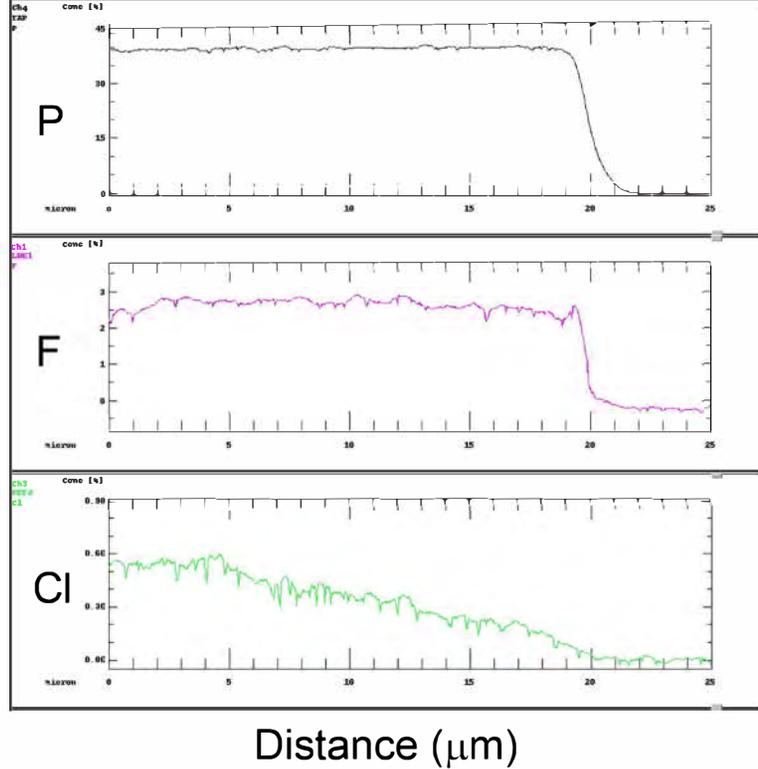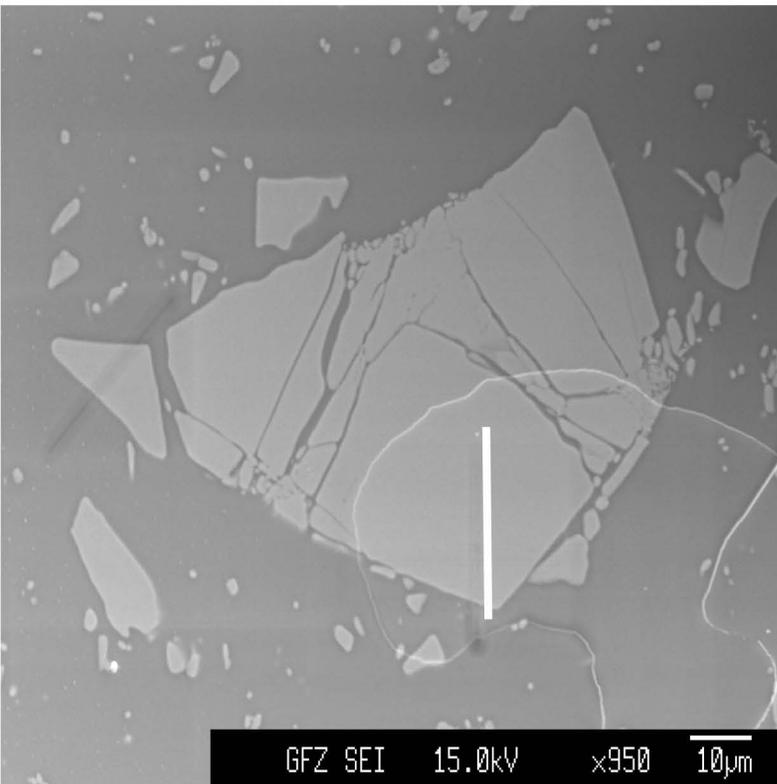
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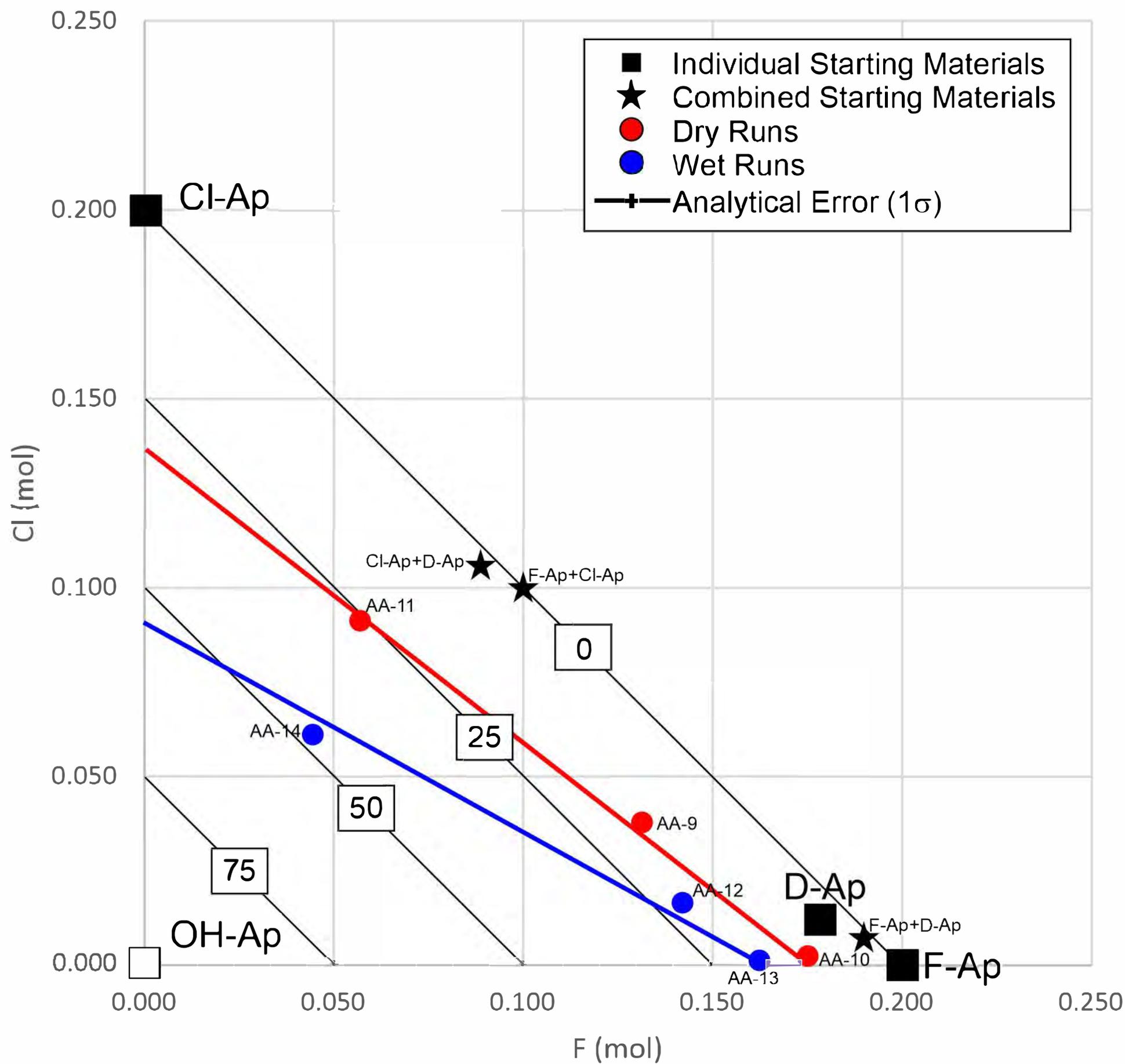
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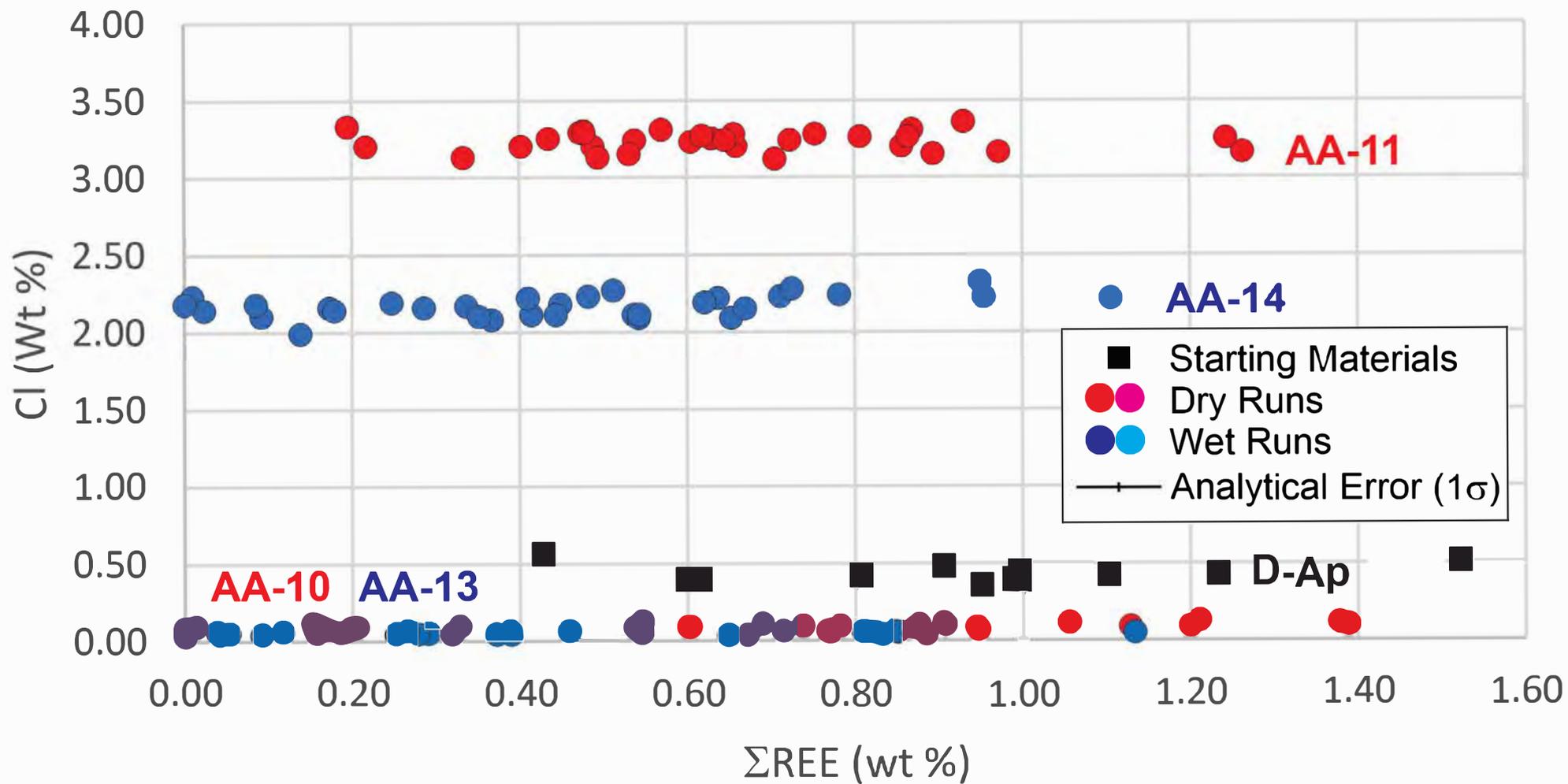
Figure 3

Figure 4

Figure 5

GFZ COMP 15.0kV   ×40 100μm

GFZ COMP 15.0kV   ×40 100μm
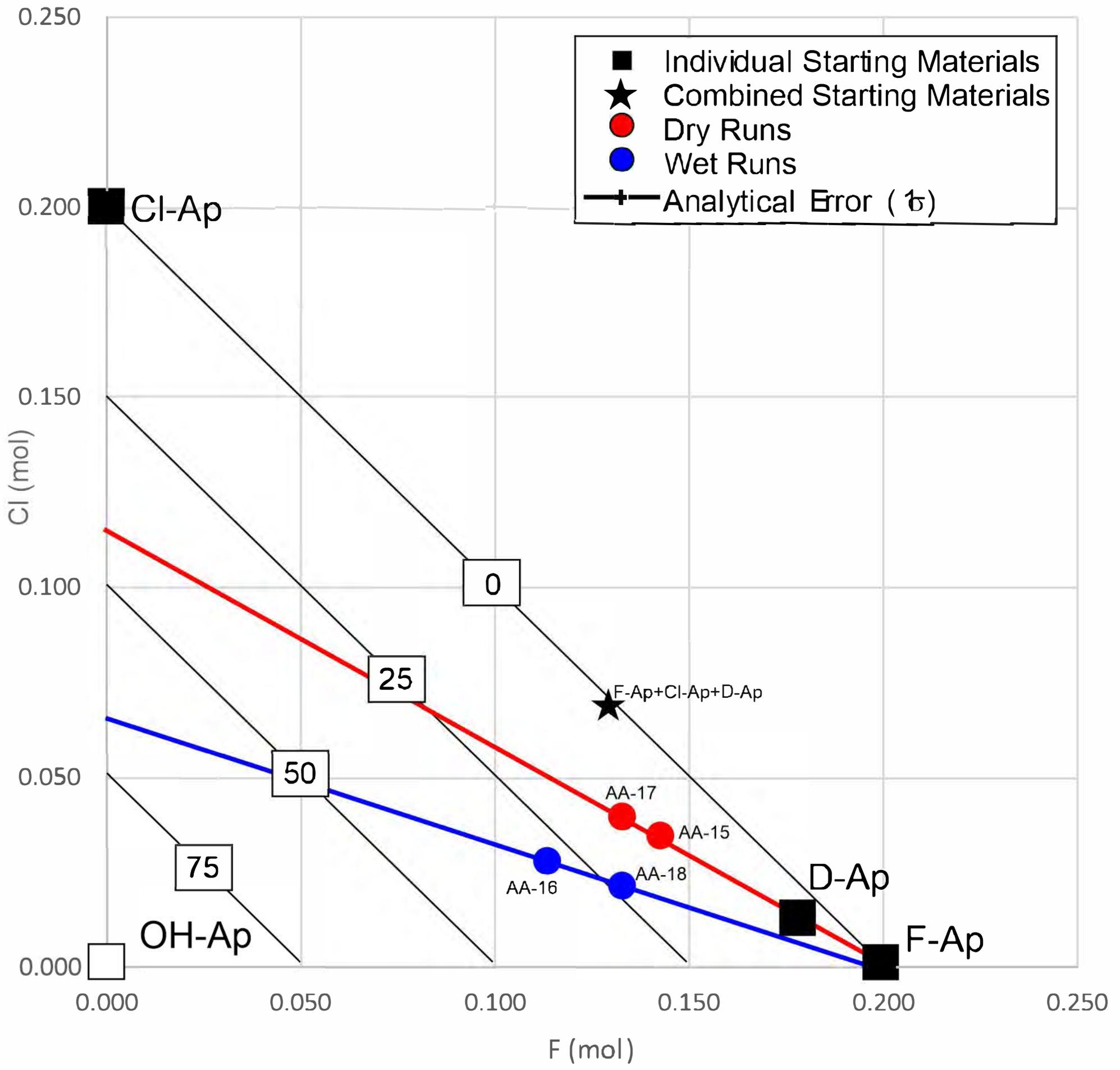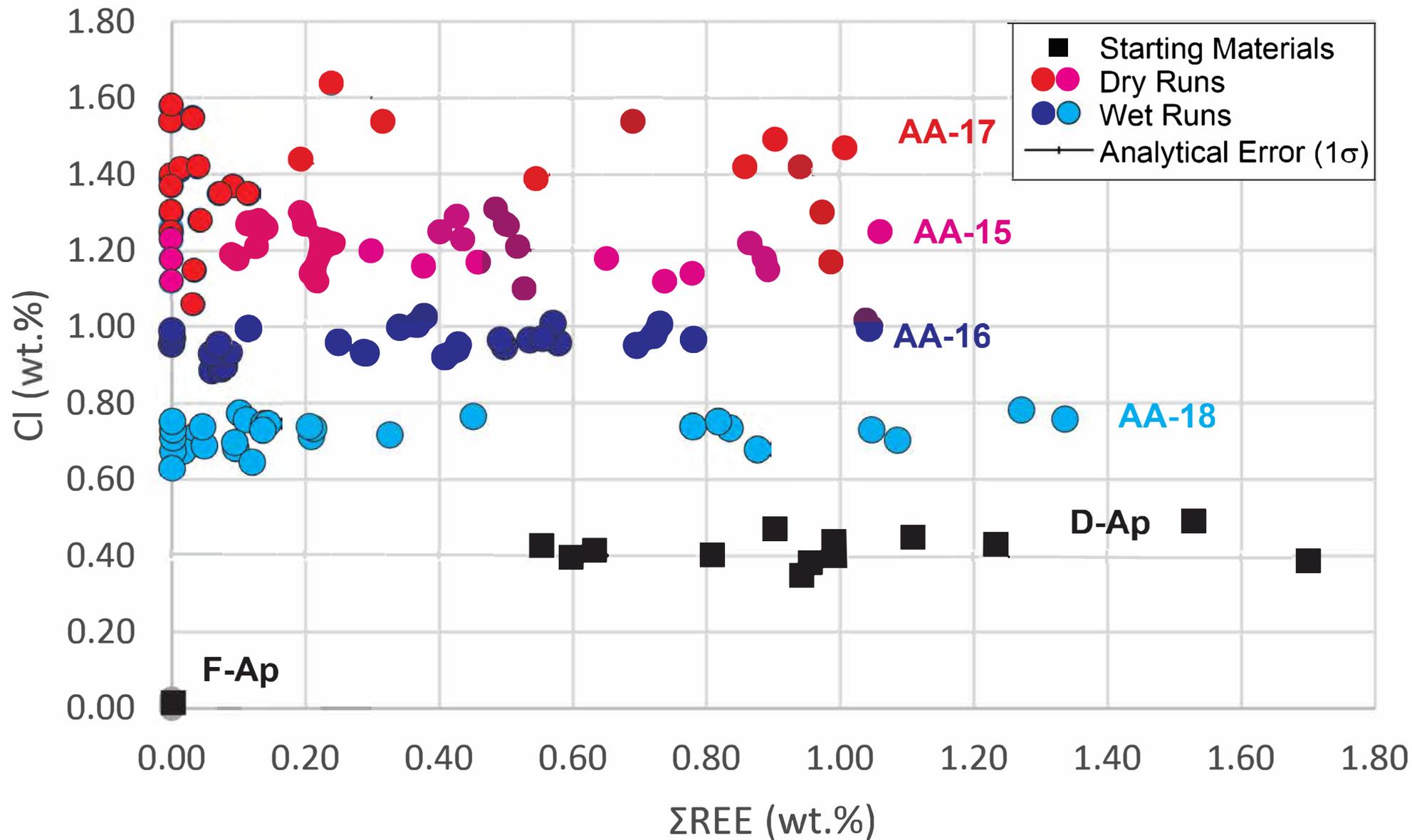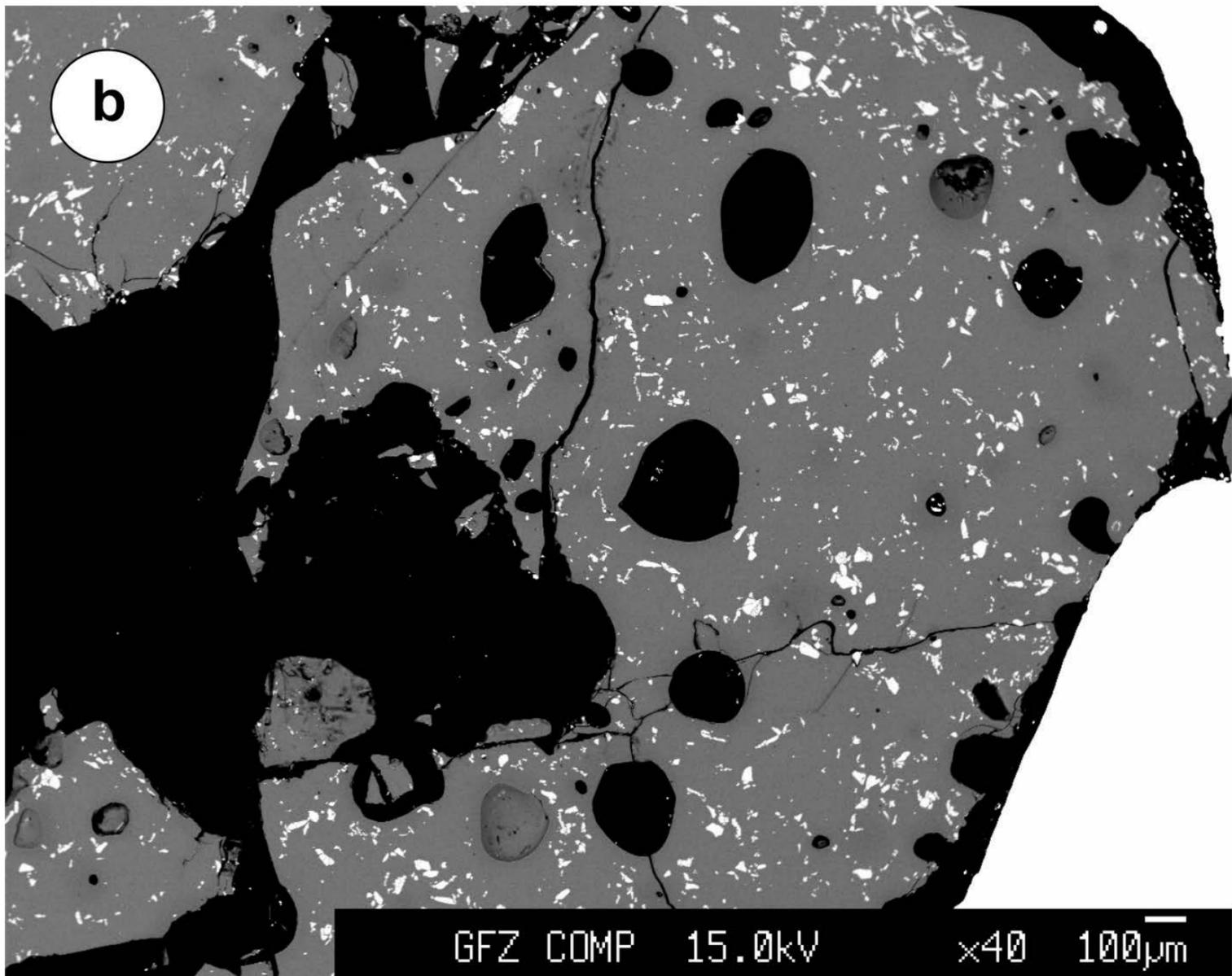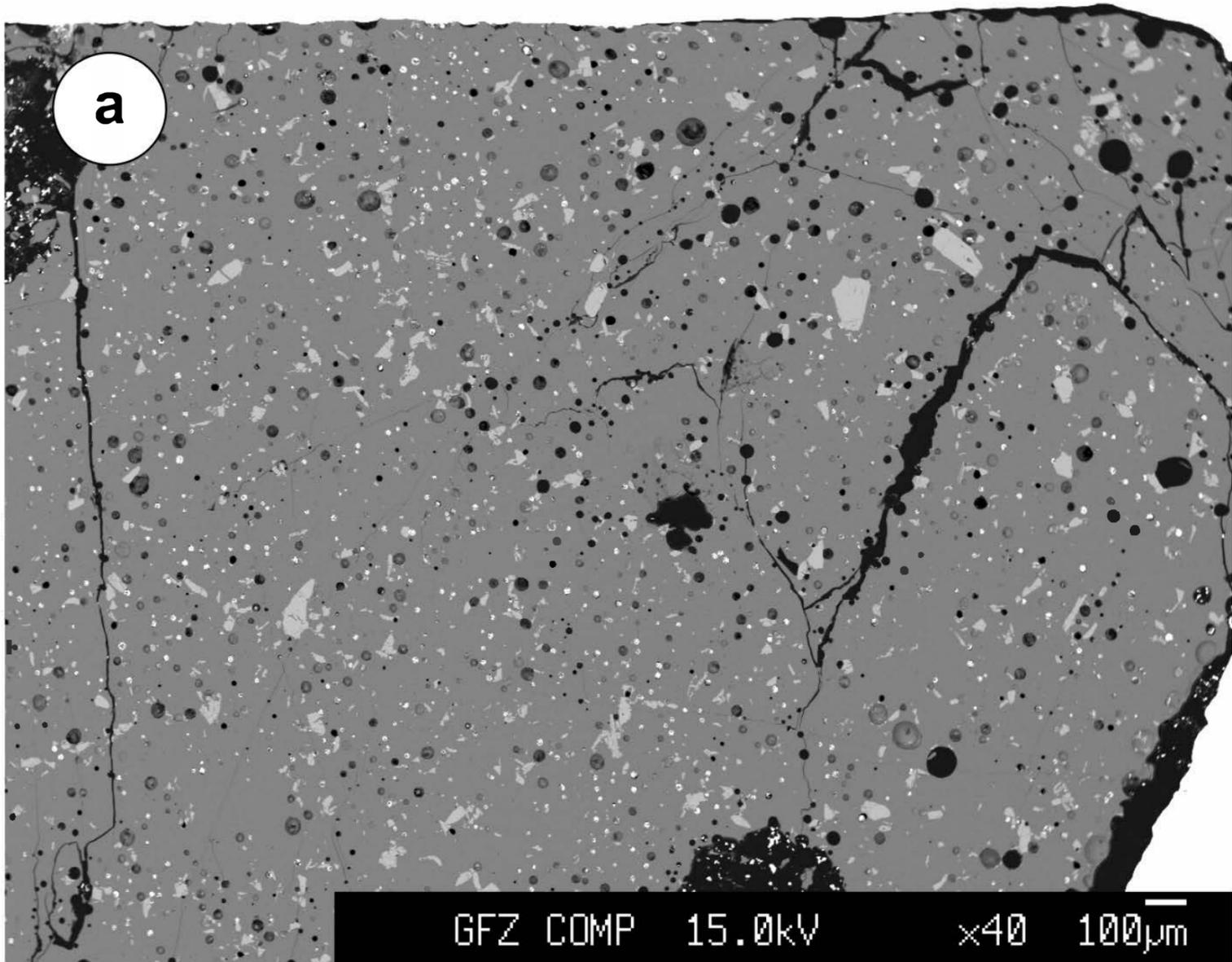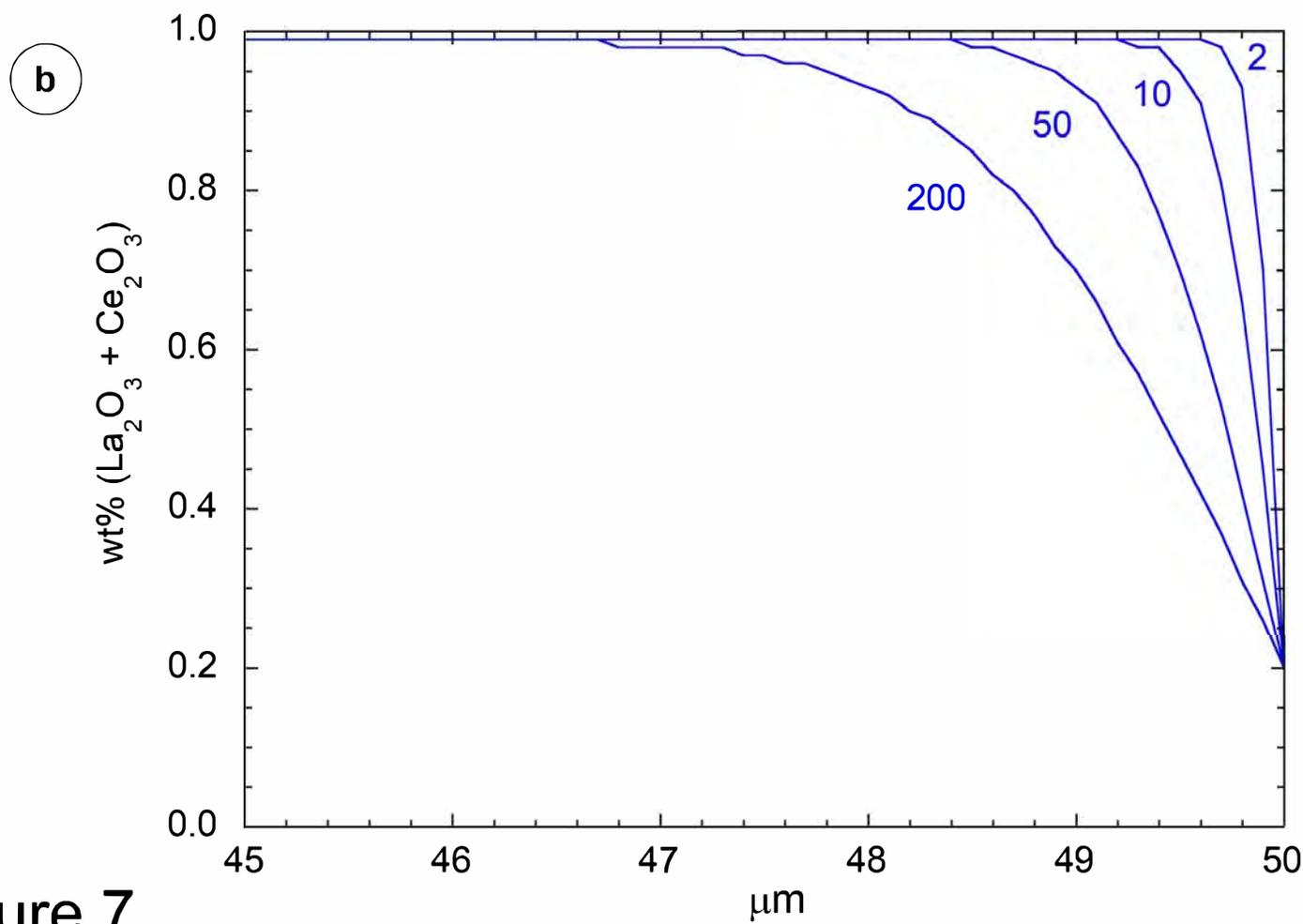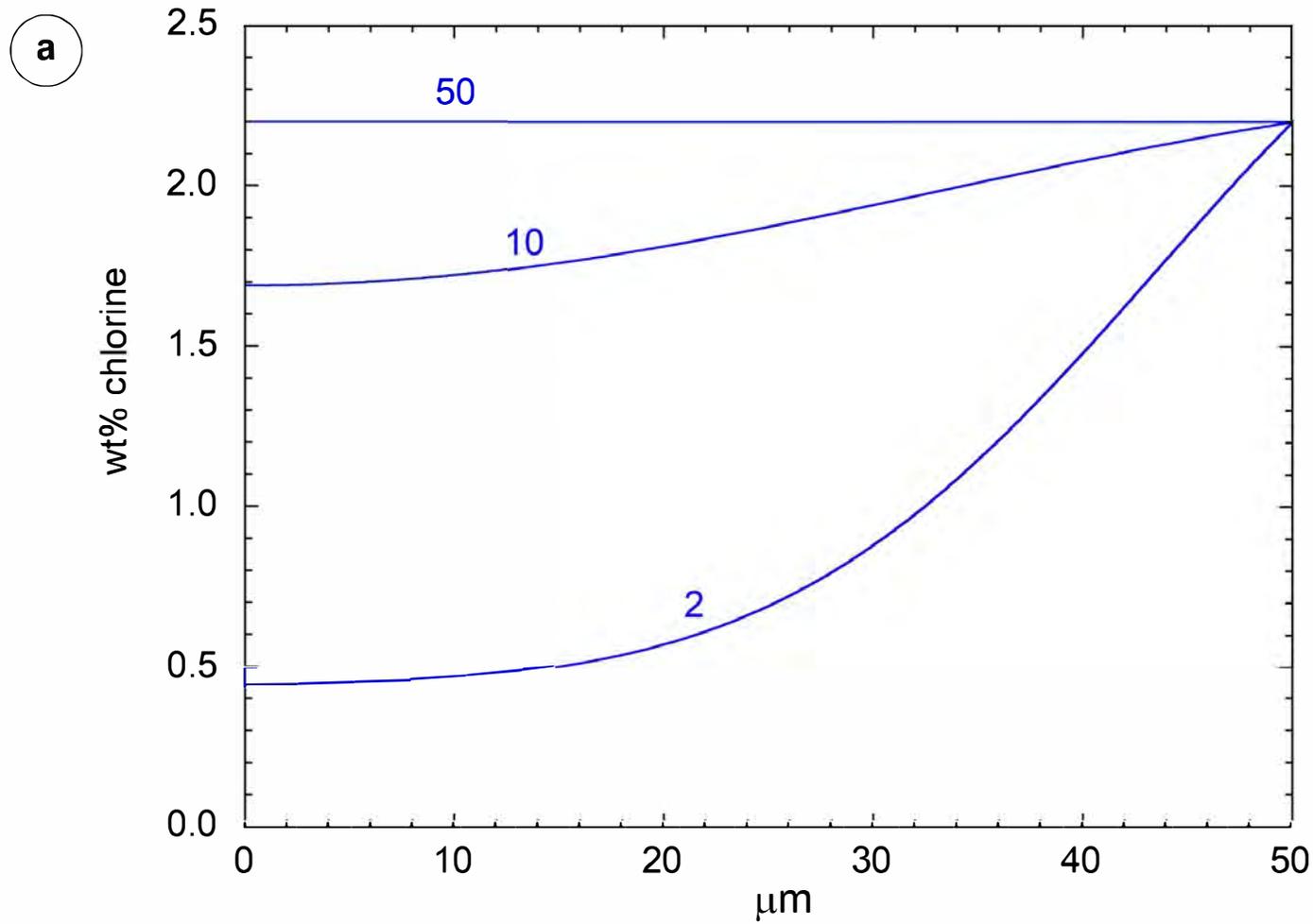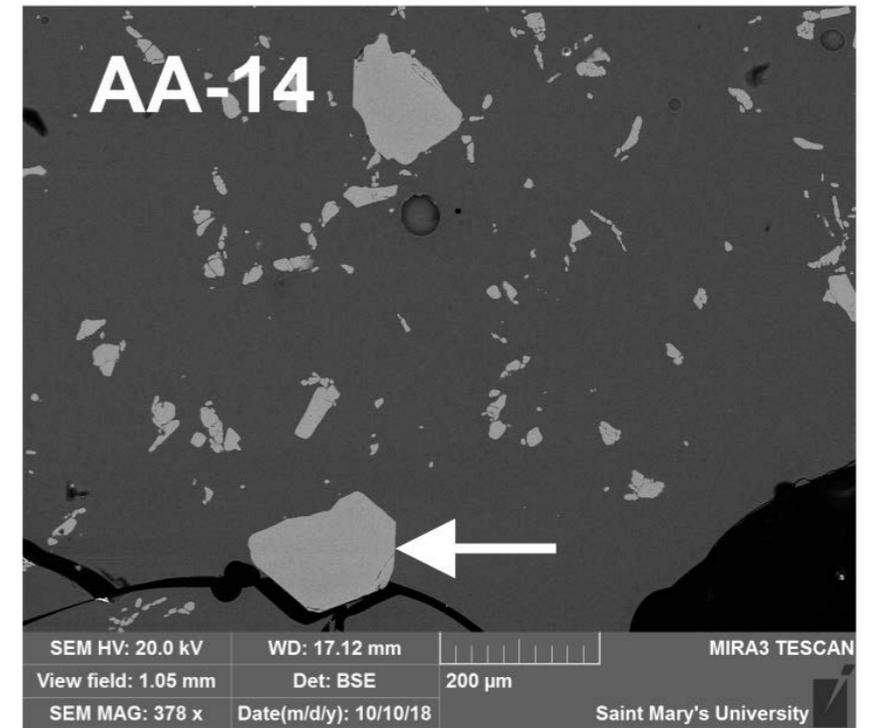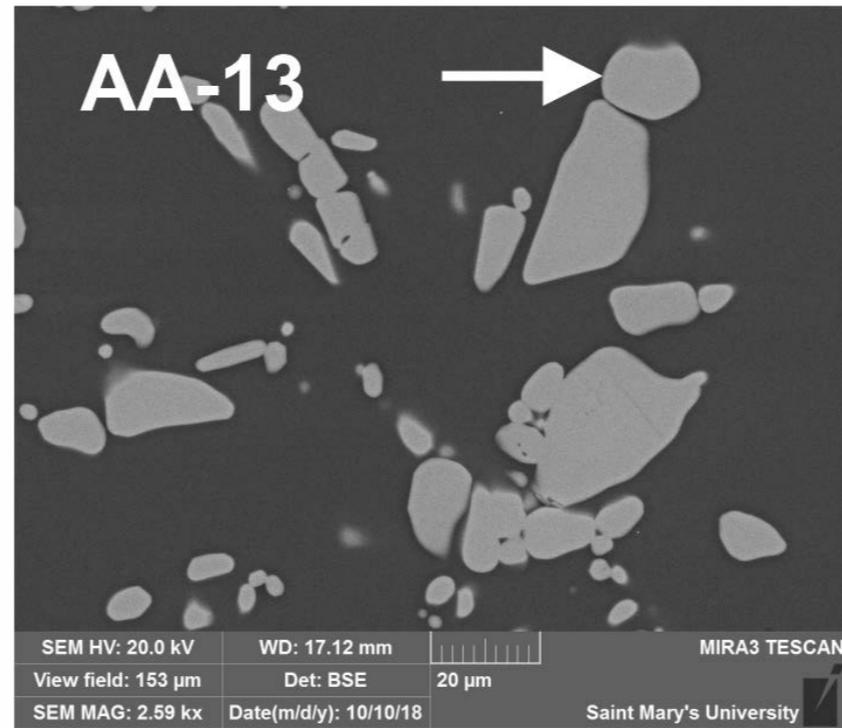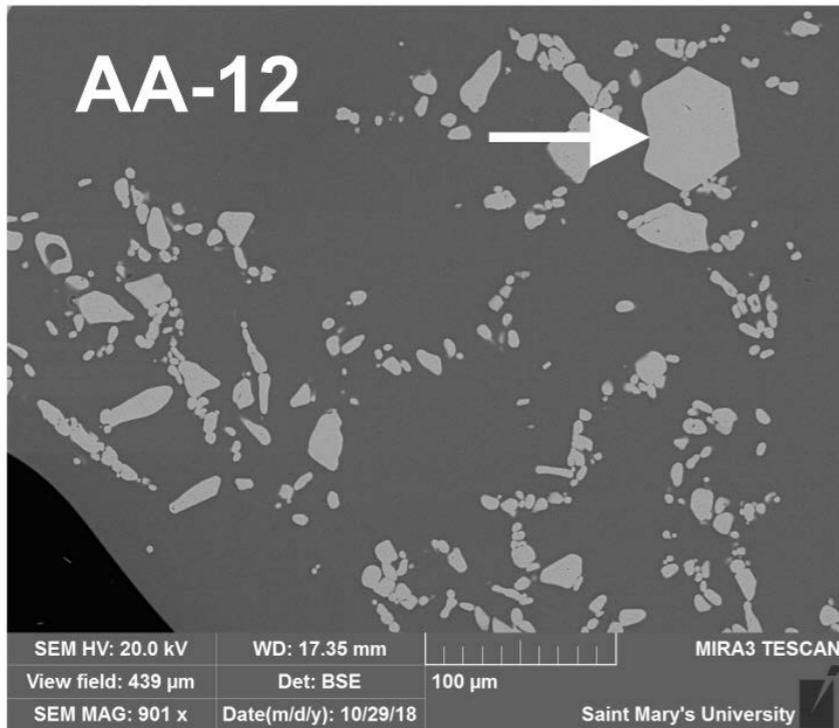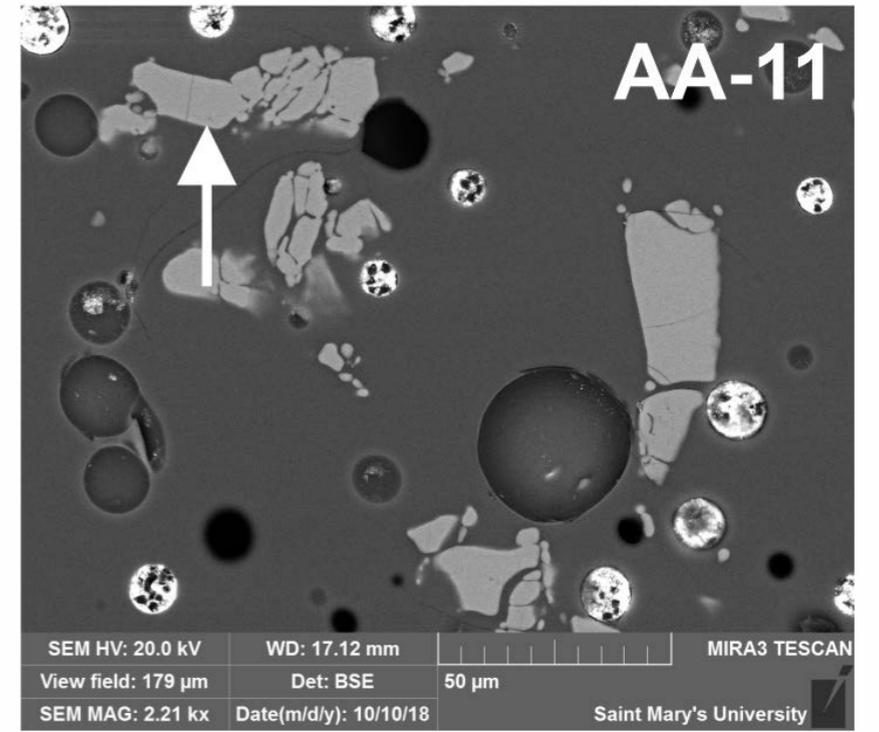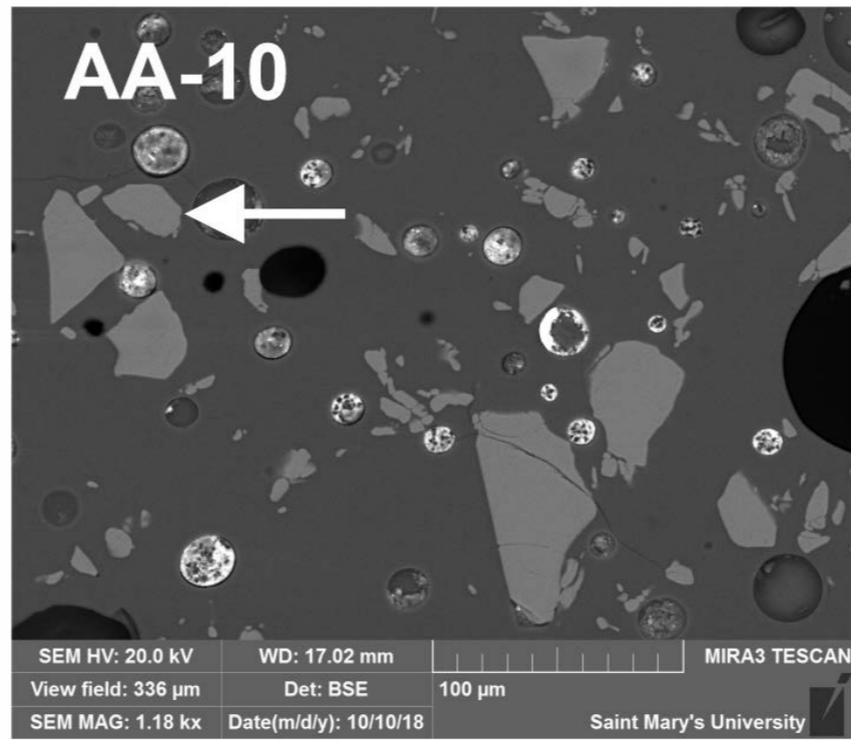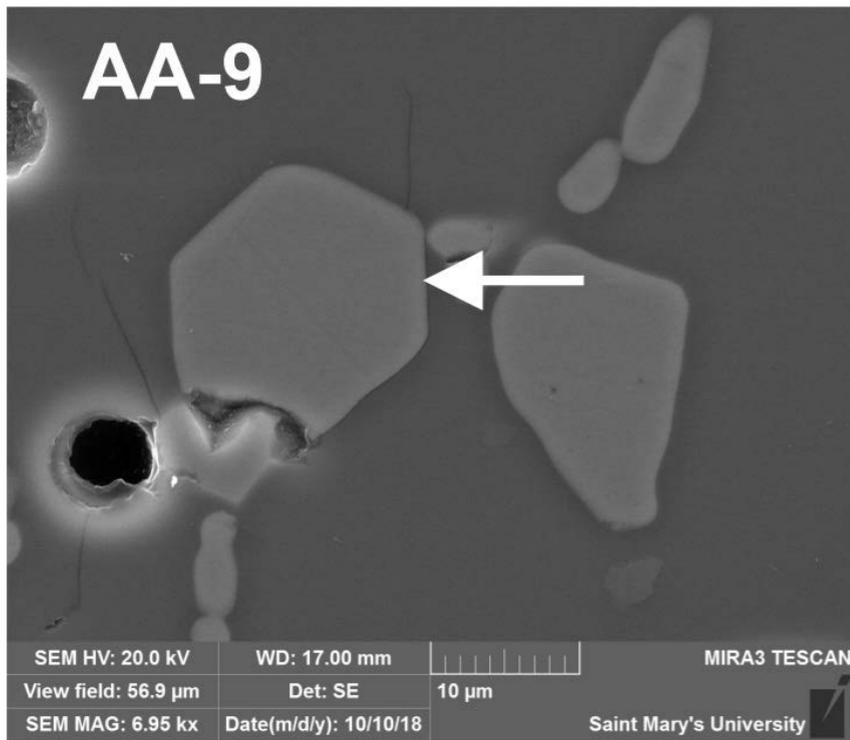
Figure 6.

Figure 7.

Figure 8.
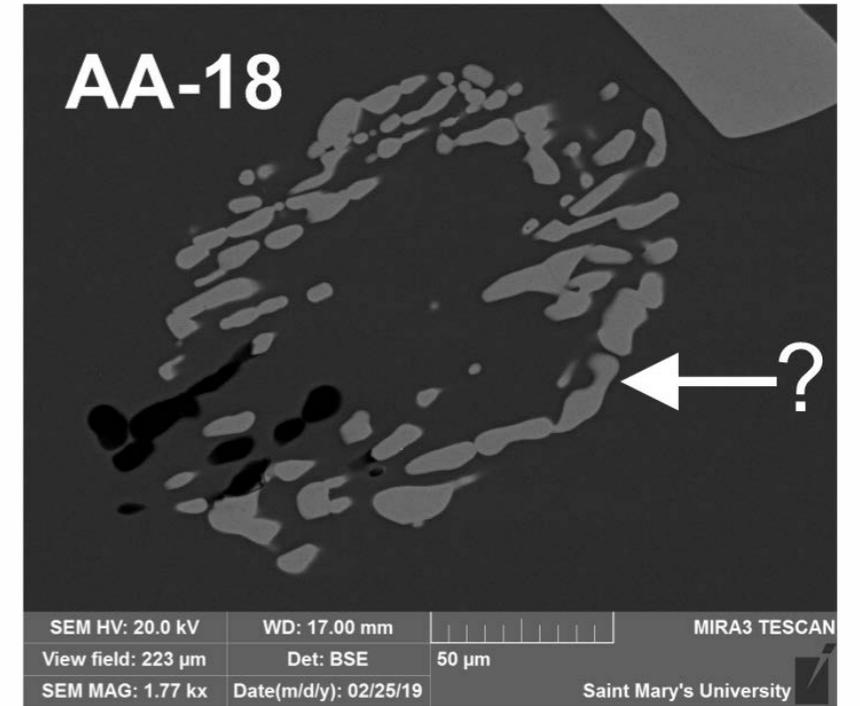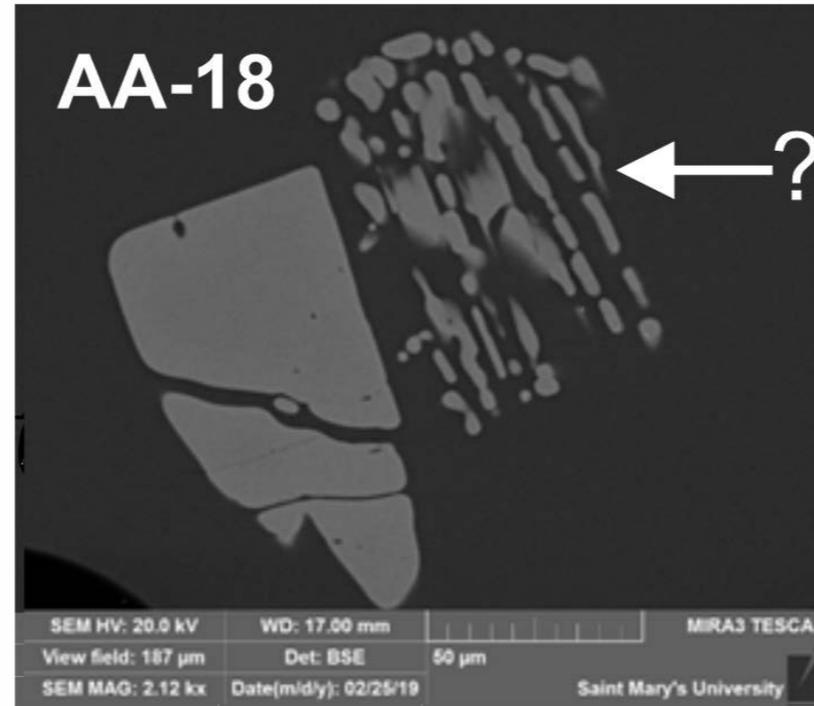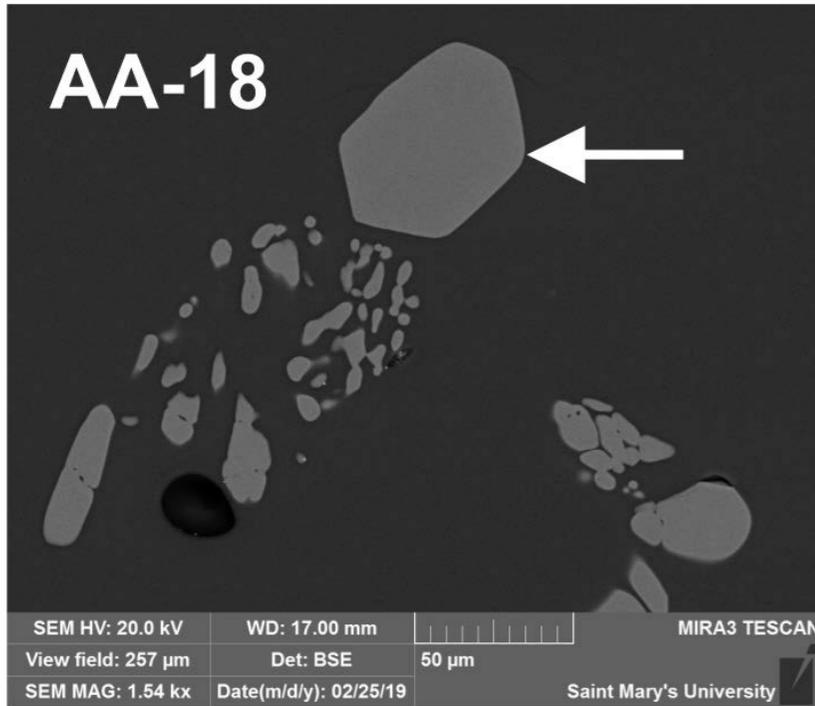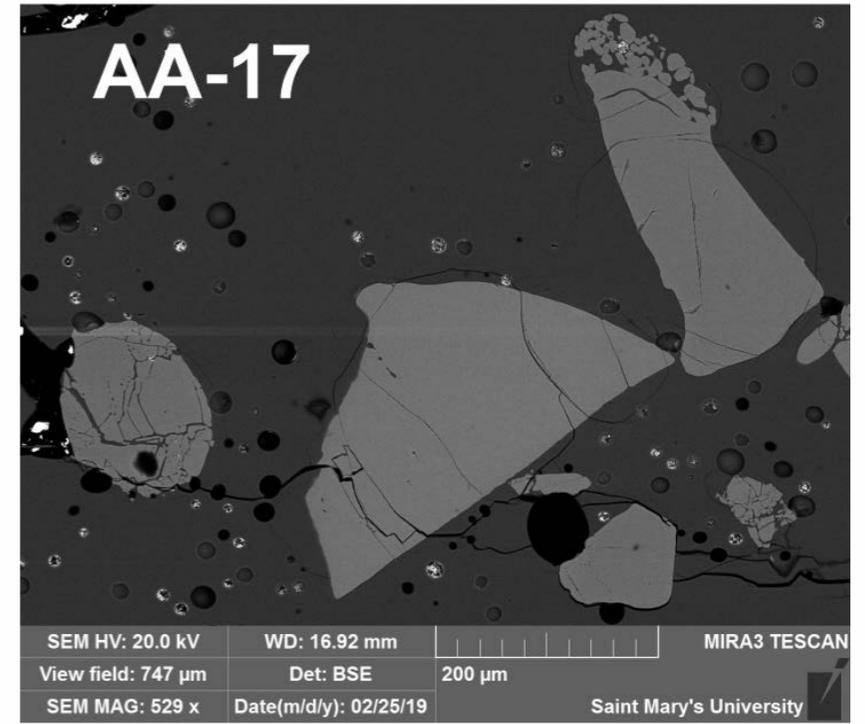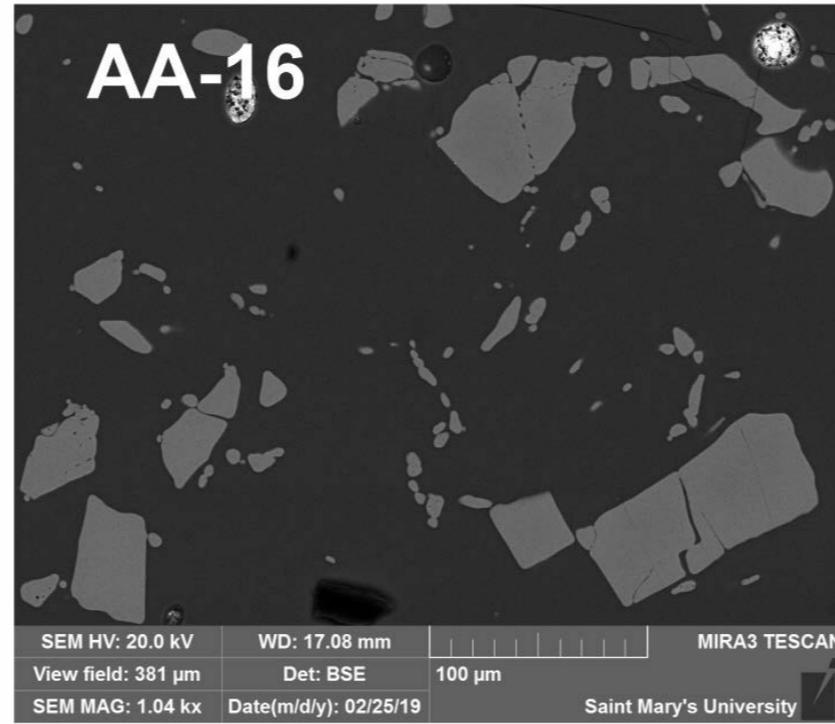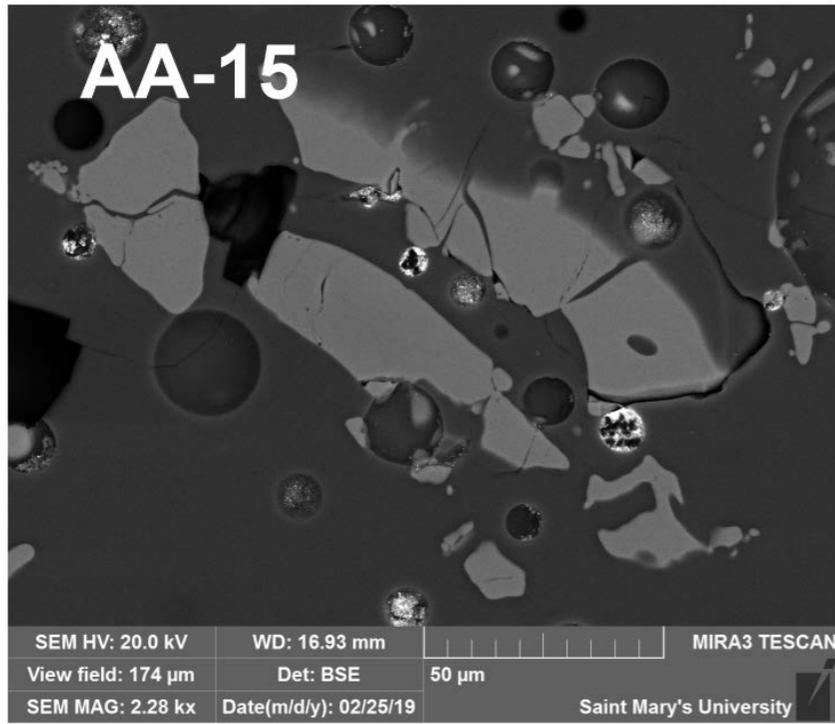
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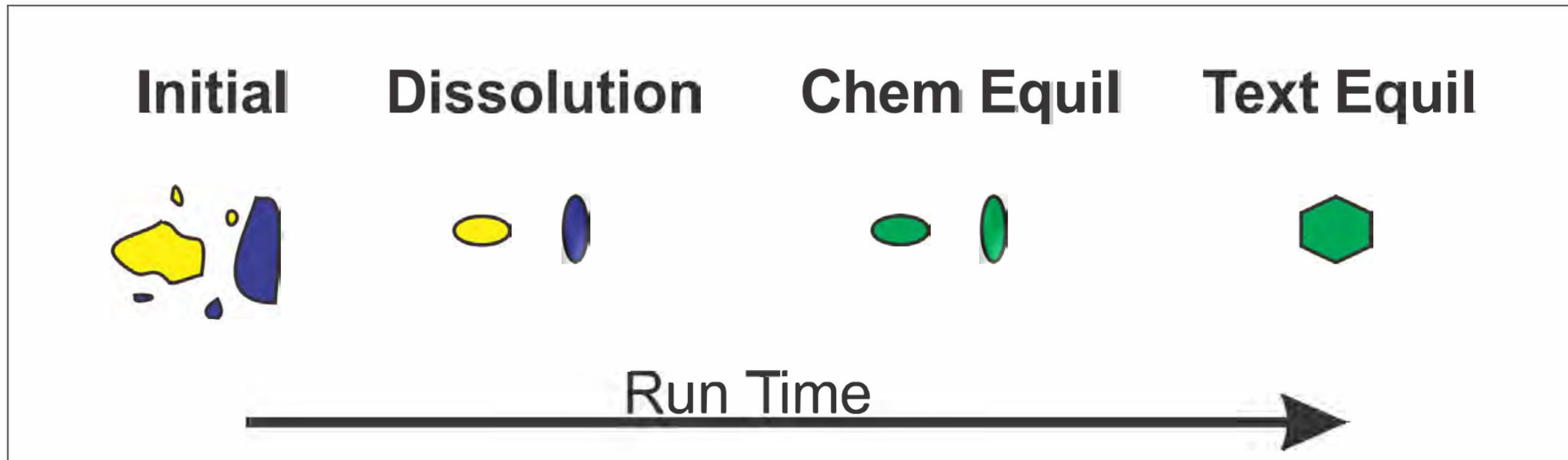
Figure 10.

Figure 11.

Figure 12.