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4 Short-wave infrared (SWIR) spectral and geochemical
5 characteristics of hydrothermal alteration at the Archean Izok
6 Lake Zn-Cu-Pb-Ag volcanogenic massive sulfide deposit,
7 Nunavut, Canada: application in exploration target vectoring
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26 Large, 1977; Seyfried et al., 1988; Gemmell and Large, 1992; Galley, 1993; Goodfellow
27 and Peter, 1994; Ohmoto, 1996). Prior to VMS deposit formation, cold seawater is
28 drawn into the upper parts of the crust, heated and a convective cell of circulating
29 hydrothermal fluids is created. As the fluid temperature increases and pH concomitantly
30 decreases, metals are leached from the host rocks by the hydrothermal fluids. The
31 dissolved metals are transported upward and precipitated at or near the seafloor where
32 the hydrothermal fluids mix with cold seawater. A key geochemical reaction along the
33 fluid flow path is the breakdown of feldspars through interactions with the acidic
34 hydrothermal fluids, and the subsequent formation of white micas and chlorite (Barrett
35 and MacLean, 1994). Herein, white mica refers to dioctahedral phyllosilicate minerals
36 that display a solid solution between paragonite-muscovite and muscovite-phengite
37 (Velde, 1965). Many VMS systems (i.e., the entire footprint of the deposit, including
38 subtle textural, geochemical, mineralogical, and mineral chemical features imparted on
39 the host rocks) have two distinct alteration styles: 1) primarily chlorite-altered, typically
40 centered on the core of the fluid upflow zone, and 2) sericite-altered, typically peripheral
41 to the chlorite-altered zone (Barrett and MacLean, 1994).

42 Although the most intense hydrothermal alteration (forming at high temperatures
43 of 300-400 °C and high water/rock ratios; Barrett and MacLean, 1994) is commonly
44 manifest within the core of the hydrothermal upflow zone, peripheral to mineralization,
45 alteration effects are more subtle (less intense), and their recognition can aid in vectoring
46 toward mineralization in an exploration program. Vectoring methods include the
47 quantification of the enrichment and depletion of particular elements, such as (expressed
48 as oxides) Na₂O, CaO and K₂O (Stephens et al., 1984). Bulk rock sodium depletion is
49 documented in the vicinity of most VMS deposits (Franklin, 1997), and several studies
50 (see Franklin et al., 1975 and references therein) have mapped the spatial variability of
51 this depletion as a proxy for alteration intensity variability throughout a study area.

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Alteration indices, such as the commonly used Ishikawa alteration index (hereafter referred to as AI; Ishikawa et al., 1976) and the chlorite-carbonate-pyrite index (CCPI; Large et al., 2001), offer a more sophisticated method of quantifying alteration intensity by tracking multiple geochemical and mineralogical parameters. The AI measures the depletion (Na₂O and CaO) and enrichment (MgO and K₂O) of alkaline earth and alkali metal oxides associated with the formation of white mica and chlorite. One disadvantage of the use of the AI is that it does not consider carbonate alteration, which can be significant in some VMS deposits (Large et al., 2001). Consequently the chlorite-carbonate-pyrite index (CCPI) is used in the present study to measure the abundance of chlorite through FeO and MgO enrichment and Na₂O and K₂O depletion. Both the AI and the CCPI range between 0 and 100%, such that the maximum value represents complete replacement of feldspar and volcanic glass by white micas, chlorite, or both.

Conventional methods of determining the chemical compositions of rocks and minerals (e.g., whole rock and electron microprobe analysis, respectively) can be time-consuming and costly. A rapid and non-destructive alternative to these methods is optical remote sensing. Many phyllosilicate minerals are infrared-active, and can be identified using their characteristic absorption features in the short-wave infrared (SWIR) wavelength region. More specifically, muscovite has a pronounced Al-OH absorption feature near 2200 nm, and chlorite group minerals have an Fe-OH absorption feature near 2260 nm (Hunt and Salisbury, 1970). The Fe-OH absorption feature is also present in biotite in the same wavelength region (Post and Noble, 1993). Like chlorite, biotite can form either during regional metamorphism or hydrothermal metasomatism (Pirajno, 2009). The wavelength position of these absorption features shifts as a function of compositional changes that take place in response to changing chemical and temperature gradients within a VMS system. High temperatures favor a decrease in the Mg and Fe content and an increase in the Al content of white mica (Duke, 1994).

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78 Moreover, the Fe contents of chlorite and biotite can increase with formation at higher
79 temperatures (Miyashiro and Shido, 1985; Cathelineau, 1988). Additionally, other
80 factors such as pressure, hydrothermal fluid chemistry, water/rock ratios and the
81 composition of the host rocks can all simultaneously influence the chemical composition
82 of the phyllosilicate minerals (Kranidiotis and MacLean, 1987). The compositional
83 changes that take place as a result of these processes are manifested in the wavelength
84 position of the Al-OH absorption feature, which shifts toward shorter wavelengths as the
85 Al content of the octahedral sites of the mineral increase, and the opposite effect, or a
86 shift toward longer wavelengths when the Mg and Fe contents of the octahedral sites
87 increase (Post and Noble, 1993; Duke, 1994). Similarly, the hydroxyl absorption
88 features of biotite and chlorite shift toward shorter wavelengths with increasing Mg, and
89 toward longer wavelengths with increasing Fe (Bassett, 1960; McLeod et al., 1987).

90 In a prior publication (Laakso et al. 2015) we examined the application of large-
91 scale airborne hyperspectral imagery to detect hydrothermal alteration zones in the Izok
92 Lake Zn-Cu-Pb-Ag VMS deposit, Nunavut, Canada, one of the largest undeveloped Zn-
93 Cu deposits in North America (Morrison, 2004). We first documented the links between
94 the position of key spectral features (Fe-OH, Al-OH) of constituent phyllosilicate
95 minerals (biotite, chlorite and white mica) in altered rhyolites and the chemistry of these
96 minerals using petrographic and mineral chemistry data. From the analysis of ground
97 hyperspectral results we then revealed a systematic trend in the Fe-OH absorption
98 feature wavelength position of biotite/chlorite with distance from the VMS deposit. A
99 spatial pattern of relatively long Al-OH absorption feature wavelength positions was
100 also observed in the vicinity of Izok Lake using ground and airborne hyperspectral
101 sensors. This area coincides with relatively long Fe-OH absorption feature positions,
102 detected by means of ground spectra. These findings showed that hydrothermal
103 alteration zones could be detected by hyperspectral remote sensing, despite the presence

104 of abundant lichen cover in the study area.

105 In the present study we have investigated the relationship between bulk rock
106 compositions and the spectral properties of the constituent phyllosilicate minerals in the
107 hydrothermal alteration zones of the Izok Lake deposit, with the aim of developing
108 methodologies that can be used to vector toward concealed mineralization here and
109 elsewhere. The present investigation extends the previous study by Laakso et al. (2015)
110 by linking hydrothermal alteration intensity metrics, extracted from lithogeochemical
111 data, to hyperspectral data obtained from rock outcrops and drill cores of the Izok Lake
112 deposit. These lithogeochemical and spectral data are used to define the fine-scale
113 spatial distribution of the alteration trends in the study area.

114 **2. Study Area**

115 Izok Lake (65°38'N, 112°48'W; Fig. 1) is a Zn-Cu-Pb-Ag VMS deposit located in
116 the Kitikmeot region of Nunavut, Canada. The total resource presently is 14.4 million
117 tonnes grading 2.52% Cu, 12.94% Zn and 71 g/t Ag (MMG Ltd., 2011). The Izok Lake
118 deposit is hosted within the Point Lake Formation, a succession of felsic and mafic
119 metavolcanic rocks that belong to the Yellowknife Supergroup of the Slave Structural
120 Province.

121 The deposit comprises five polymetallic, texturally and mineralogically complex
122 massive to semi-massive lenses of sphalerite, pyrite, chalcopyrite and galena hosted by
123 Archean (2.6 Ga) rhyolitic rocks that are regionally metamorphosed to middle
124 amphibolite facies (Bostock, 1980; Mortensen et al., 1988; Morrison, 2004). The
125 presence of the assemblage anthophyllite-cordierite-spinel-corundum, the
126 porphyroblastic textures and widespread occurrence of sillimanite collectively indicate
127 that the metamorphic conditions may have reached peak temperatures of 700 °C and
128 pressures of between 0.2 and 0.3 GPa in the vicinity of mineralization (Morrison, 2004).

129 The rocks of the study area have undergone three phases of deformation
130 (Morrison, 2004). The first phase is evidenced as a pervasive, planar fabric parallel to
131 bedding. The second phase is expressed as crenulation cleavage and lineation in the
132 northern parts of the study area. The massive sulfide lenses are located in the middle of
133 an antiform that may (in part) be a primary volcanic domal structure and (in part) a
134 structure induced by the third phase of deformation (Morrison, 2004).

135 Immediately adjacent to a set of southwest trending faults the rocks have been
136 hydrothermally altered in an asymmetric fashion (Fig. 1). The known mineralization is
137 located underneath Izok Lake in five massive sulfide lenses (North, Northwest, Central -
138 West, Central - East and Inukshuk) shown in Figure 2. The hanging wall and footwall
139 host felsic volcanic rocks are visually and geochemically very similar to each other and
140 are in places intensely altered (Morrison, 2004). The timing of hydrothermal alteration
141 is syn-volcanic and syn-mineralization (Morrison, 2004), and, therefore, our spectral
142 measurements and geochemical data are focused exclusively on the hydrothermally
143 altered rhyolitic rocks. This hydrothermal alteration is manifest by an inner core of
144 chlorite-rich rocks that is surrounded by a broad zone of sericite-rich rocks (Morrison,
145 2004). The inner alteration zone is characterized by Mg-enriched rocks comprised
146 mainly of chlorite, biotite and cordierite (Money and Heslop, 1976). The immediate
147 hangingwall rocks (predominantly rhyolite; andesite in some places) are sodium-
148 depleted and contain widespread muscovite, biotite and sillimanite (Morrison, 2004).
149 Nowak (2012) interpreted muscovite and biotite to be the peak metamorphic products of
150 the precursor syn-volcanic hydrothermal alteration minerals white mica and chlorite,
151 respectively. The lack of exhalative sediments lateral to the deposit, the primary
152 presence of stringer mineralization lateral to the massive sulfide lenses, and the presence
153 of intense alteration in the hanging wall to the deposit were among the factors that led
154 Morrison (2004) to suggest that the deposit formed through sub-seafloor mineralization

155 processes.

156 The syn-volcanic and syn-mineralization hydrothermal alteration is overprinted
157 by younger calcic metasomatism, which is evidenced by a wide range of CaO contents
158 in the rhyolitic rocks spanning from trace amounts to over 11 wt% (Morrison, 2004).
159 Nowak (2012) attributed the variation in the CaO content of the rhyolitic rocks of the
160 study area to variable dissolution of feldspar during hydrothermal alteration. However,
161 the timing and significance of this calcic metasomatism are currently not well
162 understood.

163 **3. Sampling and Methods**

164 *3.1 Outcrop spectra site selection and measurement*

165 The surface expression of the hydrothermally altered rocks was delineated by
166 collecting 455 spectral measurements and 60 samples (Fig. 1) from rhyolite outcrops
167 during summer 2010 and 2013. The area of most intense alteration extends
168 approximately 4.7 km west from the known mineralization (Fig. 1), and hence the
169 outcrop spectral measurements collected farther away from the mineralization are likely
170 from rocks that are the least altered or weakly altered in the study area. Nevertheless, all
171 the spectral measurements are included in the data analysis to obtain a complete
172 understanding of the spectral features and trends throughout the study area. The
173 rationale for site selection (and further description of data acquisition to that given
174 below) is provided in Laakso et al. (2015).

175 All measurements were obtained using a PANalytical (formerly ASD, Inc.,
176 Boulder, CO) FieldSpec Pro[®] (abbreviated hereafter as "ASD") 3 spectrometer that
177 records spectra in the 350-2500 nm wavelength range with a spectral resolution of 10
178 nm and a sampling interval of 1 nm in the short-wave infrared (SWIR; 1300-3000 nm)
179 wavelength region. The spectrometer was connected to a contact probe that has an

180 internal illumination source that ensures consistent illumination conditions during data
181 acquisition. The raw at-sensor radiance values were converted to surface reflectance
182 values by means of a SpectralonTM reflectance panel (i.e. the "white reference", SRT-99-
183 100, Labsphere, Inc., North Sutton, NH, USA), a commercially available plate made of
184 polytetrafluoroethylene (Bruegge et al., 1993). Finally, these relative reflectance values
185 were converted to absolute reflectance values by multiplying the relative reflectance
186 value of each wavelength with the reflectance factor obtained from the calibration
187 certificate of the SpectralonTM panel, in accordance with the procedure of Clark et al.
188 (2002).

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190 *3.2 Drill core sampling and laboratory spectral measurements*

191 In order to establish the character and extent of the hydrothermal alteration zones
192 of the Izok Lake deposit in the subsurface, spectroscopic data were obtained from 28
193 drill cores (Figs. 1-2). These measurements were made with PANalytical TerraSpec[®] 4
194 Hi-Res and ASD spectrometers at an average down-hole spacing of 5.5 m, resulting in
195 781 spectral readings from all lithologies intersected in the drillholes. As with the
196 outcrop spectral measurements, the drill core spectra were acquired using a contact
197 probe. The TerraSpec4 spectrometer acquires data with a spectral resolution of 6 nm and
198 sampling interval of 1 nm in the SWIR wavelength region. Each spectrum acquired from
199 the drill cores consists of 60 individual measurements taken consecutively and averaged
200 by the instrument. Conversion of radiance to reflectance was as described for outcrop
201 spectral measurements and only the drill core spectra that were acquired from the
202 rhyolite samples were analyzed.

203 In addition to acquiring spectral measurements, a visual estimate of the
204 hydrothermal alteration intensity at each spectral measurement area was recorded for a
205 subset of eight drill cores (HEN-172, HEN173, HEN-197, HEN-198, HEN-212, HEN-

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206 273, HEN-309 and HEN-340) that collectively comprise a cross-section through a
207 Central - West massive sulfide lens. For this subset, each spectral measurement has an
208 associated alteration intensity that ranges from weak, to moderate, to intense, based on
209 the textural and mineralogical properties of the rock. These were then assigned visually
210 estimated alteration intensity (VEAI) values, with 1 indicating weak alteration, 2
211 representing moderate alteration, and 3 representing intense alteration. The examined
212 drill core profiles do not show visible signs of weathering that could potentially affect
213 the interpretations of the spectral measurements.

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215 *3.3 Laboratory spectral and spatial analysis*

216 Of the 781 spectra acquired from the drill cores, 624 are from rhyolitic rocks and
217 these were investigated to delineate the vertical extent of hydrothermal alteration and
218 document any zonation present. In the case of the outcrop spectrometry, 50 of the 455
219 spectral measurements were discarded because of low signal-to-noise ratios. The
220 remaining 405 spectra and the 624 drill core spectra were hull-corrected (continuum-
221 removed) to minimize the effects of background absorption (Clark, 1999), and the hull
222 quotient minima of the Al-OH and Fe-OH absorption features were estimated manually.
223 Visualization of the spatial trends of the outcrop spectroscopic Al-OH and Fe-OH
224 absorption feature wavelength positions was done by interpolation by Kriging (Oliver
225 and Webster, 1990) using the nearest 10 values to calculate the contents of each pixel in
226 the continuous surface. The results were spatially restricted to the outcrop limits of the
227 rhyolitic rocks in the study area.

228 In a separate analysis, the Euclidean distance between the Al-OH and Fe-OH
229 absorption feature observations of the drill cores and their spatially nearest massive
230 sulfide lenses was calculated to investigate possible changes in the spectral properties of

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231 the white micas and biotite/chlorite with distance to the mineralization. The locations
232 and spatial dimensions of the massive sulfide lenses were extracted from the drill core
233 logs of MMG Ltd. In the case of outcrop spectra, the distance between the measurement
234 locations and the nearest subcropping or subsurface massive sulfide lens (see Figure 1)
235 was calculated. Finally, all measured distances were combined to construct a three-
236 dimensional model of the spatial variation of the Al-OH and Fe-OH absorption feature
237 wavelength positions.

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239 *3.4 Bulk geochemical analytical techniques*

240 A database of whole rock major element oxide analyses of 2902 rock samples
241 collected from outcrops at an average sample spacing of 43 m was provided by MMG
242 Ltd. These samples are from outcrops of intensely altered rocks proximal to
243 mineralization and outcrops of less altered rocks distal to mineralization. This database
244 was supplemented by a similar bulk compositional database of 151 drill core samples
245 (NQ core, 4.5 cm diameter, each 15 to 20 cm long) collected at 28 m intervals down-
246 hole. The drill core samples are mainly from intensely altered rocks proximal to
247 mineralization. The locations of the surface samples and drill cores are shown in Figure
248 1.

249 For the whole rock major element oxide analyses, the samples were crushed, split
250 and powdered using a hardened steel mill. Powdered samples (0.2 g) were added to a
251 lithium metaborate and lithium tetraborate flux (0.9 g), mixed and fused in a furnace at
252 1000 °C. The samples were then cooled and dissolved in 100 mL of 4% nitric acid/2%
253 hydrochloric acid. This solution was analyzed by Inductively Coupled Plasma-Atomic
254 Emission Spectroscopy (ICP-AES). The results were corrected for spectral inter-element
255 interferences. Oxide abundances were calculated from the determined elemental

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256 contents with 0.01% and 100% lower and upper limits, respectively.

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258 *3.5 Lithogeochemical data treatment (AI, CCPI, & VEAI analyses)*

259 The outcrop lithogeochemical data were used to identify large-scale variations in
260 the intensity and style of hydrothermal alteration across the study area. First, the outcrop
261 samples were restricted to rhyolite (shown in Figure 1) and the Nb, Y, Zr and TiO₂
262 values of the remaining 555 lithogeochemical analyses were used to classify the
263 volcanic rocks in the study area. This was conducted by means of the Winchester-Floyd
264 diagram (Winchester and Floyd, 1977) that is used to differentiate rock types based on
265 their characteristic proportions of the minor and trace elements that are relatively
266 immobile during the alteration of the volcanic rocks. This analysis was only conducted
267 using the outcrop lithogeochemical data because the drill core lithogeochemical database
268 lacks the requisite immobile element data.

269 The alteration intensity variation throughout the study area was further assessed
270 by calculating the Ishikawa index (AI, Ishikawa et al., 1976):

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$$AI = 100(K_2O + MgO)/(K_2O + MgO + Na_2O + CaO).$$

272 The AI values were spatially linked to corresponding outcrop spectral
273 measurements of the rhyolitic rocks to investigate the relationship between the Al-OH
274 and Fe-OH wavelength positions and intensity of hydrothermal alteration. This was
275 achieved by horizontally linking each Al-OH and Fe-OH absorption feature in the
276 outcrop spectra with the AI value calculated from its geographically nearest
277 lithogeochemical analysis. The AI was used as a measure of alteration intensity due to
278 the predominantly white mica-rich nature of the rhyolitic rocks surrounding the massive
279 sulfide lenses. The alteration intensity variation throughout the study area was further

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280 investigated by calculating the chlorite-carbonate-pyrite index (CCPI) using the
281 following equation (Large et al., 2001):
282 $CCPI = 100(\text{FeO} + \text{MgO}) / (\text{FeO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O})$.

283 The CCPI is a measure of chlorite replacement of white micas and feldspar
284 group minerals. The AI and CCPI values of the study area were then plotted into an
285 alteration box plot (Large et al., 2001) to assist in distinguishing different alteration
286 trends in the study area.

287 In order to explore the relationships between the Al-OH and Fe-OH absorption
288 features and alteration intensity in a vertical (depth) sense, 122 drill core whole rock
289 analyses of the rhyolitic rocks were correlated with their nearest Al-OH and Fe-OH
290 absorption features in the drill core spectra. The alteration intensity was estimated by
291 means of the AI and the CCPI. The AI and CCPI alteration index values ($n=122$) were
292 then combined with their spatially nearest VEGAI values ($n=172$). Only VEGAI values for
293 the rhyolitic rock units were included in this analysis. No VEGAI value was assigned to
294 an AI or CCPI value for down-hole distances between the AI, CCPI and the VEGAI
295 values of greater than five meters.

296 The AI and CCPI values were then compared with the Al-OH and Fe-OH
297 absorption features for the drill core rhyolitic rocks with the objective of associating the
298 wavelength position shifts with the vertical hydrothermal alteration intensity variation.
299 Due to the different sampling intervals of the analytical and spectral results, the latter
300 were linearly interpolated to the nearest whole rock geochemical analysis. The Al-OH
301 and Fe-OH absorption feature wavelength positions situated immediately down-hole and
302 up-hole from the geochemical analysis were used to calculate the interpolated Al-OH
303 and Fe-OH absorption feature wavelengths. If interpolation was not possible due to a
304 missing value either below or above a particular geochemical analysis, no extrapolation

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305 was performed, and the analysis was not assigned a corresponding Al-OH and Fe-OH
306 absorption feature wavelength value. This resulted in 112 Al-OH values and 97 Fe-OH
307 values that were spatially combined with their nearest rock geochemical analysis.
308 Correlations were not assigned for drill cores HEN-258, HEN-418 and HEN-444 due to
309 a lack of geochemical data.

310 Finally, the Kriging interpolation technique (Oliver and Webster, 1990) was used
311 to map and visualize the spatial distribution of the alteration intensity values throughout
312 the study area. The nearest 10 alteration intensity values, estimated by means of the AI,
313 were used to calculate the content of each pixel in the interpolation surface. In this
314 analysis, all the outcrop lithogeochemical samples that lie within the surface spatial
315 limits of the rhyolitic rocks were used ($n=1136$) in order to estimate the alteration
316 intensity variation throughout the study area using a maximum number of observations.
317 For the same reason, the vertical alteration index values of the drill core database were
318 combined with the horizontal alteration index values extracted from the surface samples.
319 This analysis was constrained to the vertical alteration index values from a maximum
320 depth of 10 m so that the vertical AI values are comparable with the horizontal AI
321 values. Here, the AI was used to estimate the hydrothermal alteration intensity both
322 vertically and horizontally, such that outcrop and drill core results could be compared.
323 Eight AI values of the drill cores HEN-172, HEN-173, HEN-192, HEN-198, HEN-234,
324 HEN-252, HEN-356 and HEN-400 are used in this analysis because there are
325 lithogeochemical data for them in the chosen depth range (~2-10 m).

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327 *3.6 Mineralogy and mineral chemistry*

328 The relationships between the Al-OH and Fe-OH absorption features and the
329 minerals present in the samples were studied by petrographic analysis of six polished

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330 thin sections (PTS) using a Nikon Labophot2[®] transmitted polarizing light microscope.
331 The samples were selected based on the presence of an Al-OH or Fe-OH absorption
332 feature, or both, and the presence or absence of biotite, chlorite and muscovite was
333 recorded at over 500 random spots within each PTS (Laakso et al., 2015).

334 The electron probe microanalyses (EPMA) of seven PTS were conducted in
335 order to investigate the relationship between the Al-OH and Fe-OH absorption feature
336 wavelength shifts and the compositions of muscovite, biotite and chlorite. The samples
337 were selected for EPMA based on the short, intermediate and long wavelength positions
338 of their Al-OH and Fe-OH absorption features. The PTS were carbon-coated and
339 analyzed using a JEOL 8230[®] electron microprobe. Mineral formulae were calculated
340 on the basis of 22 oxygens for micas (white micas and biotite) and 28 oxygens for
341 chlorite. The mineral cation compositions were then compared to the average Al-OH
342 and Fe-OH absorption feature wavelength positions of the same samples from which the
343 PTS were prepared (Laakso et al., 2015).

4. Results

4.1 Frequency distribution of Al-OH and Fe-OH absorption features

347 The Al-OH and Fe-OH absorption features of the outcrop and drill core datasets
348 show a wide range of wavelength positions suggestive of considerable chemical
349 compositional variation within the phyllosilicate minerals. This variation is discussed
350 below in the context of the proximal (0-500 m), intermediate (500-2400 m) and distal
351 (5700-6800 m) positions of these zones from mineralization.

352 Based on the petrographic analysis of the thin sections, the Al-OH absorption
353 features are associated with the white micas and the Fe-OH absorption features are

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354 associated with biotite/chlorite (Laakso et al., 2015). Furthermore, the EPMA results
355 indicate that the Al-OH absorption features of the white micas shift toward shorter
356 wavelengths with increasing Al content, and toward longer wavelengths with increasing
357 Fe+Mg content (Fig. 3; Laakso et al., 2015). Similarly, the Fe-OH absorption features of
358 biotite/chlorite shift toward shorter wavelengths with an increasing content octahedral
359 Mg, and toward longer wavelengths with an increasing octahedral Fe content (Fig. 3).

360 The summary statistical properties (minimum, maximum, median and mode) of
361 the outcrop and drill core datasets (Table 1) were calculated with the objective of
362 identifying differences in the Al-OH and Fe-OH absorption feature wavelength positions
363 of these datasets. The Al-OH and Fe-OH absorption feature wavelength position
364 frequency distributions show that both the mode and median of the Al-OH and Fe-OH
365 absorption feature wavelength positions are at shorter wavelengths in the drill core
366 spectral dataset than in the outcrop spectral dataset (Fig. 4). This indicates that the
367 chemical properties of the phyllosilicate minerals of these datasets may not be identical.
368 Moreover, the wavelength ranges of the Al-OH and Fe-OH absorptions are wider for the
369 drill core spectra than the outcrop spectra.

370 The frequency distributions of the Al-OH and Fe-OH absorption feature
371 wavelengths were compared to the normal distribution using the Shapiro-Wilk test
372 (Shapiro and Wilk, 1965). This test reveals that the Al-OH and Fe-OH wavelength
373 positions of the outcrop and drill core spectra are not normally distributed ($p=0$). The
374 non-normal data distributions of the outcrop and drill core spectral datasets are also
375 expressed as asymmetry in the frequency distributions of the data sets, which are all
376 positively skewed (Fig. 4). All data sets, with the exception of the outcrop spectra Fe-
377 OH absorption feature wavelengths, have outliers that are more than three standard
378 deviations from the sample mean. The skewed data distributions and the presence of
379 outliers in the data sets necessitated the use of non-parametric statistical methods,

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380 specifically Spearman's rank correlation analysis (rather than Pearson's) for determining
381 the relationships between the spectral and lithochemical datasets, discussed in
382 sections 4.3 and 4.4.

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384 *4.2 Evaluation of geochemical indicators of alteration intensity of the drillcore dataset*

385 Bivariate plots of the visually estimated alteration intensity (VEAI) of the drill
386 cores versus the calculated alteration indices CCPI and AI indicate that there is a
387 statistically significant (Spearman's $\rho=0.494$, $n=24$, $p=0.14$, 95% confidence level,
388 one-tailed) correlation between the CCPI and the VEA; however, there is no
389 statistically significant correlation between the AI and the VEA (Figs. 5A,B).
390 Correlations between the VEA and the AI and CCPI values were calculated using the
391 Spearman's rank correlation coefficient due to the non-normal distributions of all three
392 data sets, together with their small sample size (<30). These results suggest that the
393 CCPI shows systematic variation with the visually observable alteration intensity
394 parameters (textural and mineralogical) of the drill cores, whereas the AI does not.
395 Hence the CCPI was chosen (over the AI) to assess the relationship between the
396 alteration intensity and the Al-OH and Fe-OH wavelength positions of the drill core
397 samples.

398 *4.3 Relationships between drill core spectral and geochemical indicators*

399 A comparison between the CCPI and the Al-OH/Fe-OH absorption feature
400 wavelengths of the drill cores (Fig. 6A,B) shows a weak negative correlation
401 (Spearman's $\rho=-0.333$, $n=112$, $p=0$, 99% confidence level, two-tailed) between the
402 wavelengths of the Al-OH absorption features and the CCPI and a weak positive
403 correlation between wavelengths of the Fe-OH absorption feature and the CCPI
404 (Spearman's $\rho=0.252$, $n=97$, $p=0.013$, 95% confidence level, two-tailed). The average

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405 distance between the spectral and lithochemical data positions is 2.9 m for the Al-
406 OH absorption feature wavelength positions and 3.2 m for the Fe-OH wavelength
407 positions.

408 The vertical alteration intensity variation was examined further by selecting
409 seven drill cores (HEN-172, HEN-173, HEN-197, HEN-262, HEN-273, HEN-309 and
410 HEN-340) that lie along a NW-SE trending section (Fig. 7A). The drill holes were cored
411 in the immediate vicinity of the Central - West lens, which has the highest overall grade
412 of the massive sulfide lenses (Morrison, 2004). The drill holes define a vertical section
413 through this massive sulfide body that extends to a maximum depth of ≈ 150 m below
414 surface and dips steeply toward the north. The cross-section encompasses predominantly
415 rhyolitic rock units that surround and are crosscut by massive sulfides and intermediate
416 to mafic dykes, respectively (Fig 7B).

417 Subsurface interpolated data from cores (Figs. 7A,B) show that the highest Zn
418 and Cu values (Cu shown in Figure 7C) are located between 100 and 150 meters below
419 the surface. The complexly zoned areas are characterized by high (80-96%) CCPI values
420 in the immediate vicinity of the Cu-rich massive sulfide lens that gradually decrease to
421 lower CCPI values (46-60%) toward the surface (Fig. 7D). However, there is small-scale
422 spatial variation in these alteration intensity values such that the areas below the massive
423 sulfide lenses also show very weak alteration. The results also illustrate the inverse
424 correlation between the CCPI values and the Al-OH absorption feature wavelength
425 positions (Fig. 7E). The correlation between the spatial distribution of the CCPI and the
426 Fe-OH absorption feature wavelength positions is not as apparent in the respective cross
427 section (Fig. 7F).

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429 *4.4 Relationships between outcrop spectral and geochemical indicators*

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430 A discriminant plot of incompatible element ratios indicates that most
431 lithogeochemical samples are rhyolitic in composition (Fig. 8). Specifically, 88% of the
432 samples are classified as rhyolite, 6% rhyodacite-dacite, 3% comendite-pantellerite, 2%
433 andesite and 1% as andesite-basalt. Alkali basalt, sub-alkaline basalt, trachyandesite and
434 trachyte each comprise less than 1% of the total number of lithogeochemical samples.
435 Furthermore, the alteration box plot (Fig. 9) suggests that rhyolitic and rhyodacitic-
436 dacitic samples encompass different alteration intensities that are distributed relatively
437 evenly across the plot, but these samples are not in general associated with high CCPI
438 values. In contrast, alkali basalts, andesite, andesite-basalt and sub-alkaline basalt are in
439 general associated with high CCPI values and relatively low AI values. Comendite-
440 pantellerite compositions are commonly associated with high AI values, and relatively
441 low CCPI values. The paucity of trachyte and trachyandesite samples precludes
442 determination of their hydrothermal alteration trends in the study area. It is notable that
443 87% of the samples are located in the "hydrothermal alteration" field in the plot,
444 indicating that most samples are hydrothermally altered.

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445 The relationship between the bulk rock compositional and spectral data was
446 assessed by comparing the AI values with the Al-OH and Fe-OH absorption feature
447 wavelength positions of the outcrop spectra. Here, the AI was used as a measure of
448 alteration intensity due to the predominantly sericitic alteration of the rhyolitic rocks
449 surrounding the massive sulfide lenses.

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450 The average distance between the outcrop spectral measurements and the nearest
451 lithogeochemical sample site is 46 m in the case of the Al-OH absorption feature
452 measurements and 55 m in the case of the Fe-OH absorption feature measurements.
453 Furthermore, both the Al-OH and Fe-OH absorption feature datasets have a minimum
454 distance of 1.3 m and a maximum distance of 382 m to their nearest lithogeochemical

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455 analysis. In the case of the Al-OH absorption feature wavelength positions, 7 samples
456 are comendite-pantellerite (peralkaline rhyolites), 3 are rhyodacite-dacite, and 347 are
457 rhyolite. In the case of the Fe-OH absorption feature wavelength position measurements,
458 4 nearest lithochemical samples are comendite-pantellerite and 260 are rhyolite.

459 The Spearman rank correlation analysis suggests that there is no statistically
460 significant relationship between the Al-OH absorption feature wavelength positions and
461 AI (Fig. 10A). In contrast, there is a positive correlation between the Fe-OH absorption
462 feature wavelength positions and the AI (Spearman's $\rho=0.220$, $n=264$, $p=0$, 99%
463 confidence level, two-tailed, Fig. 10B). This correlation indicates that intense alteration
464 is associated with a shift toward longer Fe-OH absorption feature wavelength positions
465 in the outcrop spectral dataset.

466 467 *4.5 Regional map patterns of the Al-OH and Fe-OH absorption feature positions*

468 The spatial distributions of the Al-OH and Fe-OH absorption feature wavelength
469 positions extracted from the outcrop spectra display spectral shifts with distance to
470 mineralization. The intermediate areas (500–2400m) display relatively long Al-OH and
471 Fe-OH wavelength positions (Figs. 11A,B) that correlate with relatively high to
472 moderate AI values in the areas proximal (and intermediate) to the massive sulfide
473 lenses (Fig. 11C).

474 The spatial distributions of the Al-OH and Fe-OH absorption feature wavelength
475 positions extracted from the outcrop and drill core spectra were further assessed by
476 examining their correlation with distance to the nearest massive sulfide mineralization.
477 Bivariate plots, shown in Figures 12A-B, show that rocks within the proximal areas
478 display considerable variation in the Al-OH and Fe-OH wavelength positions. In

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479 general, Figure 12A shows a lack of systematic spatial trends in the Al-OH absorption
480 feature wavelength positions with distance to the mineralization. In contrast to this, the
481 Fe-OH absorption feature wavelength positions display a shift toward longer
482 wavelengths in the intermediate areas, and a shift toward shorter wavelengths in the
483 areas distal (5700-6800 m) from mineralization (Fig. 12 B).

484

485 **5. Discussion**

486 *5.1 Spectral characteristics of white micas and biotite/chlorite*

487 The wavelength positions of the Al-OH absorption features of the outcrop and
488 drill core spectra span a continuous wavelength range from 2194 nm to 2216 nm.
489 According to Herrmann et al. (2001), this range corresponds to white micas that span in
490 composition from sodic (paragonitic, or: high octahedral Al) to potassic to phengitic
491 (low octahedral Al) muscovite. Similarly, the Fe-OH absorption feature wavelength
492 positions, attributed to biotite and chlorite, display a wide and continuous range from
493 2244 nm to 2260 nm. Jones et al. (2005) suggested that this wavelength range represents
494 compositional variability from Mg-rich to Fe-rich chlorite in the short and long end of
495 the wavelength range, respectively.

496 The chemical compositional variations of these phyllosilicate minerals in the host
497 rocks in and around the Izok Lake deposit are expressed as considerable vertical and
498 horizontal spectral diversity in the immediate vicinity of the massive sulfide lenses (Fig.
499 12A,B), likely induced by intense hydrothermal alteration at varying temperatures and
500 chemical gradients. Similar hydrothermal alteration-induced spectral variation has been
501 documented in the Rosebery, Western Tharsis and Highway-Reward (Australia;
502 Herrmann et al., 2001), Myra Falls (Canada; Jones et al., 2005) and Panorama

503 (Australia, Van Ruitenbeek et al., 2012) VMS deposits.

504 The vertical alteration intensity variation, as measured by the CCPI, indicates
505 relatively weak alteration near the surface and intense alteration in the subsurface in the
506 immediate vicinity of massive sulfide mineralization at approximately 100 m depth.
507 This relationship can be explained by the occurrence of progressively higher
508 temperatures at depth of circulating hydrothermal fluids at the time of hydrothermal
509 alteration.

510 In the drill core spectra, the white micas in the immediate vicinity of the areas
511 proximal to mineralization have short Al-OH wavelength positions, whereas those in the
512 intermediate areas have relatively long Al-OH wavelength positions. The intermediate
513 zone, interpreted to be a marginal discharge area by Laakso et al. (2015), is associated
514 with intense hydrothermal alteration (Fig. 11C) that may have occurred at high
515 temperatures and high water/rock ratios synchronous with deposit formation. In the
516 distal areas, the AI values decrease and the Al-OH wavelength positions shift to slightly
517 shorter wavelengths, consistent with a more potassic white mica composition.

518 In contrast to the spatial patterns of the Al-OH absorption features of the white
519 micas, the Fe-OH wavelength positions of biotite/chlorite serve as a better-defined
520 vector to mineralization in the Izok Lake deposit area. The spatial patterns of the Fe-OH
521 absorption feature wavelength positions can be summarized as follows: the most
522 proximal alteration is characterized by relatively short Fe-OH absorption feature
523 wavelength positions that show considerable small-scale diversity, whereas the
524 intermediate areas show a shift toward longer Fe-OH absorption feature wavelength
525 positions. In the areas distal from mineralization there is a shift toward shorter Fe-OH
526 absorption feature wavelengths. These findings can be interpreted as follows: intense
527 alteration in the proximal areas is characterized by Mg-rich biotite/chlorite, whereas the

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528 areas between the proximal and distal areas have intermediate to Fe-rich biotite and
529 chlorite, and the distal areas also contain Mg-rich biotite/chlorite.

530 As discussed above, both the Al-OH and Fe-OH absorption feature wavelength
531 positions show a shift toward longer wavelengths in the intermediate areas. In these
532 areas, these trends are associated with a shift toward higher AI values of up to 98% that
533 indicate almost wholesale replacement of feldspars and glass by sericite and chlorite
534 (Large et al., 2001). In contrast, the northwestern parts of the study area display
535 relatively weak AI values of 50-80%, and long Al-OH and Fe-OH absorption feature
536 wavelength positions (up to 2209 nm and 2256 nm, respectively; Fig. 11A-C).

537 The highly variable physicochemical parameters of the hydrothermal systems
538 from which VMS deposit form result in myriad and variable documented alteration
539 styles and extents. For example, although Fe-rich chlorite has been documented in close
540 proximity to some massive sulfide lenses (e.g., Plimer and de Carvalho, 1982; MacLean
541 and Hoy, 1991; Leistel et al., 1998), other studies have documented Mg-chlorite in these
542 areas (e.g. Date et al., 1983; Urabe et al., 1983; McLeod et al., 1987; Schmidt, 1988;
543 Sánchez-España et al., 2000; Paulick et al., 2001; Hannington et al., 2003; Biel et al.,
544 2010). Regardless of the chemical composition of chlorite, altered rocks in the proximal
545 fluid upflow areas can have white micas that are either predominantly Al-rich (e.g.,
546 Urabe et al., 1983; Jones et al., 2005; Herrmann et al., 2009) or Al-poor (e.g. Biel et al.,
547 2010). Similar trends to those present in the compositional variety of the white micas
548 and biotite/chlorite group minerals of the Izok Lake deposit have been reported from
549 other VMS deposits such as the South Bay deposit in Ontario, Canada (Urabe et al.,
550 1983) and the Ambler mineral district in Alaska (Schmidt, 1988).

551 *5.2 Correlations between spectral absorption features and bulk rock compositions*

552 One of the limitations of the CCPI is that it is strongly affected by primary

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553 compositional variations in the volcanic rocks (Large et al., 2001). This phenomenon is
554 also evident in the alteration box plot (Fig. 9), in which the intermediate and mafic
555 volcanic rocks of the study area (andesite and basalt) predominantly group in the high
556 CCPI and low AI corner of the plot. As such rock types contain more ferromagnesian
557 minerals than the felsic volcanic rocks (e.g., rhyolite), the high CCPI values in these
558 rocks are controlled predominantly by their primary mineralogy and not the intensity of
559 alteration. However, lithologic variation plays a minimal role in our study because care
560 was taken to analyze only the lithogeochemical and spectral properties of the rhyolitic
561 rocks. This is also evidenced by the Winchester-Floyd diagram that indicates the
562 predominantly rhyolitic character of the outcrop lithogeochemical samples (Fig. 8).

563 Despite its limitations, the CCPI is designed to measure chloritic alteration
564 (Large et al., 2001), and hence is well suited to the study of hydrothermal alteration in
565 VMS deposits. In our study, the CCPI was chosen over the AI to estimate the alteration
566 intensity variation of the drill cores because there is no discernable correlation between
567 AI and VEAI, whereas there is a good correlation between the CCPI and VEAI. The
568 presence of chloritic alteration in the vicinity of the Izok Lake massive sulfide lenses
569 (Morrison, 2004) best explains the correlation between CCPI and VEAI.

570 The weak negative correlation between the Al-OH absorption feature
571 wavelengths of the drill core spectra and the CCPI indicates that increasing alteration
572 intensity is associated with increasing Al content of the white micas. Yang et al. (2011)
573 have documented a similar relationship between the Al-OH absorption feature
574 wavelength positions of andesitic host rocks and the AI in Hellyer VMS deposit,
575 Tasmania. Herrmann et al. (2001) reported an inverse correlation between the Al-OH
576 wavelength positions and the AI values of the Western Tharsis (Tasmania) and
577 Highway-Reward (Queensland, Australia) deposits. The investigation by Herrmann et

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578 al. (2001) in the Rosebery deposit (Tasmania) found no association between the
579 lithogeochemical and spectral datasets. Despite the correlation between the Al-OH
580 absorption feature wavelength positions of the drill core data and the nearest
581 lithogeochemical data at Izok Lake, the lack of a quantifiable relationship between the
582 Al-OH absorption features of the outcrop spectral dataset and the AI suggests that the
583 chemical composition of the white micas is an imperfect mineral exploration vectoring
584 tool in the study area.

585 Correlations between the Fe-OH wavelength positions of the spectral datasets
586 (outcrop and drill core) and the AI and CCPI alteration indices show statistically
587 significant positive correlations, suggesting that high alteration intensities are in general
588 associated with a shift toward a more Fe-rich biotite/chlorite in the study area. The
589 observed iron enrichment of these phyllosilicate minerals can result from several factors,
590 such as their formation in a high-temperature discharge zone that was characterized by
591 Fe-rich hydrothermal fluids at the time of hydrothermal alteration.

592 Despite the presence of some Fe-rich biotite and chlorite, the phyllosilicate
593 minerals associated with the highest AI and CCPI values (80-100%) have average
594 absorption feature wavelength positions of 2253 nm and 2254 nm for the drill core and
595 outcrop spectral datasets, respectively, indicative of Mg-rich compositions (Yang and
596 Huntington, 1996; Figs. 6B and 10B). Hence, the observed shift toward a more Fe-rich
597 composition is relative and does not imply that the most intense alteration is associated
598 with iron-rich chlorite and biotite. It is noteworthy that the areas proximal and distal to
599 the Izok Lake mineralization are characterized by high and low hydrothermal alteration
600 intensity values, respectively (Fig. 11C), but both areas have Mg-rich biotite/chlorite
601 that are spectrally similar (Fig. 12B). Hence, without the lithogeochemical data and field
602 observations, the distal areas might have been (mis)interpreted as being favourable to

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603 hosting mineralization. Our study therefore highlights the importance of using all
604 available geological, geochemical and mineralogical information in the application of
605 hydrothermal alteration vectoring toward VMS mineralization.

606 There are a number of external factors that influence our results. First, a
607 relatively small number of observations and data are available, and hence caution should
608 be exercised when interpreting the correlations between outcrop spectral and
609 lithogeochemical features both in the Izok Lake area and elsewhere. If the chemical
610 compositions of the white micas and biotite/chlorite do not vary exclusively as a
611 function of the alteration processes, the correlations between the spectral and
612 lithogeochemical data can reflect multiple factors that include (but are not limited to)
613 hydrothermal alteration. One factor potentially affecting the mineralogy of VMS
614 deposits is metamorphism that can recrystallize and re-equilibrate minerals at
615 metamorphic conditions that exceed greenschist facies (Dusel-Bacon, 2012). Evaluation
616 of the metamorphic overprint of the Izok Lake study area is out of scope of this
617 investigation, and can be found elsewhere. For instance, the investigation by Nowak
618 (2012) suggests that amphibolite-facies metamorphism resulted in only minor changes
619 in the chemical compositions of the rocks in the study area.

620 Another factor that may potentially influence the relationship between the
621 spectroscopic and lithogeochemical data is the sampling interval. The average distance
622 between the outcrop spectral measurement and the nearest lithogeochemical data is 50.5
623 m, and this relatively large distance may have weakened the relationship between these
624 two datasets. In contrast, the average distance between the drill core spectral
625 measurements and the nearest lithogeochemical data is only 3 m, indicating that local
626 variations in alteration type and intensity play only a minor role in the correlations
627 between the spectral and lithogeochemical data extracted from the drill cores.

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629 *5.3 Implications of the spectral features for deposit genesis*

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5 631 deposits that typically contain Fe-rich chlorite (MacLean and Hoy, 1991; Barrett and
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7 632 MacLean, 1994). In the Izok Lake deposit, however, our infrared spectroscopic data
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9 633 indicate that the proximal areas contain more Mg-rich chlorite and biotite than the
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11 634 intermediate areas farther away from the mineralization. This conclusion is supported by
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13 635 the findings of Money and Heslop (1976), who reported Mg-enrichment in rocks
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15 636 proximal to the deposit. Several studies (Schmidt, 1988; Schade et al., 1989; Paulick et
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17 637 al., 2001; Hannington et al., 2003) have similarly noted Mg-enrichment in the vicinity of
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19 638 the feeder (fluid upflow) zones of VMS deposits, and attributed these patterns to the
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21 639 influx of seawater.
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28 640 Paleo-hydrothermal upflow and discharge zones generally display the highest
29
30 641 alteration intensities in VMS deposits (Barrett and MacLean, 1994), and therefore an
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32 642 area of strong alteration located west of the known massive sulfide lenses (Fig. 11C)
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34 643 merits further exploration, as it may be associated with yet unrecognized mineralization.
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42 645 **6. Conclusions**
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46 646 Outcrop and drill core spectroscopy of the host rocks to the Izok Lake VMS
47
48 647 deposit display a wide spectral range of the Al-OH and Fe-OH absorption feature
49
50 648 wavelength positions that indicate considerable compositional variation within the
51
52 649 contained phyllosilicate minerals. This variation is attributable to variable parameters
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54 650 during the hydrothermal alteration process, possibly including the physico-chemical
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56 651 composition of the hydrothermal fluids, water/rock-ratios and temperature that have
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58 652 influenced the mineralogical and chemical composition of the alteration minerals. These
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653 processes have resulted in the formation of Al-rich white micas and Mg-rich
654 biotite/chlorite in the intensely altered rocks of the proximal areas. The Mg-rich
655 compositions of chlorite and biotite may be due to influx of seawater that resulted in
656 Mg-metasomatism. Further away from the proximal alteration is a zone of Al-poor white
657 micas and intermediate to Fe-rich biotite and chlorite that transitions to a distal zone of
658 predominantly potassic muscovite and Mg-rich biotite and chlorite.

659 The weak positive correlation between the Fe-OH absorption feature wavelength
660 positions and the alteration intensity (using AI and CCPI as proxies) is evident in both
661 the outcrop and drill core spectral datasets. There is also a statistically significant
662 correlation between the Al-OH absorption feature wavelength positions of the drill core
663 spectrometry and alteration intensity, but this is only evident in the drill core spectra,
664 and not the outcrop spectra. Hence, in the study area, the spectral properties of chlorite
665 and biotite follow the alteration intensity variation more closely than those of the white
666 micas. Although the correlation coefficients for the relationships between the Al-OH/Fe-
667 OH absorption feature wavelength positions and the alteration indices are weak, the Al-
668 OH and Fe-OH wavelength positions of the white micas and biotite/chlorite,
669 respectively, do provide a useful measure of the alteration intensity of the rocks that host
670 the Izok Lake VMS deposit. However, the weak correlations between the Al-OH and
671 Fe-OH absorption feature wavelength positions and the AI and CCPI alteration indices
672 suggest that the spectral shifts detected in these phyllosilicate minerals are better suited
673 for inferring large-scale rather than small-scale alteration patterns. Moreover, because
674 VMS deposits can have differing alteration fingerprints due to the complexity of factors
675 that induce hydrothermal alteration, caution should be exercised, and a baseline study is
676 recommended before applying the conclusions for Izok Lake to other VMS deposits
677 elsewhere.

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FIGURE LEGENDS

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3 868 **Figure 1.** Location map and geological map of the Izok Lake study area showing the
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5 869 locations of the outcrop spectroscopic sites, samples, drill cores and
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7 870 lithogeochemical samples. meas.=measurement.

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10 871 **Figure 2.** Location of the drill cores and sulfide lenses. The geology and projected
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12 872 location of massive sulfide zones are from MMG Ltd. unpublished GIS data.

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15 873 **Figure 3.** A) Reflectance spectra from drill cores HEN187 ("HEN187-0018", spectrum
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17 874 1) and HEN-186 ("HEN186-0014", spectrum 2); B) Selected range plot of hull
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19 875 quotient-corrected spectra 1 (absorption feature wavelength position: 2208 nm)
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21 876 and 2 (absorption feature wavelength position: 2195 nm) shown in A; C)
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23 877 Reflectance spectra from drill cores HEN252 ("HEN252-0012", spectrum 1) and
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25 878 HEN-188 ("HEN188-0016", spectrum 2); D) Selected range plot of hull quotient-
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27 879 corrected spectra 1 (absorption feature wavelength position: 2259 nm) and 2
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29 880 (absorption feature wavelength position: 2246 nm) shown in C.

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32 881 **Figure 4.** Frequency distribution histograms of absorption band position for: A) drill
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34 882 core Al-OH absorption; B) drill core Fe-OH absorption; C) outcrop spectra Al-OH
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36 883 absorption; D) outcrop spectra Fe-OH absorption.

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39 884 **Figure 5.** Bivariate plot of the visually estimated alteration intensity (VEAI) of the drill
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41 885 cores versus A) the calculated chlorite-carbonate-pyrite index (CCPI) (expressed
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43 886 as %); and B) the calculated Ishikawa index (AI) (expressed as %).

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46 887 **Figure 6.** Bivariate plot of the chlorite-carbonate-pyrite index (CCPI, expressed as %)
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48 888 calculated from the lithogeochemical data for the drill core samples versus A) the
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50 889 Al-OH wavelength positions (in nm) and; B) the Fe-OH wavelength positions (in
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52 890 nm).

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55 891 **Figure 7.** A vertical cross section of the lithogeochemical and spectral trends across
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57 892 seven drill cores (HEN-172, HEN-173, HEN-197, HEN-262, HEN-273, HEN-309

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893 and HEN-340). A) map view of the locations of the drill cores; B) three-
1 894 dimensional lithological map of the drill cores. Downhole variation of: C) Cu
2 895 contents (ppm); D) chlorite-carbonate-pyrite index (CCPI, %) values; E) Al-OH
3 896 absorption feature wavelength positions (nm); F) Fe-OH absorption feature
4 897 wavelength positions (nm). pegmat.=pegmatite. The Cu contents of the drill cores
5 898 are extracted across all lithologies and the CCPI, Al-OH and Fe-OH values are
6 899 extracted from the rhyolitic rock sections of the drill cores. Due to the three
7 900 dimensional nature of the profile, and the uncertainty on the spatial dimensions of
8 901 the rock units, the interpolation results are displayed across different rock units for
9 902 the full vertical section (0-200 m depth). These interpolations were created by
10 903 estimating the value of each voxel node (three-dimensional cell) using the value of
11 904 the nearest drill core observation (i.e. the "nearest neighbor"). All the sections face
12 905 west.

31 906 **Figure 8.** Nb/Y (ppm) versus Zr/TiO₂ (ppm) discrimination plot of Winchester and
32 907 Floyd (1977) for the lithogeochemical samples. Shown in the plot are the outcrop
33 908 samples from the Izok Lake study area ($n=555$).

38 909 **Figure 9.** Alteration box plot of Large et al. (2001) showing lithogeochemical samples
39 910 of the Izok Lake study area. bas.=basalt, dac.=dacite, pant.=pantellerite.

43 911 **Figure 10** Bivariate plots of: A) the Al-OH absorption feature wavelengths of the
44 912 outcrop spectra ($n=357$) versus the Ishikawa index (AI, expressed as %). The
45 913 lithogeochemical samples represent rhyolite ($n=347$), rhyodacite-dacite ($n=3$) and
46 914 comendite-pantellerite ($n=7$); B) the Fe-OH absorption feature wavelengths of the
47 915 outcrop spectra ($n=264$) versus the AI (expressed as %). The lithogeochemical
48 916 samples represent rhyolite ($n=260$) and comendite-pantellerite ($n=4$). All the
49 917 spectral measurements (Figs. A and B) are acquired from the rhyolitic rocks.

60 918 **Figure 11.** Color gradient map of the absorption feature wavelength positions extracted

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919 from the outcrop spectra for A) Al-OH and B) Fe-OH and subsetted to the spatial
920 dimensions of the approximated extent of the rhyolitic rocks in the study area.
921 Only areas proximal (327-2679 m) to the mineralization are shown in the
922 interpolation due to the sparsity of data in the more distal areas. C) Color gradient
923 map of the AI calculated from the lithogeochemical data for drill core and outcrop
924 samples.
925 **Figure 12.** Bivariate plots of the absorption feature wavelength positions of the outcrop
926 and drill core spectra versus distance from massive sulfide mineralization for A)
927 Al-OH and B) Fe-OH.

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TABLE LEGENDS

929 **Table 1.** Summary statistics of the Al-OH and Fe-OH absorption features of the outcrop
930 and drill core spectra.

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Figure 1

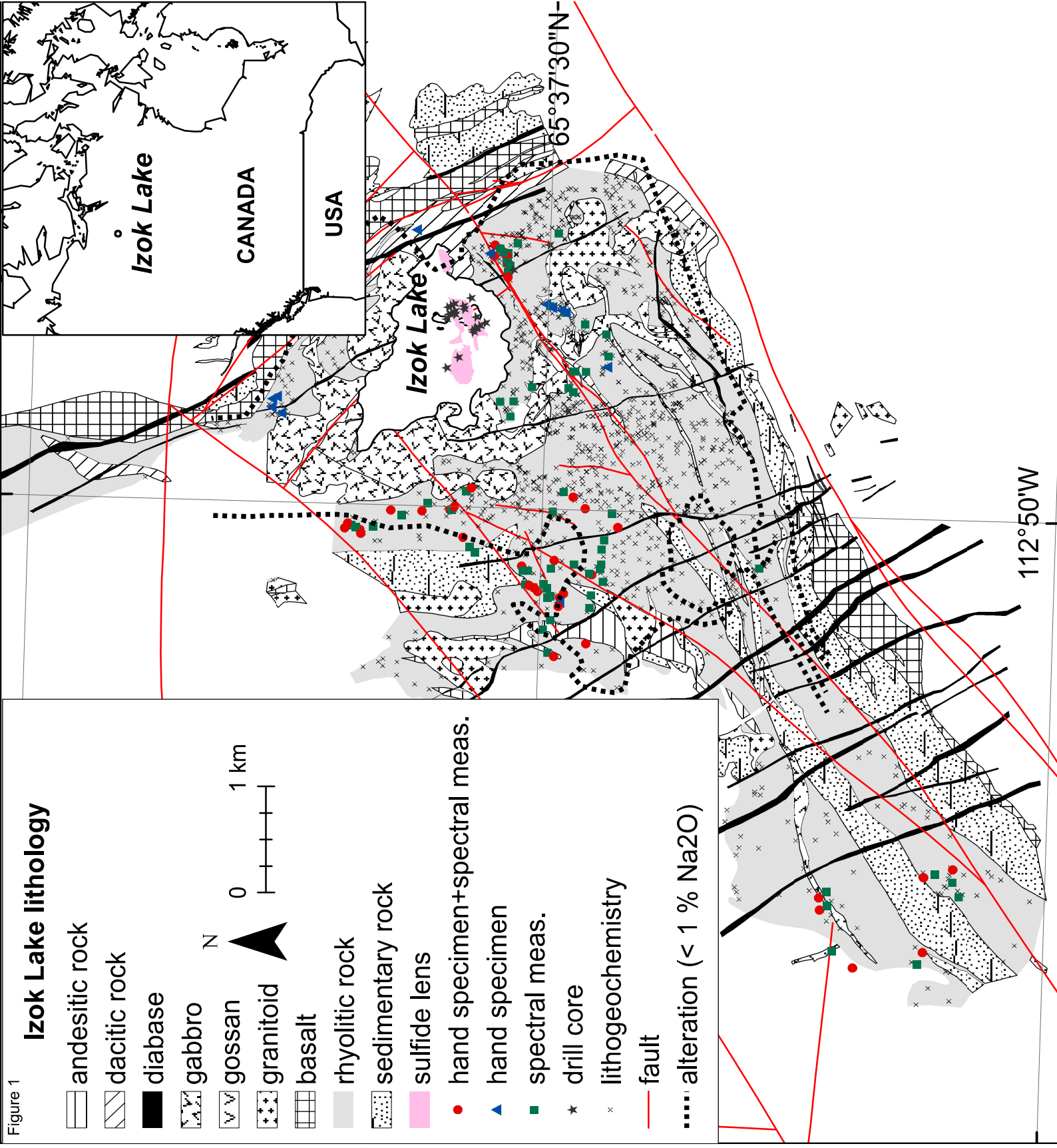
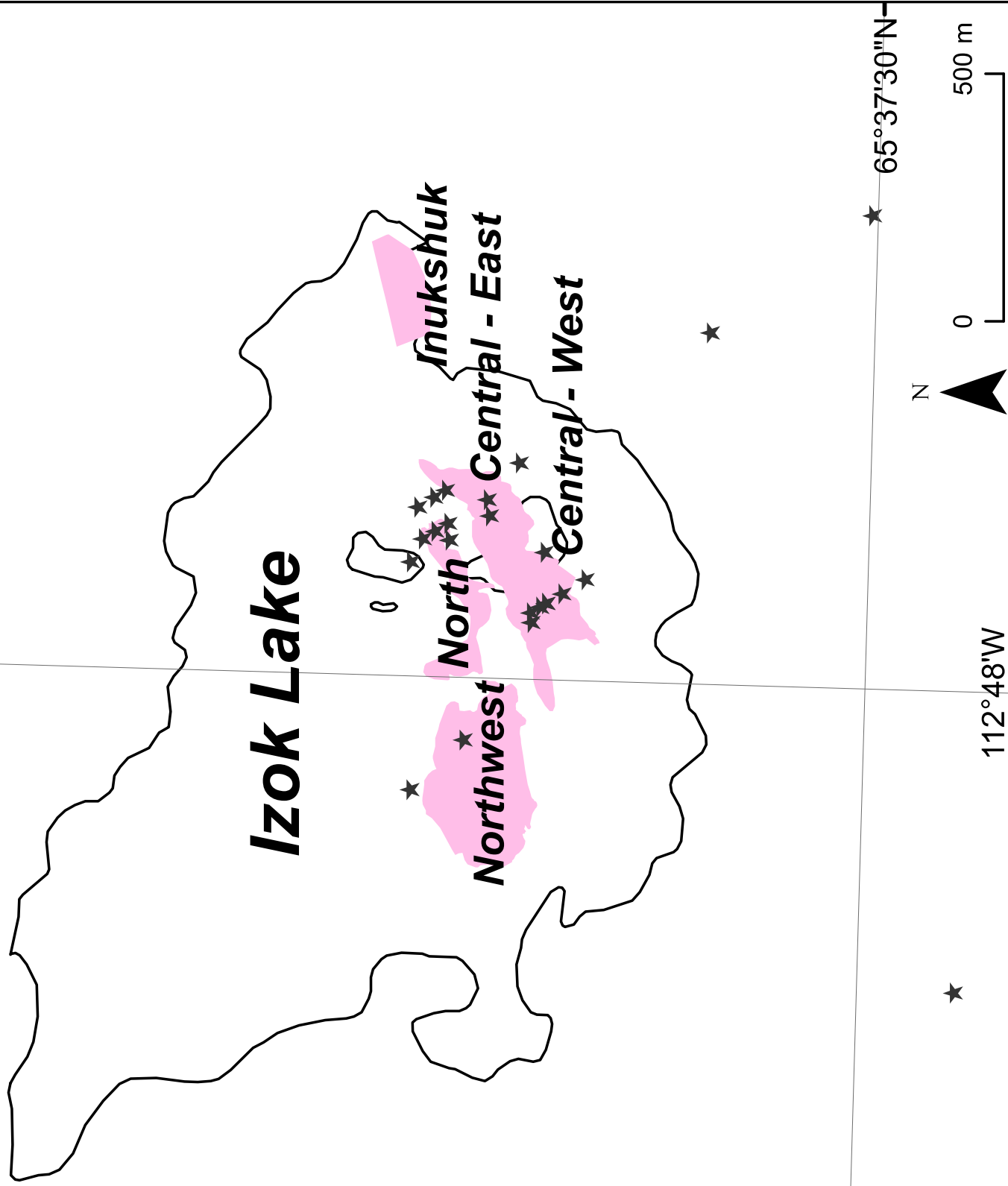


Figure 2
Sulfide lens

★ drill core



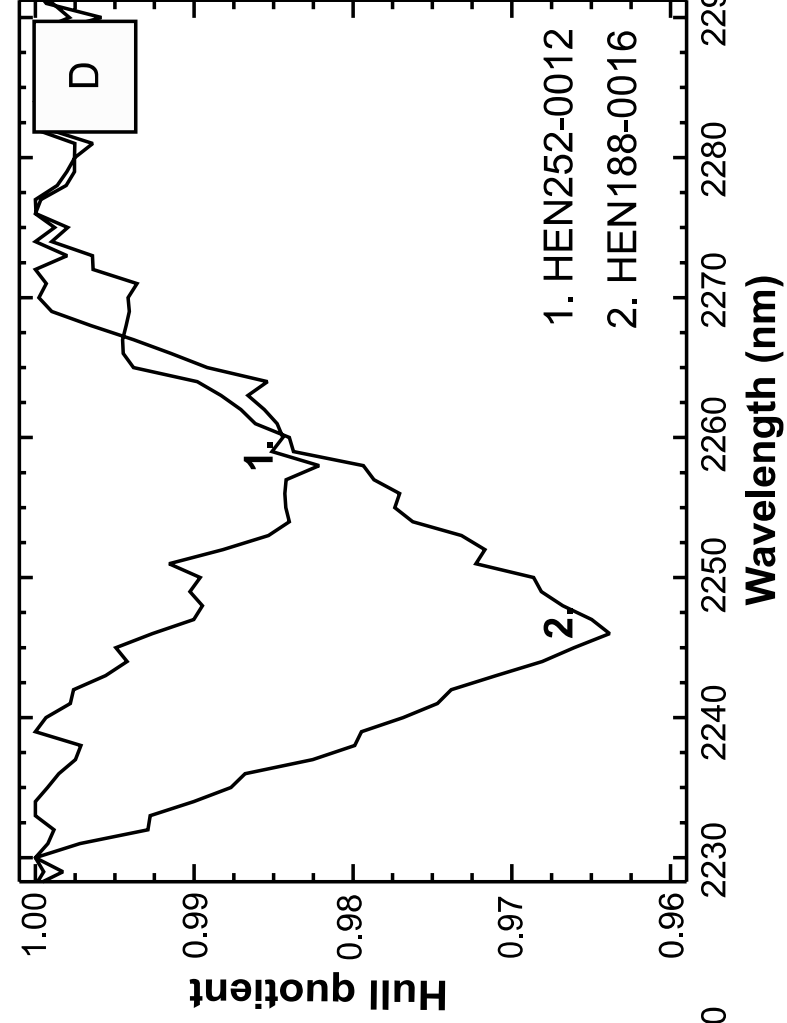
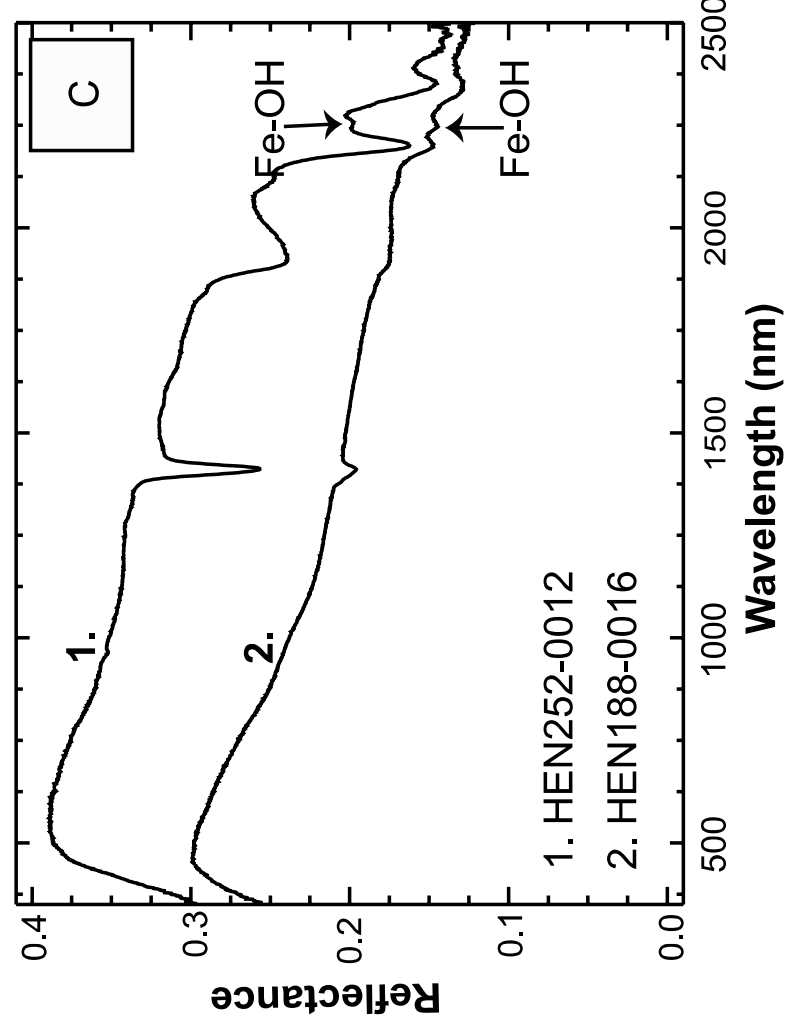
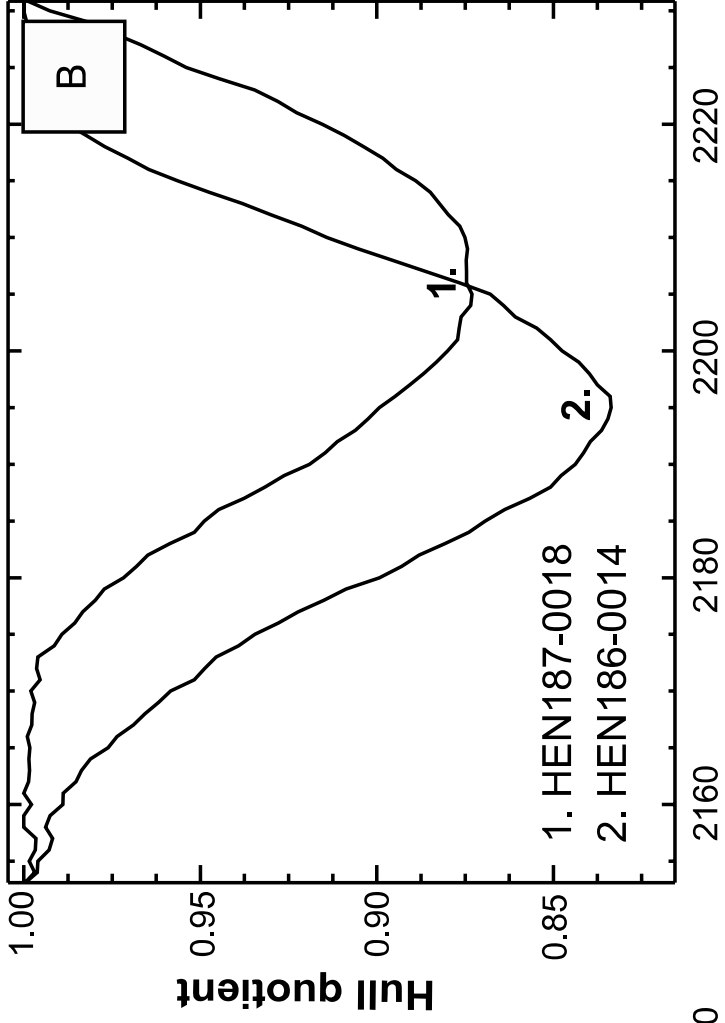
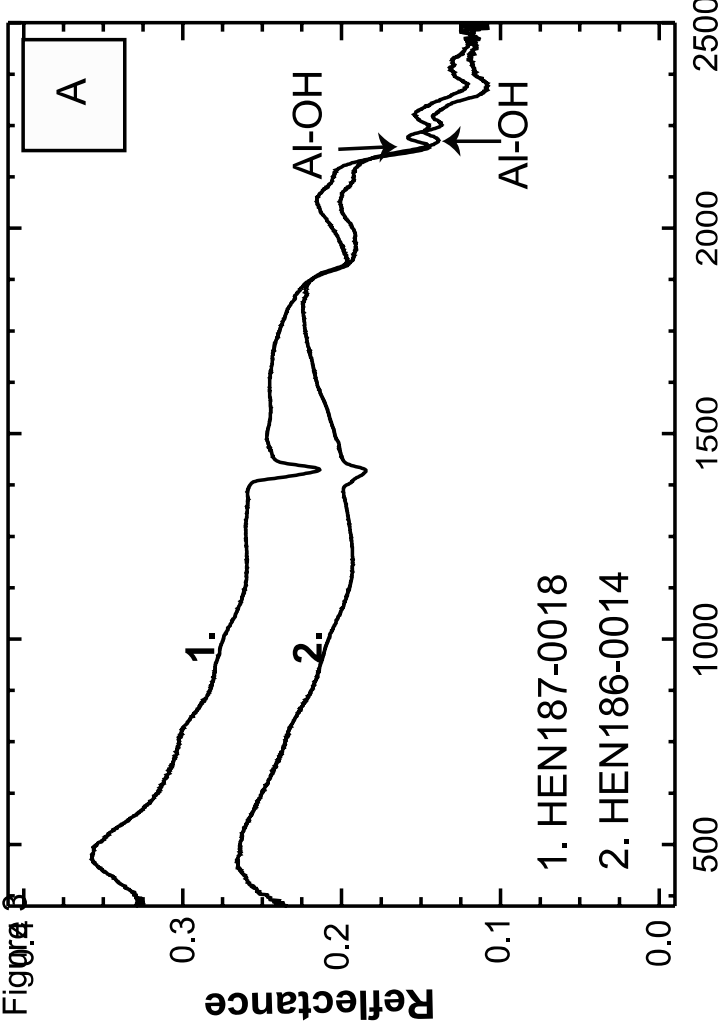


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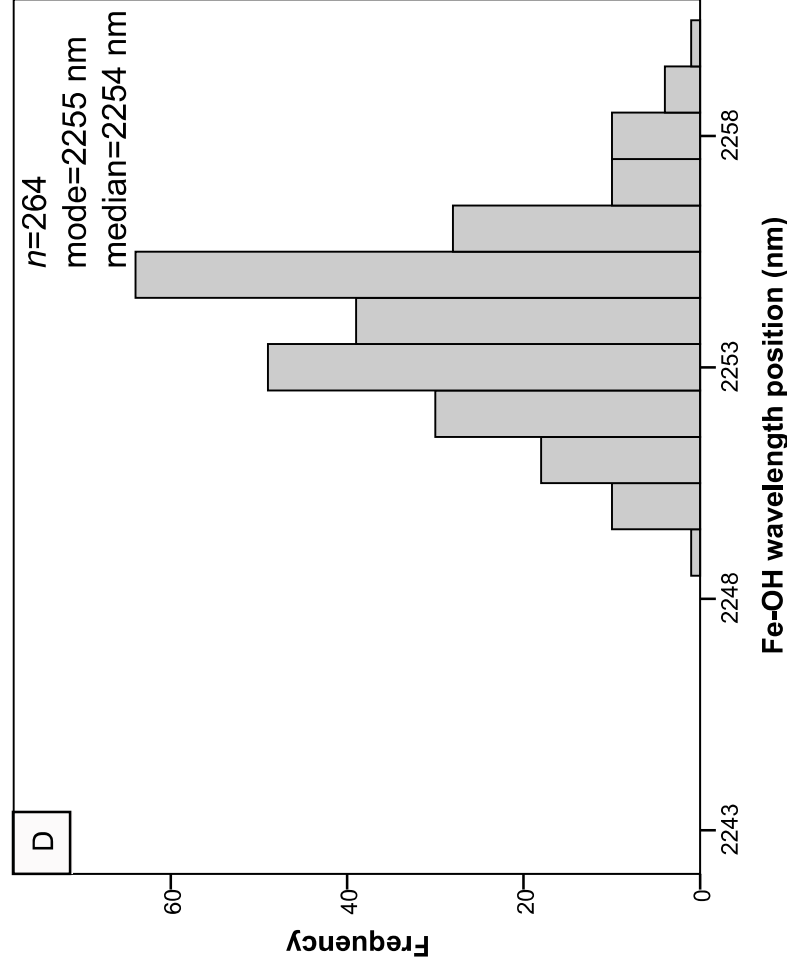
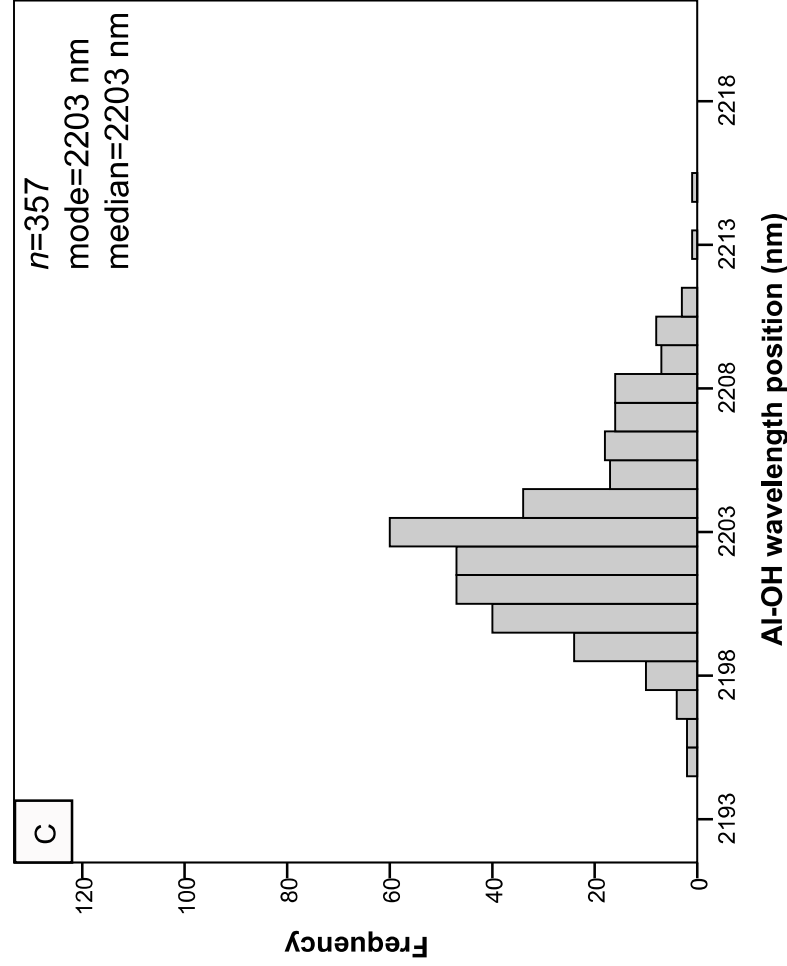
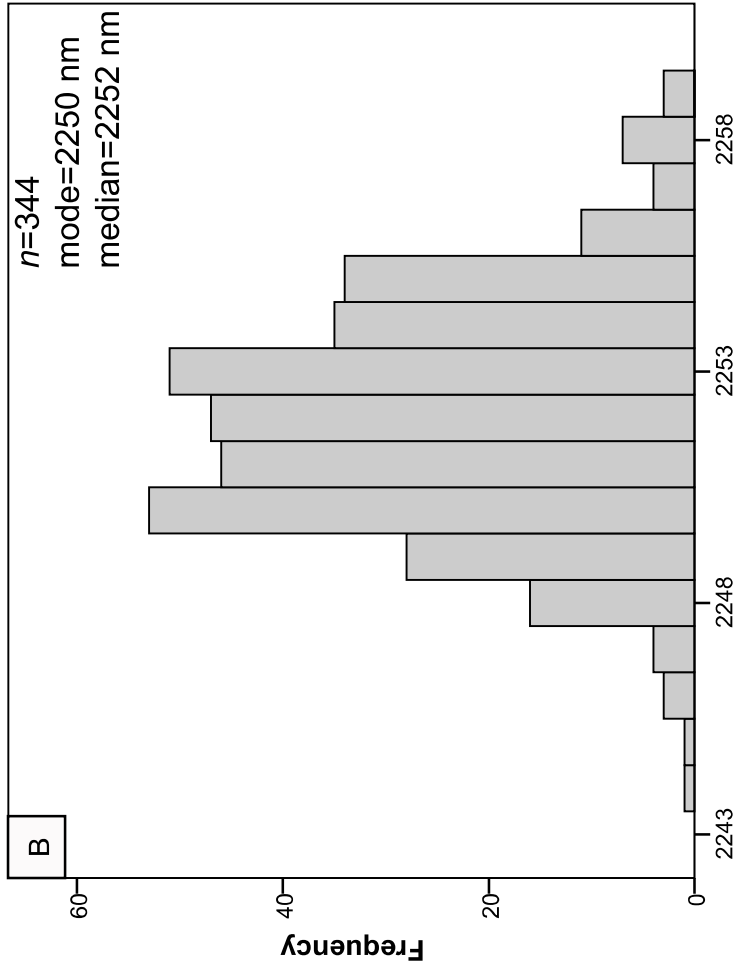
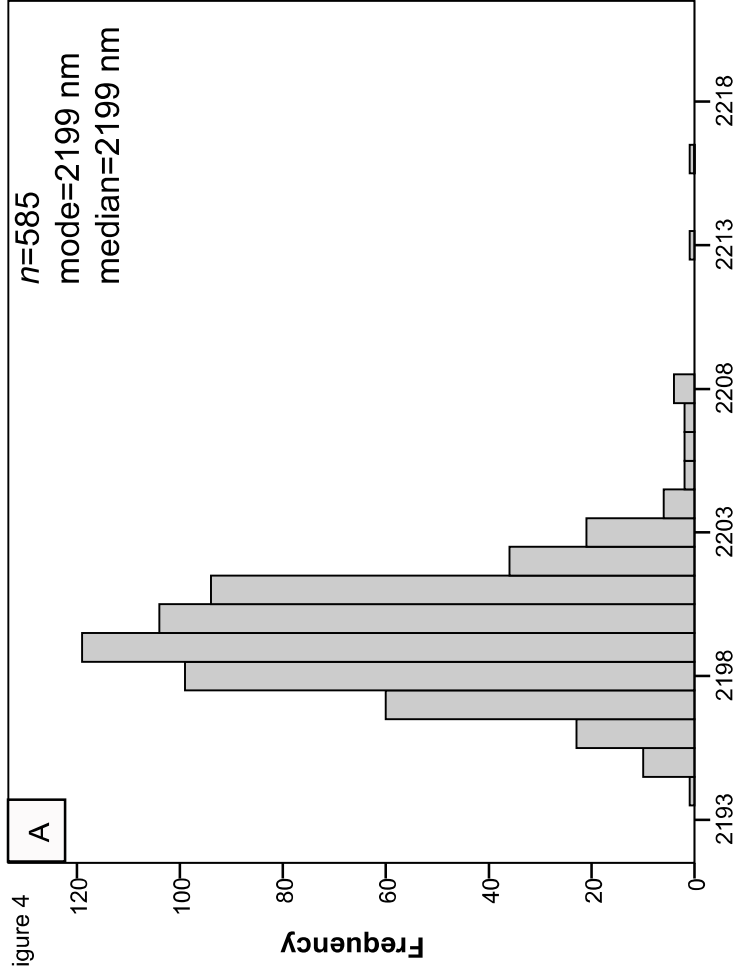
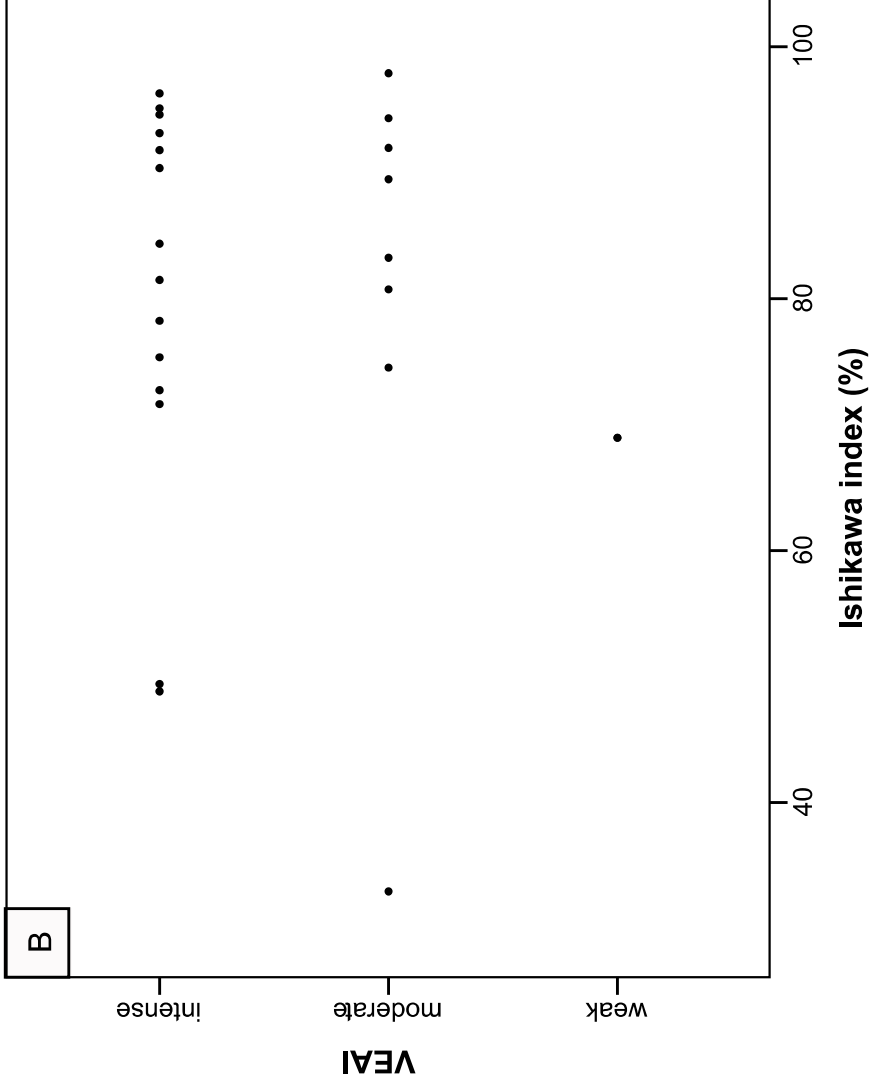
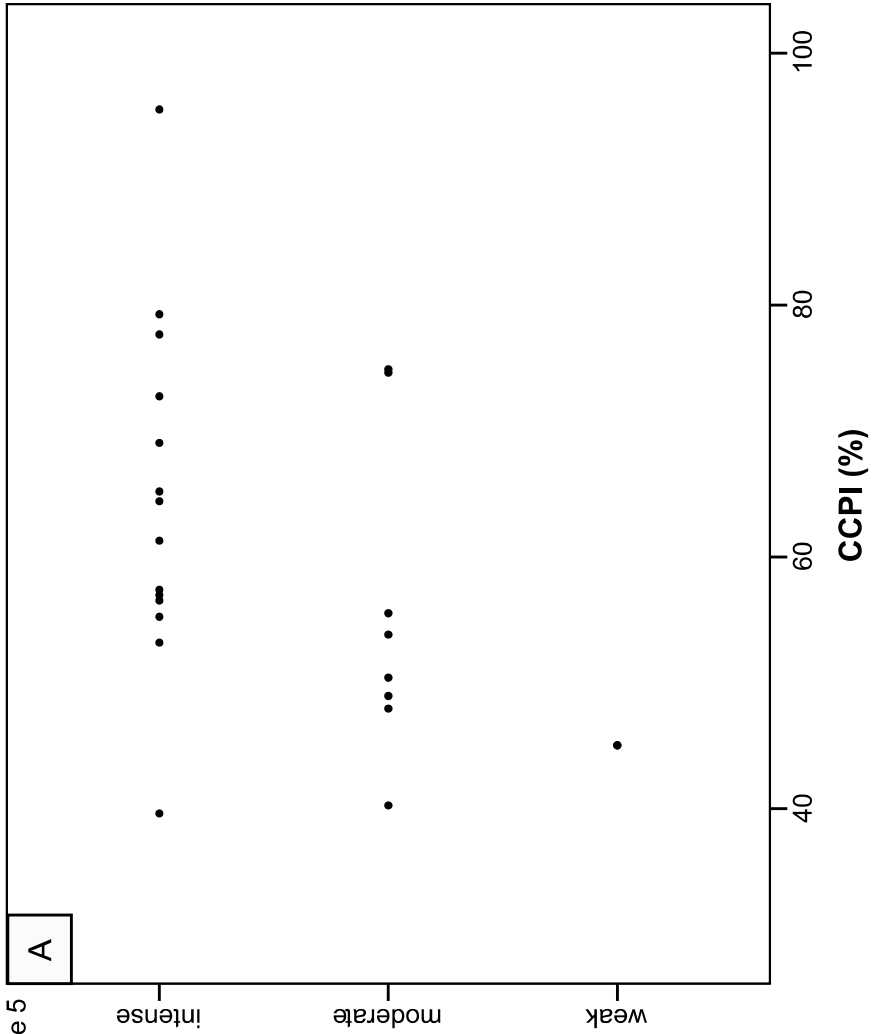


Figure 5



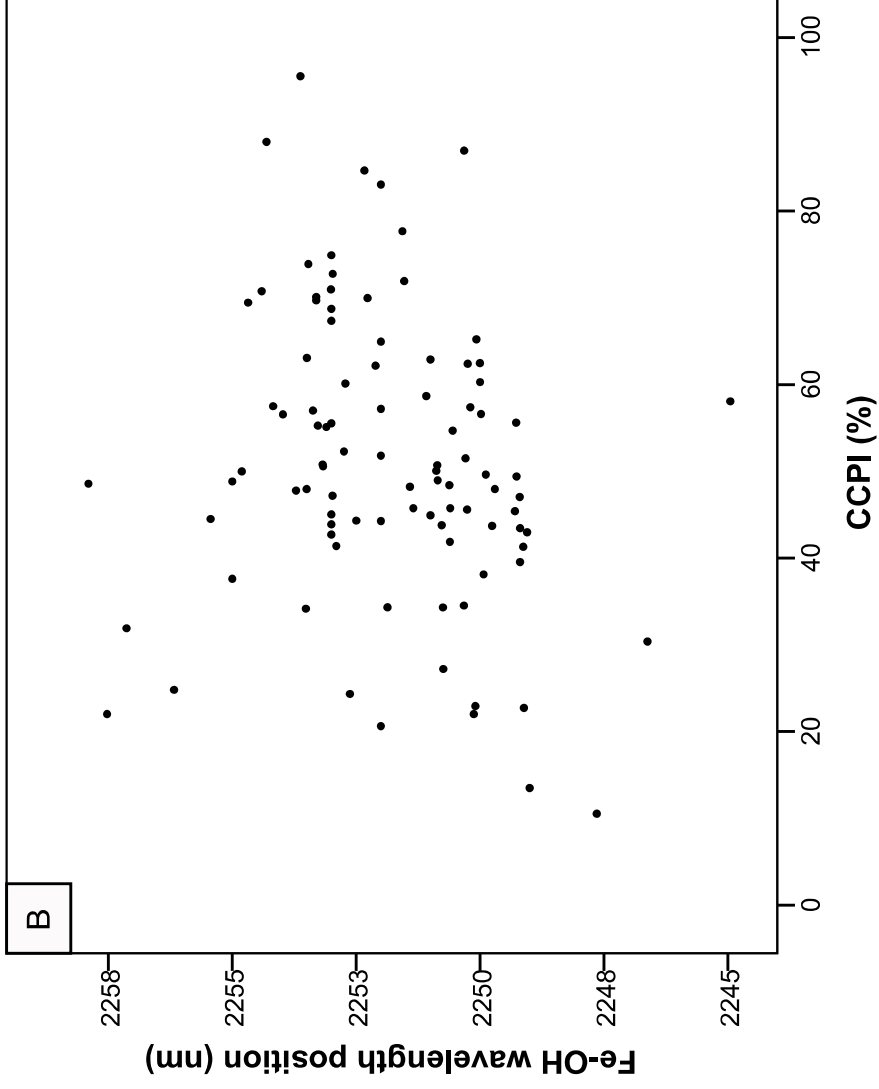
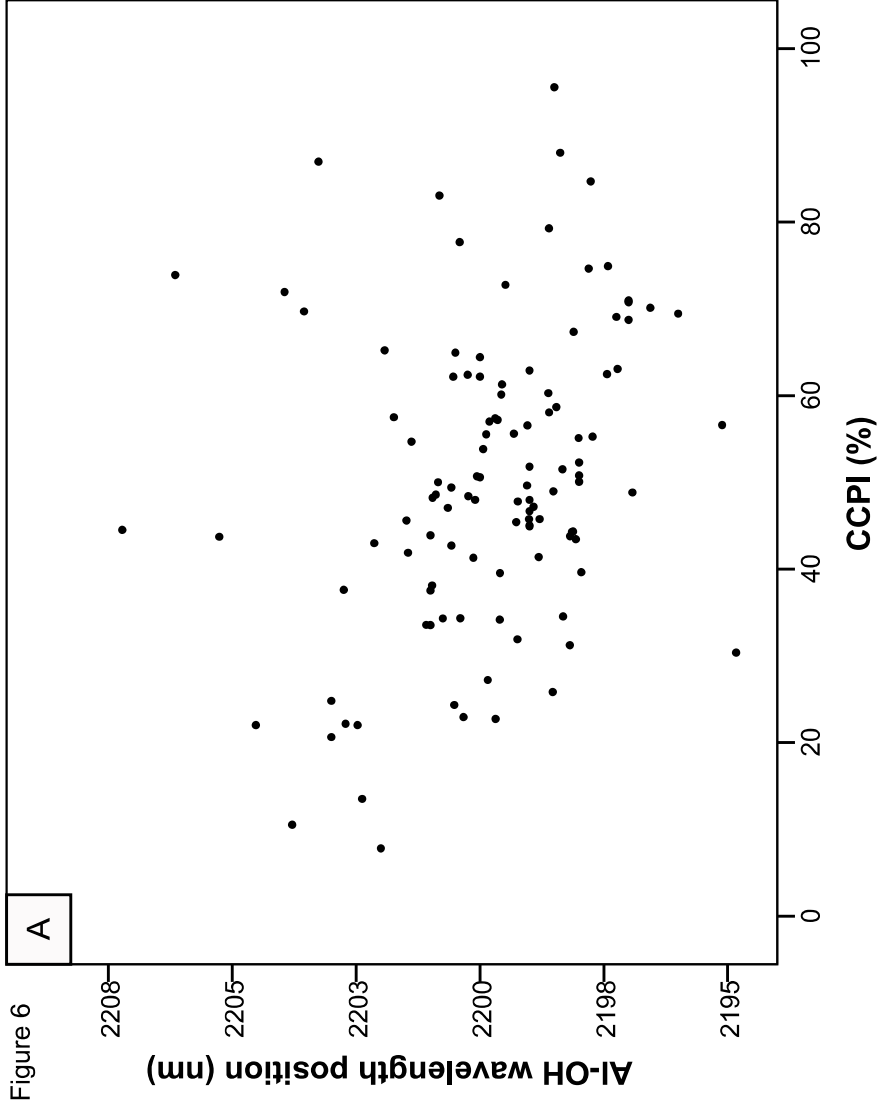


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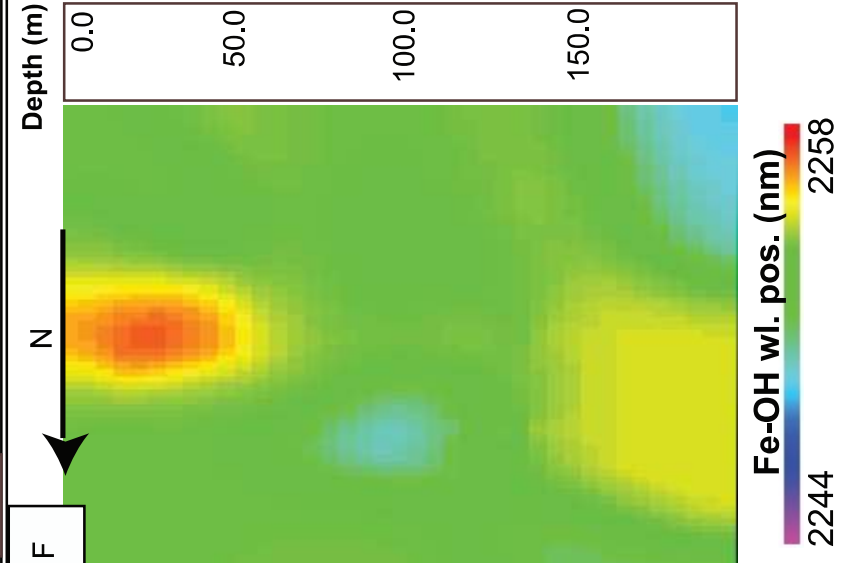
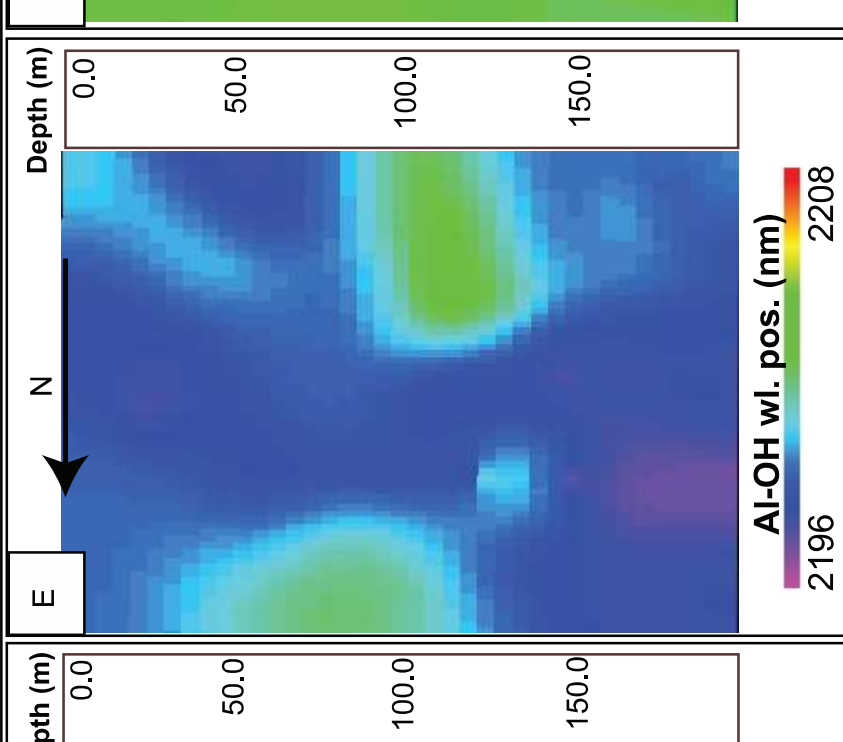
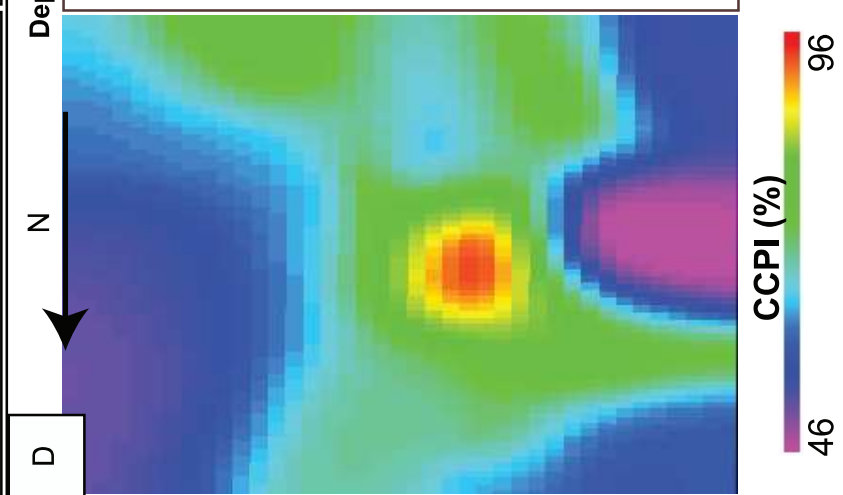
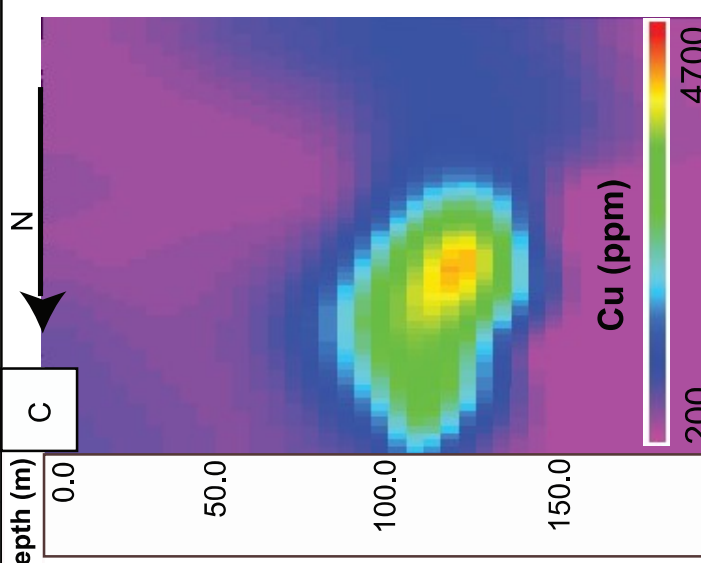
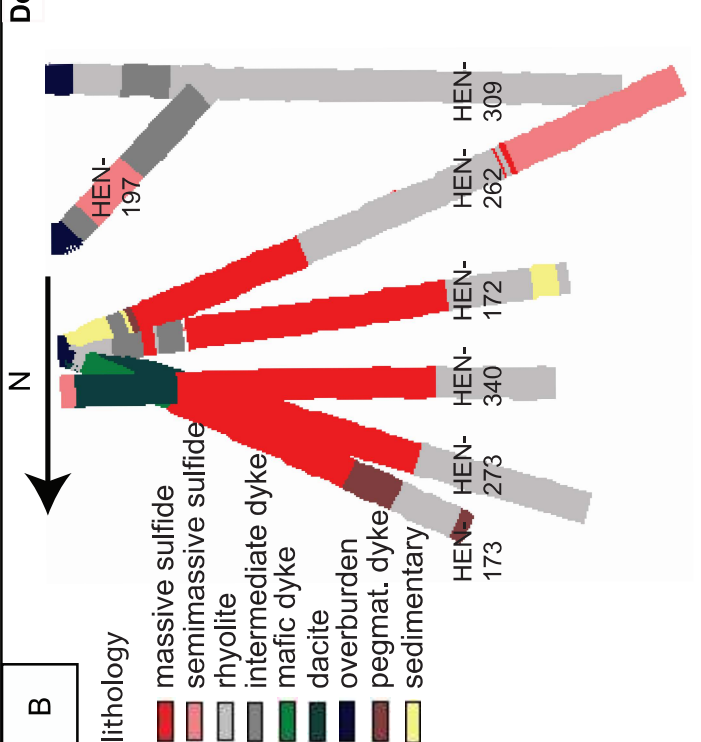
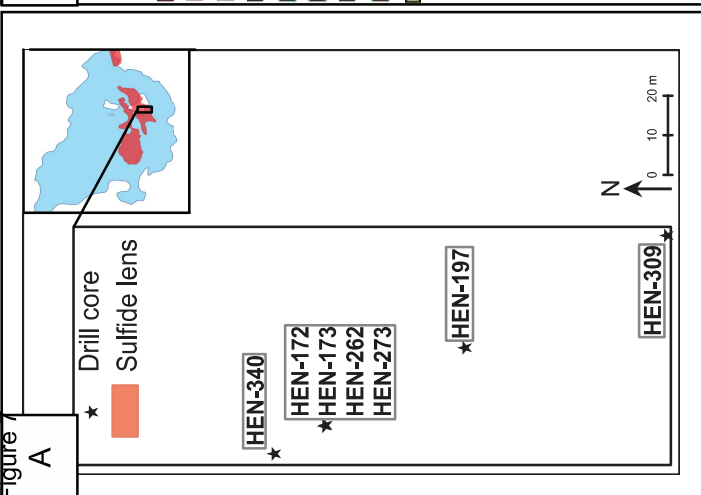


Figure 8

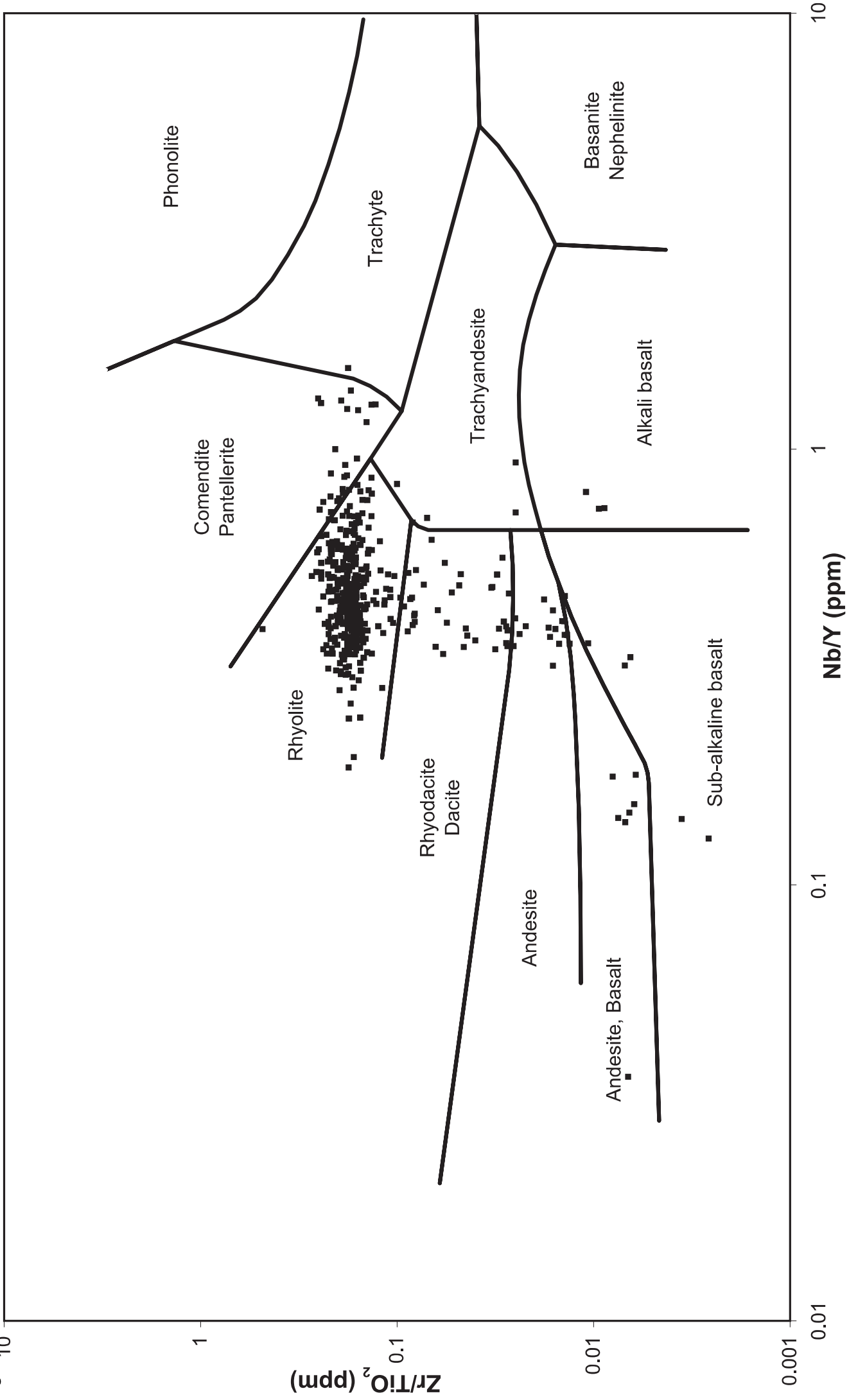


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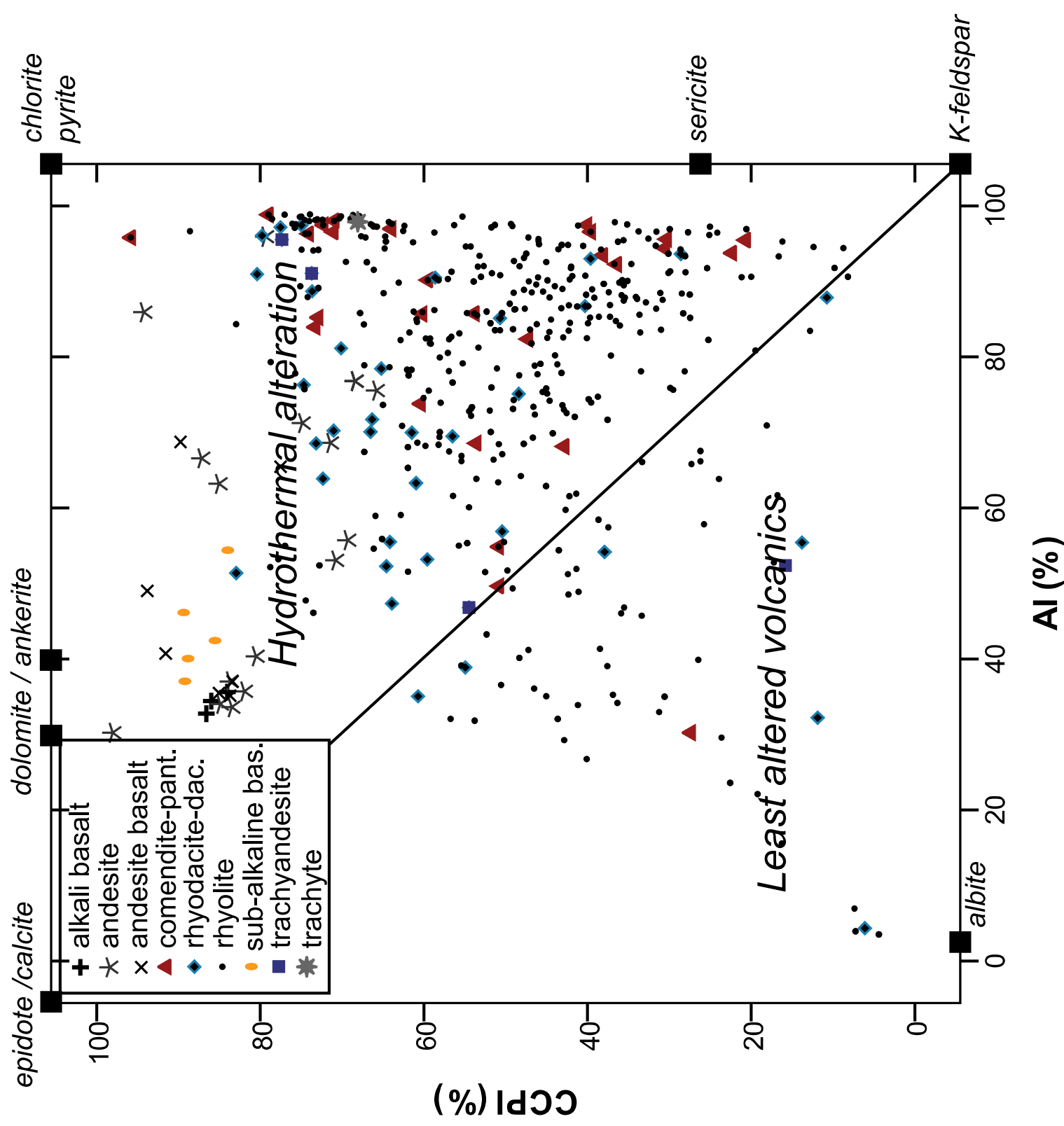
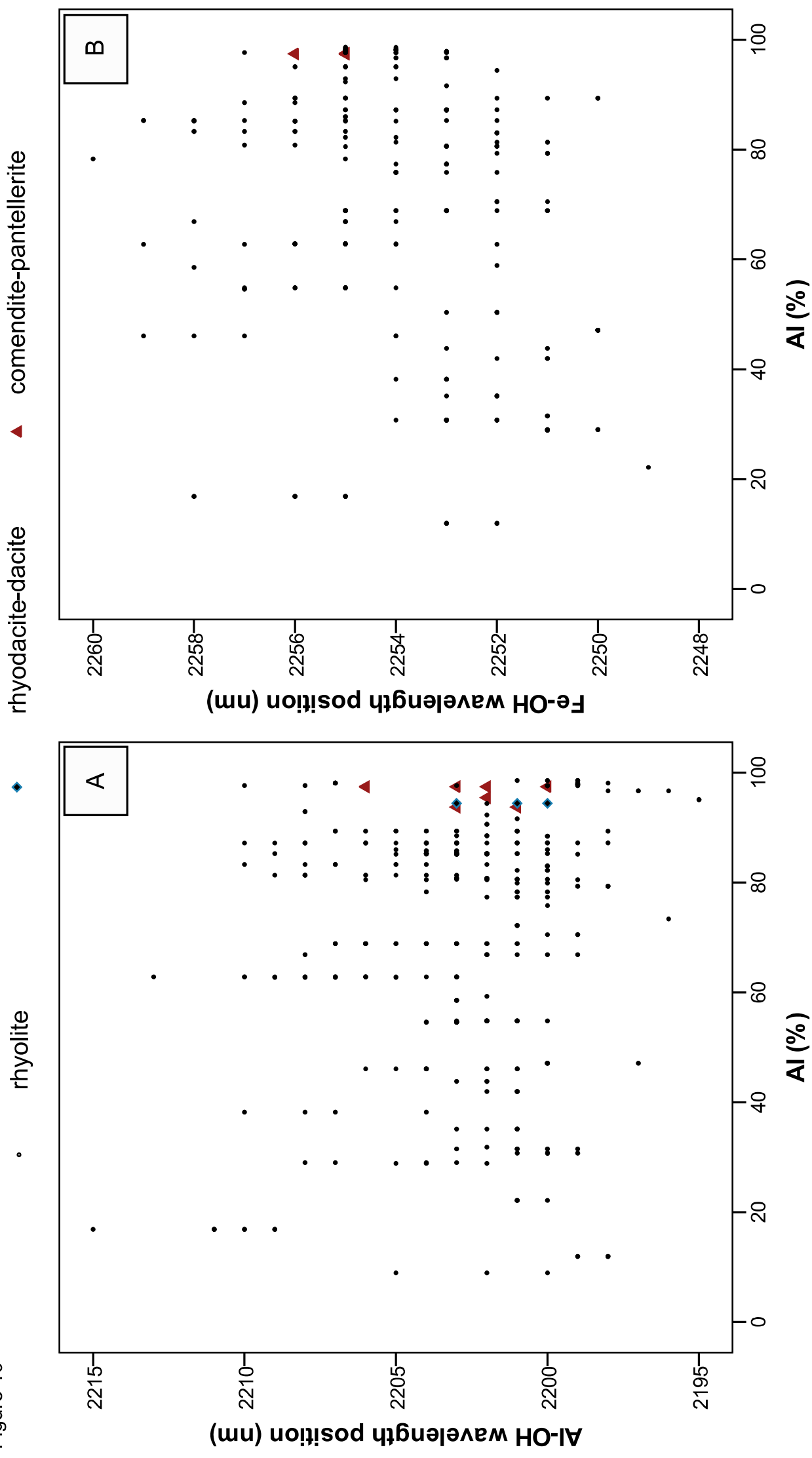


Figure 10



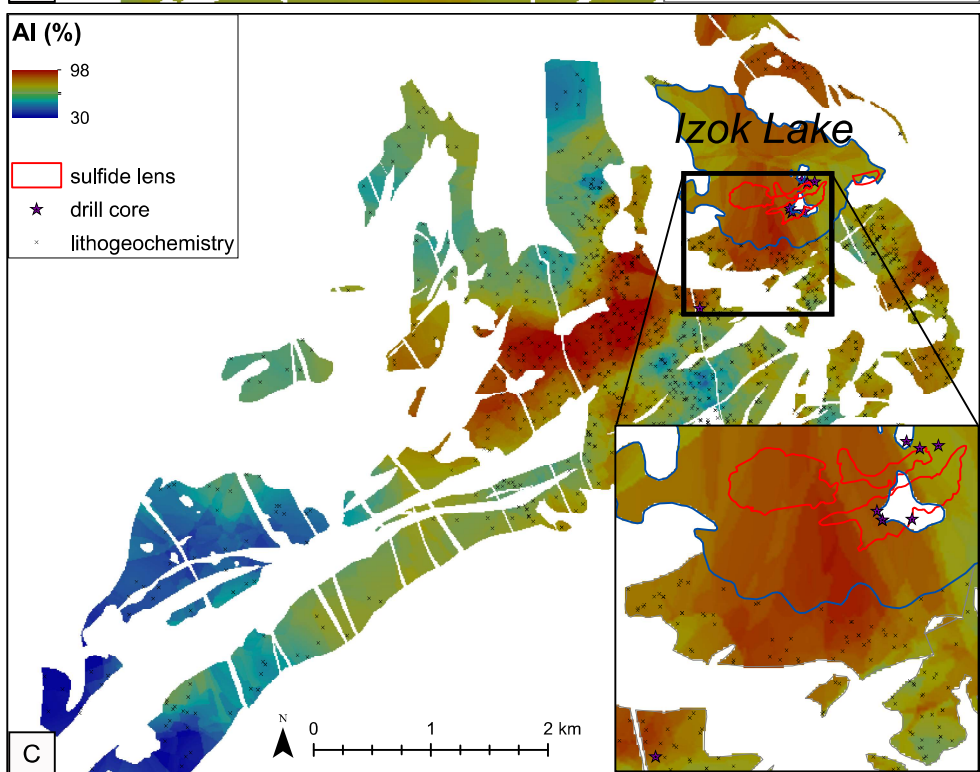
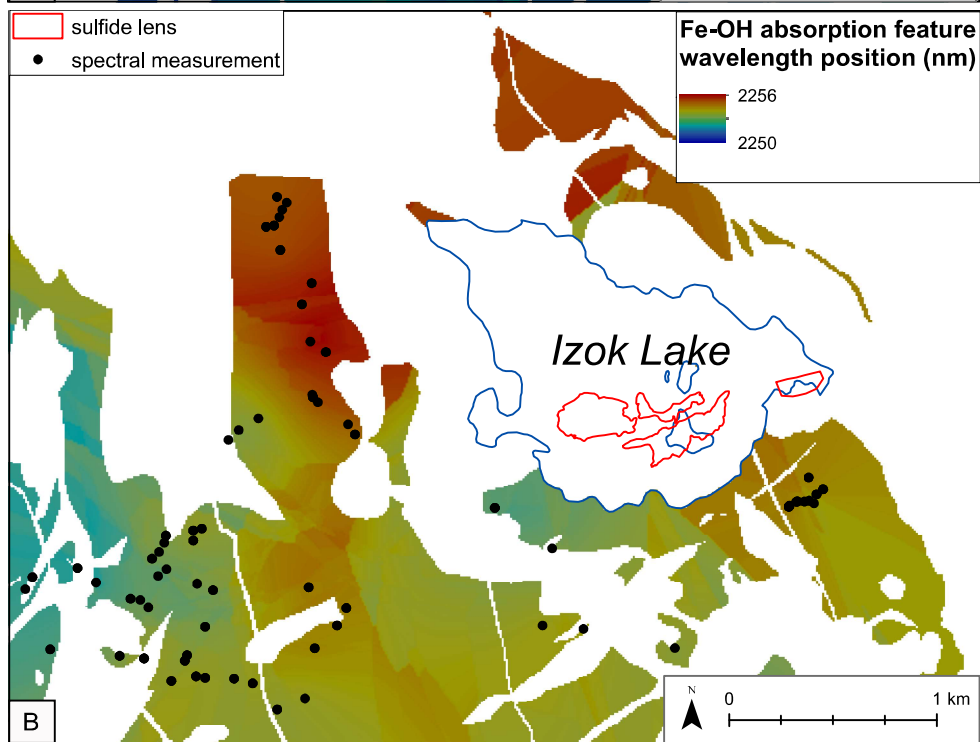
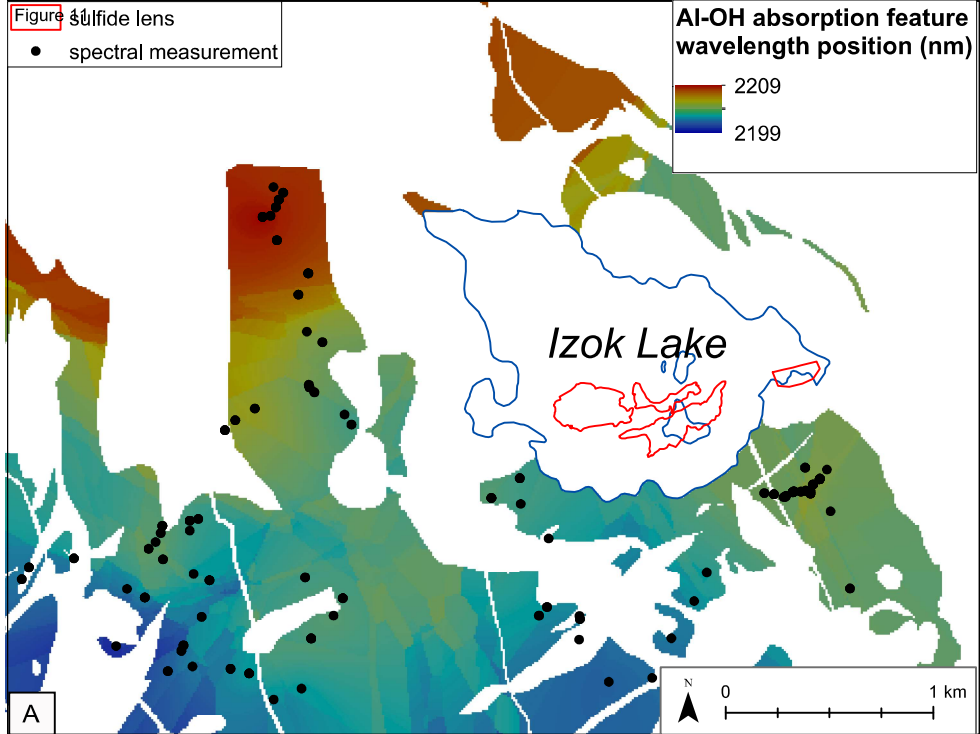


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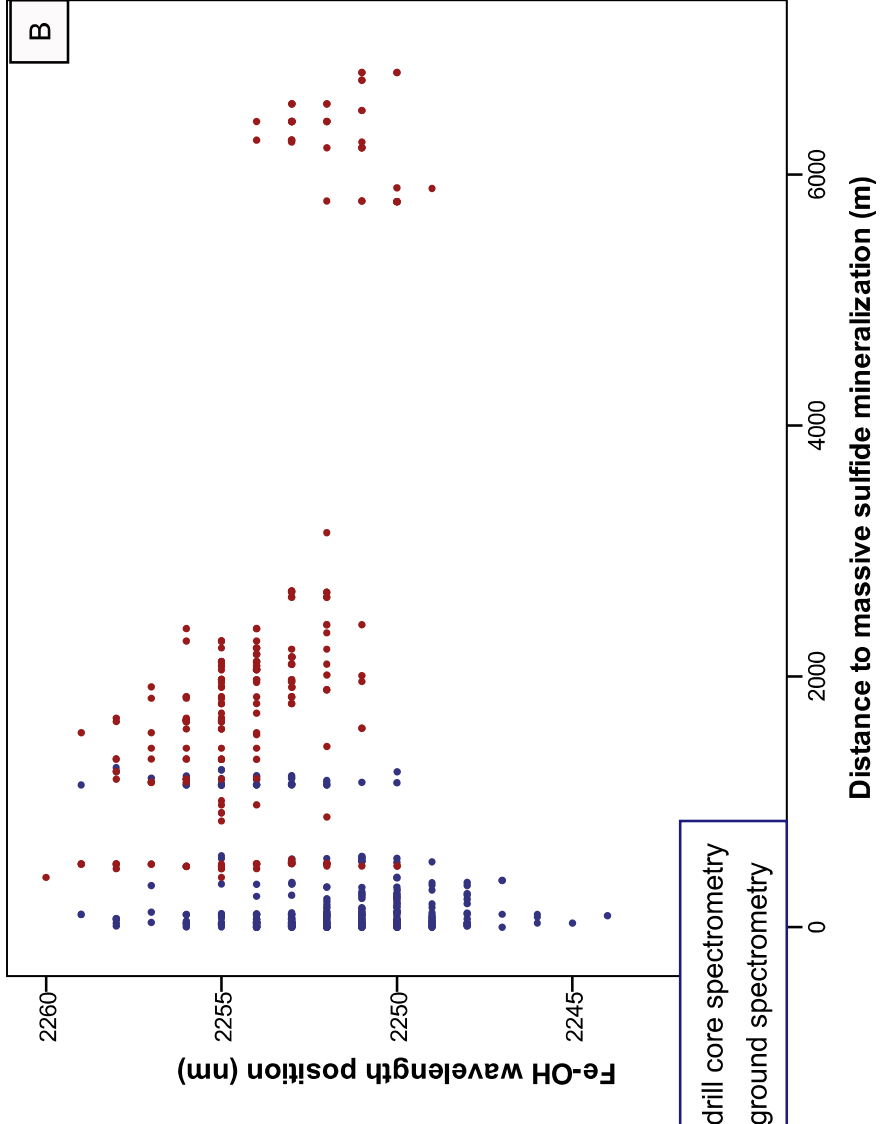
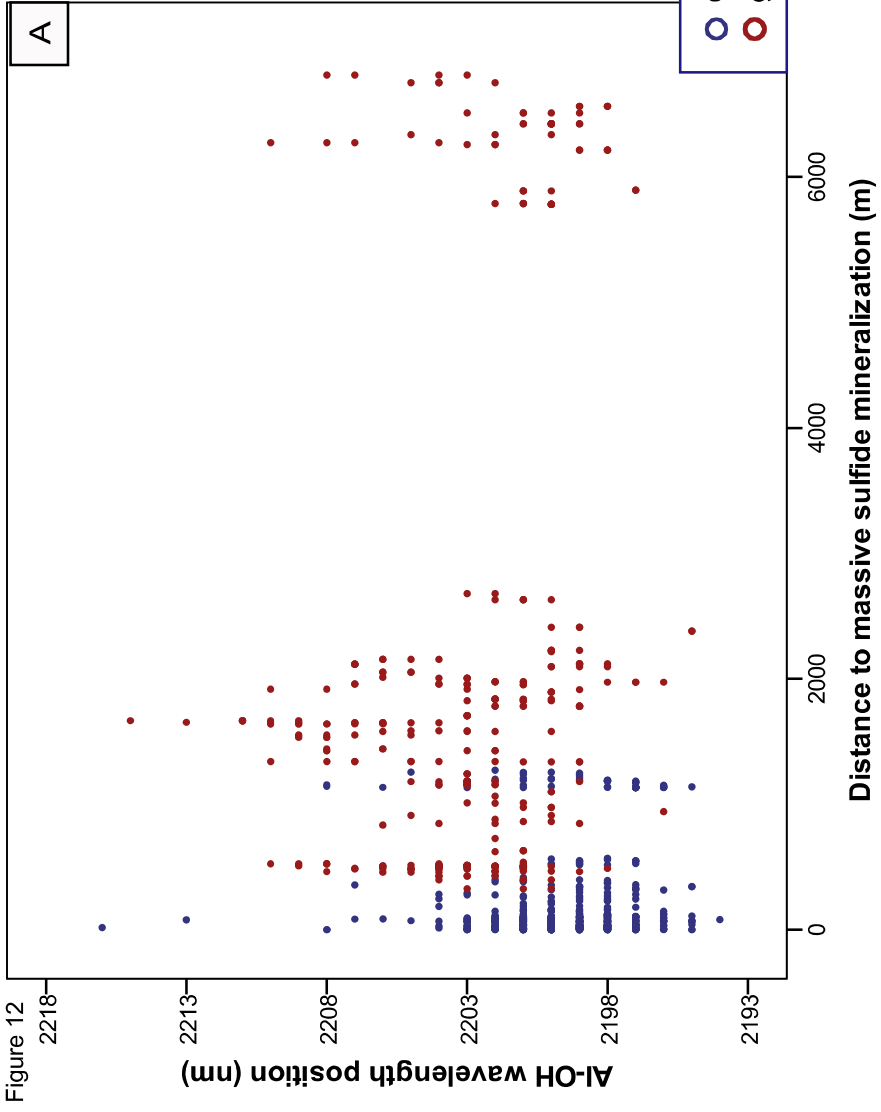


Table 1

	Min, nm	Max, nm	Median, nm	Mode, nm	Range, nm	<i>n</i>
Al-OH, ground spectrometry	2195	2215	2203	2203	21	357
Al-OH, drill core spectrometry	2194	2216	2199	2199	22	585
Fe-OH, ground spectrometry	2249	2260	2254	2255	12	264
Fe-OH, drill core spectrometry	2244	2259	2252	2250	15	344