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1 Actively forming Kuroko-type volcanic-hosted massive sulfide
2 (VHMS) mineralization at Iheya North, Okinawa Trough, Japan

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23 **ABSTRACT**

24 Modern seafloor hydrothermal systems provide important insights into the formation and
25 discovery of ancient volcanic-hosted massive sulfide (VHMS) deposits. In 2010, Integrated
26 Ocean Drilling Program (IODP) Expedition 331 drilled five sites in the Iheya North
27 hydrothermal field in the middle Okinawa Trough, back-arc basin, Japan. Hydrothermal
28 alteration and sulfide mineralization is hosted in a geologically complex, mixed sequence of
29 coarse, pumiceous, volcanoclastic and fine hemipelagic sediments, overlying a dacitic to
30 rhyolitic volcanic substrate. At site C0016, located adjacent to the foot of the actively venting
31 North Big Chimney massive sulfide mound, massive sphalerite-(pyrite-chalcopyrite±galena)-
32 rich sulfides were intersected (to 30.2% Zn, 12.3% Pb, 2.68% Cu, 33.1 ppm Ag and 0.07 ppm
33 Au) that strongly resemble the black ore of the Miocene-age Kuroko deposits of Japan. Sulfide
34 mineralization shows clear evidence of formation through a combination of surface detrital and
35 subsurface chemical processes, with at least some sphalerite precipitating into void space in
36 the rock. Volcanic rocks beneath massive sulfides exhibit quartz-muscovite/illite and quartz-
37 Mg-chlorite alteration reminiscent of VHMS proximal footwall alteration associated with
38 Kuroko-type deposits, characterised by increasing MgO, Fe/Zn and Cu/Zn with depth.
39 Recovered felsic footwall rocks are of FII to FIII affinity with well-developed negative Eu
40 anomalies, consistent with VHMS-hosting felsic rocks in Phanerozoic ensialic arc/back-arc
41 settings worldwide.

42 Site C0013, ~100 m east of North Big Chimney, represents a likely location of recent
43 high temperature discharge, preserved as surficial coarse-grained sulfidic sediments (43.2%
44 Zn, 4.4% Pb, 5.4% Cu, 42 ppm Ag and 0.02 ppm Au) containing high concentrations of As,
45 Cd, Mo, Sb, and W. Near surface hydrothermal alteration is dominated by kaolinite and
46 muscovite with locally abundant native sulfur, indicative of acidic hydrothermal fluids.
47 Alteration grades to Mg-chlorite dominated assemblages at depths of >5 mbsf (metres below
48 sea floor). Late coarse-grained anhydrite veining overprints earlier alteration and is interpreted
49 to have precipitated from down welling seawater as hydrothermal activity waned. At site
50 C0014, ~350 m farther east, hydrothermal assemblages are characterized by
51 illite/montmorillonite, with Mg-chlorite present at depths below ~30 mbsf. Recovered
52 lithologies from distal, recharge site C0017 are unaltered, with low MgO, Fe₂O₃ and base metal
53 concentrations.

54 Mineralization and alteration assemblages are consistent with the Iheya North system
55 representing a modern analogue for Kuroko-type VHMS mineralization. Fluid flow is focussed
56 laterally along pumiceous volcanoclastic strata (compartmentalized between impermeable

57 hemipelagic sediments), and vertically along faults. The abundance of Fe-poor sphalerite and
58 Mg-rich chlorite (clinochlore/penninite) is consistent with the lower Fe budget, temperature
59 and higher oxidation state of felsic volcanic-hosted hydrothermal systems worldwide compared
60 to Mid Ocean Ridge black smoker systems.

61

62 **1. INTRODUCTION**

63 Over the past 25 years our understanding of seafloor hydrothermal fields has been
64 revolutionized by the research activity of the Deep Sea Drilling Project (1968-1983), Ocean
65 Drilling Program (ODP; 1985-2003) and Integrated Ocean Drilling Program (IODP; 2004-
66 2013). In particular, the research findings of expeditions to the Trans-Atlantic Geotraverse
67 [TAG], Manus Basin and Juan de Fuca Ridge have provided important insights into the nature
68 of fluid rock interaction and fluid mixing in the development of seafloor hydrothermal systems
69 in different tectonic settings (Barriga et al., 2000; Fouquet et al., 1997; Humphris et al., 1995,
70 1998; Lackschewitz et al., 2004; Mottl et al., 1994; Paulick and Bach, 2006; Roberts et al.,
71 2003; Teagle et al., 1998; Webber et al., 2011). This work has been complemented by countless
72 other scientific and industry-funded cruises to hydrothermal fields worldwide (Connelly et al.,
73 2012; de Ronde et al., 2005; Glasby et al., 2008; Hannington et al., 2005 and references therein;
74 Ishibashi et al., 2015; McConachy et al., 2005; Petersen et al., 2014; Yeats et al., 2014; Webber
75 et al., 2015).

76 Volcanic-hosted massive sulfide (VHMS) deposits represent significant resources of
77 base and precious metals in a number of Archean Cratons and Phanerozoic volcanic arcs/back-
78 arc basins worldwide (Barrie et al., 1993; Galley et al., 1993; Herrington et al., 2005; Hollis et
79 al., 2015; van Staal, 2007). VHMS mineralization occurs as syngenetic stratiform
80 accumulations of metal sulfides that precipitated at or below the seafloor, often underlain by
81 discordant zones of stringer and disseminated sulfides (Franklin et al., 2005). The size,
82 metallogeny and grade of a deposit that forms within a volcanic succession is dependent on its
83 tectonic setting, host lithologies and any magmatic input (Barrie and Hannington, 1999; de
84 Ronde et al., 2003, 2005; Piercey, 2011). Therefore, analogues for specific types of VHMS
85 deposits are represented by different modern hydrothermal systems (e.g. Glasby et al., 2008;
86 Hannington et al., 1998; Ishibashi and Urabe, 1995; Lüders et al., 2001; Webber et al., 2015).
87 Active systems provide important insights into the formation of ancient VHMS deposits,
88 allowing fluids to be directly sampled and mineralization to be studied without the effects of
89 subsequent deformation and metamorphism.

90 Hydrothermal vents were first discovered at the Iheya North Knoll in 1995 (**Fig. 1**), and
91 this location has since become the most intensely investigated of all hydrothermal fields within
92 the middle Okinawa Trough, Japan (Aoyama et al., 2014; Chiba et al., 1996; Glasby and Notsu,
93 2003; Ishibashi et al., 2015; Kawagucci et al., 2013; Masaki et al., 2011; Shao et al., 2015;
94 Takai et al., 2011; Tsuji et al., 2012). During 2010, IODP Expedition 331 drilled five sites at
95 Iheya North. Blocks of massive and semi-massive sphalerite-(pyrite-chalcopyrite±galena)-rich
96 sulfides, that strongly resembled the ‘black ore’ of the Kuroko VHMS deposits of Japan, were
97 recovered from immediately beneath the modern seafloor (Takai et al., 2011). Samples
98 collected during IODP Expedition 331 provide a unique opportunity to understand
99 hydrothermal fluid flow and mineralization processes associated with an actively forming
100 Kuroko-style VHMS deposit in an ensialic back-arc setting. We present shipboard logging and
101 X-ray diffraction data, along with new petrographic, whole rock geochemical, mineral-
102 chemical and microstructural work on recovered lithologies.

103

104 **2. REGIONAL GEOLOGY**

105

106 The Okinawa Trough, Japan, extends for ~1200 km between the Ryukyu arc-trench system and
107 the Eurasian continent, and is regarded as an incipient intra-continental back-arc basin (Lee et
108 al., 1980; Letouzey and Kimura, 1986; Shinjo and Kato, 2000; **Fig. 1a**). It is still considered to
109 be in an early rifting stage prior to seafloor spreading (Shinjo and Kato, 2000), with a minimal
110 crustal thickness of ~8 km at its southernmost end (Klingelhoefer et al., 2009). Arc volcanism
111 predominantly occurs in the northern part of the Ryukyu Arc and in the middle and southern
112 parts of the Okinawa Trough (Shinjo et al., 2000). The transition from arc to back-arc volcanism
113 in the middle Okinawa Trough has been termed the VAMP area (Sibuet et al., 1987), with
114 present day activity in the middle and southern Okinawa Trough associated with *en echelon*
115 intra-trough grabens (Glasby and Notsu, 2003; Shinjo and Kato, 2000). The VAMP area is
116 coincident with the subduction of the WNW-ENE trending Daito Ridge (Sibuet et al., 1998;
117 **Fig. 1a**). A rift-related bimodal basaltic-rhyolitic suite, accompanied by minor intermediate
118 rocks, characterizes the middle Okinawa Trough (Ishizuka et al., 1990; Shinjo et al., 1999;
119 Shinjo and Kato, 2000; Zeng et al., 2010). Thick (~1000 m) sequences of organic-rich
120 terrigenous sediments sourced from the Yangtze and Yellow rivers overlie basement lithologies
121 (Takai et al., 2011). Due to volcanism and rifting, the VAMP area is characterized by
122 anomalously high heat flow (Yamano et al., 1986) and contains several hydrothermal fields
123 (Glasby and Notsu, 2003; Ishibashi et al., 2015). From north to south these include the Minami-

124 Ensei Knoll, Iheya North Knoll (**Fig. 1b-c**), Yoron Hole, CLAM site of the Iheya Ridge, the
125 JADE and Hakueri hydrothermal fields of the Izena Hole (also known as the Izena Cauldron)
126 (Ishibashi et al., 2015).

127

128 **3. HYDROTHERMAL ACTIVITY AT IHEYA NORTH**

129 The Iheya North Knoll hydrothermal field is located at ~1000 mbsl (metres below sea level) in
130 the middle Okinawa Trough (**Fig. 1b**). Approximately ten hydrothermal mounds aligned north
131 to south are associated with active venting and sulfide/sulfate mineralization (Ishibashi et al.,
132 2015; **Fig. 1c**). The main sulfide assemblages identified from chimney samples are dominated
133 by sphalerite, wurtzite [(Zn,Fe)S], galena, pyrite, marcasite [FeS₂] and chalcopyrite (Ueno et
134 al., 2003). Some samples also include arsenopyrite, tetrahedrite [Cu₁₂(As,Sb)₄S₁₃], tennantite
135 [Cu₃(As,Sb)₄], freslebenite [PbAgSbS₃], native arsenic, realgar [AsS] and/or covellite [CuS]
136 (Ueno et al., 2003). Gangue mineralogy is characterized by barite, gypsum, anhydrite, quartz,
137 rhodochrosite [MnCO₃], and/or native sulfur (Chiba, 1997; Ueno et al., 2003).

138 Recent studies of hydrothermal fluid chemistry at Iheya North indicate the presence of
139 high concentrations of CO₂, CH₄, NH₄⁺, B, and I, and high alkalinity, consistent with some
140 interaction between hydrothermal fluids and organic matter (Kawagucci et al., 2011), although
141 this is less pronounced than at the JADE and CLAM sites. High concentrations of K, Rb, Cs
142 and Li in interstitial water are consistent with interaction between hydrothermal fluids and
143 felsic footwall lithologies (Takai et al., 2011). North Big Chimney (NBC) marks the centre of
144 the hydrothermal field and is associated with the vigorous venting of clear fluid of 311 °C at
145 971 mbsl (Nakagawa et al., 2005; **Fig. 1c**). The chimney is 20 m high and 6 m in diameter
146 (Takai et al., 2011). Chloride concentrations lower than seawater suggest phase separation at
147 depth (Chiba et al., 1996).

148 During IODP Expedition 331, five sites were drilled at Iheya North (C0013 to C0017;
149 **Figs. 1b-c, 2**). Hydrothermal alteration and sulfide mineralization is hosted in a geologically
150 complex mixed sequence of coarse pumiceous, volcanoclastic, and fine, hemipelagic,
151 sediments, overlying dacitic to rhyolitic volcanic substrate. Site descriptions (section 5) are
152 based on shipboard data (detailed in Takai et al., 2011, 2012) and post-cruise research. Post-
153 drilling changes in fluid flow and chemistry at sites C0014 and C0016 are detailed in
154 Kawagucci et al. (2013).

155

156 **4. METHODS**

157 During IODP Expedition 331, approximately 325 powdered whole rock samples were analysed
158 by X-ray diffraction (XRD) to characterize the main alteration minerals present across the
159 Iheya North hydrothermal field. Samples of interest were also examined using polished thin
160 sections and scanning-electron microscopy (SEM). Post-cruise research focussed primarily on
161 the whole rock geochemical, mineral-chemical and microstructural characterization of
162 recovered lithologies.

163 Shipboard SEM analysis was conducted using a GEOL 5770 SEM equipped with
164 backscatter and energy dispersive spectroscopy detectors operating at an accelerating voltage
165 of 15 kV. Samples for XRD were systematically analysed from every 1.5 m section of core
166 obtained during hydraulic piston coring and extended shoe coring, and for every 0.75 m core
167 section for Baker Hughes INTEQ (BHI) cores. Additional samples were analysed as deemed
168 appropriate. Samples were freeze-dried prior to powdering in a ball mill. Powders were
169 analysed on a PANalytical CubiX PRO (PW3800) diffractometer. Further detail is provided by
170 Takai et al. (2011).

171 For post-cruise research, samples from site C0016 were imaged using both secondary
172 electrons (SE) and backscattered electrons (BSE) in a Zeiss Ultraplus field emission gun (FEG)
173 SEM at the CSIRO facilities, Kensington, Western Australia, operated at a chamber pressure
174 of 2×10^{-6} mbar and an accelerating voltage of 20 kV.

175 Twenty-five specimens (samples IN01-IN25) representative from each of the five sites
176 (C0013 to C0017) were submitted for whole-rock geochemical analysis to Bureau Veritas
177 Geoanalytical Laboratory, Canning Vale, Western Australia, to characterize the geochemistry
178 of the host sequence and the intensity of hydrothermal alteration. Samples were predominantly
179 composed of variably hydrothermally altered and/or mineralized, felsic pumiceous
180 volcanoclastic sediments and basement rocks, with one sample of hemipelagic clay (IN08;
181 **Table 1**). Major element concentrations (plus S, Cu, Pb, Zn, Ba) were determined on fused
182 glass beads (using a 12:22 flux ratio and 4% lithium nitrate) by X-ray Fluorescence (XRF).
183 Trace elements were determined on the same fused discs by laser ablation inductively coupled
184 plasma mass spectrometry (LA-ICP-MS). Gold, Pt and Pd were analysed by lead-collection
185 fire assay with element concentrations quantified by ICP-MS. Carbon concentrations were
186 measured by total combustion using a Carbon-Sulfur Analyser. Loss on ignition (LOI) was
187 calculated using a robotic thermogravimetric system set to 110 and 1000 °C. Sulfate
188 concentrations were determined by digestion with hydrochloric acid and evaporation to dryness
189 twice before a final leach in hydrochloric acid. Results are presented in **Table 1**.

190 Accuracy (% RD) was monitored using mineralized (to 34.6% Zn, 13.2% Pb, 3.1% Cu)
191 and unmineralized international standards. Precision (% RSD) was monitored by repeat
192 analysis of samples from Iheya North. Accuracy and precision can be considered good to
193 excellent after Jenner (1996) for all elements determined by XRF, except for Al₂O₃, MgO, MnO
194 and P₂O₅ in some instances where concentrations were near detection (i.e. 0.01 wt.%).
195 Accuracy for elements determined by LA-ICP-MS was good to excellent (<10% RD) except
196 for As at low concentrations, and Cd. Precision was also poor (>10% RSD) for Cd and
197 consequently these data should be treated with caution. Accuracy and precision for Au, Pt, Pd
198 and C were good to excellent for all standards used after Jenner (1996).

199 Mineral compositions of chlorite and white mica from site C0016B were determined at
200 the Natural History Museum, London, on a Cameca SX-50 Electron Microprobe (EMP)
201 equipped with a wavelength dispersive system (WDS). Operating conditions were at 20 keV
202 and 20 nA. Counting times ranged from 10 to 50 s for spot analysis. Chlorite mineral formulae
203 were calculated using the worksheets of Tindle (2015).

204 For EBSD analysis, round samples (25 mm in diameter) were polished using colloidal
205 silica for 5 hours on a Buehler Vibromat 1, and for 1 hour on the Leica Microsystems EM
206 RES101 instrument (after Halfpenny, 2010; Halfpenny et al., 2013). Full crystallographic
207 orientation data were obtained from automatically indexed Kikuchi diffraction patterns
208 collected using a Bruker e-flash detector fitted to a Zeiss Ultraplus FEG SEM at the CSIRO
209 facilities, Kensington. Coincident EDS data were collected using a Bruker XFlash 5030
210 detector. The SEM was operated using an accelerating voltage of 20 kV and a 120 µm aperture,
211 which in high current mode produced a beam current of 12.1 nA. The EBSD data were collected
212 using the Bruker Quantax Espirit 1.9 software, using a resolution of 200 x 150 pixels, a 12 ms
213 exposure time and a step size between measurements of 1.7 µm. If the pattern quality was poor
214 then the software was unable to find the correct crystallographic solution and the point was not
215 indexed. Non-indexed points are common in areas of poor surface quality, on grain boundaries,
216 cracks, void space and where the surface is contaminated. Unfortunately, not all of the sample
217 was prepared well enough for EBSD analysis, due to the various hardnesses of the constituent
218 phases, this has led to areas of non-indexing. The EBSD data were post-processed using Oxford
219 Instruments Channel 5 software to remove mis-indexed points and interpolate non-indexed
220 points (Prior et al., 2009; Halfpenny, 2010). The corrected data files were then used to generate
221 the maps presented.

222

223 5. RESULTS

224 **5.1 Hydrothermal alteration and mineralization at Iheya North**

225 **Site C0016 (North Big Chimney)**

226 Site C0016 is located at North Big Chimney (**Fig. 1c**). Although hole C0016A at the
227 summit of NBC failed to recover core, a variety of lithologies were obtained from hole C0016B
228 drilled at its base (**Fig. 3f-j**). From 45 m of drilling at C0016B, only 2.1 m of core was recovered
229 (4.7% recovery). Between 0 and 9 mbsf, blocks of massive and semi-massive sphalerite-rich
230 sulfide were recovered (**Fig. 3f–1 to 3**), along with a 15cm section of silicified and mineralized
231 volcanic rock altered to illite/muscovite clay (confirmed by XRD; **Fig. 3g**). Recovered sections
232 of clastic-textured massive/semi-massive sulfide (**Fig. 3f – blocks 1 to 3**) are characterized by
233 rounded 1-5 mm fragments of clay-altered and hard siliceous volcanic rock, cemented by a
234 matrix of sphalerite (~60%), pyrite (~15%) and quartz, with lesser galena and chalcopyrite
235 (**Figs. 3f; 4a**). Silicification is variable, with the uppermost block containing coarser grained
236 (2-3 mm) sphalerite-pyrite-galena-(chalcopyrite) associated with late anhydrite veining (**Fig.**
237 **3f**). The second section of core obtained from 9-27 mbsf (31 cm total recovery) included two
238 pieces of hydrothermally altered, silicified and mineralized volcanic rock with clastic textures,
239 found either side of a 12 cm piece of coarsely crystalline white acicular anhydrite cut by thin
240 veins of sphalerite-pyrite (**Fig. 3h - blocks 5-7**). The third section of core (from 27-45 mbsf)
241 comprised almost 1m of quartz-chlorite altered volcanic rock exhibiting stockwork veining of
242 quartz-chlorite-pyrite and late anhydrite (**Fig. 3i-j – blocks 8-9**). XRD analysis identified the
243 chlorite as clinocllore (Mg-chlorite) – subsequently confirmed by electron microprobe
244 analysis. Two generations of veining have been recognized: (i) early sugary, 2-3 cm wide
245 quartz-chlorite-pyrite veins which form a dark network; and (ii) late vuggy pyrite-anhydrite
246 veins, from hairline to 1 cm in thickness.

247

248 **Site C0013 (a site of recent hydrothermal activity):**

249 Site C0013, located ~100 m east of NBC (**Fig. 1c**), is characterized by numerous areas
250 of patchy diffuse flow and chemosynthetic animal colonies, where the seafloor is covered by
251 pumiceous breccias and barite-anhydrite-carbonate crusts, with hemipelagic sediment in
252 depressions (Takai et al., 2012). Site C0013 occurs in a zone of relatively high heat flow,
253 estimated before drilling to be ~3 °C/m (Takai et al., 2012). Eight holes were sited to a
254 maximum depth of 54.3 mbsf (hole C0013E; **Fig. 2a**). Melting of plastic core liners severely
255 limited drilling to depth, with core liners starting to soften and deform at 12 mbsf and 82 °C.
256 Following capping and casing of the deepest hole, strong hydrothermal discharge was noted by
257 ROV from the casing pipe, with thermoseal temperature-sensitive strips indicating

258 temperatures >250 °C. Two days later blackish water was discharging directly from the hole
259 beneath the guide base.

260 Eight holes were drilled at site C0013 (A to H). Due to their close proximity, core from
261 these holes exhibit a broadly consistent vertical distribution (**Fig. 2a**). From 0 to ~4 mbsf
262 moderately hydrothermally altered sulfidic sediment was recovered from several holes,
263 characterized by detrital sulfide (sphalerite-pyrite-covellite), sulfate (anhydrite-barite),
264 kaolinite-muscovite (confirmed by XRD) and locally, native sulfur. Native sulfur occurs as
265 veinlets, cements (**Fig. 3c**), and coatings in voids (**Fig. 3d**). Rapid lateral and vertical variations
266 in the composition and grain size of the sulfidic sediments suggest they originated locally,
267 probably from the breakdown of nearby hydrothermal mounds and/or chimney structures. Thin
268 horizons (~10 cm) can exceed 50% sulfide (e.g. C0013E). Covellite is much less abundant than
269 sphalerite and pyrite (**Fig. 4e-f**), and framboidal pyrite was also observed (**Fig. 4g-h**). The
270 sediment is commonly poorly sorted, medium- to coarse-grained, and contains anhydrite
271 crystal fragments and lesser barite. Anhydrite shows evidence for incipient dissolution and
272 replacement by gypsum (**Fig. 4i**). SEM analysis also identified galena and tetrahedrite-
273 tennantite intergrowths with sphalerite, and an unknown silver arsenide phase associated with
274 opaline silica (**Fig. 4j**). Underlying pale grey to white sediments (from ~4 to ~5.5 mbsf) are
275 characterized by an assemblage of kaolinite-muscovite-anhydrite, with trace fine-grained
276 disseminated pyrite.

277 From ~5.5 to ~26 mbsf, site C0013 is dominated by pale bluish-grey to white mottled
278 hydrothermal clay. Mg-chlorite (clinochlore) was identified as the main alteration mineral by
279 XRD, and occurs with coarse (4-5 cm) rounded nodules of brecciated, drilling-disturbed veins
280 of white, opaque, anhydrite ± dolomite ± talc ± calcite ± quartz ± sphalerite ± pyrite (**Fig. 3a**),
281 which show evidence for erosion. Fine-grained disseminated pyrite and sphalerite are present
282 in low abundances (<1%), and rare irregular veins of anhydrite-sulfide and quartz-sulfide cut
283 the Mg-chlorite altered sediments.

284 Quartz and Mg-chlorite altered volcanic basement was recovered from below ~26 mbsf
285 in holes C0013D and C0013E (**Fig. 3b**). The rocks are unique in their hardness and distinct
286 quartz stockwork veining (most of which are barren of sulfides). Petrographic analysis has
287 revealed that ~40% of the rock is composed of volcanic glass, with the remainder devitrified
288 and replaced by quartz-chlorite and minor biotite. Rare mineralized quartz veins contain
289 sphalerite, pyrite, covellite, and in one interval, fine intergrowths of native copper and organic
290 carbon (**Fig. 3e**). Overlapping the zones of kaolinite and Mg-chlorite alteration, abundant 1-2
291 cm euhedral anhydrite crystals occur in the core (**Fig. 2a**).

292

293 **Site C0014 (distal alteration and mineralization):**

294 Site C0014 is located 350 m east of site C0013 (**Fig. 1c**) and
295 ~450 m from the NBC hydrothermal mound. A distinct colony of clams and a rocky seafloor
296 characterize the site (Takai et al., 2012). Seven holes were drilled to a maximum depth of 136.7
297 mbsf (hole C0014G; **Fig. 2b**). Compared to the two sites described above, site C0014 is
298 dominated by lower temperature alteration assemblages and is only weakly mineralized (**Fig.**
299 **2b**). From 0 to 8-10 mbsf, hemipelagic ooze and pumiceous volcanoclastic sediments exhibit
300 little evidence of hydrothermal alteration (except weak oxidation in holes C0014F and
301 C0014G), with quartz, muscovite and calcite the most abundant phases determined by XRD.
302 Sulfides commonly occur as fine-grained disseminated and framboidal pyrite grains. An
303 underlying zone of pale grey mottled clay is characterized dominated by quartz-muscovite and
304 alteration minerals illite-montmorillonite with lesser kaolinite.

305 Below ~25-30 mbsf (to the maximum depth of 136.7m; hole C0014G) Mg-chlorite
306 becomes an important alteration phase irrespective of lithology (**Fig. 2b**). Unlike at site C0013,
307 detrital muscovite and quartz persist. Anhydrite is present, but is significantly less abundant
308 with only mm-scale irregular veinlets, with halite below 57 mbsf. After casing and capping,
309 diffuse hydrothermal fluids were observed by ROV, discharging from the seafloor through the
310 space between the wall of the hole and the casing pipe (Takai et al., 2012). Thermoseal strips
311 indicated the diffusing fluids were >240 °C (Takai et al., 2012).

312 In the illite-montmorillonite and Mg-chlorite zones little sulfide mineralization was
313 observed. Pyrite occurs in trace amounts disseminated throughout the core (**Fig. 4k**) and very
314 rarely as coarser veins (with sphalerite-galena-chalcopyrite; **Fig. 4l**). XRD analysis also
315 identified covellite in some sections of core, although none was identified under binocular
316 microscope.

317

318 **Site C0015**

319 Site C0015 is located ~600 m northwest of NBC (**Fig. 1b**). Hole C0015C was the deepest
320 at the site, drilled to only 9.4 mbsf. No hydrothermal alteration was observed. Evidence for
321 weak oxidation in the uppermost layers included orange to brown iron oxide staining on pumice
322 fragments. The area is characterized by a low surface temperature gradient of 1 °C/m (Takai et
323 al., 2012). Together with the presence of iron oxides and characteristic major element
324 compositions of interstitial water samples close to those of seawater, the relatively low

325 temperature gradient suggests that the site represents a background site, unrelated to the
326 hydrothermal system (Takai et al., 2012).

327

328 **Site C0017 (a distal recharge site)**

329 Site C0017 is located ~1.6 km east of North Big Chimney (**Fig. 1b**) and is characterized
330 by extremely low heat flow, with a surface thermal gradient an order of magnitude lower than
331 the average non-hydrothermal, trough-filling sediments of the middle Okinawa Trough (Takai
332 et al., 2012). Hole C0017D was the deepest (150.6 mbsf) across all sites during IODP
333 Expedition 331, recording a temperature of only 90 ± 5 °C at the base of the hole. Sediment
334 types encountered were homogeneous hemipelagic mud, pumiceous sediment, and
335 volcanoclastic-pumiceous breccia and mixed sand with erosional bases. No alteration was
336 observed except weak to moderate oxidation, which was reflected in a yellow to brownish
337 colouration in sediments, orange to brown iron oxide staining on pumice fragments, and 1-2
338 mm botryoidal aggregates of Fe-Si oxyhydroxides. Geochemical results, including reversals in
339 alkalinity, ammonium and phosphate pore water concentrations, combined with downhole
340 temperature measurements, indicate that this oxidized zone resulted from cold seawater influx
341 (Takai et al., 2011, 2012). Notably, sulfides were absent at shallow depths, with trace pyrite
342 consistently present below 94 mbsf.

343

344 **5.2 Texture analysis**

345 EBSD analysis was performed as it reveals information on crystal orientation, grain boundaries
346 and phase distribution (Prior et al., 1999). EBSD data may be used to understand the controlling
347 mineralization processes and determine any subsequent modification. Three samples were
348 analysed, all from site C0016 - two samples of sphalerite-rich semi-massive sulfides (16B-2,
349 16B-3; **Fig. 3f**- blocks 2 and 3 respectively) and a quartz-chlorite altered volcanic rock with
350 stringer and disseminated sulfides (16B-9; **Fig. 3** – block 9). For both samples of semi-massive
351 sulfide, two areas were analysed (denoted by A and B).

352 For EBSD analysis, the interface between two grains is termed the grain boundary.
353 Where the minimum misorientation angle is $>10^\circ$ these are termed high angle grain boundaries
354 (HAGBs) (Halfpenny et al., 2012). Low angle grain boundaries (LAGBs) or sub-grain
355 boundaries have misorientation angles of $<10^\circ$ and are composed of an array of dislocations
356 (Halfpenny et al., 2006; Trimby et al., 1998). LAGBs represent intra-grain variations due to
357 modification of the grains post-mineralization. There are some special orientations where there
358 is a relationship between the lattices on either side of a boundary. One such structure is a

359 coincident site lattice (CSL), which describes the number of atoms that are shared on the
360 boundary between the grains. For coherent twin boundaries $\Sigma 3$, one in three atoms is shared.
361 If the crystallographic orientations of an individual phase are fully random, then there is no
362 distinct texture. However, in some geological systems grains can align due to mineralization
363 and deformation processes producing a crystallographic preferred orientation (CPO)
364 (Halfpenny, 2011; Halfpenny and Prior, 2009). If a CPO is identified it may be used to interpret
365 the underlying processes which caused grain alignment (Fougerouse et al., 2016a; Fougerouse
366 et al., 2016b).

367 Sample 16B-2 is dominated by sphalerite, with lesser pyrite, chalcopyrite, quartz,
368 chlorite and graphite. Two areas within this sample were analysed - 16B-2A (**Fig. 5a-c**) and
369 16B-2B (**Fig. 5d-f**). In the prior, sphalerite exhibits a variable grain size with the grain diameter
370 varying from 10-20 μm . The sphalerite exhibits $\Sigma 3$ ($60^\circ \pm 5^\circ$ about $\langle 111 \rangle$) CSLs (red lines) and
371 very little substructure development as there are few LAGBs (white lines) (**Fig. 5c**). None of
372 the indexed phases in area 16B-2A exhibit a CPO. In area 16B-2B, the sphalerite exhibits a
373 coarser grain size with a maximum of grain diameter of 47 μm . Sphalerite grains contain
374 multiple $\Sigma 3$ CSL's (**Fig. 5f**). All phases measured show little to no internal deformation (no
375 LAGBs) and no CPO has been developed.

376 Sample 16B-3 contains sphalerite as the main phase with quartz, chlorite, pyrite,
377 chalcopyrite, anhydrite and minor amounts of graphite (**Fig. 5g-l**). In area 16B-3A, the
378 sphalerite is coarse grained, contains $\Sigma 3$ CSLs and some of the sphalerite grains exhibit lobate
379 grain boundaries (**Fig. 5i**). In area 16B-3B, the sphalerite is extremely coarse grained and
380 exhibits lobate grain boundaries (**Fig. 5j & k**). There is a small area which contains finer
381 grained sphalerite and pyrite crystals (**Fig. 5l**). None of the indexed phases in sample 16B-3
382 exhibit a CPO or internal deformation (**Fig. 5l**).

383 Sample 16B-9 is from a pyrite vein and the mineralogy is dominantly pyrite and quartz
384 with some chlorite (**Fig. 5m & n**). The pyrite exhibits a bimodal grain size distribution between
385 coarse ($>40 \mu\text{m}$ in diameter) and fine grains ($<40 \mu\text{m}$ in diameter). The quartz crystals range
386 from euhedral to anhedral, but all grains exhibit little to no internal deformation (**Fig. 5o**). No
387 CPO is observed.

388

389 **5.3. Whole rock geochemistry**

390 Massive sulfide from site C0016B (sample IN01) contains high concentrations of Zn
391 (30.2%), Pb (12.3%) and Cu (2.68%), and elevated Mo (35.4 ppm), Ag (33.1 ppm), Sb (25.6
392 ppm) and Au (0.07 ppm) with respect to unmineralized samples from Iheya North. Low

393 concentrations of lithophile elements, such as SiO₂ (4.9 wt.%), Al₂O₃ (0.21 wt.%), MgO (0.28
394 wt.%) and K₂O (0.11 wt.%), are consistent with large mass gains of Fe, S and base metals (see
395 following section). Underlying felsic rocks (**Fig. 6a**) from site C0016 contain significantly
396 lower levels of Fe, Zn, Cu, Pb, Sb, Mo, Ag and Au (**Table 1**). Increasing MgO, Cu/Zn and
397 Fe/Zn occur down hole in C0016B. MgO values are low (0.3 wt.%) in massive sulfides (IN01),
398 ~1.0 wt.% in underlying silicified volcanic rocks (IN02-IN04), and 5.2-5.8 wt.% in quartz-
399 chlorite altered rocks at depth (IN05-IN06). Quartz-chlorite altered rocks are also characterized
400 by much higher Fe/Zn (917-1044) and Cu/Zn ratios (0.5-0.6) than overlying lithologies (<6.0
401 Fe/Zn and <0.1 Cu/Zn). SiO₂, K₂O, sulfide and sulfate concentrations are erratic down hole
402 C0016B due to varying degrees of silicification, sulfide mineralization and anhydrite veining.
403 Na₂O concentrations are consistently ~0.1 wt.% throughout, indicative of extensive feldspar
404 destruction or an absence of albite in the rhyolitic precursor. On the Box Plot of Large et al.
405 (2001a; see figure caption for description), samples from C0016B plot on a chlorite-pyrite-
406 (sericite) trend, away from the least altered dacite field, characterized by high CCPI
407 (Carbonate-chlorite-pyrite Index) and Alteration Index values (**Fig. 6b**).

408 Samples from site C0013 are in many respects geochemically similar to those from site
409 C0016 (**Table 1**). A sample of coarse grained sulfidic sediment from C0013 (IN13) is
410 characterized by high Zn (43.2%), Fe₂O₃ (9.6%), Cu (5.4%), Pb (4.4%), As (1.5%), Ag (42
411 ppm), Cd (980 ppm) Sb (104 ppm) and Mo (59 ppm). This is consistent with the presence of
412 abundant coarse sphalerite (overgrown by pyrite), covellite (**Fig. 4e**) and chalcopyrite
413 identified under binocular microscope in near surface sulfidic sediments. Galena and sulfosalts,
414 including tetrahedrite-tennantite, were identified by SEM and are intergrown with sphalerite.
415 High concentrations of Zn (3.46%) and Cu (1.89%) also occur in samples with visible sulfide
416 veining at depth (e.g. sample IN16). SiO₂, K₂O, MgO, Fe₂O₃, Na₂O, S and base metal
417 concentrations are erratic throughout the sampled sections. Samples from C0013 with
418 significant anhydrite are characterized by high CCPI and low Alteration Index values near the
419 calcite mineral node of the Box Plot (**Fig. 6b**).

420 Zinc concentrations from the relatively distal site C0014 (to 0.01% Zn) are consistently
421 lower than at sites C0013 and C0016. Hydrothermal alteration at C0014 is dominated by quartz
422 and muscovite with minor kaolinite, illite/montmorillonite, and Mg-chlorite at depth. This is
423 reflected by varying concentrations of SiO₂, K₂O, Na₂O, CaO, MgO and Al₂O₃. Na₂O
424 concentrations are significantly higher (0.3-0.92 wt.%) than at proximal sites C0013 and
425 C0016. Iron and base metal concentrations are low in all samples (<4.47 wt.% Fe₂O₃ and
426 <0.02% Cu+Pb+Zn) due to the lack of sulfides. Discounting rare anhydrite-rich units, samples

427 from C0014 are characterized by high Alteration Index and moderate CCPI values, typical of
428 a distal sericite-chlorite-pyrite trend (Large et al., 2001a; **Fig. 6b**). At site C0014, Sb
429 concentrations reach a maximum of ~7.1 ppm, which are significantly lower than at proximal
430 sites C0016 and C0013.

431 Samples of felsic pumice and clay from sites C0015 and C0017 are characterized by
432 low MgO (0.37-0.62 wt.%), Fe₂O₃ (2.3-5.3 wt.%), LOI (<6 wt.%) and base metal
433 concentrations (<0.04% Cu+Pb+Zn). SiO₂ concentrations for pumice samples (67.8-69.4
434 wt.%) are typical of unaltered felsic rocks. All three samples analysed plot within the least
435 altered dacite and rhyolite fields on the Box Plot of Large et al. (2001a) (**Fig. 6b**), containing
436 low concentrations of Au, Ag, Bi, Cu, Mo, Pb, Sb, Te, Tl and Zn (**Table 1**).

437
438 **Immobile element geochemistry:** Most lithologies sampled from Iheya North are of felsic
439 composition (**Fig. 6a**), characterized by high Zr/TiO₂ ratios. Three clay-rich samples plot closer
440 to the intermediate field of Pearce (1996), along with massive sulfides from C0016B. These
441 include one sample of hemipelagic clay (IN08), and two samples dominated by
442 illite/montmorillonite (IN19, IN20). Felsic lithologies (both pumiceous volcanoclastic
443 sediments and coherent volcanic basement) are of FII to FIIIa affinity according to the VHMS
444 fertility diagrams of Lesher et al. (1986) and Hart et al. (2004) (**Fig. 6c**); and straddle the
445 volcanic arc and A-type fields of Pearce et al. (1984; **Fig. 6d**). This latter diagram is shown
446 simply to highlight the HFSE enrichment of the felsic rocks (after Piercey, 2011). With
447 increasing mass gain at sites C0016, C0013 and C0014, Nb and Y concentrations will be diluted
448 at a constant ratio as both elements are immobile (see arrow in **Fig. 6d**). All samples analysed
449 herein display prominent negative Eu anomalies on chondrite-normalized REE diagrams, with
450 slightly elevated LREE concentrations and flattish HREE profiles (**Fig. 6e**). Elevated HFSE
451 concentrations (e.g. **Fig. 6d**), and Sc/V and Sc/TiO₂ ratios, are consistent with felsic rocks
452 associated with VHMS deposits in ensialic settings worldwide (see Piercey, 2011; Hollis et al.
453 2015 and references therein).

454
455 **Mass change:** Mass change values were calculated for selected samples from across the Iheya
456 North hydrothermal field using the isocon method of Grant (1986, 2004). Isocons were fitted
457 using a range of immobile elements: Al, Ga, Hf, La, Nb, P, Ta, Tb, Ti, Th, Y, Yb, Zr (**Figure**
458 **7**). Element concentrations are scaled for plotting convenience using the values listed in **Table**
459 **2**. Sample IN07 (grey woody pumice) from site C0017 was used for a least altered composition,
460 consistent with shipboard XRD and petrographic analysis. Although this pumice may have

461 been introduced from elsewhere, its similar Zr/TiO₂, Nb/Y, La/Yb_{CN} and Zr/Y ratios (**Fig. 6**)
462 suggest it is of similar composition to the altered felsic volcanic/volcaniclastic rocks of sites
463 C0016, C0013 and C0014. Calculated mass change values are illustrated in **Figure 8** and
464 provided in **Table 3**. Mineralized and hydrothermally altered samples from sites C0016, C0014
465 and C0013 show significant mass gains in Cu-Pb-Zn-Fe-S-Au-Ag-As-Sb-Bi-Mo-Sr-Sn-Te-Tl-
466 Mg-LOI±Si±Ca and losses of Na-K-Cs-Eu-Rb±Ba (**Fig. 8**). Mass change is most pronounced
467 in the massive sulfides from site C0016, with large gains of Fe, S, Cu, Pb, Zn and a range of
468 trace metals (e.g. Ag, As, Mo, Sb, Te) as to be expected, decreasing downhole (samples IN01,
469 IN02 and IN05: **Fig. 8**). Less well mineralized footwall rocks show smaller gains of Fe, S, base
470 and trace metals. Erratic gains of Si and Mg are due to variable silicification and chloritization.
471 Samples from more distal sites C0013 and C0015 (represented by IN15 and IN09 respectively)
472 have lower mass gains and losses than samples from site C0016. The clustering of mobile
473 elements around the isocon of sample IN09 (**Fig. 7**) is consistent with the unaltered nature of
474 site C0015, with only minor losses of SiO₂, and gains of Sr and Ba (**Fig. 8**).

475

476 **5.4 Mineral chemistry**

477 Three samples from site C0016 were characterized by electron microprobe analysis: 16B-1
478 (sphalerite-rich massive sulfide, from 0-9 mbsf; **Figure 3f-1**), 16B1-3 (silicified and anhydrite-
479 sulfide veined volcanic rock, from 0-9 mbsf; **Fig. 3g**), and 16B-8 (quartz-chlorite altered
480 volcanic rock from 27-45 mbsf; **Fig. 3i**). Chlorite analyses (n=42) plot consistently within the
481 clinocllore and penninite fields (**Fig. 9**), characterized by extremely low Fe/Fe+Mg and
482 moderate Si. Chlorite geothermometers (MacLean and Kranidotis, 1987; Zhang and Fyfe,
483 1995) yield average temperature estimates of 218-235 °C for sphalerite-rich massive sulfides
484 (sample 16B-1), and 225-241 °C for quartz-chlorite altered volcanic rock (sample 16B-8).

485 White mica was analysed from sample 16B1-3 (a silicified and anhydrite-sulfide veined
486 volcanic rock from 0-9mbsf) and was not identified in the other two samples discussed above.
487 Mg/(Fe+Mg) ratios are high 0.90-0.94 and Na/(Na+K) ratios low (0.02). Al_{iv} values of 0.94-
488 1.01 are indicative of phengitic white mica compositions.

489

490 **6. DISCUSSION**

491 **6.1 Fluid/rock interaction and active VHMS mineralization at Iheya North**

492 The recovery of massive sphalerite-(pyrite-chalcopyrite±galena)-rich sulfides from below the
493 seafloor at Iheya North represents an extraordinary achievement for the IODP. At site C0016,

494 recovered blocks of sphalerite-rich massive sulfide from the base of North Big Chimney show
495 clear microstructural evidence of formation via a combination of surface detrital and subsurface
496 chemical processes (**Fig. 4c**), with no subsequent deformation as highlighted by EBSD analysis
497 (**Fig. 5**). At least two episodes of sphalerite mineralization have been recognized. Early Fe-
498 poor sphalerite appears to be detrital in origin and occurs as 0.5 mm subhedral, slightly rounded
499 crystals with inclusions of chalcopyrite. This generation is overgrown by pyrite (\pm galena), and
500 in turn by chalcopyrite (**Fig. 4d**). A second generation of Fe-poor sphalerite most likely
501 occurred as the system cooled, prior to final seawater influx represented by late coarse
502 anhydrite crystals (**Fig. 4b**). This second generation includes colloform- and atoll-textured
503 aggregates (**Fig. 4c**).

504 Massive sulfides are polymetallic and characterized by high Zn (30.2%), Pb (12.3%)
505 and Cu (2.68%), plus elevated Ag (33.1 ppm) and Sb (25.6 ppm) concentrations. Low Au
506 concentrations (maximum 0.07 ppm) may be a result of phase separation at depth, as indicated
507 by chloride concentrations that are lower than seawater (Chiba et al., 1996) and flashing (rapid
508 boiling) during IODP drilling (Takai et al., 2011). This is consistent with the lower confining
509 pressures from shallower water depths of the middle Okinawa Trough (<1000 m; Chiba, 1997)
510 when compared to the PACMANUS (~1650 m) and DESMOS (~2000 m) systems of the
511 Manus Basin, and similar hydrothermal fields of the Lau Basin (e.g. Valu Fa Ridge, ~1700 m)
512 (Ishibashi and Urabe, 1995).

513 Altered volcanic rocks at site C0016 beneath massive sulfides exhibit quartz-
514 muscovite/illite and quartz-Mg-chlorite alteration (**Fig. 10**), reminiscent of the proximal
515 footwall alteration typically associated with ancient VHMS deposits (Large et al., 2001a,b;
516 Piercey, 2009). Low concentrations of SiO₂, Al₂O₃, MgO and K₂O in massive sulfides resulted
517 from large mass gains of Fe, S and base metals (**Fig. 8**).

518 At site C0013, a likely location of recent high temperature discharge, intense
519 hydrothermal alteration obliterates primary mineralogy and texture. Near surface alteration is
520 dominated by kaolinite and muscovite with locally abundant native S, which is indicative of
521 the presence of acidic fluids. The entire sequence grades to Mg-chlorite dominated assemblages
522 at depths of >5 mbsf (**Fig. 10**). Coarse-grained surficial sulfidic sediments at site C0013 contain
523 ~43.2% Zn, 4.4% Pb, 5.4% Cu and 42 ppm Ag, with high concentrations of As, Cd, Mo, Sb
524 and W. These sediments are interpreted to represent collapsed chimney structures. They
525 contain significantly higher Zn, Cu, Ag, Sb and As concentrations than massive sulfides from
526 hole C0016B.

527 Distinctive white coarse rounded nodules of anhydrite±dolomite±talc±calcite±quartz±
528 sphalerite±pyrite (**Fig. 3a**) likely precipitated from down welling seawater at an early stage in
529 the evolution of the hydrothermal system (**Fig. 11a**). These anhydrite veins were subsequently
530 reworked during the main phase of hydrothermal activity (**Fig. 11b**). The presence of yellow
531 native sulfur cement in the top of hole C0013E (**Fig. 3c**) indicates that the sediment was
532 infiltrated by liquid native sulfur at temperatures between 112 and 119 °C (Takai et al., 2011).
533 The transition from kaolinite-muscovite to chlorite-rich alteration assemblages with increasing
534 depth (**Fig. 11b**) is similar to the gradation from paragonitized to chloritized rocks below the
535 TAG hydrothermal field. The major difference in mineralogy between these two fields is due
536 to lack of Fe in the system and abundance of K available from the leaching of underlying felsic
537 basement. A zone of coarse-grained crystalline anhydrite that overlaps the kaolinite and Mg-
538 chlorite alteration zones is interpreted to have precipitated from down welling seawater that
539 penetrated the sediments when hydrothermal activity at the site waned (**Fig. 11c**). Volcanic
540 basement at site C0013 consists of hard quartz and Mg-chlorite altered volcanic breccia with
541 scattered quartz-sulfide (sphalerite-pyrite±covellite±native Cu) veining and trace fine
542 disseminated pyrite within clasts.

543

544 **6.2. Distal hydrothermal alteration, mineralization and system recharge**

545 Site C0014 represents a more distal locality to the main zone of hydrothermal activity, ~450 m
546 from NBC and ~350 m from site C0013 (**Fig. 10**). At site C0014, covellite and sphalerite
547 mineralization is significantly less abundant. Anhydrite is present from ~57 mbsf as mm-scale
548 irregular veinlets, but is in much lower abundance than at proximal site C0013. Pyrite occurs
549 only in trace amounts and is rarely present as coarser veins. Mg-chlorite alteration occurs from
550 ~30 mbsf, at much greater depths than sites C0016 and C0013. Higher Na₂O concentrations at
551 site C0014 and lower Sb contents than site C0013 are consistent with the more distal location
552 of site C0014 (e.g. Large et al., 2001b; Piercey, 2009).

553 Recovered lithologies from distal sites C0015 and C0017 are unaltered, with low MgO,
554 Fe₂O₃, LOI, CCPI, AI, base metal concentrations and VHMS ‘pathfinder’ elements (e.g. Sb,
555 Sn, Cd, Tl; Large et al., 2001b; Piercey, 2009). Downhole temperature profiles at C0017 are
556 also indicative of lateral fluid flow recharge into the system approximately 1.6 km east of NBC
557 (Takai et al., 2011). Site C0015 is interpreted to represent a background locality where porous
558 strata are saturated with seawater.

559

560 **6.3. A modern analogue for Kuroko-type VHMS mineralization**

561 Recent interest surrounding the potential to mine modern seafloor massive sulfide
562 (SMS) deposits, such as the Solwara 1 deposit of the Manus Basin (Golder Associates, 2012;
563 Yeats, 2012), has highlighted the importance of identifying robust modern analogues for
564 different styles of VHMS mineralization. For instance, the Cu-Zn rich TAG site, a sediment-
565 starved system on the Mid Atlantic Ridge (e.g. ODP Expedition 158), has been compared to
566 Cyprus-type VHMS deposits (Hannington et al., 1998). IODP Expedition 331 was the first time
567 an active hydrothermal system in a continental back-arc setting has been drilled by the ODP /
568 IODP (Takai et al., 2011, 2012). VHMS deposits which form in these settings fall into the
569 Kuroko-type class (Barrie and Hannington, 1999; Galley et al., 2007; Piercey, 2011).

570 Kuroko-type VHMS deposits are typically polymetallic (Zn-Pb-Cu-Ag-Au), of high
571 grade (Piercey, 2007), and hosted in bimodal felsic flow-dominated sequences where felsic
572 rocks are in greater abundance than mafic rocks and there are less than 15% of siliciclastic
573 rocks in the host succession (Galley et al., 2007; Piercey, 2011). On idealized cross sections,
574 Kuroko-type VHMS deposits are developed on felsic flow complexes, such as rhyolite domes
575 with associated tuffs and breccias (Franklin, 1981). Eight zones of massive/semi-massive
576 mineralization were recognized by Eldridge et al. (1983) which may be present, and three zones
577 associated with the underlying chloritic stockwork. In descending order from the top of the
578 deposit the massive zones are: i) tetsusekiei (quartz-hematite±barite±sulfide), ii) barite ore
579 (barite>sulfide), iii) massive black ore (sphalerite±barite>pyrite-galena>tetrahedrite); iv) semi-
580 massive black ore (sphalerite±barite>pyrite>chalcopyrite-quartz), v) massive yellow ore
581 (chalcopyrite-pyrite>quartz); vi) powdery yellow ore (pyrite>chalcopyrite); vii) massive
582 pyrite ore (pyrite>>chalcopyrite>>sphalerite), and viii) massive gypsum-anhydrite ore (Ca
583 sulfates>>sulfides). These zonations typically occur within a broadly stratiform mound, with
584 the first seven forming imperfectly concentric shells, often with gradational contacts (unless
585 reworked) (Eldridge et al., 1983). An underlying discordant zone of siliceous ore is often
586 associated with the underlying chloritic stockwork with a general zonation from yellow ore
587 (quartz>pyrite>chalcopyrite) in the middle, toward a more sphalerite-galena rich mineral
588 assemblage at the base of the overlying lens, and a quartz>pyrite>>chalcopyrite mineralogy at
589 depth (Eldridge et al., 1983). Classic examples of Kuroko-type VHMS deposits are found in
590 the Honshu arc of Japan in the Hokuroku district, with deposit clusters associated with back-
591 arc rifting (Yamada and Yoshida, 2011), the Mount Read volcanic belt of SE Australia (Large
592 et al., 2001b), Buchans Group of Newfoundland (Piercey et al., 2007), and Skellefte district of
593 northern Sweden (Allen et al., 1996).

594 At Iheya North, massive sulfides intercepted at the base of North Big Chimney strongly
595 resemble the black ore of the Miocene-age Kuroko deposits of Japan (Sato, 1974, 1977), with
596 equivalents to the yellow, gypsum and siliceous ores also recognized by Ishibashi et al. (2013).
597 Massive sulfides are polymetallic and characterized by high Zn (30.2%), Pb (12.3%) and Cu
598 (2.68%), and elevated Ag (33.1 ppm) and Sb (25.6 ppm) concentrations. These metal
599 concentrations are consistent with massive sulfides from Kuroko-type VHMS deposits
600 worldwide (e.g. Barrie and Hannington, 1999; Galley et al., 2007; Large et al., 2001b; Piercey,
601 2007, 2009), in addition to the increased abundance of pyrite with respect to sphalerite at depth
602 - both on the local scale within the massive sulfide and overall in the sequence (e.g. Sato, 1977;
603 Eldridge et al., 1983). This is also reflected by higher Fe/Zn ratios with depth at site C0016.
604 The clastic nature of the massive and semi-massive sulfides at site C0016 is also consistent
605 with observations from the Kuroko deposits of Japan (e.g. Kuroda, 1977; Eldridge et al., 1983).

606 The quartz-Mg-chlorite basement present at sites C0016, C0013 and C0014 is typical
607 of high-temperature hydrothermal alteration associated with VHMS systems (Galley et al.,
608 2007; Piercey, 2009). All rocks analysed from C0016 show large gains in SiO₂ and MgO, with
609 the latter increasing downhole (**Fig. 8**). It is important to note the reduced depth of the Mg-
610 chlorite alteration towards NBC - from ~30 mbsf at site C0014 to ~6 mbsf at site C0013 (**Fig.**
611 **10**). Aoyama et al. (2014) highlight that this zone at site C0014 corresponds with shifts in Mg,
612 K and SO₄ pore water chemistry and $\delta^{34}\text{S}$ values. Whereas the unaltered sediment at site C0014
613 (**Fig 2b**) is saturated with seawater, the Mg-chlorite altered zone is dominated by hydrothermal
614 fluid and has yielded significantly higher temperatures (Takai et al., 2011). Bacteriogenic
615 sulfate reduction is only evident in the unaltered sediments (Aoyama et al., 2014).

616 Decreasing Na₂O concentrations in felsic volcanic and volcanoclastic rocks at Iheya
617 North with proximity to NBC is consistent with observations from ancient Kuroko-type VHMS
618 deposits (Date et al., 1983; Hashiguchi et al., 1983; Piercey, 2009). For example, Date et al.
619 (1983) recognized a Na₂O-depleted dacite mass with the lateral dimensions of 1.5 by 3 km
620 immediately below the ore horizon associated with the Fukazawa deposits. This was interpreted
621 to reflect feldspar destruction and sericite formation at relatively low pH and high temperatures.
622 It was hypothesised that much of the sodium lost from footwall lithologies was added to the
623 rocks in zones I (distal; forming analcime) and IV (proximal; forming Na-montmorillonite in
624 the hanging-wall). In the Miocene footwall rocks of the Uwamuki deposits, Urabe et al. (1983)
625 noted a mineralogical zonation from core to margin of quartz-sericite, sericite-chlorite-quartz,
626 remnant albite-sericite-chlorite-quartz and kaolinite-quartz-sericite-chlorite±albite.

627 Recovered footwall felsic volcanic rocks from site C0016 (and elsewhere) are of FII to
628 FIII affinity with well-developed negative Eu anomalies, similar to felsic volcanic rocks
629 hosting ancient Kuroko-type VHMS deposits that formed in Phanerozoic ensialic back-arc
630 settings worldwide (e.g. Leat et al., 1986; McConnell et al., 1991; Piercey, 2011). In some
631 instances the period of VHMS mineralization may be associated with a shift in immobile
632 element characteristics of the host lithologies (i.e. higher HFSE concentrations in pre-ore felsic
633 rocks; Yamada and Yoshida, 2011). However, this features has also been observed in bimodal-
634 mafic or Noranda-type VHMS systems (e.g. Golden Grove & Teutonic Bore; Hollis et al.,
635 2015).

636 Chlorite analyses from site C0016 plot consistently within the Mg-rich clinocllore and
637 penninite fields (**Fig. 9**). These compositions are similar to chlorite associated with the SE
638 Australian Kuroko-type VHMS deposits such as Thalanga, and some analyses of footwall
639 chlorite at Hellyer (**Fig. 9**). Fe/Fe+Mg ratios from Iheya North are significantly lower than
640 values reported at other active hydrothermal fields such as TAG and PACMANUS, plus
641 Noranda-type (i.e. bimodal-mafic) VHMS deposits (e.g. Noranda belt, Mattagami Lake; **Fig.**
642 **9**). Work by McLeod and Stanton (1984) on the SE Australian Kuroko-type VHMS deposits
643 (e.g. Woodlawn, Que River) observed that chlorite associated with sphalerite-rich ore had
644 significantly lower Fe/Fe+Mg ratios than chalcopyrite-rich samples. This is entirely consistent
645 with chlorite geothermometers which utilise Fe/Fe+Mg ratios (e.g. MacLean and Kranidotis,
646 1987), as higher temperatures would be expected for chalcopyrite precipitation. Fe-poor
647 sphalerite and Mg-rich chlorite compositions at Iheya North are consistent with the overall low
648 Fe-budget of the system, and Zn-rich nature of the mineralization.

649 Chlorite geothermometers which utilise Fe/Fe+Mg ratios (MacLean and Kranidotis,
650 1987; Zhang and Fyfe, 1995) yield average temperature estimates of 218-235 °C for sphalerite-
651 rich massive sulfides and 225-241 °C for quartz-chlorite altered volcanic rocks characterized
652 by higher Cu/Fe and Cu/Zn ratios. These temperatures are consistent with hydrothermal fluids
653 associated with Kuroko-type VHMS mineralization (e.g. Kalogeropoulos and Scott, 1983;
654 Shikazono et al., 1983), with temperatures of >250 °C when associated with chalcopyrite.
655 EBSD data also reveal higher temperature microstructures downhole at site C0016, and
656 temperature induced grain boundary migration through more lobate HAGBs (e.g. 16B-3B, **Fig.**
657 **5l**).

658

659 **6.4. Role of sediments on fluid flow and chemistry**

660 Although there is less interaction between hydrothermal fluids and sediments at Iheya North
661 than the JADE and CLAM sites of the middle Okinawa Trough (Glasby and Notsu, 2003), high
662 alkalinity, NH_4^+ , CH_4 and CO_2 at Iheya North are still indicative of some reaction with organic
663 matter. Anomalously high alkalinity and NH_4^+ at the CLAM site of the middle Okinawa
664 Trough, coupled with significantly higher $\delta^{34}\text{S}$ of sulfate than ambient seawater indicate that
665 sulfate reduction plays a dominant role in decomposing organic material (see Glasby and
666 Notsu, 2003). Oxidation of significant quantities of H_2S in organic matter at Iheya North,
667 evident from the local presence of native S, coupled with Mg-fixation in chlorite ultimately
668 resulted in the stabilization of the potassic alteration assemblages observed during IODP
669 Expedition 331. Sediment input has also previously been used to explain higher concentrations
670 of Pb (13.5%), Zn (31.4%), Sb (1,140 ppm), As (1,730 ppm) and Ag (465 ppm) in chimney
671 samples from Iheya North (average values from Ueno et al., 2003) than in Kuroko-type
672 deposits (Glasby and Notsu, 2003). Lead in the JADE deposits is derived from both sediments
673 and volcanic rocks (Halbach et al., 1997; Zeng et al. 2000), similar to the Kuroko-type VHMS
674 deposits of Japan (Fehn et al., 1983). For comparison, the influence of sediment in mafic
675 dominated hydrothermal systems is provided by ODP legs to the un-sedimented TAG VHMS
676 mound and the sedimented Middle Valley (summarized by Shanks, 2012).

677 More recent work by Keith et al. (2014) has linked Fe/Zn ratios in sphalerite to the
678 influence of $f\text{S}_2$ and $f\text{O}_2$ on Fe partitioning between fluids and sphalerite. It was stated that
679 sphalerite from sediment-hosted vents has systematically higher S concentrations and Fe/Zn
680 ratios than those of the sediment-starved vents. This is again consistent with data presented by
681 Ishibashi et al. (2015) from the middle Okinawa Trough. Whereas the Iheya North, Yoron,
682 Minami-Ensei, Irabu and Hatoma fields are characterized by low Fe/Zn ratios in sphalerite
683 (FeS typically <5 mol %), data from the more sedimented JADE and Yonaguni IV fields
684 progressed to considerably higher values (Ishibashi et al., 2015). The CLAM site in particular
685 is characterized by a thick blanket of muddy sediments, with associated Zn-mineralization
686 dominated by wurtzite (Glasby and Notsu, 2003). Proton-induced X-ray emission mapping has
687 confirmed the Fe-poor nature of the sphalerite from site C0016 massive sulfides, plus an
688 association between sphalerite and high Cd (Yeats & Laird, unpublished).

689 As impermeable hemipelagic sediments are interlayered with volcanoclastic sediments
690 through the upper part of the Iheya North stratigraphy (**Fig. 2**), hydrothermal fluids are
691 channelled laterally in porous and permeable volcanoclastic units, and vertically predominantly
692 through faults (Takai et al., 2011; **Fig. 10**). Locally sourced woody pumice and pumiceous
693 pyroclastic flow deposits have been recovered by numerous gravity cores obtained from the

694 central valley of Iheya North Knoll (Oiwane et al., 2008). In all cores, thick pumice layers with
695 coarse to fine grain sizes were found just below the seafloor. These layers often contain
696 abundant gas-filled voids accompanied by elemental sulphur and sulfide minerals, deposited
697 by a gas-rich hydrothermal fluid (Oiwane et al., 2008). Shipboard pore-water chemistry also
698 shows clear evidence for the compartmentalization of hydrothermal fluids due to the presence
699 of thick sequences of hemipelagic sediment (Takai et al., 2011).

700

701 **7. CONCLUSIONS**

702 The mineralization and alteration assemblages intercepted during IODP Expedition 331 at
703 Iheya North provide a relatively complete (though fragmental) profile through a developing
704 Kuroko-type VHMS system. At site C0016, located adjacent to the foot of the actively venting
705 NBC massive sulfide mound, massive sphalerite-(pyrite-chalcopyrite±galena)-rich sulfides
706 were recovered that strongly resemble the black ore of the Miocene-age Kuroko deposits of
707 Japan. Sulfide mineralization shows clear evidence of formation through a combination of
708 surface detrital and subsurface chemical processes, with at least some sphalerite precipitating
709 into void space in the rock. Underlying volcanic rocks exhibit quartz-muscovite/illite and
710 quartz-Mg-chlorite alteration reminiscent of VHMS proximal footwall hydrothermal
711 alteration.

712 Site C0013, ~100 m east of NBC, represents a likely location of recent high temperature
713 discharge, with surficial coarse-grained sulfidic sediments containing high concentrations of
714 As, Mo, Sb and W. Near surface alteration is dominated by kaolinite and muscovite with locally
715 abundant native sulfur, indicative of acidic fluids, grading to Mg-chlorite dominated
716 assemblages at depths of >5 mbsf. Late coarse-grained anhydrite veining overprints earlier
717 alteration and is interpreted to have precipitated from down welling seawater as hydrothermal
718 activity waned. At site C0014, ~150 m farther east, hydrothermal assemblages are
719 characterized by illite/montmorillonite, with Mg-chlorite present at ~30 mbsf. Recovered
720 lithologies from distal, recharge site C0017 are unaltered.

721 The metal tenors and alteration assemblages at Iheya North are significantly different
722 from those observed at deposits hosted in Mid Ocean Ridge (Cyprus-type) and primitive arc
723 (e.g. Noranda-type) environments. Mineralization and alteration assemblages are consistent
724 with the Iheya North system representing a modern analogue for Kuroko-type VHMS
725 mineralization. Fluid flow is focussed laterally along pumiceous volcanoclastic strata
726 (compartmentalized between impermeable hemipelagic sediments), and vertically along faults.

727

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749

750 **LIST OF FIGURES**

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752 Trough, Japan (modified after Ishibashi et al., 2015; Shinjo & Kato, 2000). **(b-c)**
753 Bathymetric maps of the Iheya North hydrothermal field and IODP Expedition 331 drill
754 sites (after Ishibashi et al., 2015; Takai et al., 2011). NBC, North Big Chimney.

755 **Figure 2.** Sedimentary logs for the deepest holes at sites C0013 and C0014 with alteration
756 assemblages determined by shipboard XRD indicated. **(a)** Hole C0013E. **(b)** Hole
757 C0014G.

758 **Figure 3.** Key lithologies recovered from sites C0013 **(a-e)** and C0016 **(f-j)**. All core recovered
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760 from hole C0013D. Note the large white nodules of anhydrite with truncated internal
761 structures, indicating physical or chemical erosion after precipitation. **(b)** Quartz and

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763 sphalerite, pyrite and covellite. **(c)** Native sulfur bearing sediment at the top of hole
764 C0013E. As the sulfur occurs as veinlets and cements this implies it was liquid when the
765 interval formed. **(d)** Native S crystalline linings on gaseous or fluid filled voids in silty
766 mud from hole C0013F. **(e)** Native Cu (confirmed by SEM) and organic carbon present
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773 rock recovered from between 27-45 mbsf, which displays a network of quartz-chlorite-
774 pyrite veins. **(j)** Quartz-chlorite-pyrite veining cut by a later anastomosing pyrite-
775 anhydrite vein network, in quartz-chlorite altered volcanic basement (recovered from the
776 core catcher; from 27-45 mbsf).

777 **Figure 4.** Petrographic and backscattered SEM photomicrographs of samples recovered from
778 Iheya North. **(a)** Massive sulfide from site C0016B showing intergrown pyrite-
779 chalcopyrite-sphalerite-galena (reflected light). Chalcopyrite has overgrown pyrite, with
780 sphalerite showing chalcopyrite disease. **(b)** Coarsely crystalline anhydrite overgrowing
781 quartz and sulfide in sphalerite-rich massive sulfides from site C0016B. **(c)**
782 Colloform/atoll textured sphalerite overgrowing pyrite and chalcopyrite in massive
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785 by pyrite and chalcopyrite. **(e)** Covellite present in sulfidic sediments from site C0013
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788 in sulfidic sediments at site C0013 (image taken under binocular microscope). **(h)** SEM
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793 clay from C0014G **(l)** SEM photomicrograph of a polymetallic sulfide vein from site
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795 **Figure 5. (a, d, g, j, m)** Reflected light photomicrographs of the areas analysed by coincident
796 EDS/EBSD. **(b, e, h, k, n)** phase maps created from EDS data (sphalerite = dark blue,
797 quartz = red, pyrite = orange, chalcopyrite = lime green, chlorite = aqua blue, graphite =
798 grey, anhydrite = pink). **(c, f, i, l, o)** EBSD data plotting the phases (sphalerite = blue,
799 quartz = red, pyrite = orange, chalcopyrite = lime green) overlain on the pattern quality
800 map, with high angle grain boundaries (HAGB) in black, low angle grain boundaries
801 (LAGB) in white, and sigma 3 coincident site lattices (CSL) in red. *Samples: Figure 5a-*
802 *f: sphalerite-rich semi-massive sulfide (C0016B, block 2 in Figure 3f). Figure 5g-l:*
803 *sphalerite rich semi-massive sulfide (C0016B, block 3 in Figure 3f). Figure 5m-o quartz*
804 *and Mg-chlorite altered volcanic rock with stringer sulfides (C0016B, block 9 in Figure*
805 *3j)*

806 **Figure 6.** Whole rock geochemical variation at Iheya North. **(a)** Pearce (1996) whole rock
807 Zr/TiO₂ vs. Nb/Y discrimination diagram for the classification of hydrothermally altered
808 volcanic and volcanoclastic rocks. All samples plot within the felsic (rhyolite/dacite) field
809 except for 5 samples which contain significant quantities of hemipelagic/hydrothermal
810 clay (IN08 and IN19-20 respectively) or are strongly mineralized (IN01). **(b)** Alteration
811 Box Plot of major element mobility (after Large et al. 2001a). CCPI (Chlorite-Carbonate-
812 Pyrite Index) = 100 (MgO + FeO) / (MgO + FeO + Na₂O + K₂O). AI (Ishikawa Alteration
813 Index) = 100 (K₂O + MgO) / (K₂O + MgO + Na₂O + CaO). The Ishikawa Alteration
814 Index quantifies the intensity of sericite and chlorite alteration that occurs in footwall
815 rocks proximal to Kuroko-type VHMS deposits. High AI is associated with the
816 breakdown of sodic plagioclase and volcanic glass and their replacement by sericite and
817 chlorite. The Chlorite-Carbonate-Pyrite Index quantifies increases in MgO and FeO
818 associated with Mg-Fe chlorite development, which commonly replaces albite, K
819 feldspar or sericite. It also is affected by Mg-Fe carbonate alteration, and enrichments in
820 pyrite, magnetite and hematite. Mineral nodes and common alteration trends associated
821 with hydrothermal alteration are shown. **(c)** Zr/Y vs. Y fertility plot of Leshner et al. (1986)
822 for the VHMS prospectivity of felsic rocks. Inset image shows the La/Y_{bcn} vs. Y_{bcn}
823 fertility plot of Hart et al. (2004). Samples analysed from Iheya North are predominantly
824 of FII to FIIIa affinity and similar to VHMS associated felsic rocks in ensialic arc settings
825 worldwide. **(d)** Nb vs. Y diagram highlighting the HFSE enrichment of the least altered
826 felsic rocks at Iheya North. Large mass gains of mobile elements (e.g. Fe, S, Si, Mg, Zn)
827 result in the dilution of Nb and Y while maintaining immobile-element ratios. **(e)**
828 Chondrite normalized REE diagram illustrating the slight LREE enrichment, flattish

829 HREE profiles and pronounced negative Eu anomalies for most samples. Chondrite
830 normalization values from McDonough and Sun, 1995).

831 **Figure 7.** Isocon diagrams for representative samples from Iheya North (after the method of
832 Grant, 1986, 2004). Isocons were fitted using a range of immobile elements (shown in
833 red). Element concentrations are scaled for plotting convenience using the values listed
834 in Table 2. **(a)** IN01, sphalerite-rich massive sulfide from site C0016 (see **Figure 3a**). **(b)**
835 IN02, silicified volcanic rock with disseminated sulfides from site C0016 that underlies
836 massive and semi-massive sulfide (see **Figure 3f**). **(c)** IN05, quartz-Mg-chlorite altered
837 volcanic rock with stringer sulfides from site C0016 (see **Figure 3h**). **(d)** IN15, quartz-
838 chlorite altered volcanic rock from depth at site C0013. **(e)** IN09, unaltered pumice with
839 trace oxidized yellow clay staining from site C0015. **(f)** Schematic cartoon for the
840 interpretation of isochon diagrams.

841 **Figure 8.** Calculated mass change values for selected samples from sites Iheya North after
842 Grant (1986, 2004). Mass change was calculated using the immobile element isocons and
843 equations in **Figure 7**. Large mass gains of Zn-Pb-Cu-Fe-S occur in IN01. Underlying
844 silicified (IN02) and quartz-chlorite altered volcanic rocks also show large gains in
845 Si±Mg, whereas samples from C0013 (IN15) and C0015 (IN09) show significantly
846 reduced mass gains.

847 **Figure 9.** Chlorite chemistry for samples analysed from hole C0016B compared to other active
848 hydrothermal systems and ancient VHMS deposits. Data compiled from: Arctic VHMS
849 deposit, Alaska (Schmidt 1988), Heath Steel B Zone VHMS deposit, New Brunswick,
850 Canada (Lentz et al., 1997), Hellyer VHMS deposit, western Tasmania, Australia
851 (Gemmell and Fulton, 2001), Horne VHMS deposit, Noranda, Quebec (MacLean and
852 Hoy, 1991), Iberian Pyrite belt, SW Spain (Sánchez-España et al., 2000), Mattagami
853 Lake, Quebec, Canada (Costa et al., 1983), PAC-MANUS (Paulick and Bach, 2006),
854 TAG (Sturz et al., 1998), Thalanga VHMS deposit, northern Queensland, Australia
855 (Paulick et al., 2001), Turkey VMS deposits (Catagay, 1993), Wolverine volcanic-
856 sediment hosted deposit, Finlayson Lake, Canada (Bradshaw et al., 2008).

857 **Figure 10.** Schematic cartoon for the Iheya North hydrothermal field.

858 **Figure 11.** Schematic model for evolution of hydrothermal activity at site C0013. **(a)** Eroded
859 anhydrite veining/nodules occur within a mixed sequence of felsic volcanoclastic rocks
860 and hemipelagic sediments on an unaltered volcanic basement. **(b)** Hydrothermal activity
861 is associated with the alteration of the volcanic basement to quartz-Mg-chlorite and Mg-
862 chlorite-talc in the overlying sediments, and venting at the seafloor. The uppermost

863 portion of the sedimentary sequence is characterized by a lower temperature assemblage
864 of kaolinite-muscovite, indicative of acidic fluids. (c) As hydrothermal activity ceases,
865 cool seawater infiltrates the sediment precipitating coarsely crystalline anhydrite above
866 the 150 °C isotherm. Sulfide chimneys collapse to form occurrences of sulfide-rich
867 sediment, which contain varying base metal concentrations.

868

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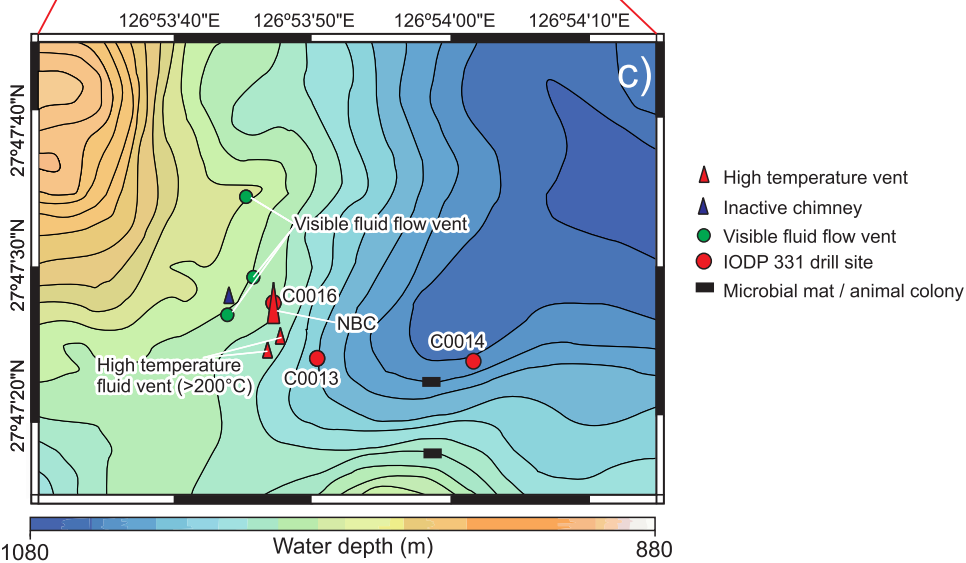
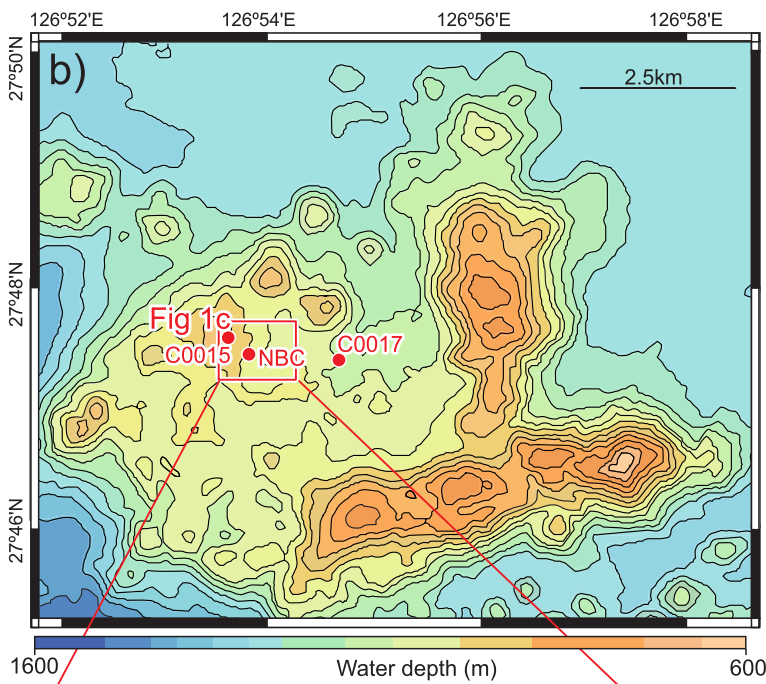
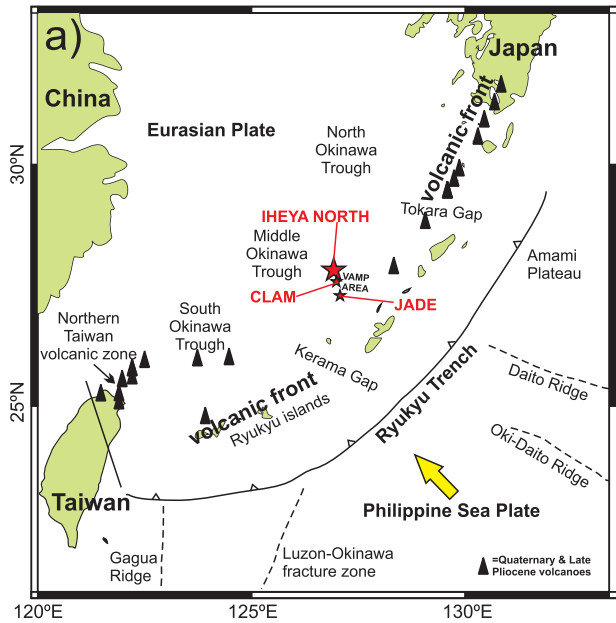
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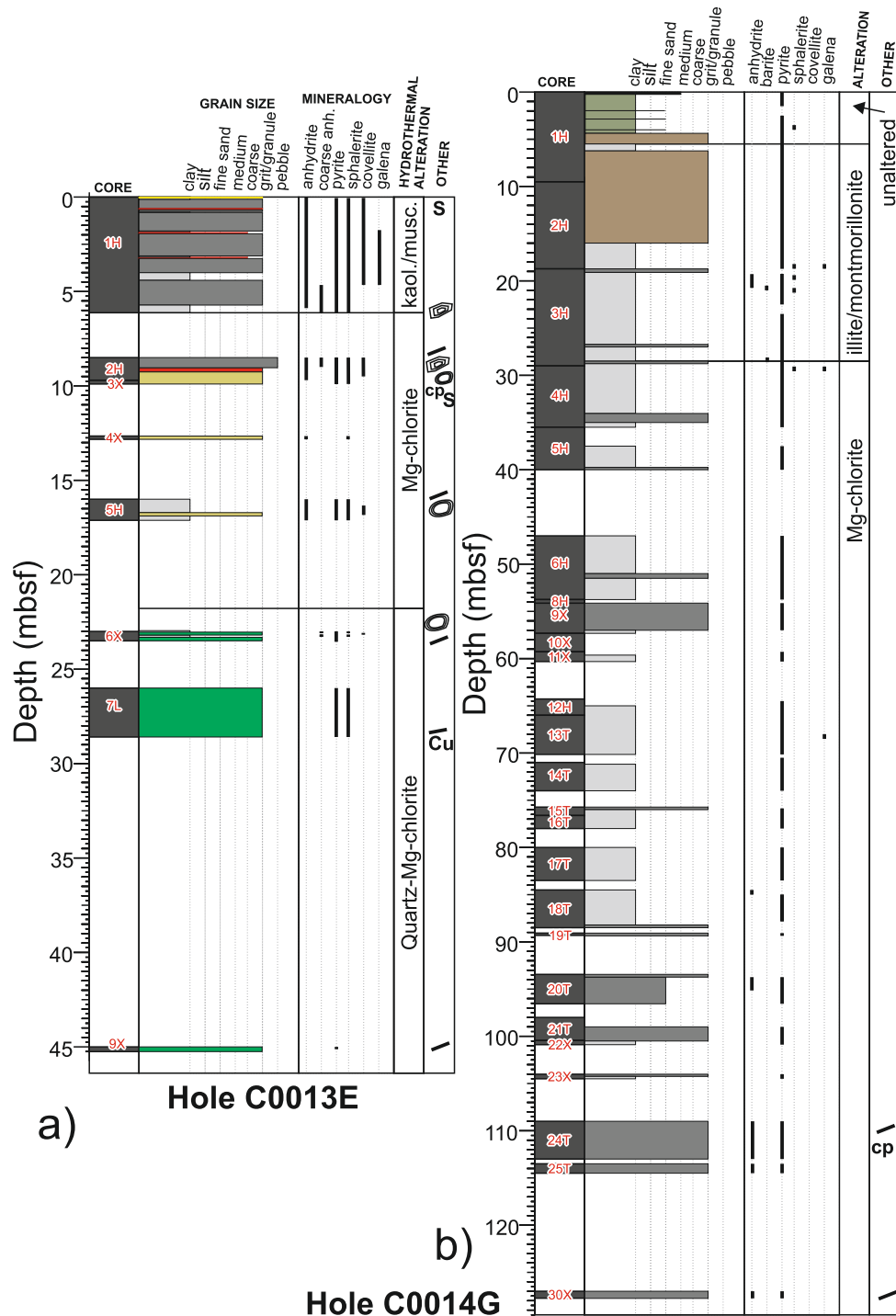
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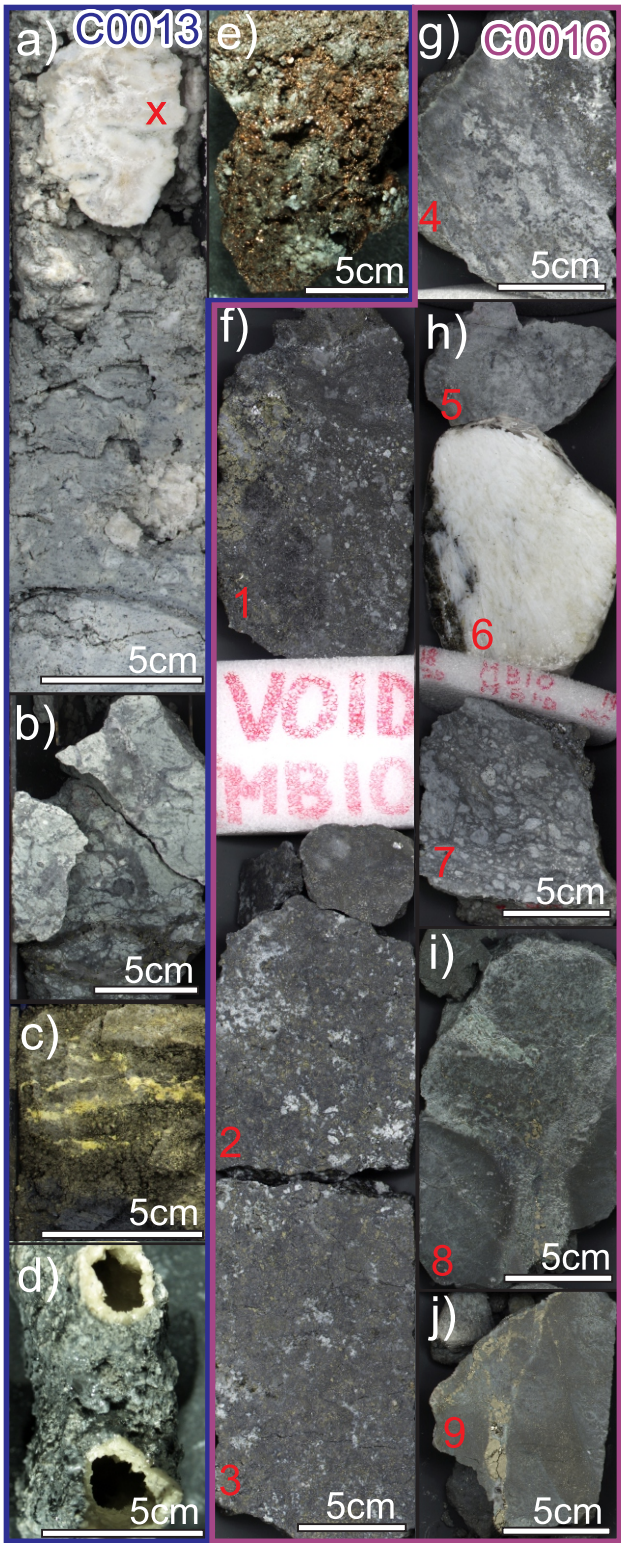


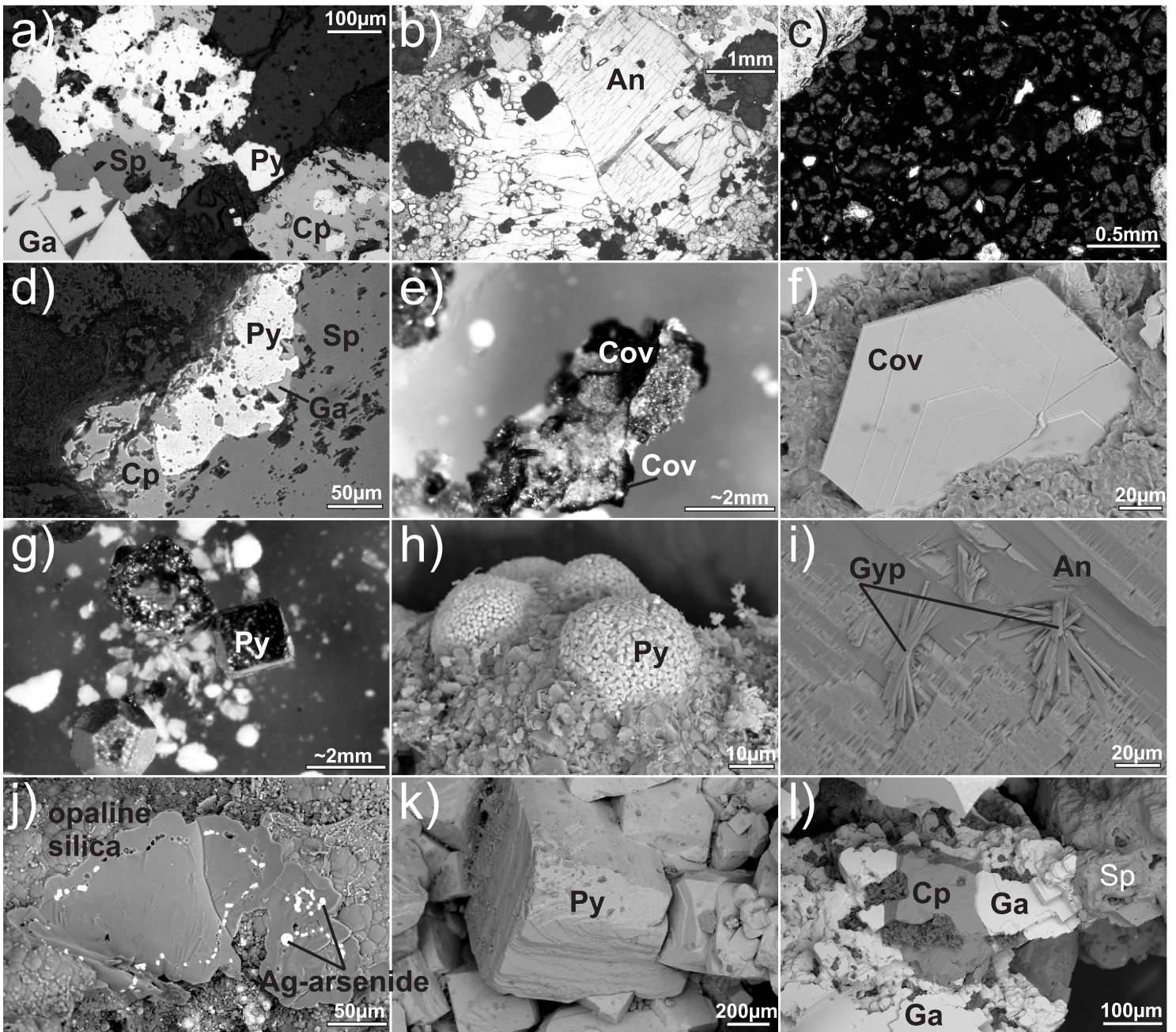


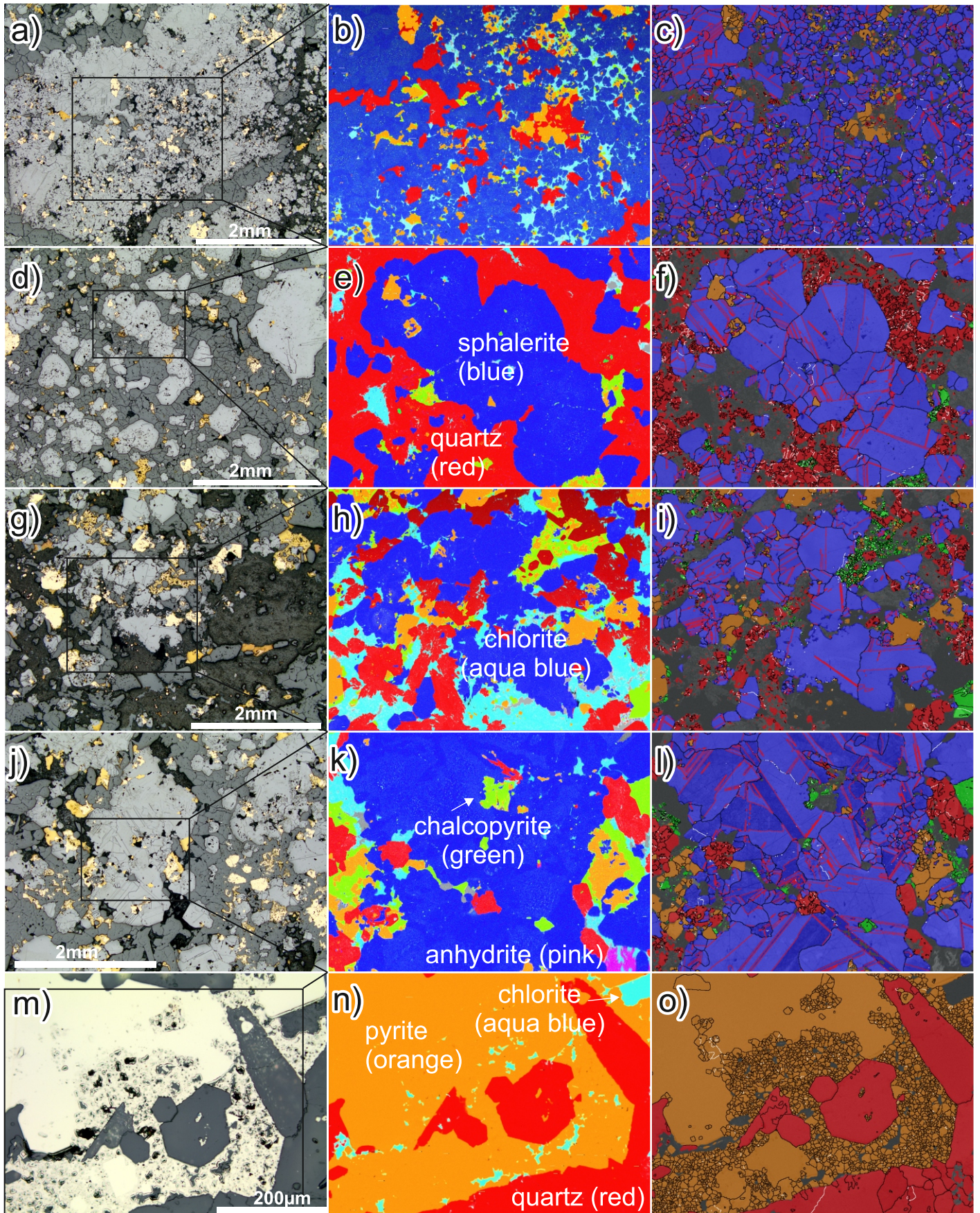
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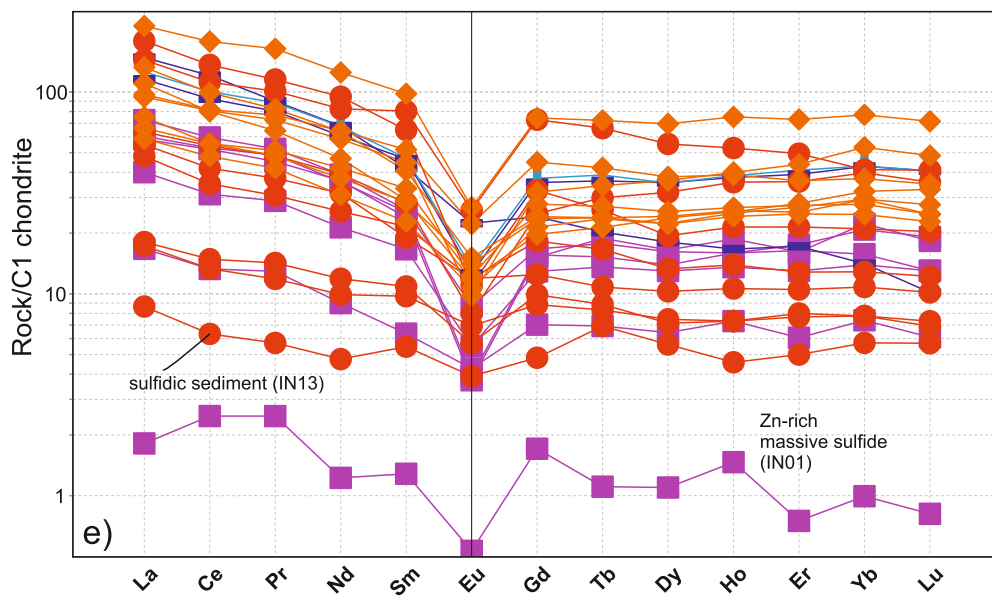
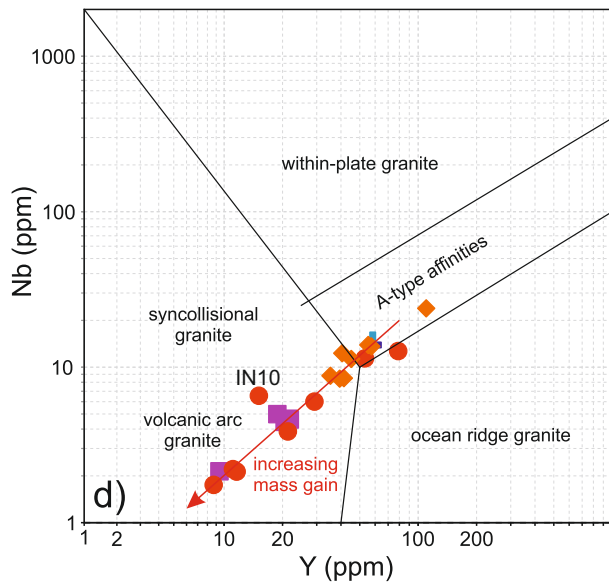
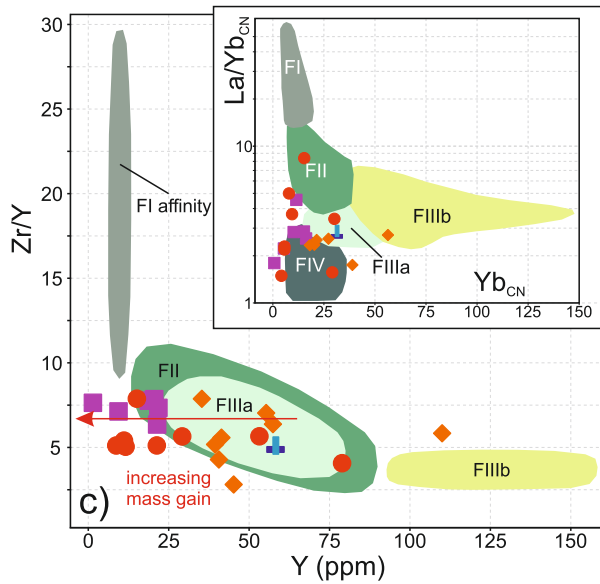
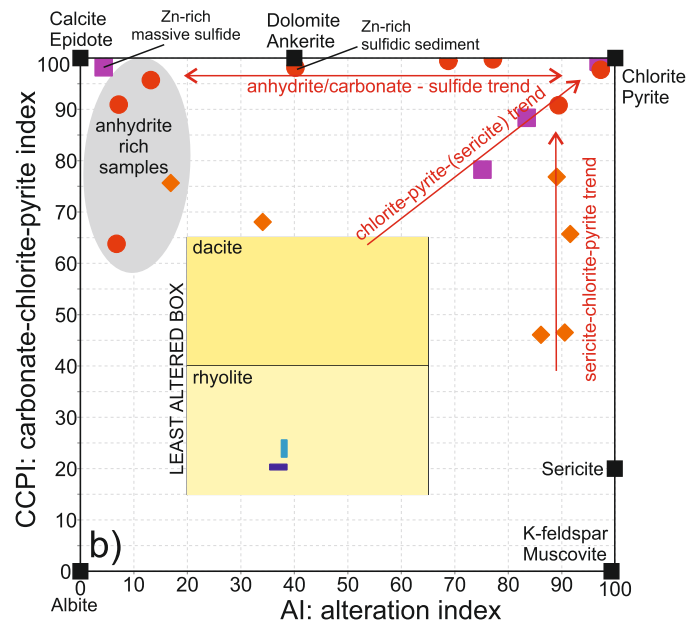
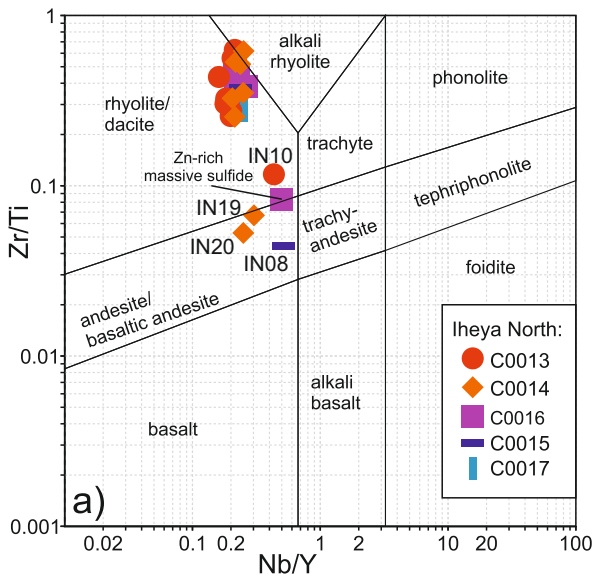
- Medium- to coarse-grained sulfidic sediment.** Sulfides dominated by pyrite-sphalerite with minor galena and covellite. Some coarse (1-4 cm) fragments of cemented sulfide aggregates.
 - Reduced mud (unaltered).** Dark olive green colour, with foraminifera and very fine disseminated pyrite.
 - Hydrothermal clay.** Light to medium grey colour. May contain pseudoclasts of harder clay after pumice(?).
 - Unaltered/weakly-altered pumiceous grit/gravel.** Pumice clasts in a coarse sand matrix with dark olive green mud. Often clast supported.
 - Hydrothermal grit/gravel.** Scattered large (1-2cm) aggregate clasts set in a clay-sand matrix. Locally sulfide rich (to ~5%). Grey to black colour, occasionally paler. Can be clast- or matrix-supported. Pumice replaced by white to pale grey clay.
 - Hydrothermal grit with native sulfur.** Pale grey to yellow colour. Patches of white clay. Small aggregates of altered volcanic rocks.
 - Anhydrite-carbonate-silica vein material embedded in dark and white clay.**
 - White to pale grey volcanic breccia.** Strongly altered volcanic rock comprising clasts in a silicified network of quartz veins (hairline to 1cm in width). Clasts are <0.5cm to >5cm, poorly-sorted, subangular to subrounded, and in some areas jig-saw fit.
- Sulfide vein.
 - Broken anhydrite crystals (to 5mm in size) - veins disturbed by drilling?
 - Native sulfur stringers and/or blebs.
 - Large (4-5cm), white, hard, anhydrite-clay-sulfide nodules (grown *in situ*?). May also contain dolomite, calcite, quartz and/or talc.
 - cp** Presence of trace chalcopyrite.
 - Cu** Presence of native copper in basement.

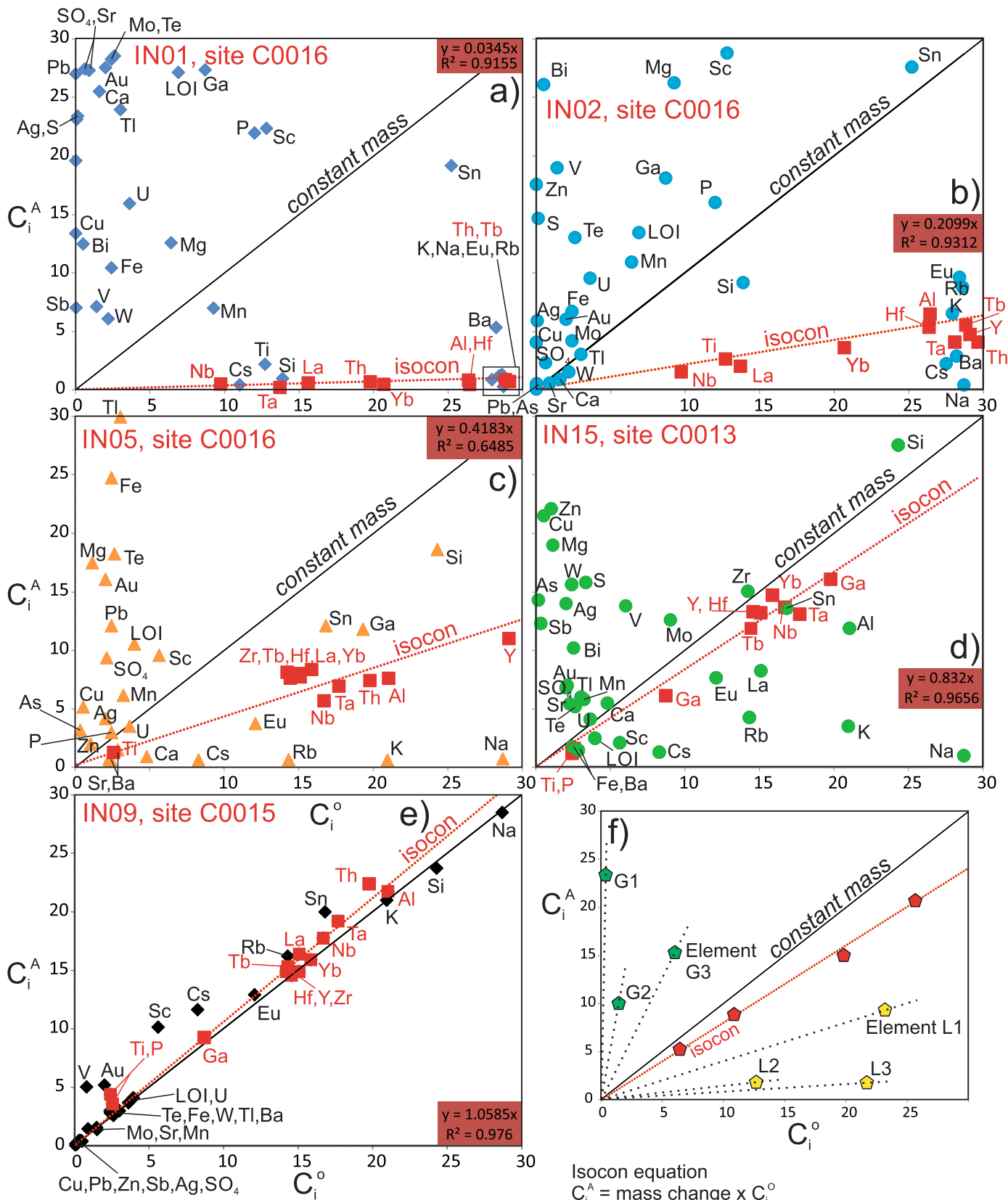
Note: Sections of re-drilled core not shown.











- ◆ Immobile element used for isochron
- ◆ Mobile element - removed from rock (below isochron)
- ◆ Mobile element - added to rock (above isochron)

Isocon equation

$$C_i^A = \text{mass change} \times C_i^o$$

Relative magnitude of mass gains/losses for mobile elements:

G1>G2>G3 (i.e. steeper slope from origin of graph)

L3>L2>L1 (i.e. shallower slope from origin of graph)

Note: The isochron plots below the line of constant mass, therefore the rock has gained mass.

