

1 **Barite from the Saf'yanovka VMS deposit (Central Urals) and Semenov-1 and -**
2 **3 hydrothermal sulfide fields (Mid-Atlantic Ridge): A comparative analysis of**
3 **formation conditions**

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41 sulfur isotopic compositions, VMS deposit

42

43 **Abstract**

44

45 Hydrothermal and diagenetic barites from colloform and clastic pyrite-rich ores from the weakly
46 metamorphic Saf'yanovka volcanogenic massive sulfide deposit (Devonian, Central Urals) were
47 studied in comparison with barite from similar modern seafloor deposits from the mid-Atlantic
48 Ridge (Semenov-1 and Semenov-3 hydrothermal fields). Hydrothermal barites from all the studied
49 deposits exhibit similar morphology: they occur as tabular crystals or their aggregates. In contrast,
50 diagenetic barite from clastic ores of the Saf'yanovka deposit occur as compact aggregates of
51 deformed, broken, or slightly curved tabular crystals with stylolite boundaries. The variable Sr
52 contents in the studied barites show no relationship with the genetic types. The average $\delta^{34}\text{S}$ values
53 of hydrothermal barite from both ancient and modern colloform sulfides (+22.9 ‰, Saf'yanovka
54 deposit; +21.2‰, Semenov-1 field) match those of Silurian–Devonian and contemporary seawater,
55 respectively. The lower $\delta^{34}\text{S}$ of hydrothermal barite from clastic sulfides of the Semenov-3 field
56 (+19.6 ‰), which is associated with high-Se, high-temperature chalcopyrite, indicates light sulfur
57 contribution from oxidation of fluid H_2S . The higher average $\delta^{34}\text{S}$ of diagenetic barite from clastic

58 ores of the Saf'yanovka deposit (+28.1‰) is interpreted to reflect partial thermochemical reduction
59 of seawater sulfate due to interaction with ferrous minerals and/or organic matter.

60 In spite of different geodynamic setting, hydrothermal barite from colloform ores from the
61 Saf'yanovka deposit (back-arc basin) and Semenov-1 field (slow-spreading mid-oceanic ridge)
62 were formed under similar low- to moderate-temperature conditions (172–194 °C and 83–233 °C,
63 respectively) from relatively low-salinity fluids (1.6–4.5 and 0.6–3.8 wt.% NaCl_{eq}, respectively).
64 Variations in salinity values from higher- to lower-than seawater reflect phase separation in the
65 parent fluids. High contents of CO₂, CH₄, and N₂ (up to 1.58, 0.05, and 0.006 mol%, respectively)
66 in fluid inclusions from the Saf'yanovka deposit are attributed to reactions with abundant
67 hydrothermal fauna and C-bearing sediments. The presence of SO₂ and CO₂ in fluid inclusions from
68 the Semenov-1 field is ascribed to contributions from a magmatic fluid. Hydrothermal barite from
69 Semenov-3 clastic sulfides crystallized at higher-temperature (266–335 °C) from higher-salinity
70 fluids (4.8–9.2 wt.% NaCl_{eq}). The high salinity may again indicate a contribution from a magmatic
71 fluid, consistent with high measured CO₂ content in fluid inclusions (1.6 mol%). Diagenetic barite
72 from the Saf'yanovka clastic ores was formed at moderate temperatures (140–180 °C) from low- to
73 moderate-salinity pore fluids (1.4–5.4 wt.% NaCl_{eq}). The variable salinity may reflect contributions
74 from various water sources, e.g., connate seawater, silicate dehydration, and transformation of
75 primary hydrothermal barite with low-salinity fluid inclusions.

76 Combining our new data with those for other seafloor hydrothermal barites the following
77 systematics can be defined. Barite precipitated on chimney rims or associated with pyrite-rich,
78 colloform, massive sulfides forms at relatively low to moderate temperatures (<230 °C), barite
79 associated with polymetallic-rich sulfides forms at moderately high temperatures (210–280 °C), and
80 barite in assemblage with chalcopyrite records the highest temperatures (265–335 °C). The main
81 source of sulfur is seawater for both hydrothermal and diagenetic barite; additional contribution of
82 isotopically light sulfur from partial oxidation of H₂S or of isotopically heavy sulfur from bacterial
83 sulfate reduction may occur in hydrothermal barite, whereas a contribution from isotopically heavy

84 sulfur remaining after thermochemical or bacterial partial reduction of seawater sulfate appears to
85 be common in diagenetic barite.

86

87 **Introduction**

88

89 Barite may form in seafloor environments by a number of processes, such as (i) hydrogenetic
90 precipitation from the water column (i.e., ‘marine’ barite), (ii) diagenetic precipitation from pore
91 fluids in sediments, (iii) precipitation from cold seeps, and (iv) precipitation from low-temperature
92 (<120 °C) to high-temperature (>300 °C) hydrothermal fluids venting on the seafloor in various
93 geodynamic settings (e.g., Sasaki et al. 1995; Hou et al. 2001; Paytan et al. 2002; de Ronde et al.
94 2003; Petersen et al. 2004; Hein et al. 2007; Griffith and Paytan 2012). The conditions of formation
95 of seafloor barite are recorded in its habit, chemical and isotopic composition, and fluid inclusions
96 (Paytan et al. 2002). Barite is a common gangue mineral in both modern seafloor sulfide-rich,
97 hydrothermal vent systems and in their ancient counterparts, which are represented by on-land,
98 volcanic-hosted massive sulfide (hereafter, VMS) deposits. The direct comparison of barite in
99 ancient and modern hydrothermal systems can be difficult because the primary hydrothermal
100 features of ancient deposits are often modified by later metasomatic or metamorphic processes.

101 In this paper, we compare barite in colloform and clastic pyrite-rich ores from the Paleozoic
102 Saf’yanovka VMS deposit, Central Urals (Fig. 1), with barite in colloform and clastic pyrite-rich
103 ores from the modern Semenov-1 and -3 hydrothermal fields, Mid-Atlantic Ridge (hereafter, MAR)
104 (Fig. 2). In spite of their different geodynamic setting (back-arc spreading center for the
105 Saf’yanovka deposit, cf. Yazeva et al., 1991, vs mid-oceanic ridge for the Semenov-1 and -3
106 hydrothermal fields, Beltenev et al., 2007), these deposits were chosen for their significant
107 similarities of pyrite-rich ores in terms of textures and mineral assemblages, characterized by
108 predominance of iron disulfides and presence of abundant barite. Moreover, the weakly
109 metamorphic character of the Saf’yanovka deposit, which allowed preservation of its delicate

110 primary hydrothermal structures (uncommon for Paleozoic VMS deposits, which are often modified
111 by later metasomatism or metamorphism), enabled a detailed comparison with its modern
112 counterparts. By comparing previous data for barite from these deposits with our newly acquired
113 geochemical, isotopic and fluid inclusion data and with published data on other ancient and modern
114 seafloor hydrothermal deposits, we will investigate the major distinctive features of different types
115 of barites (hydrothermal vs. diagenetic) and the systematics between temperatures of barite
116 formation and mineralogy and textures of associated sulfides.

117

118 **Geological outlines of the studied deposits**

119

120 **Saf'yanovka deposit**

121

122 The Saf'yanovka massive sulfide deposit, discovered in 1985, is situated in the Sverdlovsk district,
123 9 km northeast of the town of Rezh in the Central Urals (Fig. 1a). The deposit is located in the East
124 Uralian megazone, in the Rezh ore district. The geological setting, host rocks, and ore mineralogy
125 of the Saf'yanovka deposit have been studied in detail and are described in Yazeva et al. (1991),
126 Koroteev et al. (1997), Maslennikov (2006), Maslennikova and Maslennikov (2007), Safina and
127 Maslennikov (2009), Soroka et al. (2010), Murzin et al. (2010), Chuvashov et al. (2011), and
128 Yaroslavtseva et al. (2012). The deposit is thought to have formed in a Devonian back-arc basin
129 which hosts a rhyolite–dacite–andesite–basalt association (Yazeva et al. 1991; Koroteev et al.
130 1997). The area of the deposit consists of a stack of three main tectonic slivers; (i) a ~50 m-thick
131 lower sliver composed of Late Devonian basalts and basaltic andesites, (ii) a ~500 m-thick ore-
132 hosting middle sliver composed of Middle Devonian dacites and rhyolites, interlayered with
133 volcano-sedimentary rocks and black shales, and (iii) an upper sliver, up to 300 m-thick, composed
134 of Middle Devonian serpentinites, gabbro, limestones and basalts, interlayered with Upper
135 Devonian–Lower Carboniferous cherts (Fig. 1b; Yazeva et al. 1991; Koroteev et al. 1997).

136 The deposit includes ten ore lenses up to 40 m-thick, which occur in three stratigraphic
137 horizons at depths of 190 to 400 m. In the central part of the deposit, the sulfide bodies are
138 separated by volcano-sedimentary layers ranging in thickness from several cm to over 10 m. At
139 their margins, the sulfide bodies are alternated with black shales (C_{org} 2.7–3.5 wt%) up to 5 m-thick
140 (Yaroslavtseva et al. 2012). A 5–7 m-thick zone of nearly monomineralic barite lies directly
141 beneath the ore bodies, at a depth of about –200 m.

142 The main ore body exposed by the open pit is up to 200 m thick and is split on its flanks into
143 several segments by subvolcanic rhyolite bodies (Fig. 1b; Yazeva et al. 1991; Koroteev et al. 1997).
144 A few barite–sphalerite layers with thicknesses of about one meter occur on the southern margin of
145 the main ore body. The deposit is remarkable considering the low degree of metamorphism (lower
146 greenschist facies) of the host rocks and massive sulfide ores (Yazeva et al. 1991), which allowed
147 preservation of delicate primary structures such as fine-grained colloform ores, black-smoker
148 chimneys, and fossilized hydrothermal fauna (Maslennikov 2006; Maslennikova and Maslennikov
149 2007). The sulfide ores include several types: massive Cu–Zn, Cu and Fe ores with dominant,
150 massive, banded and breccia-like structures, stockwork Cu ores consisting of a chalcopyrite-pyrite
151 network in hydrothermally altered volcanic rocks, and Cu–Zn coarse-grained disseminated ores at
152 the contacts with massive ores.

153 Based on detailed ore-facies mapping, the major, vertical, conical sulfide lens, the core of
154 which is composed of massive Cu–Zn ores with relics of quartz–sphalerite–chalcopyrite black-
155 smoker chimneys, has been interpreted as a remnant sulfide mound (Fig. 1c; Maslennikov 2006).
156 According to the ore-facies reconstruction, colloform pyrite ores with barite and quartz at the top of
157 the sulfide body are thought to represent fragments of seafloor hydrothermal crusts. Sulfide breccias
158 and sandstones with clasts derived from massive and colloform sulfides and black smoker
159 chimneys, cemented by quartz or barite, are widespread on the flanks of the sulfide layers. Stringer–
160 disseminated Cu and Cu–Zn ores, comprising more than half of the reserves of the deposit, are

161 localized beneath the major ore body (Yazeva et al. 1991). Veins composed of coarse-crystalline
162 chalcopyrite and pyrite are fragmented and cemented by quartz and barite.

163 Preliminary data on homogenization temperatures of fluid inclusions in barite from colloform
164 (160–190 °C) and clastic (130–170 °C) ores and in vein barite in massive ores (160–200 °C) were
165 reported in Safina et al. (2012).

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167

168 Semenov-1 and Semenov-3 fields

169

170 The inactive Semenov-1 and Semenov-3 hydrothermal fields are part of the large Semenov massive
171 sulfide cluster that was discovered in 2007 during the 30th cruise of the Russian R/V *Professor*
172 *Logachev* by the Polar Marine Geosurvey Expedition (PMGE) in collaboration with
173 VNIIOkeangeologia, Saint Petersburg, Russia (Beltenev et al. 2007). The Semenov cluster is
174 located between the Fifteen Twenty and Marathon transform fracture zones on the western wall of
175 the mid-ocean rift valley, on a EW-trending seamount approximately 10 km-long and 4.5 km-wide
176 (Beltenev et al. 2007; Fig. 2). The substrate of the Semenov cluster is believed to be a detachment
177 fault structure, which exposes deep oceanic basement rocks on the seafloor (Smith et al. 2008;
178 McLeod et al. 2009). The hydrothermal fields of the Semenov cluster are located between depths of
179 2400 and 2950 m. The large vertical extent of the mineralization is mainly due to the structure of
180 the Semenov-4 field, which is the largest field in the cluster (several square kilometer-wide). This
181 field is characterized by significant post-depositional faulting, which allowed exposure of
182 stockwork veining in substrate basalts (Beltenev et al. 2007; Jamieson et al. 2014).

183 Serpentinized ultramafic rocks (mainly harzburgites) were recovered from the northern,
184 southern, and western slopes of the seamount (Beltenev et al. 2007; Fig. 2). Other igneous rocks are
185 given by gabbros, olivine gabbros, gabbronorites, ferrogabbros, plagiogranites, tonalites, and
186 diorites. Volcanic and subvolcanic rocks are represented by aphyric and plagiophyric pillow lavas

187 (locally with well-preserved chilled glasses) and dolerites, respectively (Pertsev et al. 2012).

188 Hydrothermal alteration is shown by the formation of serpentized harzburgites, talcites,

189 chloritized mafic rocks, talc-chlorite rocks, and amphibolites.

190 The Semenov-1 hydrothermal field ($13^{\circ} 30.87' \text{ N}$, $44^{\circ} 59.24' \text{ W}$) is situated near the base of
191 the seamount, at a depth of 2570–2620 m (Fig. 2). It consists of a single mound or, probably, a
192 series of coalesced sulfide mounds and their eroded products, each covered by metalliferous
193 sediments and hydrothermal crusts (unpublished report of PMGE, 2007; Beltenev et al. 2007, 2009;
194 Ivanov et al. 2008). The max size of the sulfide mound seen on the seafloor is $\sim 175 \times 200$ m. The
195 samples dredged in 2007 included serpentized ultramafic rocks, altered basalts, and massive
196 sulfides containing up to 20 volume percent of barite (Beltenev et al. 2007). Beltenev et al. (2009)
197 also reported dredging small amounts of inactive chalcopyrite-rich chimneys. Recently,
198 Melekestseva et al. (2014) reviewed the mineralogy, geochemistry, fluid inclusions data, and sulfur
199 isotopic compositions of minerals hosted by colloform and fine-grained, barite-rich massive sulfides
200 from the Semenov-1 hydrothermal field. It was shown that the Semenov-1 barite-rich marcasite–
201 pyrite assemblages were formed from low-salinity fluids produced by phase separation of a Ba-rich
202 hydrothermal fluid. Thermodynamic modeling showed that the formation of the Semenov-1 Ba-rich
203 massive sulfides requires both a mafic substrate and a magmatic volatile contribution to the parent
204 fluid.

205 The Semenov-3 hydrothermal field ($13^{\circ} 30.70' \text{ N}$, $44^{\circ} 55.00' \text{ W}$) is located on the
206 northeastern slope of the seamount at depths between 2400 and 2600 m, and is associated with
207 altered basalts (Fig. 2). Sulfide breccia containing marcasite–pyrite clasts enclosed by sulfide–
208 quartz cement, with numerous fractures and cavities encrusted with barite crystals, were also
209 recovered from the seafloor in 2007, while massive sulfides dominated by pyrite and marcasite
210 were dredged in 2009 (Beltenev et al. 2007, 2009).

211

212 **Analytical methods**

213

214 Barite-bearing samples from the Saf'yanovka deposit were collected from the main ore body in
215 2007–2010 from the open pit that was operating at the time. Massive sulfides from the Semenov-1
216 and -3 hydrothermal fields were collected using dredge station 30L186 and TV-grab station 30L292
217 (hereafter referred to as st. 186 and st. 292, respectively) from the Semenov-1 field and dredge
218 station 30L284 (hereafter, st. 284) from the Semenov-3 field, respectively, during the 2007 cruise of
219 the R/V *Professor Logachev* (Table 1).

220 Ten hand samples from the Saf'yanovka deposit and nine from the Semenov-3 field were
221 studied macroscopically during this study. In addition, forty polished sections from Saf'yanovka
222 and twenty from Semenov-3 were studied by transmitted and reflected light microscopy at the
223 Institute of Mineralogy (IMin UB RAS), Miass, Russia. Major element compositions of barite from
224 the Saf'yanovka deposit was analyzed at the IMin UB RAS using a REMMA-202M electron
225 microscope equipped with a Link ED-System with a 1 μm electron beam, a 15 nA beam current, a
226 20 kV accelerating voltage and a counting time of 120 s for peaks; the standard used was MINM-
227 25-53 from ASTIMEX Scientific Limited (mineral mount no. 01-044). Similarly, major elements
228 for barite from the Semenov-3 fields were determined at IGG-CNR, Padova, Italy, using a
229 CAMECA “CAMEBAX” SX-50 electron microprobe equipped with four vertical WDS
230 spectrometers, a 1 μm electron beam, a 15 nA beam current, 15 kV accelerating voltage, and a
231 counting time of 10 s for peaks and 10 s for background; the analytical standards were pure barite
232 for Ba and S, celestite for Sr, wollastonite for Ca, sphalerite for Zn and galena for Pb. The contents
233 of several minor and trace elements in selected barite samples were measured on an ELAN 9000
234 (PerkinElmer) quadrupole mass-spectrometer at the Zavaritsky Institute of Geology and
235 Geochemistry (IGG UB RAS), Yekaterinburg, Russia, calibrated against the USGS rock standard
236 BCR-2, using In as an internal standard.

237 Sulfur isotopic compositions of barite from the Saf'yanovka deposit and Semenov-3
238 hydrothermal field (reported as $\delta^{34}\text{S}$ per mil relative to the international standard CDT) were

239 analyzed using a DELTA Plus XL, Thermo Finnigan mass-spectrometer using an NBS-127
240 standard at the Center of Analytical Researches, Karpinsky All-Russian Geological Institute
241 (VSEGEI), St. Petersburg, Russia, and a Delta+ Advantage, Thermo Finnigan mass-spectrometer
242 using NBS-123 and IAEA-S-1 standards at IMin UB RAS.

243 Primary fluid inclusions (cf. Roedder 1984) were studied using double-polished sections using
244 a THMSG-600 (LINKAM) equipment at the Laboratory of Thermobarogeochemistry, Faculty of
245 Geology, South-Urals State University, Miass Branch, Russia. Homogenization, eutectic, and final
246 ice melting temperatures were measured. Freezing experiments were always made first. For the
247 Saf'yanovka deposit, which is associated with black shales, a pressure correction of +10 °C (Potter
248 1977) was made, based on the estimated pressure of formation of the deposit of 100–150 bar
249 (Maslennikov 2006), which corresponds to the depth of deposition of modern black-shale sediments
250 in the Red Sea and Black Sea (i.e., 1400 ± 500 m; Murdmaa 1987). For the Semenov-1 and
251 Semenov-3 fields, a pressure correction of +25 °C was made, assuming a pressure of ~250–260
252 bars, which corresponds to a hydrostatic pressure regime under a water column of 2570–2620 m for
253 the Semenov-1 and 2400–2600 m for the Semenov-3 fields (Beltenev et al. 2007). The salt
254 compositions of the fluids were estimated after Borisenko (1977), who provided eutectic
255 temperatures for 38 aqueous salt systems and combined them into five major groups: (i) LiCl-
256 bearing (–74.8 to –78 °C); (ii) CaCl₂-bearing (–49.8 to –55 °C); (iii) MgCl₂-, FeCl₂-, and FeCl₃-
257 bearing (–35 to –38 °C); (iv) NaCl- and KCl-bearing (–21.2 to –23.5 °C); and (v) sulfate- and
258 carbonate-bearing (–1.2 to –6 °C). The salinities of the fluids were calculated from the temperatures
259 of final ice melting following the methods of Bodnar and Vityk (1994).

260 Fluid inclusions in pure barite crystals from the Saf'yanovka deposit and the Semenov-3 field
261 were further analyzed by pyrolysis–gas chromatography, which involves gas extraction from 50–150
262 mg samples by heating to 500 °C in a microfurnace. The compositions of the extracted gases were
263 determined using a Tsvet-100 gas chromatograph equipped with a P-75 pyrolytic device at the
264 Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences

265 (GEOKHI RAS, Moscow) following (Mironova et al. 1992), The gases were accumulated in a
266 precolumn at liquid nitrogen temperature and, then, rapidly introduced into a chromatographic
267 column. Gases were determined using (i) a thermal conductivity detector (katharometer) for the
268 registration of inorganic gases and water and (ii) a flame ionization detector for the registration of
269 hydrocarbon gases. The duration of decrepitation was 3 min that is sufficient for the opening of
270 inclusions in the samples but too short for the occurrence of secondary gas-forming reactions. The
271 sensitivity of gas component determination was the following (μl): $\text{N}_2 - 0.1$, $\text{CH}_4 - 4 \times 10^{-2}$, $\text{CO}_2 -$
272 3×10^{-2} , $\text{H}_2\text{O} - 5 \times 10^{-5}$.

273

274 **Ore microscopy**

275

276 Barite was found in both colloform (Saf'yanovka, Semenov-1) and clastic (Saf'yanovka, Semenov-
277 3) sulfide ores. The microstructural and paragenetic features of the barite-bearing ores are described
278 here in detail.

279

280 *Colloform sulfides*

281

282 Saf'yanovka deposit

283 Samples from the upper part of the main sulfide body are characterized by colloform, zonal, and
284 porous structures (Fig. 3a). In this sector, the hydrothermal precipitates are dominantly composed of
285 pyrite and marcasite, with abundant quartz and barite, and minor chalcopyrite, sphalerite, tennantite,
286 and galena. Barite forms tabular crystals up to 0.2 mm long and fills cavities in the sulfide matrix
287 (Fig. 4a). It is associated with early quartz crystals up to 0.5 mm long and is cut by later, small-
288 crystalline quartz. Locally, barite hosts small (10–20 μm) inclusions of pyrite and sphalerite.
289 Crystalline aggregates of pyrite contain relics of an earlier, fine-grained, laminar, nodular and
290 globular pyrite. The nodular pyrite is characterized by an outer rim of zonal crystalline pyrite.

291 Marcasite occurs as spear to tabular crystals and their aggregates, which are intergrown with
292 crystalline pyrite. Rare small inclusions (up to 10 μm) of chalcopyrite, sphalerite, tennantite, and
293 galena occur in pyrite.

294

295 Semenov-1 field

296 The main mineralogical and petrographical characteristics of the Semenov-1 hydrothermal field
297 were described previously by Melekestseva et al. (2014). They are briefly summarized here and
298 further integrated with additional specific details on barite. The massive sulfides are represented by
299 porous, finely crystalline (st. 186), and colloform, nodular, porous, crystalline and banded (st. 292)
300 marcasite–pyrite aggregates that contain barite and opal (Fig. 3b). At both sites, barite is the major
301 gangue mineral, reaching up to 20 volume percent in single specimens from st. 186, and ~5 to 7
302 volume percent in those obtained from st. 292 (Melekestseva et al. 2014). Tabular barite crystals
303 form elongated aggregates up to several mm long and ~1 mm thick, or pockets made up of rosettes
304 ~1.5 mm across (Fig. 4b). Barite crystals are characterized by growth zoning, which is marked by
305 pores and an abundance of fluid inclusions. Early and late generations of barite can be
306 distinguished. For example, early, relatively large (up to 1 mm) barite crystals are in part
307 pseudomorphically replaced by sulfides and are themselves mantled by sulfides. Later, much
308 smaller (~50 μm) barite crystals overgrow the late-generation sulfides.

309 At st. 186, a fine-crystalline (~10 μm) pyrite is associated with quartz and is overgrown by a
310 coarse-crystalline pyrite. At st. 292, tiny (~1 μm) pyrite globules, clustered into framboids (up to 20
311 μm), are partially replaced by pyrite crystals (up to 20 μm). Marcasite occurs as two generations of
312 spear and tabular crystals (10 μm –1 mm), which are overgrown by a crystalline pyrite. Numerous
313 small (up to 40 μm) sphalerite grains and occasional inclusions of galena were observed in both
314 pyrite and barite. Fine inclusions of chalcopyrite (1–2 μm) and pyrrhotite (up to 8 μm) were
315 observed in crystalline pyrite as small inclusions. Chalcopyrite is also intergrown with sphalerite, or
316 forms “chalcopyrite disease” in sphalerite. Isocubanite was rarely found as isometric inclusions (up

317 to 50 μm) in sphalerite. Sulfides and barite from st. 186 are coated by a thin (~ 20 to 50 μm) rim of
318 opal. Hematite forms numerous clots in the late opal, or occasional globules on the sulfides. Late
319 Fe-hydroxides and jarosite pseudomorphically replace the sulfides.

320

321 *Clastic ores*

322

323 Saf'yanovka deposit

324 The margins of the main Saf'yanovka ore body are host to numerous clastic ores (e.g., Safina and
325 Maslennikov 2009). On its southern flank, sulfide breccias are found which are cemented by barite,
326 quartz and, locally, by carbonaceous silty sandstones (Fig. 3c). The breccias are mainly composed
327 of pyrite and marcasite with lesser sphalerite, galena, quartz, and barite and sporadic chalcopyrite
328 and tennantite.

329 Barite occurs in the cement as compact aggregates of deformed, broken, or slightly curved
330 tabular crystals up to 1 mm in size (Fig. 4c) or as relict crystals in clasts of colloform pyrite ores.
331 Small (~ 10 μm) pyrite crystals, intimately intergrown aggregates of sphalerite and galena, and rare
332 grains of chalcopyrite and tennantite are locally observed in barite crystals. Chains of finely
333 crystalline quartz are observed between individual plates of barite, or within them. Angular pyrite
334 clasts up to 3 cm in size are characterized by colloform, framboidal, crystalline, granular, laminar,
335 nodular and/or globular structures. Clasts of laminar and nodular pyrite are interpreted to represent
336 fragments of seafloor hydrothermal crusts, fossilized fauna from the outer-zone of mineralized
337 material, and black smoker chimneys. Clasts of framboidal pyrite are cemented by fine-grained
338 anhedral pyrite, marcasite or gangue minerals, and served as a core for the late pyrite aggregates.
339 Some clasts, where pyrite replaces pyrrhotite, contain individual or clustered, elongated, oval and
340 round pseudomorphs after near-hydrothermal fauna, set in a fine-grained clastic sulfide matrix.
341 Clasts of radial aggregates and occasional dendrites of marcasite are common. Relics of colloform

342 pyrite are locally found in fine-grained marcasite. Sphalerite, galena, tennantite, and chalcopyrite
343 are observed as small (3–5 μm) inclusions in the pyrite clasts.

344

345 Semenov-3 field

346 Sulfide breccias are composed of angular clasts of colloform, concentric-zonal, massive, and porous
347 marcasite–pyrite aggregates up to 10 cm across that are cemented by fine-grained clastic sulfides
348 and quartz (Fig. 3d). Pyrite, marcasite, and quartz are the dominant minerals, and are accompanied
349 by lesser amounts of barite, chalcopyrite, hematite, and jarosite, and occasional bornite, sphalerite,
350 pyrrhotite, and covellite.

351 Tabular barite crystals up to 1 mm in size fill numerous fractures and cavities in the
352 marcasite–pyrite clasts and cement and form druses or rosettes up to 0.5 cm thick (Fig. 4d). They
353 are locally associated with late chalcopyrite. Quartz forms the cement of the breccias and overgrows
354 the pyrite clasts and barite crystals. Colloform and nodular pyrite clasts consist of porous dendritic
355 early pyrite and zonal crystals of later pyrite. Marcasite occurs as radial aggregates up to 1 mm in
356 size made of spear crystals or of intergrown, zonal crystals with rhombic sections. Pyrite and
357 marcasite are also closely associated with concentric-zonal aggregates. Chalcopyrite is found as
358 individual round grains, anhedral aggregates, and occasional euhedral crystals in the cement and
359 fractures and pores of the marcasite–pyrite aggregates locally associating with barite. Bornite forms
360 small ($\sim 10 \mu\text{m}$) grains surrounded by chalcopyrite in the cement or in the late quartz rims. Micron-
361 sized covellite rims are developed around the chalcopyrite grains. Small (up to $10 \mu\text{m}$) subhedral
362 sphalerite and pyrrhotite grains occur in the pyrite clasts. Hematite is found as globules in the quartz
363 rims around pyrite or as acicular crystals in cement. Jarosite zones up to $50 \mu\text{m}$ thick are developed
364 in the marginal and central portions of marcasite–pyrite clasts.

365

366 **Chemical composition of barite**

367

368 Strontium is the most abundant minor component in barite based on microprobe and ICP-MS
369 analyses (Tables 2 and 3). Barite from the Saf'yanovka deposit contains less SrO (up to 1.05 wt% in
370 microprobe analyses and 2530 to 3100 ppm Sr in ICP-MS analyses) than that from the Semenov-1
371 (up to 4.12 wt% SrO and 7050 ppm Sr; Melekestseva et al., 2014) or Semenov-3 (up to 3.36 wt%
372 SrO and 3410 ppm Sr) hydrothermal fields. However, in general, there is no univocal relationship
373 between SrO contents in barite and the various ore facies.

374 Barite from Semenov-1 field contains minor to trace PbO (0.02–0.16 wt%), CaO (0.01–0.38
375 wt%), ZnO (0.01–0.05 wt%) and FeO (0.12–0.40 wt%). Semenov-3 barite is zoned, with higher
376 SrO (up to 4.73 wt%) and PbO (up to 0.5 wt%) contents in the core, and lower contents (0.24–1.06
377 wt% and < 0.1 wt%, respectively) in the margins. Barite from the Saf'yanovka colloform ores
378 contains only minor admixtures of CaO (0.03–0.11 wt%), which was not detected in barite derived
379 from the clastic ores.

380 At Saf'yanovka, barite from the clastic ores is enriched in several trace elements (i.e., Cu, Zn,
381 Pb, Ga, As, Hg, Bi, Mn, and Sr) when compared with barite from the colloform ores (Table 3).
382 Barite from the colloform ores has relatively increased contents of nickel only (i.e., 15.1 vs 6.6
383 ppm). The contents of Ge, Se, Cd, Tl, Sb, Te, Co, Y, and V are relatively low (and similar) in both
384 varieties of barite.

385 Similarly, barite from the Semenov-3 breccias is enriched in many trace elements (Cu, Pb, Ga,
386 Ge, Cd, Sb, Co, Ni, and V) relative to barite from the Semenov-1 finely crystalline sulfides.
387 However, barite from the Semenov-3 clastic sulfides has lower contents of Zn, Mn, and Sr. Other
388 trace elements (i.e., As, Se, Te, Tl, Bi, and Y) show no significant variations between the two
389 varieties of barite.

390

391 **Sulfur isotopic composition of barite**

392

393 The sulfur isotopic compositions of the analyzed barites vary within a single deposit, or cluster
394 (Table 4). The $\delta^{34}\text{S}$ values of barite from the Saf'yanovka colloform ores show a relatively wide
395 range (from +20.9 to +25.5‰), whereas the $\delta^{34}\text{S}$ values of barite from the Saf'yanovka clastic ores
396 are higher and show a narrower range (from +27.0 to +29.2‰). The $\delta^{34}\text{S}$ values of barite from the
397 Semenov-1 colloform sulfides (from +21.0 to +21.3‰; Melekestseva et al. 2014) are higher than
398 those of barite from the Semenov-3 clastic sulfides (from +18.7 to +20.6‰).

399

400 **Fluid inclusion data**

401

402 Fluid inclusions in barite from the Saf'yanovka colloform ores are 10 to 40 μm in size and are
403 characterized by negative-crystal to subround shapes. The negative-crystal inclusions are mostly
404 one-phase (liquid), whereas subround inclusions are vapor-rich and two-phase (liquid + vapor). In
405 the liquid two-phase inclusions the vapor bubbles occupy 20–30 volume percent of the inclusions.
406 In the vapor-rich inclusions the relative proportion of liquid and vapor was difficult to assess.
407 Similar fluid inclusions ranging 5 to 30 μm in size are unevenly distributed in barite from the
408 Saf'yanovka clastic ores.

409 Rare angular, round, or spindle-like fluid inclusions (8–12 μm , occasionally up to 20 μm long)
410 are uniformly distributed in barite within the Semenov-1 field (Melekestseva et al. 2014). The
411 majority of them are two-phase fluid inclusions composed of liquid and a vapor bubble, which
412 occupies 5–10 vol.% of the inclusions. More rare, small groups of two-phase inclusions, partly
413 showing negative crystal shapes, consist of liquid and a larger vapor bubble, which occupies up to
414 over 50 vol% of the inclusion. At the Semenov-3 field, negative-crystal or elongated fluid
415 inclusions <10 μm in size are unevenly distributed in barite. Both one- (liquid) and two-phase
416 (liquid + vapor) inclusions, with a vapor bubble occupying 15–20 volume percent of the inclusion
417 are found.

418 The results of heating and cooling measurements on liquid-rich, two-phase inclusions are
419 summarized in Table 5. Upon heating, the inclusions in barite from colloform sulfides homogenize
420 to the liquid phase at 162 °C to 184 °C (average and median 173 °C, mode 177 °C) in the
421 Saf'yanovka samples, and at 58 °C to 199 °C (average, median and mode at 150 °C) at the
422 Semenov-1 samples (Fig. 5a, c). The homogenization temperatures of fluid inclusions in barite from
423 clastic sulfides range from 130 °C to 170 °C (with two modes at 135–140 °C and 155–160 °C,
424 average at 150 °C, and median at 149 °C) in the Saf'yanovka samples and from 241 °C to 310 °C
425 (average, median and mode at 275 °C) in the Semenov-3 samples (Fig. 5e,g). Effects of possible
426 stretching of fluid inclusions were minimized by studying mostly small-sized, round inclusions, as
427 suggested by Ulrich and Bodnar (1988). The relatively narrow ranges of homogenization
428 temperatures and absence of high-*T* outliers within each sample population (Fig. 5a), as well as the
429 lack of correlation between homogenization temperatures and inclusion size further suggest that
430 stretching was effectively minimized. The above data should therefore be reliable.

431 Final temperatures of ice melting are –0.9 to –2.7 °C (Saf'yanovka colloform ores), –0.5 to –
432 2.8 °C (Semenov-1 colloform sulfides), –0.8 to –3.3 °C (Saf'yanovka clastic ores), and –3.0 to –6.0
433 °C (Semenov-3 clastic sulfides). According to Bodnar and Vityk (1994), these values correspond to
434 salinities of 1.6 to 4.5 wt% NaCl_{eq} (average, median and mode of 2.9 wt%), of 0.6 to 3.8 wt% NaCl
435 equivalent (average, median and mode of 2 wt%), 1.4 to 5.4 wt% NaCl_{eq} (average of 3.9 wt%,
436 median of 4.2, and two modes at 2.5–3.0 wt% and 4.5–5.0 wt%), and 4.8–9.2 wt% NaCl_{eq}
437 (average, median and mode of 6.7 wt%; Figs. 5b, d, f, h), respectively. The temperature vs. salinity
438 dependence is either absent (Saf'yanovka and Semenov-3) or weakly positive (Semenov-1 barite)
439 (Fig. 6).

440 The eutectic temperatures of fluid inclusion in barite from the Saf'yanovka and Semenov-1
441 colloform sulfides vary from –21.7 to –22.3 °C and from –2.2 to –6.6 °C, respectively. These values
442 are compatible with a NaCl–Na₂CO₃–H₂O system, with possible addition of Na₂SO₄ and NaHCO₃
443 for the Saf'yanovka deposit and with Na₂SO₄–K₂SO₄–H₂O and Na₂SO₄–NaHCO₃–H₂O systems for

444 the Semenov-1 field (cf. Borisenko 1977; see also Melekestseva et al. 2014). The eutectic
445 temperatures of fluid inclusions in barite from the clastic ores range from -22.0 to -22.3 °C in the
446 Saf'yanovka deposit and from -21.1 to -21.8 °C in the Semenov-3 field. These values are
447 compatible with a NaCl-dominated composition, with possible addition of Na_2SO_4 and NaHCO_3 for
448 the Saf'yanovka breccias (cf. Borisenko 1977).

449 Gas chromatography data (Table 6) show that the fluid inclusions, as expected, are dominated
450 by H_2O . Inclusions in barite from the Saf'yanovka colloform ores are enriched in CH_4 , CO_2 , and
451 CO relative to those from the Saf'yanovka clastic ores. Inclusions in barite from the Semenov-3
452 clastic ores have higher contents of CO_2 than those from the Saf'yanovka clastic ores and have the
453 highest CO_2/CH_4 ratios. Other potential volatile components, such as H_2S , SO_2 or various
454 hydrocarbons, which are typical of hydrothermal vents (e.g. Gieskes et al. 1988; de Ronde et al.
455 2003, 2011), were below detection limits in all analyzed samples. These data can be compared with
456 those of Krylova and Melekestseva (2011), who qualitatively estimated by Raman spectroscopy the
457 composition of vapor in fluid inclusions in barite from Semenov-1 st. 186: spectra in the range
458 $1100\text{--}2000\text{ cm}^{-1}$ showed peaks at 1150 cm^{-1} , compatible with the presence of SO_2 , and at 1370 and
459 1388 cm^{-1} , indicating the presence of CO_2 (cf., Naumov et al. 1986; Frezzotti et al. 2012).

460

461 **Discussion**

462

463 Barite is a common gangue mineral in ancient VMS deposits of the Kuroko type associated with
464 felsic rocks (cf. Sato 1977; Scott 1980; Ohmoto 1996) and in modern arc-related and sediment-
465 hosted hydrothermal fields (cf., Gieskes et al. 1988; Hannington and Scott 1988; Shadlun et al.
466 1992; Binns and Scott 1993; Fouquet et al. 1993a; Goodfellow and Franklin 1993; Halbach et al.
467 1993; Herzig et al. 1993; Zierenberg et al. 1993; Davis et al. 2003; de Ronde et al. 2003, 2005;
468 Glasby et al. 2008; Berkenbosch et al. 2012; Hein et al. 2014). Barite is instead rare in most mafic-
469 hosted hydrothermal fields on slow-spreading ridges (Fouquet et al. 1993b; Rona et al. 1993;

470 Duckworth et al. 1995; Halbach et al. 1998) and in their ancient, Cyprus-type VMS analogs (cf.
471 Constantinou and Govett 1972; Ixer et al. 1984; Hannington et al. 1998). The abundance of barite in
472 the Semenov-1 and -3 hydrothermal fields, as well as in the Lucky Strike, Menes Gwen, and
473 Krasnov hydrothermal fields of the MAR (Fouquet et al. 1994; Bogdanov et al. 2006; Cherkashev
474 et al. 2008), is thus somewhat anomalous. The Fe-disulfide-rich and barite-rich composition of the
475 colloform and clastic ores of the backarc-hosted Saf'yanovka VMS deposit is similar to that of the
476 Semenov-1 and -3 hydrothermal fields, which suggests similar formation condition, in spite of
477 different geodynamic setting. The significance of such similarities is discussed below.

478

479 Textural-structural and mineralogical features

480

481 The abundance of finely crystalline, porous, nodular, banded, and colloform structures, the
482 predominance of pyrite and marcasite, and the presence of barite with less abundant SiO₂ phases in
483 *colloform* sulfides from both the Saf'yanovka deposit and Semenov-1 hydrothermal field suggest
484 formation under comparable physico-chemical conditions. The morphological features of barite
485 crystals and aggregates in colloform sulfides from both deposits are typical of hydrothermal barites
486 (cf. Paytan et al. 2002; de Ronde et al. 2005; Berkenbosch et al. 2012). The abundance of pyrite and
487 marcasite points to the predominance of Fe over chalcophile metals and relatively high sulfur
488 activity (Hannington and Scott 1989). Despite the strict association of barite and sulfides,
489 precipitation of barite in colloform sulfides from the Saf'yanovka deposits and Semenov-1 field
490 appears to postdate and predate, respectively, that of the accompanying sulfides, therefore it
491 remains unclear whether barite and sulfides could have been part of the same paragenesis. Similar
492 low- to medium-temperature massive sulfides with simple mineral compositions and dominant
493 pyrite and marcasite are well documented at the flanks of seafloor sulfide mounds (e.g., TAG and
494 Snake Pit hydrothermal fields, Mid-Atlantic Ridge; Fouquet et al. 1993; Rona et al. 1993). Barite
495 chimneys with pyrite were reported on the flanks of the Loki's Castle and Jan Mayen hydrothermal

496 fields in the Arctic mid-Oceanic Ridge (Eickmann et al. 2010; Pedersen et al. 2010). These
497 conditions appear to be distinct from those of seafloor, barite-rich assemblages recovered from arc-
498 related hydrothermal systems, where barite is mostly associated with Cu-rich or polymetallic
499 sulfides: e.g., Cu-rich and Zn-rich chimneys at the Brother volcano (de Ronde et al. 2003), Cu-rich
500 chimneys in the PACMANUS hydrothermal field (Binns and Scott 1993) or sphalerite-dominated
501 chimneys in hydrothermal fields of the Lau basin (Herzig et al. 1993). At the same time, the pyrite-
502 rich samples recovered from the Brother volcano showed the presence of anhydrite instead of barite
503 (de Ronde et al. 2005). The Fe-rich sulfides with barite from the White Lady hydrothermal field in
504 the North Fiji basin represent spires rather than colloform massive sulfides (Bendel et al. 1993). The
505 Fe-rich assemblage with barite from the JADE hydrothermal field in the Okinawa Trough replaces
506 primary Cu- and Zn-rich assemblages (Halbach et al. 1993).

507 *Clastic* ores from the Saf'yanovka deposit resemble those from the Semenov-3 hydrothermal
508 field in several respects. That is, the combination of sulfide clasts with colloform, finely crystalline,
509 banded, and massive textures, the significant proportions of sulfide-quartz cement, the presence of
510 host-rock clasts, the mineral composition (i.e., major and accessory sulfides), and the abundance of
511 barite and quartz. Barite in breccias from both deposits was formed after the cementation of the
512 breccia. Barite from the Saf'yanovka clastic ores precipitated after formation of diagenetic pyrite
513 framboids and metacrystals, and its compact aggregates are similar to those of diagenetic barite
514 from oceanic sediments (Paytan et al. 2002). The barite crystals are deformed and locally show
515 stylolite boundaries as a result of burial and compaction (Fig. 4c). Therefore, its origin can be
516 defined as 'anadiagenetic' (cf. Fairbridge 1967). In contrast to Saf'yanovka deposit, barite in clastic
517 sulfides from the Semenov-3 field is most probably a product of mixing of late hydrothermal fluid
518 with seawater. It occurs in large cavities in clasts and cement, forms radial aggregates of large
519 tabular crystals, which are typical of active hydrothermal chimneys (e.g., Fouquet et al. 1993a; de
520 Ronde et al. 2003), is locally associated with late chalcopyrite with high Se content (638–1201 ppm,
521 unpublished LA-ICP-MS analysis by I.Yu. Melekestseva). The high Se contents in chalcopyrite are

522 considered as evidence of high-temperature and highly reducing conditions (Maslennikov et al.
523 2009). A late hydrothermal origin is consistent with $^{230}\text{Th}/\text{U}$ dating of massive sulfides from station
524 30L284, which showed multi-stage hydrothermal activity at the Semenov-3 hydrothermal field with
525 at least four peaks at ~90, 51, 47, and 35 ka (Kuznetsov et al. 2011).

526

527 Formation conditions of barite

528

529 Pressure-corrected homogenization temperatures of fluid inclusions in barite from the barite-rich
530 *colloform* sulfides are 172–194 °C for the Saf'yanovka deposit and 83–224 °C for the Semenov-1
531 field (Table 5). The widespread presence of marcasite, which forms at temperatures <240 °C
532 (Murowchick and Barnes 1986), is consistent with formation of the colloform sulfide–barite
533 association at moderate to low temperatures. Assuming isotopic equilibrium was attained, the $\delta^{34}\text{S}$
534 fractionation between barite and colloform sulfides at Semenov-1 would yield a temperature of 239
535 °C. This estimate is consistent with fluid inclusions data if uncertainties of sulfur isotope
536 thermometry are taken into account (± 10 to ± 40 °C; cf. Seal 2006). The same calculation for the
537 Saf'yanovka samples yielded a temperature of 265 °C, which clearly indicates isotopic
538 disequilibrium, consistent with the interpreted late origin of barite relative to the colloform sulfides.
539 The formation temperatures estimated for the colloform sulfides–barite associations (172–225 °C)
540 are consistent with the typical formation conditions of seafloor white smokers, in which barite is
541 predominant over other gangue minerals (<300 °C; Hannington et al. 1995).

542 The pressure-corrected homogenization temperatures of fluid inclusions in barite in the
543 Saf'yanovka *clastic* ores (140–180 °C), which we interpret to be anadiagenetic based on
544 microtextural features (see above), are within the range of diagenetic processes (up to 200 °C; e.g.,
545 Yapaskurt 2005). The higher homogenization temperatures of fluid inclusions in barite from the
546 Semenov-3 clastic sulfides (266–335 °C) reflect its formation from a relatively high-temperature

547 hydrothermal fluid, which is also supported by its association with late Se-rich chalcopyrite (see
548 above).

549 The relationship between barite formation temperatures and mineralogy of associated sulfides
550 is in line with estimates from other modern seafloor hydrothermal sites. In general, pure barite
551 precipitated on chimney rims or found as massive fragments records relatively low temperatures
552 (ca. 150–200 °C), barite associated with sphalerite and polymetallic sulfides records moderately
553 high temperatures (214–280 °C), and barite associated with chalcopyrite–pyrite records the highest
554 temperatures (up to at least 290 °C) (Herzig et al. 1993; Petersen et al. 2004; de Ronde et al. 2003).

555

556 Chemical composition of barite

557

558 Strontium is one of the most abundant minor components in barite (Deer et al. 1962; Hanor 2000).
559 The barites studied have low SrO contents (0.00–4.73 wt%), especially those from the Saf'yanovka
560 deposit (up to 1.05 wt%). Reported SrO contents in different genetic types of barite, including
561 examples from ancient massive sulfide deposits and modern hydrothermal sulfide fields, are highly
562 variable. For example, both ancient and modern seafloor hydrothermal barites typically contain
563 small amounts of SrO (e.g., 0.6–3.5 wt% SrO, Franklin Seamount, Woodlark basin, Binns et al.
564 1993; 0.07–0.22 wt% SrO, Devonian Balta-Tau VMS deposit, South Urals, Holland 2002; average
565 0.50 wt% SrO, Mesoproterozoic stratiform Pb-Zn-Cu±Au-Ba deposits, South Africa, McClung et
566 al. 2007). Modern seafloor specimens rarely exceed 10 wt% of SrO (e.g., up to 11.85 wt% SrO,
567 barite–sulfide edifice, Loihi Seamount, Hawaii, Davis et al. 2003; up to 11.9 wt% SrO, barite
568 chimneys, Gulf of Mexico, Fu et al. 1994). Low to intermediate SrO contents are reported in marine
569 biotic barite (e.g., <0.05 wt% SrO, central North Pacific seafloor; Bertram and Cowen 1997) and in
570 cold-seep barite (1.05–5.45 wt% SrO, shallow hemipelagic sediments with sulfides, Middle Valley
571 field, Juan de Fuca Ridge, Goodfellow and Blaise 1988; up to 4 wt% SrO, Deryugin Basin, Sea of
572 Okhotsk, Greinert et al. 2002; 0.15–1.52 wt% SrO, San-Andreas fracture zone, Pacific Ocean; Hein

573 et al. 2007). Overall, the range of SrO contents in barite appears to be irrespective of its origin,
574 suggesting that the degree of strontium enrichment may either be related to fluctuation of Sr
575 contents in the parent fluid or reflect variable mixing of these fluids with seawater. Mixing with Sr-
576 rich seawater may account for variable Sr contents in Saf'yanovka (and perhaps Semenov)
577 hydrothermal barite, because barite from deeper, stockwork pyrite–sphalerite ores contain less Sr
578 (up to 944 ppm) (Murzin et al. 2010). Higher Sr levels in diagenetic barite from the Saf'yanovka
579 clastic ores may indicate contribution from connate seawater and from alteration of clasts of
580 plagioclase-rich host rocks.

581 The measured contents of Cu and Zn (Pb) in barite from the Saf'yanovka *colloform* ores and
582 the higher contents of Zn in barite from the Semenov-1 field are probably related to micro-
583 inclusions of sulfides (e.g., sphalerite, chalcopyrite and galena), which were recognized during the
584 petrographic study. The higher Sn contents in barite from the Semenov-1 field may also be
585 attributed to sphalerite inclusions, since sphalerite may contain Sn as trace element (Cook et al.
586 2009). The relatively high contents of Ni (and Co) found in Semenov-1 barite are not unusual for
587 seafloor hydrothermal barite (cf. Davis et al. 2003; Ludwig et al. 2006). These high contents may
588 derive from seawater, as significant sorption of these elements occurs on barite after a long period
589 of interaction with seawater (Jewell and Stallard 1991). A similar process was proposed for Ni-
590 enriched barite from inactive carbonate edifices at the Lost City low-temperature ultramafic-
591 associated field (Ludwig et al. 2006). Incorporation of Co and Ni from seawater rather than from
592 the parent fluid is supported by the trace element compositions of associated pyrite and marcasite,
593 which are both Co- and Ni-free (Melekestseva et al. 2014). The higher Mn contents in barite from
594 the Semenov-1 field relative to other studied barites may also have derived from seawater.

595 Barites from the Saf'yanovka and Semenov-3 *clastic* ores are enriched in several trace
596 elements when compared to barite from the colloform sulfides. In particular, the enrichment of
597 Semenov-3 chalcopyrite-associated barite in several chalcophile elements (e.g., Cu and, to a lesser
598 extent, Ga, Ge and Sb) is probably a real feature, since no micro-inclusions of chalcopyrite were

599 observed in such barite. By contrast, the relatively high contents of Co (44 ppm) and Ni (437 ppm)
600 probably reflect the presence of inclusions of clastic crystalline pyrite, which contain high Co (266–
601 1444 ppm) and Ni contents (216–127 ppm Ni; I. Melekestseva, unpublished data). The higher Zn,
602 Pb, As, Te, Hg, and Bi contents in barite from the Saf'yanovka clastic ores are probably due to
603 micro-inclusions of sphalerite, tennantite, and galena observed during the petrographic studies.

604

605 Sources of sulfur

606

607 The average $\delta^{34}\text{S}$ value for barite from *colloform* ores of the Saf'yanovka deposit (+22.9‰)
608 corresponds to that of Silurian–Devonian seawater (+23 to +24‰, Claypool et al. 1980). The
609 average $\delta^{34}\text{S}$ value for barite from colloform sulfides of the Semenov-1 field (+21.2‰;
610 Melekestseva et al., 2014) matches the composition of contemporary seawater (+21.2‰, Rees et al.
611 1978). These results clearly indicate a seawater source for SO_4^{2-} for both hydrothermal barites.

612 The average $\delta^{34}\text{S}$ values for barite from *clastic* ores of the Saf'yanovka deposit (+28.1‰) are
613 significantly higher than that of Silurian–Devonian seawater (+23 to +24‰, Claypool et al. 1980),
614 which may indicate partial reduction of seawater sulfate and concurrent isotopic enrichment of the
615 residual sulfate (Shanks et al. 1995). Sulfate sulfur may be reduced by bacterial or thermochemical
616 reduction (Machel 2001). Bacterial sulfate reduction, which is typically invoked for diagenetic
617 barites (Paytan et al. 2002; Hein et al. 2007), is believed to occur from 0 °C to about 60–80 °C
618 (Machel 2001). Thermochemical sulfate reduction is common at temperatures of 100–180 °C
619 (Machel 2001) and may arise from interaction with ferrous minerals and/or organic matter in the
620 shallower parts of hydrothermal system (Shanks et al. 1995; de Ronde et al. 2003). The pressure-
621 corrected homogenization temperatures of fluid inclusions in barite from clastic ores of the
622 Saf'yanovka deposit (140–180 °C) support thermochemical rather than biological sulfate reduction.

623 All measured $\delta^{34}\text{S}$ values of barite from the Semenov-3 field (average = +19.6‰) are lower
624 than that of seawater, which suggests partial sulfate contribution from the oxidation of isotopically

625 lighter H₂S in vent fluid or sulfide minerals (Shanks et al. 1995). This is in agreement with the
626 association of barite with late-stage chalcopyrite, which is believed to have precipitated from a
627 relatively reduced, H₂S-bearing fluid (see above). Similar $\delta^{34}\text{S}$ values lower than seawater were
628 reported in barite from the Axial Seamount, Juan de Fuca Ridge (+16.1 to +21.2‰; Hannington and
629 Scott 1988) and Franklin Seamount, Woodlark Basin (+19.2 to +20.9‰; Binns et al. 1997).

630

631 Fluid compositions

632

633 Salinities of liquid-rich fluid inclusions in hydrothermal barite from Saf'yanovka and Semenov-1
634 colloform sulfides are mostly lower than seawater (3.2 wt% NaCl equiv.; Bischoff and Rosenbauer
635 1984; see Fig. 6) and among the lowest reported for massive sulfide deposits and seafloor
636 hydrothermal fields (e.g., Lecuyer et al. 1999; Dahlmann et al. 2001; de Ronde et al. 2003; Petersen
637 et al. 2004; Bortnikov et al. 2004; Scotney et al. 2005; Simonov et al. 2006). The coexistence with
638 vapor-rich inclusions suggests that the fluid was boiling during barite formation, so that the original
639 fluid could have been even less saline. Following a widely accepted view (e.g., Cowann and Cann
640 1988; Massoth et al. 1989; Butterfield et al. 1990; Bortnikov et al. 1997; de Ronde et al. 2003; von
641 Damm et al. 1998; 2003; Petersen et al. 2004; Suzuki et al. 2006), Melekestseva et al. (2014)
642 interpreted the low salinity of fluid inclusions in Semenov-1 barite as being due to phase separation
643 of an aqueous fluid below the seafloor and this conclusion may be extended to barite in
644 Saf'yanovka colloform sulfides.

645 The calculated salinities of the fluid inclusions in late hydrothermal barite from the Semenov-
646 3 breccia are 1.5 to 2.9 times that of seawater (Table 4). Relatively high salinities are typical of
647 fluid inclusions in many hydrothermal sulfide fields. However, in most cases, the salinities show a
648 range of values from near- or less-than-seawater values, to higher-than-seawater values (e.g., Binns
649 et al. 1993; Herzig et al. 1993; Petersen et al. 2000; Lüders et al. 2001; Bogdanov et al. 2002; de
650 Ronde et al. 2003; Bortnikov et al. 2004; 2005; Cazañas et al. 2008). This range is invariably

651 explained by phase separation, followed by remixing of separated vapor and liquid phases during
652 ascent, probably with some brine loss at depth (e.g., at the TAG field with salinities of 1.9 to 6.2
653 wt.% NaCl equiv.; Petersen et al. 2000). Such a variability of salinity values is not observed in our
654 Semenov-3 samples. However, the high salinity values may still be a result of phase separation, if
655 only the high-density brines were trapped or if they were expelled independently at a late stage (cf.
656 Gruen et al. 2014). As an alternative, the high salinities may be related to a contribution of
657 magmatic fluid (cf. Nehlig 1993; de Ronde et al. 2011). Taking into account the high CO₂ contents
658 of the fluid inclusions (Table 6), a magmatic contribution is likely. The variable salinity of fluid
659 inclusions in anadiagenetic barite from the Saf'yanovka clastic ores (1.4–5.4 wt% NaCl equiv.), for
660 which a late hydrothermal origin is not supported (see above), probably reflects involvement of
661 several sources of water: (i) connate seawater (Fairbridge 1967), (ii) high-salinity water from
662 dehydration of layered silicates (cf. Kelly and Delaney 1987) and (iii) low-salinity water released
663 from fluid inclusions in dissolved or mechanical deformed primary hydrothermal barite.

664 In general, volatiles in the fluid inclusions in the studied barite are dominated by H₂O
665 followed by CO₂ with lesser amount of CO, CH₄, and N₂. The presence of CO₂ may be related to
666 contribution from different sources (magma, seawater, interaction with organic matter or host
667 rocks). In case of Saf'yanovka colloform ores with plentiful fauna relics, the high CO₂ contents may
668 be provided by oxidation of CH₄ (according to reaction $\text{CH}_4 + 2 \text{O}_2 = 2 \text{H}_2\text{O} + \text{CO}_2$) or organic
669 matter. The high contents of CO₂ in Semenov-3 barite are most likely due to magmatic contribution
670 (cf. Butterfield et al. 1990; Lilley et al. 2003; de Ronde et al. 2003), consistent with the higher
671 salinity of fluid inclusions. The presence of SO₂ (1150 cm⁻¹) and CO₂ (1370 and 1388 cm⁻¹) peaks
672 in the Raman spectra of the fluid inclusions from Semenov-1 field (Krylova and Melekestseva,
673 2011) may also reflect magmatic contribution to the hydrothermal fluid similar to that observed at
674 some high-temperature seafloor sulfide edifices such as Brothers volcano of the Kermadec arc (de
675 Ronde et al. 2011) or NW Rota-1 volcano of the Mariana arc (Butterfield et al. 2011), or at other arc
676 magmatic-hydrothermal sites such as Kasuga seamount also of the Mariana arc, or hot spot

677 volcanoes such as McDonald seamount and Loihi seamount (McMurty et al. 1993). Based on
678 thermodynamic modeling, a magmatic contribution has also been suggested as essential for the
679 formation of Fe-disulfide–barite-rich association at Semenov-1 (Melekestseva et al. 2014).

680 The higher contents of CH₄ in fluid inclusions from the Saf'yanovka colloform ores may be
681 related to decomposition of hydrothermal fauna or interaction with black shales (cf. Lilley et al.
682 1993, 2003; de Ronde et al. 2003). Although an abiogenic origin of CH₄ cannot be excluded (cf.
683 Lilley et al. 1993), the abundant near-hydrothermal macro- and microfauna and the presence of
684 associated black shales at the Saf'yanovka deposit support its biogenic genesis.

685 The source for N₂ in the Saf'yanovka barites is uncertain, because it may be derived from
686 seawater (Lilley et al. 2003; Steele et al. 2010), from magmas (cf. de Ronde et al. 2003) or from
687 oxidation of hydrothermal ammonium and its microbial assimilation (Lam et al. 2004; Lang et al.
688 2012). A derivation from oxidation of hydrothermal ammonium, which may be originated from the
689 decomposition of seafloor organic matter in sediments (Lilley et al. 1993), is a plausible
690 hypothesis, given the presence of black shales and macro- and microfauna at the Saf'yanovka
691 deposit. A magmatic source cannot be excluded, but it seems less likely, since no other magmatic
692 indicators are found in the studied barite. The increase of one order of magnitude in the proportion
693 of N₂ in barite from the Saf'yanovka clastic ores appears consistent with its diagenetic formation, as
694 nitrogen may be generated during thermal decomposition of organic matter in clay-rich sedimentary
695 rocks (cf. Littke et al. 1995; Hao et al. 2002).

696 Overall, the analyzed fluid inclusions in barite at Saf'yanovka and Semenov-1 and -3 have
697 lower H₂O, significantly higher CO₂ and CH₄, and comparable N₂ contents relative to barite in
698 massive sulfides from the Brothers volcano, Kermadec arc (de Ronde et al. 2003), or barites from
699 the Myojinsho and Myojin Knoll vent sites, Izu-Bonin arc (Sasaki et al. 1995). This suggests that
700 the parent fluids were either more volatile-rich or less diluted by seawater, similar to what proposed
701 for the Myojinsho and Myojin Knoll vent sites (cf. de Ronde et al. 2003). The presence of CO in the
702 studied fluid inclusions indicates that the hydrothermal fluids from the Saf'yanovka deposit and

703 Semenov-3 field were not fully oxidized in comparison with the above mentioned hydrothermal
704 sites.

705

706 **Conclusions**

707

708 The comparative study of barite from colloform and clastic ores from the Paleozoic Saf'yanovka
709 VMS deposit and modern inactive Semenov-1 and -3 hydrothermal fields indicates that morphology
710 is the most distinctive feature in different types of barite. Hydrothermal barite in both ancient and
711 modern colloform ores shows undeformed, tabular to platy morphology, with or without formation
712 of rosette aggregates. This type of barite may locally be replaced by sulfides. In contrast, non-
713 hydrothermal, diagenetic barite (observed in the Saf'yanovka clastic ores) occurs as compact
714 aggregates of deformed, broken, or slightly curved platy or tabular crystals. Stylolite boundaries
715 characteristically occur between the deformed crystals. Stylolites and deformation indicate
716 development of pressure and strain during anadiagenetic crystallization within the buried clastic
717 ores.

718 The chemical and sulfur isotopic compositions of barite and the compositions of fluid
719 inclusions in it show a significant variability, but wide overlaps are observed between different
720 genetic types. The variable contents of Sr, the main minor component in barite, essentially reflect
721 variable contribution of this element from seawater (for both hydrothermal and non-hydrothermal
722 barite) and, possibly, from plagioclase-rich host rocks (for non-hydrothermal barite). Apparent
723 variations in several trace elements are mostly ascribed to contamination from sulfide micro-
724 inclusions. The sulfur isotopic compositions of hydrothermal barite generally indicate seawater as
725 the main source of sulfur, although additional contribution of isotopically light sulfur from partial
726 oxidation of H₂S (Semenov-3 field, this study; Axial Seamount, Hannington and Scott 1988;
727 Franklin Seamount, Binns et al. 1997; Hine Hina field, Herzig et al. 1998) or of isotopically heavy
728 sulfur from bacterial sulfate reduction (Loki's Castle field, Eickmann et al. 2010) is also

729 documented. A contribution from isotopically heavy sulfur remaining after partial reduction of
730 seawater sulfate appears to be common in non-hydrothermal, diagenetic barite, although the
731 mechanism of sulfur reduction may vary (i.e., thermochemical sulfate reduction for the Saf'yanovka
732 deposit studied in this work vs. bacterial sulfate-reduction for diagenetic barite; cf. Paytan et al.
733 2002; Hein et al. 2007).

734 In spite of different geodynamic setting, barite-bearing pyrite-rich colloform ores from the
735 Saf'yanovka VMS deposit (back-arc basin) and Semenov-1 and -3 hydrothermal fields (slow-
736 spreading mid-oceanic ridge) were formed under similar, low- to moderate-temperature conditions
737 (83–233 °C). Temperatures as high as 335 °C are estimated for some late-stage hydrothermal
738 barites from Semenov-3 clastic sulfides, which are associated with Se-rich chalcopyrite. Diagenetic
739 barite in Saf'yanovka clastic pyrite ores records moderate temperatures of 140–180 °C. Combining
740 our new data with those for other seafloor hydrothermal barites the following systematics can be
741 defined: barite precipitated on chimney rims or associated with pyrite-rich colloform sulfides forms
742 at relatively low to moderate temperatures (ca. 80–230 °C); barite associated with sphalerite-rich
743 and polymetallic massive sulfides forms at moderately high temperatures (210–280 °C), and barite
744 associated with chalcopyrite records the highest temperatures (265–335 °C).

745

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747

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759

760 FIGURE CAPTIONS

761

762 Fig. 1. (a) Geological sketch of the Central Urals (simplified after Puchkov 1993) with location of
763 the Saf'yanovka deposit. (b) cross-section of the deposit, simplified after unpublished report of
764 Korovko et al. (2004). (c) reconstruction of the sulfide mound, modified after
765 Maslennikov (2006). Stars indicate sampling sites: sample KLF (left) and sample Saf007
766 (right).

767

768 Fig. 2. Location of the Semenov-1 and -3 hydrothermal fields within the Semenov massive sulfide
769 cluster (after Ivanov et al. 2008; Beltenev et al. 2009).

770

771 Fig. 3. Macroscopic structures of barite-bearing ores from the Saf'yanovka deposit and massive
772 sulfides from the Semenov-1 and Semenov-3 hydrothermal fields: (a) colloform ore,
773 Saf'yanovka deposit, sample KLF; (b) fine-crystalline massive sulfides, Semenov-1 field, sample
774 186; (c) pyrite breccia, Saf'yanovka deposit, sample Saf007; (d) pyrite breccia from the Semenov-3
775 field, sample 284. Aggregates of barite are indicated by arrows.

776

777 Fig. 4. Morphology of barite from the Saf'yanovka deposit and Semenov-1 and -3
778 hydrothermal fields: (a) platy barite crystals replaced by quartz, Saf'yanovka colloform ores,
779 sample KLF; (b) platy barite crystals (Ba) in finely crystalline groundmass of early pyrite and
780 quartz (Py-I + Q), with a veinlet of late pyrite (Py-II), Semenov-1 field, sample 186-1; (c) massive,
781 platy barite crystals cut by granular quartz along the deformed, locally, stylolitic (arrows)
782 boundaries, Saf'yanovka clastic ores, sample Saf007; (d) quartz-rimmed barite rosette on a
783 pyrite clast, Semenov-3 field, sample 284-10. Photos (a) and (c) – thin sections, transmitted light;
784 photos (b) and (d) – polished sections, reflected light.

785

786 Fig. 5. Histograms of homogenization temperatures and salinities of fluid inclusions in barite
787 from the Saf'yanovka colloform ores (a–b; sample KLF) and Semenov-1 fine-crystalline massive
788 sulfides (c–d; samples 186-1 and 292-1), Saf'yanovka (e–f, sample Saf007) and Semenov-3 (g–
789 h, sample 284) pyrite breccias.

790

791 Fig. 6. Variations of salinity vs. homogenization temperature for fluid inclusions in barite from (a)
792 Saf'yanovka colloform ores, (b) Semenov-1 fine-crystalline massive sulfides, (c) Saf'yanovka and
793 (d) Semenov-3 pyrite breccias..

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796 References

797 Beltenev V, Ivanov V, Rozhdestvenskaya I, Cherkashov G, Stepanova T, Shilov V, Pertsev A, Davydov M, Egorov I,
798 Melekestseva I, Narkevsky E, Ignatov V (2007) A new hydrothermal field at 13°30' N on the Mid-Atlantic
799 Ridge. *InterRidge News* 16:9–10

800 Beltenev V, Ivanov V, Rozhdestvenskaya I, Cherkashov G, Stepanova T, Shilov V, Davydov M, Laiba A, Kaylio V,
801 Narkevsky E, Pertsev A, Dobretsova I, Gustaitis A, Popova Ye, Amplieva A, Evrara C, Moskalev L, Gebruk A
802 (2009) New data about hydrothermal fields on the Mid-Atlantic Ridge between 11°–14° N: 32nd cruise of R/V
803 Professor Logatchev. *InterRidge News* 18:14–18

804 Bendel V, Fouquet Y, Auzende J-M, Lagabrielle Y, Grimaud D, Urabe T (1993) The White Lady hydrothermal field,
805 North Fiji back-arc basin, Southwest Pacific. *Econ Geol* 88:2237–2245

806 Berkenbosch HA, de Ronde CEJ, Gemmel JB, McNeill AW, Goemann K (2012) Mineralogy and Formation of Black
807 Smoker Chimneys from Brothers Submarine Volcano, Kermadec Arc. *Econ Geol* 107:1613–1633

808 Bertram MA, Cowen JP (1997) Morphological and compositional evidence for biotic precipitation of marine barite. *J*
809 *Marine Res* 55:577–593

810 Binns RA, Scott SD, Bogdanov YA, Lisitzin AP, Gordeev VV, Gurchich EG, Finlayson EJ, Boyd T, Dotter LE, Wheller
811 GE, Muravyev KG (1993) Hydrothermal oxide and gold-rich sulfate deposits of Franklin Seamount, Western
812 Woodlark Basin, Papua New Guinea. *Econ Geol* 88:2122–2153

813 Binns RA, Parr JM, Gemmel JB (1997) Precious metals in barite-silica chimneys from Franklin Seamount, Woodlark
814 Basin, Papua New Guinea. *Marine Geol.* 142:119–141

815 Bischoff JL, Rosenbauer RJ (1984) The critical point and two-phase boundary of seawater, 200–500 °C. *Earth Planet*
816 *Sci Lett* 68:172–180

817 Bodnar RJ, Vityk MO (1994) Interpretation of microthermometric data for H₂O-NaCl fluid inclusions. In: De Vivo B
818 and Frezzotti ML (Eds) *Fluid inclusions in minerals: methods and applications*. Pontignana-Siena, pp 117–130

819 Bogdanov YuA, Bortnikov NS, Vikent'ev IV, Lein AYu, Gurchich EG, Sagalevich AM, Simonov VA, Ikorskii SV,
820 Stavrova OO, Apollonov VN (2002) Mineralogical–geochemical peculiarities of hydrothermal sulfide ores and
821 fluids in the Rainbow field associated with serpentinites, Mid-Atlantic Ridge (36°14'N). *Geol Ore Dep* 44:444–
822 473

823 Bogdanov YuA, Lein AYu, Sagalevich AM, Dorofeev SA, Ul'yanova NV (2006) Hydrothermal sulfide deposits of the
824 Lucky Strike vent field, Mid-Atlantic Ridge. *Geochem. Intern.* 44:403–418.

825 Borisenko AS (1977) Study of salt composition of fluids inclusions in minerals with a criometry. *Geol Geophys* 8:16–
826 28

827 Bortnikov NS, Krylova TL, Bogdanov YA, Vikentyev IV and Nosik LP (1997) The 14°45'N hydrothermal field, Mid-
828 Atlantic Ridge: Fluid inclusion and sulfur isotope evidence for submarine phase separation. In: Papunen H (ed)
829 *Mineral Deposits: Research and Exploration. Where do they meet*. Proc 4th Biennial SGA Meet, Turku,
830 Finland. Balkema, Rotterdam 353–356

831 Bortnikov NS, Simonov VA, Amplieva EE, Borovikov AA (2014) Anomalously high concentrations of metals in
832 fluid of the Semenov modern hydrothermal system (Mid-Atlantic Ridge, 13°31' N): LA-ICP-MS study of
833 fluid inclusions in minerals. *Dokl Earth Sci* 456(2): 714–719

834 Bortnikov NS, Simonov VA, Bogdanov YuA (2004) Fluid inclusions in minerals from modern sulfide edifices:
835 Physicochemical conditions of formation and evolution of fluids. *Geol Ore Dep* 46:64–75

836 Bortnikov NS, Vikent'ev IV (2005) Modern base metal sulfide mineral formation in the World Ocean. *Geol Ore Dep*
837 47:13–44

838 Butterfield DA, Massoth GJ, McDuff RE, Lupton JE, Lilley MD (1990) Geochemistry of hydrothermal fluids from
839 Axial Seamount hydrothermal emissions study vent field, Juan de Fuca Ridge: Subseafloor boiling and
840 subsequent fluid-rock interaction. *J Geophys Res* 95:12895–12921

841 Butterfield DA, Nakamura K-I, Takano B, Lilley MD, Lupton JE, Resing JA, Roe KK (2011) High SO₂ flux, sulfur
842 accumulation, and gas fractionation at an erupting submarine volcano. *Geology* 39(9):803–806

843 Cazañas X, Alfonso P, Melgarejo JC, Proenza JA, Fallick AE (2008). *Geology, fluid inclusion and sulphur isotope*
844 *characteristics of the El Cobre VHMS deposit, Southern Cuba*. *Mineral Dep* 43:805–824

845 Cherkashov G, Bel'tenev V, Ivanov V, Lazareva L, Samovarov M, Shilov V, Stepanova T, Glasby GP, Kuznetsov V
846 (2008) Two new hydrothermal fields at the Mid-Atlantic Ridge. *Marine Geores Geotechn* 26:308–316

847 Chernyshev IV, Bortnikov NS, Chugaev AV, Golubev VN, Fouquet Y, Amplieva EE, Stavrova OO (2011)
848 Variation scale and heterogeneity of the lead isotope composition in sulfides from hydrothermal fields of
849 the Mid-Atlantic Ridge: Evidence from high-precision MC-ICP-MS isotopic data. *Dokl. Earth Sci.* 437(2):
850 507–512

851 Chuvashov BI, Anfimov AL, Soroka EI, Yaroslavtseva NS (2011) New data on age of ore-hosting sequence of the
852 Saf'yanovka deposit, Central Urals, based on foraminifers. *Dokl Earth Sci* 439(2):1076–1078.

853 Claypool GE, Holser WT, Kaplan IR, Sakai H, Zak I (1980) The age curves of sulphur and oxygen isotopes in marine
854 sulphates and their mutual interpretation. *Chem Geol* 28:199–260

855 Constantinou G, Govett GJS (1972) Genesis of sulphide deposits, ochre and umber of Cyprus. *Trans. Inst. Min. Metall.*
856 81:B34–B46

857 Cook NJ, Ciobanu CL, Pring A, Skinner W, Shimizu M, Danyushevsky L, Saini-Eidukat B, Melcher F (2009) Trace
858 and minor elements in sphalerite: A LA-ICPMS study. *Geochim Cosmochim Acta* 73:4761–4791

859 Cowan J, Cann J (1988) Supercritical two-phase separation of hydrothermal fluids in the Troodos ophiolite
860 *Nature* 333:259–261

861 Dahlmann A, Wallmann K, Sahling H, Sarthou G, Bohrmann G, Petersen S, Chin CS, Klinkhammer GP (2001) Hot
862 vents in an ice-cold ocean: Indications for phase separation at the southernmost area of hydrothermal activity,
863 Bransfield Strait, Antarctica. *Earth Planet Sci Lett* 193:381–394

864 Davis AS, Clague DA, Zierenberg RA, Wheat CG, Cousens BL (2003) Sulfide formation related to changes in the
865 hydrothermal system on Loihi seamount, Hawai'i, following the seismic event in 1996. *Can Mineral* 41:457–472

866 Deer WA, Howie RA, Zussman J (1962) *Rock-forming minerals*. Vol. 5. Non-Silicates. London, Longmans

867 de Ronde CEJ, Faure K, Bray CJ, Chappell DA, Wright IC (2003) Hydrothermal fluids associated with seafloor
868 mineralization at two southern Kermadec arc volcanoes, offshore New Zealand. *Miner Dep* 38:217–233

869 de Ronde CEJ, Hannington MD, Stoffers P, Wright IC, Ditchburn RG, Reyes AG, Baker ET, Massoth GJ, Lupton JE,
870 Walker SL, Greene RR, Soong CWR, Ishibashi J, Lebon GT, Bray CJ, Resing JA (2005) Evolution of a
871 submarine magmatic–hydrothermal system: Brothers volcano, southern Kermadec arc, New Zealand. *Econ Geol*
872 100:1097–1133

873 de Ronde CEJ, Massoth GJ, Butterfield DA, Christenson BW, Ishibashi J, Ditchburn RG, Hannington MD, Brathwaite
874 RL, Lupton JE, Kamenetsky VS, Graham IJ, Zellmer GF, Dziak RP, Embley RW, Dekov VM, Munnik F, Lahr J,
875 Evans LJ, Takai K (2011) Submarine hydrothermal activity and gold-rich mineralization at Brothers Volcano,
876 Kermadec Arc, New Zealand. *Miner Dep* 46:541–584

877 Duckworth RC, Knott R, Fallick AE, Ricard D, Murton BJ, Van Dover C (1995) Mineralogy and sulphur isotope
878 geochemistry of the Broken Spur sulphides, 29° N, Mid-Atlantic Ridge. In: Parson LM, Walker CL, and Dixon
879 DR (eds) *Hydrothermal Vents and Processes*. Geol Soc, London, Spec Public 87:175–190

880 Eickmann B, van Zuilen MA, Thorseth IH, Pedersen R, (2010) Barite chimneys from two hydrothermal sites along the
881 slow-spreading Arctic Ridge system: Initial isotope and mineralogical results. American Geophysical Union, Fall
882 Meeting, abstract #OS21A-1482

883 Fairbridge RW (1967) Phases of diagenesis and authigenesis. In: *Diagenesis in Sediments*. Larsen G and Chilingar GV
884 (Eds). Elsevier, Amsterdam, pp. 19–89

885 Fouquet Y, von Stackelberg U, Charlou JL, Erzinger J, Herzig PM, Muehe R, Wiedicke M (1993a) Metallogenesis in
886 back-arc environments: the Lau Basin example. *Econ Geol* 88:2154–2181

887 Fouquet Y, Wafik A, Cambon P, Mevel C, Meyer G, Gente P (1993b) Tectonic setting and mineralogical and
888 geochemical zonation in the Snake Pit sulfide deposit (Mid-Atlantic Ridge at 23°C N). *Econ Geol* 88:2018–2036

889 Fouquet Y, Charlou J-L, Costa I, Donvall JP, Radford-Knoery J, Pellé H, Ondréas H, Lourenço N, Ségonzac M, Tivey
890 MK (1994) A detailed study of the Lucky Strike hydrothermal site and discovery of a new hydrothermal site:
891 Menez Gwen; preliminary results of the DIVA1 Cruise (5–29 May, 1994). *InterRidge News* 3(2):14–17

892 Frezzotti ML, Tecce F, Casagli A (2012) Raman spectroscopy for fluid inclusion analysis. *J Geochem Explor* 112:1–20

893 Fu B, Aharon P, Byerly GR, Roberts HH (1994) Barite chimneys on the Gulf of Mexico slope: Initial report on their
894 petrography and geochemistry. *Geo-Marine Lett* 14:81–87.

895 Gieskes JM, Simoneit BRT, Brown T, Shaw T, Wang Y-C, Magenheimer A (1988) Hydrothermal fluids and petroleum
896 in surface sediments of Guaymas Basin, Gulf of California: A case study. *Can Mineral* 26:589–602

897 Glasby GP, Iizasa K, Hannington M, Kubota H, Notsu K (2008) Mineralogy and composition of Kuroko deposits from
898 northeastern Honshu and their possible modern analogues from the Izu-Ogasawara (Bonin) Arc south of Japan:
899 Implications for mode of formation *Ore Geol Rev* 34:547–560

900 Goodfellow WD, Blaise B (1988) Sulfide formation and hydrothermal alteration of hemipelagic sediment in Middle
901 Valley, Northern Juan de Fuca Ridge. *Can Mineral* 26: 675–696

902 Goodfellow WD, Franklin JM (1993) Geology, mineralogy, and chemistry of sediment-hosted clastic massive sulfides
903 in shallow cores, Middle Valley, northern Juan de Fuca Ridge. *Econ Geol* 88:2037–2068

904 Greinert J, Bollwerk SM, Derkachev A, Bohrmann G, Suess E (2002) Massive barite deposits and carbonate
905 mineralization in the Derugin Basin, Sea of Okhotsk: precipitation processes at cold seep sites. *Earth Planet Sci*
906 *Lett* 203:165–180

907 Griffith EM, Paytan A (2012) Barite in the ocean – occurrence, geochemistry and palaeoceanographic applications.
908 *Sedimentology* 59(6):1817–1835

909 Gruen G, Weis P, Driesner T, Heinrich CA, de Ronde CEJ (2014) Hydrodynamic modeling of magmatic–hydrothermal
910 activity at submarine arc volcanoes, with implications for ore formation. *Earth Planet Sci Letters* 404:307–318

911 Halbach P, Pracejus B, Maerten A (1993) Geology and mineralogy of massive sulfide ores from the central Okinawa
912 Trough, Japan. *Econ Geol* 88:2210–2225

913 Halbach P, Blum N, Münch U, Plüger W, Garbe-Schönberg D, Zimmer M (1998) Formation and decay of a modern
914 massive sulfide deposit in the Indian Ocean. *Miner Deposita* 33:302–309

915 Hanor JS (2000) Barite-celestine geochemistry and environments of formation. In: *Reviews in Mineralogy &*
916 *Geochemistry – Sulfate Minerals*. Alpers CN, Jambor JL and Nordstrom DK (Eds). Mineral Soc America,
917 Washington, D.C., 40, pp 193–275

918 Hannington MD, Scott SD (1988) Mineralogy and geochemistry of a hydrothermal silica-sulfide-sulfate spire in the
919 caldera of Axial Seamount, Juan de Fuca Ridge. *Can Miner* 26:603–625

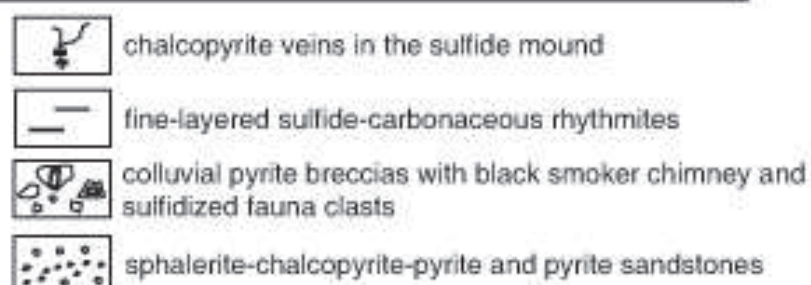
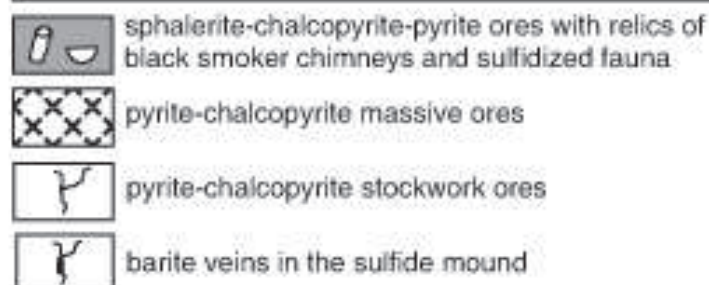
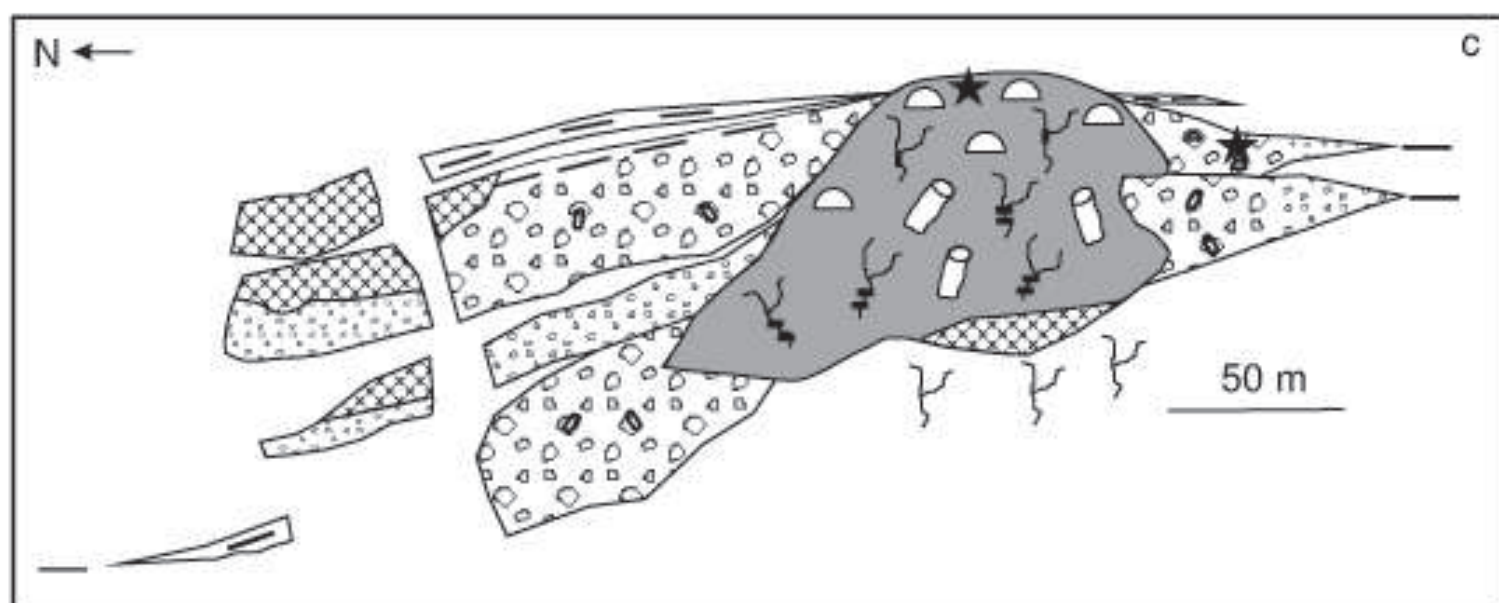
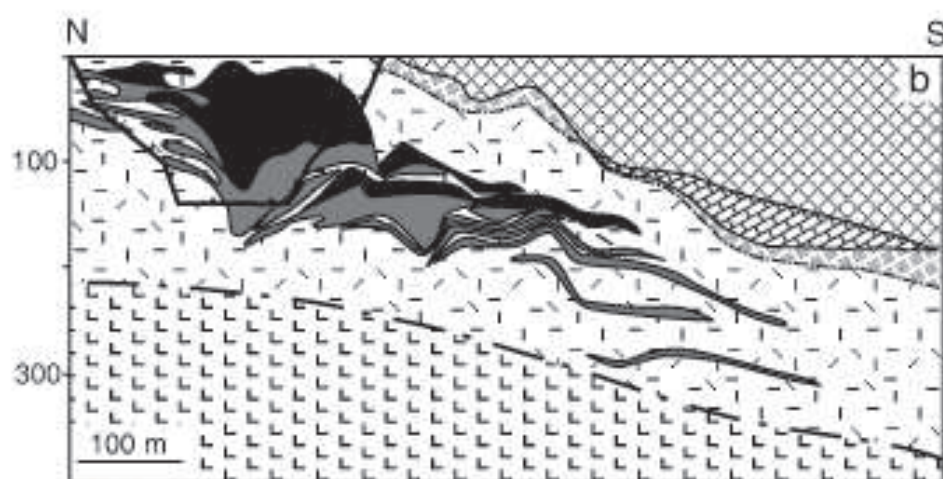
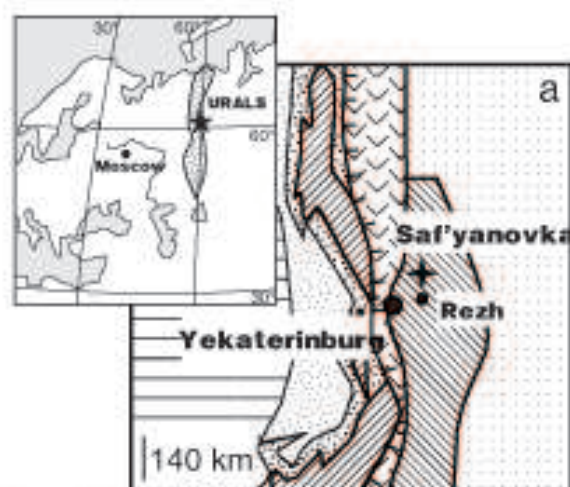
920 Hannington MD, Scott SD (1989) Sulfidation equilibria as guides to gold mineralization in volcanogenic massive
921 sulfides: Evidence for sulfide mineralogy and the composition of sphalerite. *Econ Geol* 84:1978–1995

- 922 Hannington MD, Jonasson IR, Herzig PM, Petersen S (1995) Physical and chemical processes of seafloor
923 mineralization at mid-ocean ridges. In: Humphris SE, Zierenberg RA, Mullineaux LS, Thomson RE (Eds.)
924 Seafloor hydrothermal processes. *Geophys Monogr* 91:115–157
- 925 Hannington MD, Galley AG, Herzig PM, Petersen S (1998) Comparison of the TAG mound and stockwork complex
926 with Cyprus-type massive sulfide deposits. In: Herzig PM, Humphris SE, Miller DJ, Zierenberg RA (eds) *Proc*
927 *ODP Sci Results* 158:389–415
- 928 Hao Fang, Zou Huayao, Huang Baojia (2003) Natural gas generation model and its response in accumulated fluids in
929 the Yinggehai basin. *Sci China (Series D)* 46(11):1103–1112
- 930 Hein JR, Zierenberg RA, Maynard JB, Hannington MD (2007) Barite-forming environments along a rifted continental
931 margin, Southern California Borderland. *Deep-Sea Res II* 54:1327–1349
- 932 Hein JR, de Ronde CEJ, Koski RA, Ditchburn RG, Mizell K, Tamura Y, Stern RJ, Conrad TA, Ishizuka O, Leybourne
933 MI (2014) Layered Hydrothermal Barite-Sulfide Mound Field, East Diamante Caldera, Mariana Volcanic Arc.
934 *Econ Geol* 109:2179–2206
- 935 Herzig PM, Hannington MD, Fouquet Y, von Stackelberg U, Petersen S (1993) Gold-rich polymetallic sulfides from
936 the Lau back arc and implications for the geochemistry of gold in sea-floor hydrothermal systems of the
937 Southwest Pacific. *Econ Geol* 88:2182–2209
- 938 Holland NG (2002) The formation of an ancient gold-rich volcanogenic massive sulphide deposit: a study of the Balta-
939 Tau deposit in the Southern Urals of Russia. PhD thesis. University of Southampton
- 940 Hou Z, Khin Z, Qu X, Ye Q, Yu J, Xu M, Fu D, Yin X (2001) Origin of the Gacun Volcanic-Hosted Massive Sulfide
941 Deposit in Sichuan, China: Fluid Inclusion and Oxygen Isotope Evidence. *Econ Geol* 96:1491–1512
- 942 Ivanov VN, Beltenev VE, Stepanova TV, Lazareva LI, Smovarov ML (2008). Sulfide ores of the new hydrothermal
943 fields at 13°31' N MAR. In: Zaykov VV, Belogub EV and Melekestseva IYu (Eds) *Metallogeny of ancient and*
944 *modern oceans-2008. Ore-bearing complexes and ore facies. Miass, IMin UB RAS*, pp 19–22 (in Russian)
- 945 Ixer RA, Alabaster T, Pearce JA (1984) Ore petrography and geochemistry of massive sulphide deposits within the
946 Semail Ophiolite, Oman. *Trans. Min. Metall. Sect. B* 93:B114–B124
- 947 Jamieson JW, Petersen S, Augustin N, Steinführer A, Escartín J, & ODEMAR Scientific Party (2014) Seafloor massive
948 sulfide formation on oceanic core complexes: Recent exploration of the Semyenov and Irinovskoe hydrothermal
949 fields, Mid-Atlantic Ridge. In: *Minerals of the Ocean-7 & Deep-Sea Minerals and Mining-4*. St. Petersburg,
950 VNIIOKeangeologiya, pp. 42–45
- 951 Jewell PW, Stallard RF (1991) Geochemistry and Paleooceanographic Setting of Central Nevada Bedded Barites. *J Geol*
952 99(2): 151–170
- 953 Kelley DS, Delaney JR (1987) Two-phase separation and fracturing in mid-ocean ridge gabbros at temperatures greater
954 than 700 °C. *Earth and Planetary Science Letters* 83:53–56.
- 955 Krylova MA, Melekestseva IYu (2011) Raman spectroscopy of barite from the Semenov-1 hydrothermal field
956 (13°30.87'N, Mid-Atlantic Ridge). In: Anfilogov VN (Ed) *Minerals: Structure, Properties and Methods of*
957 *Investigations*. Miass, IMin UB RAS, pp 194–196 (in Russian)
- 958 Koroteev VA, Yazeva RG, Bochkarev VV, Moloshag VP, Korovko AV, Sheremet'ev YuS (1997) Geological position
959 and composition of ores from the Saf'yanovka deposit, Central Urals. Yekaterinburg, IGG UB RAS (in Russian)
- 960 Kuznetsov V, Maksimov F, Zhelezov A, Cherkashov G, Bel'tenev V, Lazareva L (2011) ²³⁰Th/U chronology of ore
961 formation within the Semyenov hydrothermal district (13°31' N) at the Mid-Atlantic Ridge. *Geochronometria*
962 38(1):72–76
- 963 Lam P, Cowen JP, Popp BN, Jones RD (2008) Microbial ammonia oxidation and enhanced nitrogen cycling in the
964 Endeavour hydrothermal plume. *Geochim et Cosmochim Acta* 72:2268–2286
- 965 Lang SQ, Früh-Green GL, Bernasconi SM, Butterfield DA (2013) Sources of organic nitrogen at the serpentinite-hosted
966 Lost City hydrothermal field *Geobiology* 11:154–169
- 967 Lecuyer C, Dubois M, Marignac C, Gruau G, Fouquet Y, Ramboz C (1999) Phase separation and fluid mixing in
968 subseafloor back arc hydrothermal systems; a microthermometric and oxygen isotope study of fluid inclusions in
969 the barite-sulfide chimneys of the Lau Basin. *J Geophys Res* 104:911–928
- 970 Lilley MD, Butterfield DA, Olson EJ, Lupton JE, Macko SA, McDuff RE (1993) Anomalous CH₄ and NH₂⁺
971 concentrations at an unsedimented mid-ocean-ridge hydrothermal system. *Nature* 364:45–47
- 972 Lilley MD, Butterfield DA, Lupton JE, Olson EJ (2003) Magmatic events can produce rapid changes in hydrothermal
973 vent chemistry. *Nature* 422:878–881
- 974 Littke R, Krooss B, Idiz E, Frielingsdorf J (1995) Molecular nitrogen in natural gas accumulations: generation from
975 sedimentary organic matter at high temperatures. *AAPG Bulletin* 79(3):410–430
- 976 Lüders V, Pracejus B, Halbach P (2001). Fluid inclusion and sulfur isotope studies in probable modern analogue
977 Kuroko-type ores from the JADE hydrothermal field (Central Okinawa Trough, Japan). *Chem Geol* 173:45–58
- 978 Ludwig KA, Kelley DS, Butterfield DA, Nelson BK, Früh-Green G (2006) Formation and evolution of carbonate
979 chimneys at the Lost City hydrothermal field. *Geochim Cosmochim Acta* 70: 3625–3645
- 980 Machel HG (2001) Bacterial and thermochemical sulfate reduction in diagenetic settings – old and new insights.
981 *Sediment Geol* 140:143–175
- 982 Maslennikov VV (2006) Lithogenesis and formation of massive sulfide deposits. Miass, IMin UB RAS (in Russian)
- 983 Maslennikova SP, Maslennikov VV (2007) Sulfide chimneys of Palaeozoic black smokers on the example of the Urals.
984 Yekaterinburg, UB RAS (in Russian)

- 985 Maslennikov VV, Maslennikova SP, Large RR, Danyushevsky LV (2009) Study of trace element zonation in vent
986 chimneys from the Silurian Yaman-Kasy volcanic-hosted massive sulfide deposit (Southern Urals, Russia) using
987 laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS). *Econ Geol* 104:1111–1141
- 988 Massoth GJ, Butterfield DA, Lupton JE, McDuff RE, Lilley MD, Jonasson IR (1989) Submarine venting of phase-
989 separated hydrothermal fluids at Axial Volcano, Juan de Fuca Ridge. *Nature* 340:702–705.
- 990 McLeod CJ, Searle RC, Murton BJ, Casey JF, Mallows C, Unsworth SC, Achenbach KL, Harris M (2009) Life cycle of
991 oceanic core complexes. *Earth Planet Sci Lett* 287:333–344
- 992 McClung CR, Gutzmer J, Beukes NJ, Mezger K, Strauss H, Gertloff E (2007) Geochemistry of bedded barite of the
993 Mesoproterozoic Aggeneys-Gamsberg Broken Hill-type district, South Africa. *Min Dep* 42:537–549
- 994 McMurty GM, Sedwick PN, Fryer P, VonderHaar DL, Yeh H-W (1993) Unusual geochemistry of hydrothermal vents
995 on submarine arc volcanoes: Kasuga Seamounts, Northern Mariana Arc. *Earth Planet Sci Lett* 114:517–528
- 996 Melekestseva IYu, Kotlyarov VA, Khvorov PV, Ivanov VN, Bel'tenev VE, Dobretsova IG (2010) Noble-metal
997 mineralization in the Semenov-2 hydrothermal field (13°31' N), Mid-Atlantic Ridge. *Geol Ore Dep* 52(8):800–
998 810
- 999 Melekestseva IYu, Tret'yakov GA, Nimis P, Yuminov AM, Maslennikov VV, Maslennikova SP, Kotlyarov VA,
1000 Beltenev VE, Danyushevsky LV, Large R (2014) Barite-rich massive sulfides from the Semenov-1 hydrothermal
1001 field (Mid-Atlantic Ridge, 13°30.87' N): Evidence for phase separation and magmatic input. *Marine Geol*
1002 349:37–54
- 1003 Mironova OF, Salazkin AN, Garanin AV (1992) Comparison of results of gas analysis of fluid inclusions by
1004 mechanical and thermal destruction. *Geokhimiya* 1:78–87.
- 1005 Murdmaa IO (1987) Facies of oceans. Moscow, Nauka (in Russian)
- 1006 Murowchick JB, Barnes HL (1986) Marcasite precipitation from hydrothermal solutions. *Geochim Cosmochim Acta*
1007 50:2615–2659
- 1008 Murzin VV, Varlamov DA, Yaroslavtseva NS, Moloshag VP (2010) Mineralogy and structure of barite–sulfide veins of
1009 the Saf'yanovka massive sulfide deposit. In: Popov VA (ed) Ural mineralogical collection, pp. 12–19 (in
1010 Russian)
- 1011 Naumov VB, Akhmanova MV, Sobolev AV, Dhamelncourt P (1986) Application of laser Raman-microprobe to a study
1012 of gas phase of inclusions in minerals. *Geokhimiya* (7):1027–1034
- 1013 Nehlig P (1993) Interactions between magma chambers and hydrothermal systems: oceanic and ophiolitic constraints. *J*
1014 *Geophys Res* 98 (B11):19621–19633
- 1015 Ohmoto H (1996) Formation of volcanogenic massive sulfide deposits: The Kuroko perspective. *Ore Geol Rev* 10:135–
1016 177
- 1017 Paytan A, Mearon S, Cobb K, Kastner M (2002) Origin of marine barite deposits: Sr and S isotope characterization.
1018 *Geology* 30(8): 747–750.
- 1019 Petersen S, Herzig PM, Hannington MD (2000) Third dimension of a presently forming VMS deposit: TAG
1020 hydrothermal field, Mid-Atlantic Ridge, 26° N. *Mineral Dep* 35:233–259
- 1021 Petersen S, Herzig PM, Schwarz-Schampera U, Hannington MD, Jonasson IR (2004) Hydrothermal precipitates
1022 associated with bimodal volcanism in the Central Bransfield Strait, Antarctica. *Miner Dep* 39:358–379
- 1023 Pedersen RB, Tore Rapp H, Thorseth IH, Lilley MD, Barriga FJAS, Baumberger T, Flesland K, Fonseca R, Früh-Green
1024 GL, Jorgensen SL (2010) Discovery of a black smoker vent field and vent fauna at the Arctic Mid-Ocean Ridge.
1025 *Nature Communications*, DOI: 10.1038/ncomms1124
- 1026 Pertsev AN, Bortnikov NS, Vlasov EA, Beltenev VE, Dobretsova IG, Ageeva OA (2012) Modern sulfide deposits of
1027 the Semenov ore region (Mid-Atlantic Ridge, 13°30' N): Types of associated rocks of the oceanic core complex
1028 and their hydrothermal alteration. *Geol Ore Dep* 54(5):334–346
- 1029 Potter RW (1977) Pressure corrections for fluid-inclusion homogenization temperatures based on the volumetric
1030 properties of the system NaCl–H₂O. *US Geol Surv J Res* 5:603–607
- 1031 Puchkov VN (1993) Paleooceanic structures of the Urals. *Geotectonics* 3:18–34 (in Russian)
- 1032 Rees CE, Jenkins WJ, Monster J (1978) The sulfur isotopic composition of ocean water sulfate. *Geochim Cosmochim*
1033 *Acta* 42:377–381
- 1034 Roedder E (1984) Fluid inclusions. *Mineral Soc America Rev Mineral* 12, 646 p
- 1035 Rona PA, Hannington MD, Raman CV, Thompson G, Tivey MK, Humphris SE, Lalou C, Petersen S (1993) Active and
1036 relict sea-floor hydrothermal mineralization at the TAG hydrothermal field, Mid-Atlantic Ridge. *Econ Geol*
1037 88:1989–2117
- 1038 Safina NP, Maslennikov VV (2009) Sequence of mineral formation in clastic ores of the Saf'yanovka volcanic-hosted
1039 copper massive sulfide deposit, the Central Urals. *Geol Ore Dep* 51(7):633–643
- 1040 Safina NP, Ankusheva NN., Murzin VV (2012) Physico-chemical formation conditions of barite from the ore facies of
1041 the Saf'yanovka VHMS deposit, Central Urals. *Litosfera* 3:110–126.
- 1042 Sasaki M, Iizasa K, Sawaki T (1995) Characteristics of gases in fluid inclusions from the Nurukawa Kuroko deposit and
1043 submarine sulfide deposits of the Izu–Ogasawara arc, Japan. *Res Geol* 45:1–10
- 1044 Sato T (1977) Kuroko deposits: their geology, geochemistry and origin. *Geol. Soc. London Spec. Publ.* 153–161.
- 1045 Scotney PM, Roberts S, Herrington RJ (2005) The development of volcanic hosted massive sulfide and barite–gold
1046 orebodies on Wetar Island, Indonesia. *Miner Dep* 40:76–99

- 1047 Scott S (1980) Geology and structural control of Kuroko-type massive sulfide deposits. In: *The Continental Crust and*
1048 *Its Mineral Deposits* (D.W. Strangway, ed.). Geol. Assoc. Can. Spec. Pap. 20:705–740
- 1049 Seal RR II (2006) Sulfur isotope geochemistry of sulfide minerals. *Rev Min Geochem* 61:633–677
- 1050 Shadlun TN, Bortnikov NS, Bogdanov YuA, Tufar W, Muravyev K, Gurchich EG, Muravitskaya, Korina EA, Topa T
1051 (1992) Mineral composition and origin of massive sulfide ores in the Manus backarc basin (Pacific Ocean). *Geol*
1052 *Rudn Mestorozh* 34(5):3–21
- 1053 Shanks WC III, Böhlke JK, Seal RR II (1995) Stable isotopes in mid-ocean ridge hydrothermal systems: interactions
1054 between fluids, minerals and organisms. In: Humphris SE, Zierenberg RA, Mullineaux LS, Thomson RE (eds)
1055 *Seafloor hydrothermal processes*. Geophys Monogr 91:194–221
- 1056 Simonov VA, Kovyazin SV, Terenya EO, Maslennikov VV, Zaykov VV, Maslennikova SP (2006) Physicochemical
1057 parameters of magmatic and hydrothermal processes at the Yaman-Kasy massive sulfide deposit, the southern
1058 Urals. *Geol Ore Dep* 48(5):369–383
- 1059 Smith DK, Escartín J, Schouten H, Cann JR (2008) Fault rotation and core complex formation: significant processes at
1060 slow-spreading mid-ocean ridges (Mid-Atlantic Ridge, 13°–15°N). *Geochem. Geophys. Geosyst.* 9.
1061 doi:10.1029/2007GC001699.
- 1062 Soroka EI, Moloshag VP, Petrishcheva VG (2010) Al-bearing mineral assemblage with alunite in ore-hosting rocks of
1063 the Saf'yanovka VMS deposit, Central Urals. *Litosfera* 6:112–119.
- 1064 Steele JH, Thorpe SA, Turekian KK (2010) Marine chemistry and geochemistry: a derivative of encyclopedia of ocean
1065 sciences. 2nd edition. London, Elsevier. 631 p.
- 1066 Suzuki R, Ishibashi J-I, Nakaseama M, Konno U, Tsunogai U, Gena K, Chiba H (2006) Diverse range of mineralization
1067 induced by phase separation of hydrothermal fluid: Case study of the Yonaguni Knoll IV hydrothermal field in
1068 the Okinawa Trough back-arc basin. *Res Geol* 58:267–288
- 1069 Thompson G, Humphris SE, Schoeder B, Sulanowska M, Rona P (1988) Active vents and massive sulfides at 26° N
1070 (TAG) and 23° N (Snakepit) on the Mid-Atlantic Ridge. *Can Mineral* 26: 697–711
- 1071 von Damm KL, Bray AM, Buttermore LG, Oosting SE (1998) The geochemical controls on vent fluids from the Lucky
1072 Strike vent field, Mid-Atlantic Ridge. *Earth Planet Sci Lett* 160:521–536
- 1073 von Damm KL, Lilley MD, Shanks WCIII, Brockington M, O'Grady KM, Olson E, Graham A, Proskurowski G, Bray
1074 AM and the SouEPR Science Party (2003) Extraordinary phase separation and segregation in vent fluids from the
1075 southern East Pacific Rise. *Earth Planet Sci Lett* 206:365–378
- 1076 Yapaskurt OV (2005) Aspects of postsedimentation lithogenesis theory. *Lithosphere* 3:3–30
- 1077 Yaroslavtseva NS, Maslennikov VV, Safina NP, Leshchev NV, Soroka EI (2012) Black shales of the Saf'yanovka
1078 massive sulfide deposit, Middle Urals. *Lithosphere* (2):106–124
- 1079 Yazeva RG, Moloshag VP, Bochkarev VV (1991) Geology and ore parageneses of the Saf'yanovka massive sulfide
1080 deposit in the Central Urals back thrust. *Geol Ore Dep* 33(4):76–58
- 1081 Zierenberg RA, Koski RA, Morton JL, Bouse RM (1993) Genesis of massive sulfide deposits on a sediment-covered
1082 spreading center, Escanaba Trough, southern Gorda Ridge. *Econ Geol* 88:2069–2098

Figure



Figure

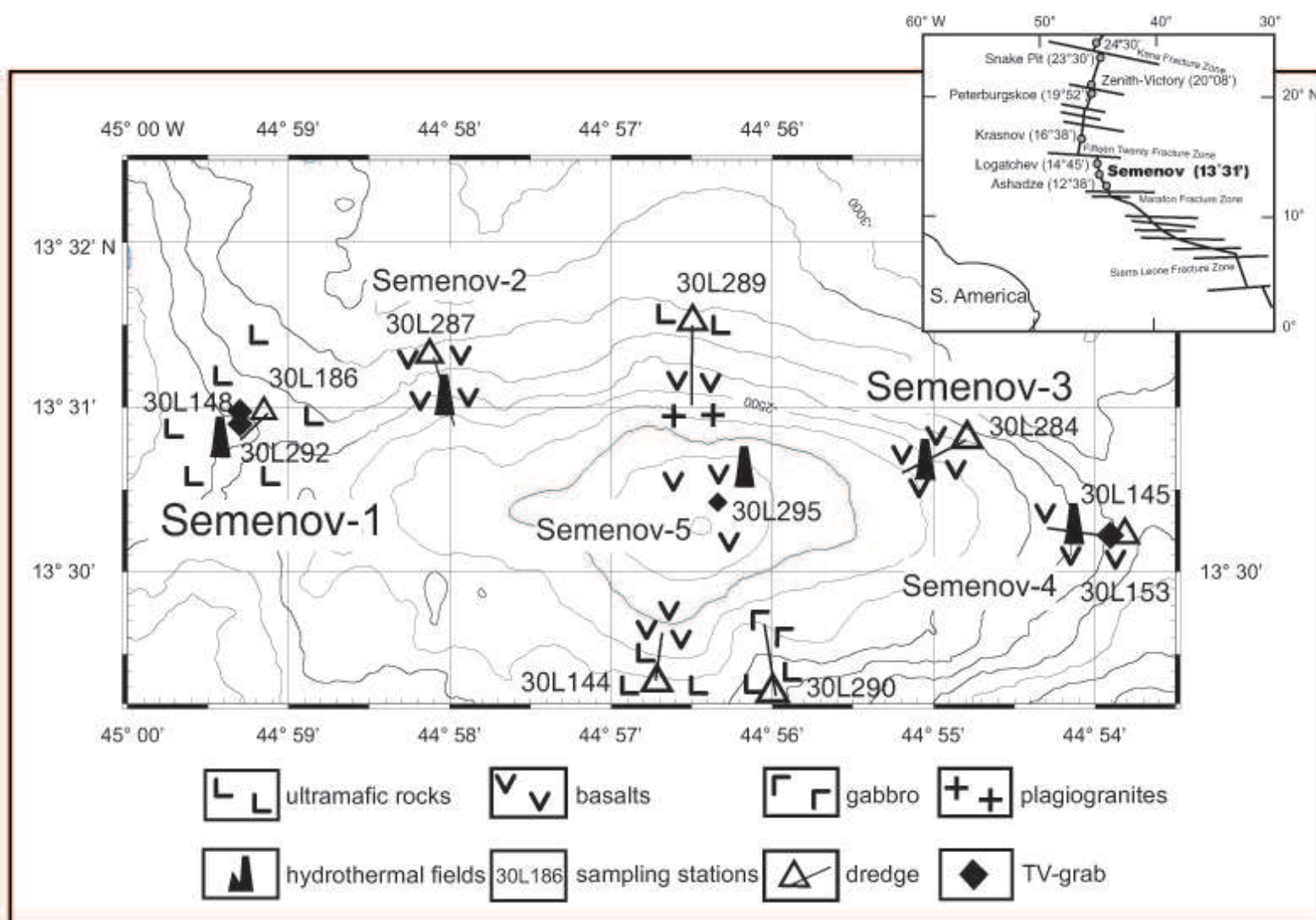


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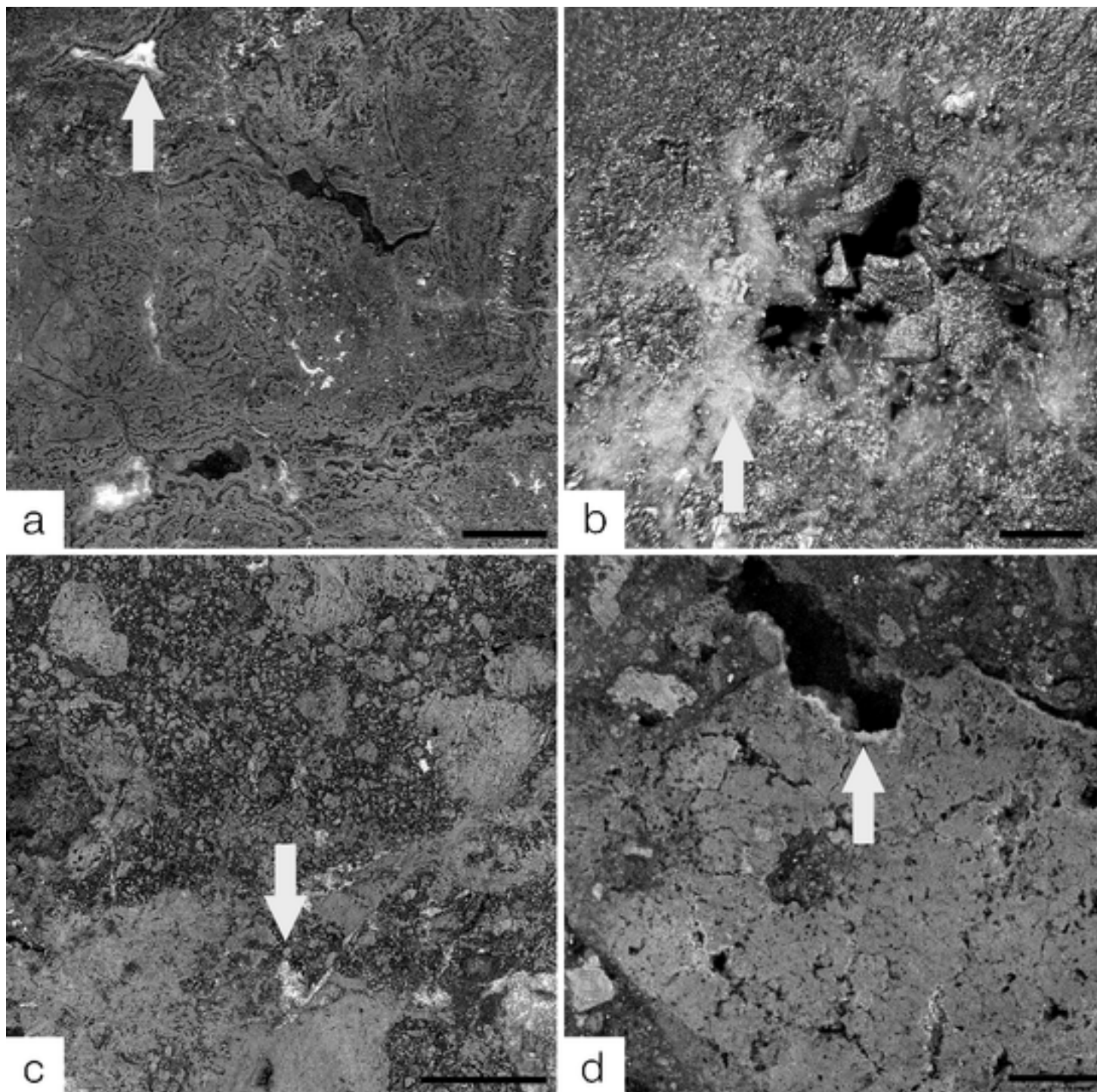
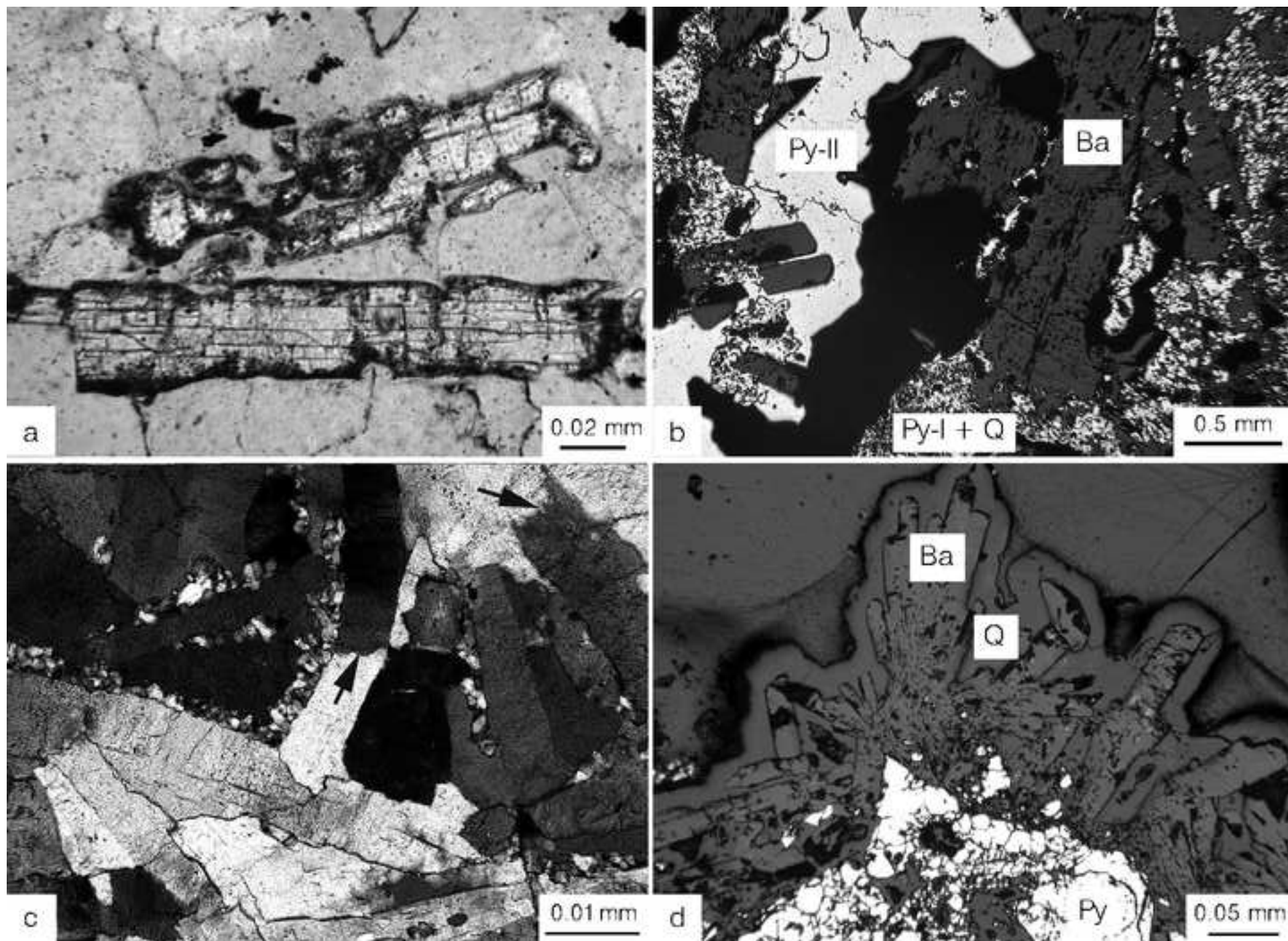
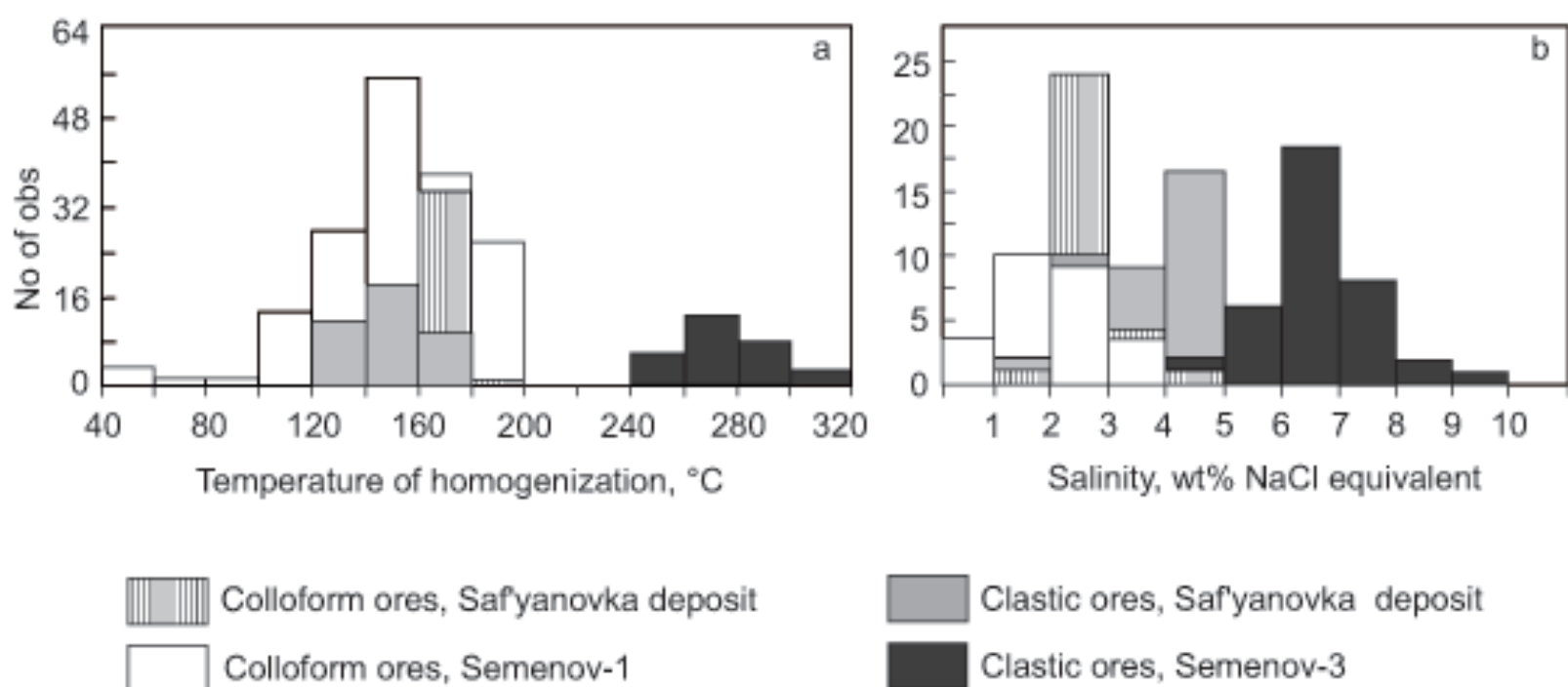


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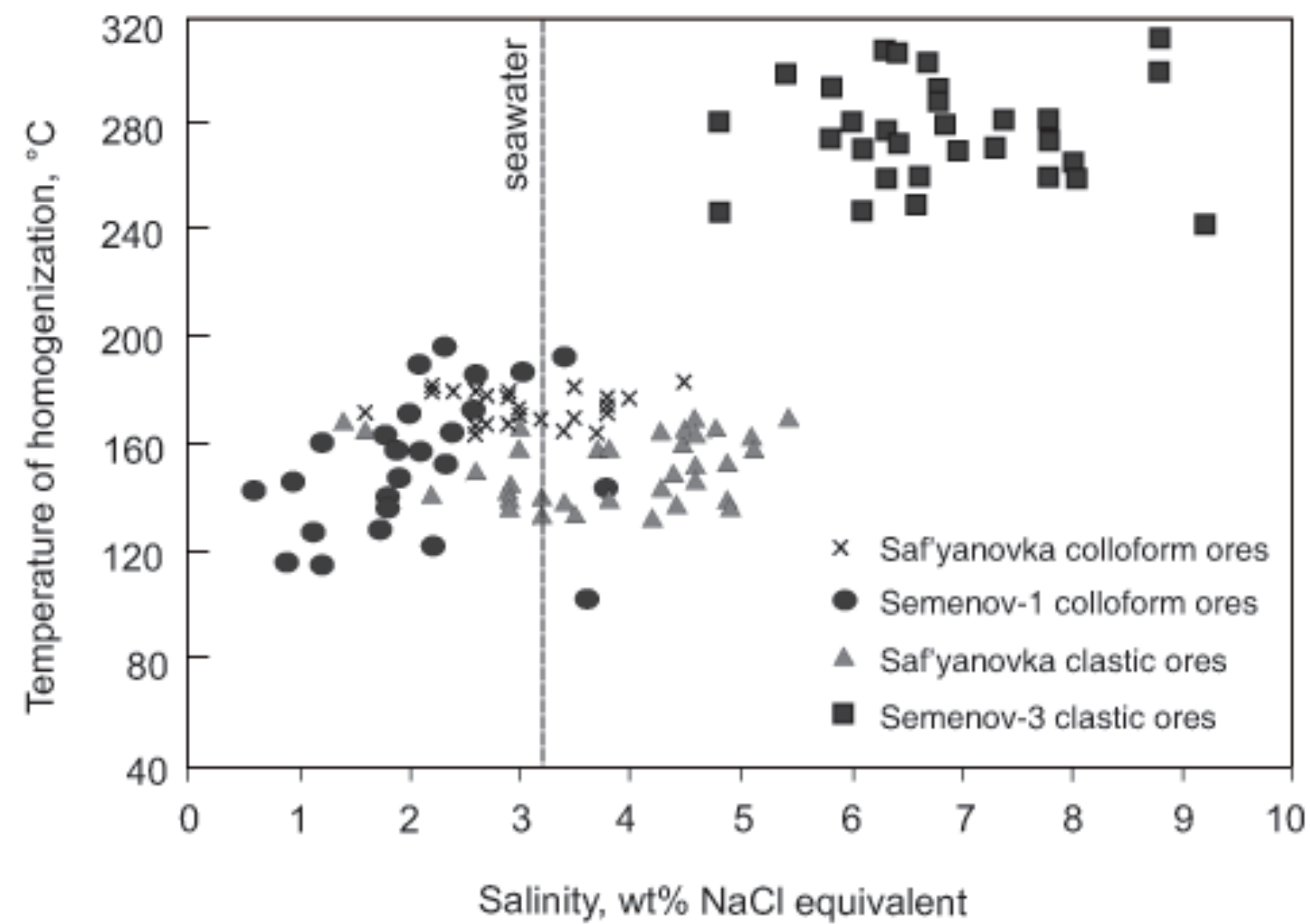


Table 1 Coordinates of sampling stations at the Semenov-1 and -3 hydrothermal fields

Stations	Latitude		Longitude		Depth	
	Start	Finish	Start	Finish	Start	Finish
Semenov-1 field						
Dredge, st. 186	13.30.960 N	13.30.802 N	44.59.130 W	44.59.297 W	2646 m	2592 m
TV-grab, st. 292	13 30.872 N		44 59.237 W		2595 m	
Semenov-3 field						
Dredge, st. 284	13 30.801 N	13 30.601 N	44 54.800 W	44 55.195 W	2616 m	2393 m

Table 2 Average electron microprobe analyses of barite, wt%

Oxides	Saf'yanovka colloform ores, sample KLF (n = 7)	Semenov-1 fine-crystalline sulfides		Saf'yanovka clastic ores, sample 007, (n = 3)	Semenov-3 clastic ores, sample 284 (n = 9)
		sample 186 (n = 5)	sample 292 (n = 8)		
BaO	65.03 (0.35)	66.61 (1.2)	61.64 (1.37)	65.06 (0.36)	64.17 (1.51)
SrO	0.57 (0.25)	1.09 (0.68)	3.41 (1.10)	0.35 (0.61)	1.74 (1.49)
SO ₃	34.27 (0.34)	33.48 (0.1)	34.15 (0.61)	34.42 (0.11)	33.60 (0.51)
Total	99.89	101.26	99.25	99.83	99.18

n, number of analyses

Standard deviation is given in brackets

Barite also contains (average, wt%) 0.11 FeO (sample 292); 0.06, 0.05 PbO (samples 186, 284, respectively); 0.01, 0.02, 0.19, 0.01 CaO (samples KLF, 186, 292, 284, respectively); 0.03 and 0.04 ZnO (samples 186 and 284, respectively)

Table 3 Trace element composition of barite, ppm

Elements	Colloform ores	Breccia	Fine-crystalline sulfides	Breccia
	Saf'yanovka deposit sample KLF	sample Saf007	Semenov-1 field sample 186	Semenov-3 field sample 284
Cu	142	201	89	444
Zn	171	293	235	158
Pb	15	136	16	42
Ga	n.d.	0.3	0.1	0.3
Ge	0.1	0.1	0.1	0.4
As	n.d.	2	n.d.	n.d.
Se	0.2	0.3	0.3	0.2
Cd	n.d.	0.01	0.02	1
Sn	n.d.	n.d.	2	n.d.
Sb	1	1.4	3	6
Te	0.02	0.1	0.1	0.01
Hg	n.d.	3	n.d.	n.d.
Bi	0.03	0.4	0.01	0.03
Co	0.1	0.1	32	44
Ni	15	7	335	438
Mn	1	8	34	5
Sr	2529	3095	7051	3408

n.d., not detected.

The contents of Cu, Zn, Pb, Co, Ni, Cd, As, Se, Sb, Te, Tl, Mo, V, Cr, Mn, Sr, and U for the Semenov-1 barite are taken from (Melekestseva et al., 2014).

Table 4 Sulfur isotopic data ($\delta^{34}\text{S}_{\text{CTD}}\text{‰}$) for barite from the Saf'yanovka deposit and Semenov-1 and -3 hydrothermal fields

Sample	$\delta^{34}\text{S}_{\text{CTD}}\text{‰}$
Saf'yanovka deposit, colloform ores	
Klf	+25.5
Klf-1	+22.7
Klf-1a	+22.1
Klf-2a	+23.5
Klf-3	+23.2
Klf-5	+20.9
<i>Average</i>	+22.9 (1.5)
Saf'yanovka deposit, clastic ores	
Saf-007	+27.0
Saf-007-1	+28.8
Saf-007-2	+28.0
Saf-007-3	+28.4
Saf-007-4	+27.3
Saf-007-5	+29.2
<i>Average</i>	+28.1 (0.9)
Semenov-1 field, colloform ores*	
186	+21.0
292	+21.3
<i>Average</i>	+21.2 (0.2)
Semenov-3 field, clastic ores	
284-1	+20.6
284-2	+18.7
284-3	+19.1
284-4	+19.9
<i>Average</i>	+19.6 (0.8)

*, data from Melekestseva et al. 2014; standard deviation is given in brackets.

Table 5 Summary of the fluid inclusion data for barite of the studied deposits

T_e , °C	Major salts in the fluids	T_m , °C	Salinity, wt.% NaCl-eq.	T_{hom} , °C	Pressure, bar	T_f , °C
Colloform ores, Saf'yanovka deposit						
-21.7 to -22.3 (n = 6)	NaCl-Na ₂ CO ₃ -H ₂ O ± NaHCO ₃ and Na ₂ SO ₄	-0.9 to -2.7 (n = 35)	1.6-4.5	162-184 (n = 35)	100 to 150	172-194
Fine-crystalline sulfides, Semenov-1 field (Melekestseva et al., 2014)						
-6.6 to -2.2 (n = 30)	Na ₂ SO ₄ -K ₂ SO ₄ -H ₂ O and Na ₂ SO ₄ -NaHCO ₃ -H ₂ O	-0.5 to -2.8 (n = 26)	0.6-3.8	58-199 (n = 180)	250	83-224
Clastic ores, Saf'yanovka deposit						
-22.0 to -22.3 (n = 7)	NaCl-H ₂ O ± NaHCO ₃ and Na ₂ SO ₄	-0.8 to -3.3 (n = 44)	1.4-5.4	130-170 (n = 44)	100 to 150	140-180
Clastic sulfides, Semenov-3 field						
-21.1 to -21.8 (n = 8)	NaCl-H ₂ O	-3.0 to -6.0 (n = 31)	4.8-9.2	241-310 (n = 31)	250	266-335

T_e , eutectic temperature; T_m , final temperature of ice melting; T_{hom} , homogenization temperature; T_f , minimum temperature of formation.

Pressure estimations are described in the text.

n is the number of measurements.

Table 6 Vapor composition of fluid inclusions in barite from the Saf'yanovka deposit and Semenov-3 field (mol%) in comparison with data on some hydrothermal fields and VMS deposits

Deposits	H ₂ O	CO ₂	CO	CH ₄	N ₂
Saf'yanovka deposit, colloform ores	96.91	1.58	1.5	0.05	0.006
Saf'yanovka deposit, clastic ores	98.93	0.64	0.41	0.02	0.02
Semenov-3 field, clastic ores	98.10	1.60	0.30	0.01	n.d.
Brother Volcano ^a	99.979	0.013	n.d.	0.002	0.006
Rumble II West ^b	99.946	0.037	n.d.	0.002	0.006
Miojinsho ^d	99.4	0.35	n.d.	0.0027	0.048
Kita-Bayonaise ^d	99.4	0.24	n.d.	0.0042	0.045

^ade Ronde et al. 2003, sample X573/G (barite+sulfides)

^bde Ronde et al. 2003, sample X656/A (barite+sulfides)

^cour calculations

^dSasaki et al. 1995