Deep-sea drilling of the 13°30' N Oceanic Core Complex: assessing links between fluid flow, metal enrichment and seafloor massive sulfide deposit formation near Semenov-1

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Abstract

Deep-sea drilling is a key tool in assessing the economic viability of seafloor massive sulfide (SMS) deposits. Drilling can be used to understand links between fluid flow, faulting and mineralization. Of particular interest on the seafloor due to their relative enrichment in Ni and Co, is an underexplored sub-

class of SMS deposits that are associated with or hosted within ultramafic lithologies. We present initial results from sub-surface drilling near the Semenov-1 SMS deposit located on the 13°30' N oceanic core complex on the Mid-Atlantic Ridge. Drilling recovered samples from up to 20.7 meters below seafloor (mbsf). In the recovered core samples, a transition from chlorite and clay-rich breccias in the upper 7.5 mbsf to serpentinite, magnesite, dolomite and talc bearing rocks with locally mylonitic fabrics was observed. The contact between mafic and ultramafic lithologies marks the transition from brittle to ductile deformation regimes. Pyrite and marcasite occur throughout the drilled interval, commonly as disseminations. Pyrrhotite and isocubanite only occurred near the seafloor (~2 mbsf) and are associated with native Au grains. Pyrite at 7.5 mbsf was notably enriched in Ni, whereas deeper pyrite contained higher Se. The average $\delta^{34}S$ value for all sulfide minerals is 0.0±5‰ (1σ, *n=114 spots*) indicating sulfur was largely contributed from the leaching of igneous host rocks, and that magmatic volatile degassing is not an important process contributing to metal enrichment at Semenov-1. The source of sulfur or processes affecting isotopic fractionation also varied over time leading to large variations of ~15‰ across individual pyrite grains. We interpret the drilled section as representing a cross-section through a basaltic veneer to the underlying upper detachment fault surface providing evidence for the complex nature of hydrothermal systems associated with core complexes.

Introduction

Our understanding of mineralizing processes in hydrothermal systems and associated seafloor massive sulfide (SMS) deposits is largely based on samples collected at the seafloor. By comparison, very little is known about the processes occurring beneath the seafloor. The extent of mineralization below the seafloor is significant in sedimented environments (Nozaki et al., 2021) and some volcanogenic massive sulfide (VMS) deposits on-land (Doyle and Allen, 2003; Piercey, 2011). Understanding the sub-seafloor distribution of sulfide mineralization is a critical question to address at a time when seafloor massive sulfide deposits are being considered as future mineral resources (Boschen et al., 2013; Miller et al., 2018). It remains unknown if comparable sub-seafloor mineralization exists in detachment-fault hosted SMS

deposits, as does the geometry of hydrothermal fluid movement within the fault zone. Understanding the extent of sulfide mineralization (Nozaki et al., 2021), and distribution and content of metals below the seafloor (Humphris et al., 1995; Martin et al., 2022; Murton et al., 2019) will allow more accurate resource assessments to be conducted in the future (Hannington et al., 2011; Jamieson et al., 2014). Furthermore, investigating the extent of sub-seafloor mineralization will advance our understanding of interactions between vent-hosted ecosystems, fluid flow, faulting and mineralization, which is required to assess the possible impacts of deep-sea mining (Van Dover, 2011).

To investigate the potential for subsurface mineralization and to understand the architecture of a seafloor detachment fault, deep-sea drilling is required, which is expensive and technologically challenging. In this study we present data from a poorly-understood sub-class of SMS deposits that are spatially associated with ultramafic lithologies (Fouquet et al., 2013; Patten et al., 2022). In 2021, project ULTRA (Ultramafic-hosted mineral Resource Assessment) conducted deep-sea drilling near the ultramafic-hosted Semenov-1 hydrothermal mound at 13°30' N on the Mid-Atlantic Ridge. At 13°30' N, ultramafic and lower-crustal lithologies are exhumed at the seafloor along a detachment fault forming an Oceanic Core Complex (OCC; Escartín et al., 2017; MacLeod et al., 2009). The Semenov-1 deposit forms a mound-structure with no visible hydrothermal venting and is, accordingly, regarded as inactive (Jamieson and Gartman, 2020). Drilling <10 m from the break of slope defining the base of the mound penetrated to a depth of 20.7 meters below the seafloor (mbsf). In this study we present initial observations from drill core analysis including visual observations, alteration mineralogy, sulfide mineralogy, geochemistry and sulfur isotopic composition ($\delta^{34}S$) of sulfide minerals, to investigate links between fluid flow and mineralization within a detachment fault.

Geological Setting

The 13°30'N OCC is located on the western flank of the axial rift valley on the Mid-Atlantic Ridge (Fig. 1A). The OCC detachment surface is delineated by well-developed corrugations that are continuous in the

direction of spreading for ~10 km (Escartín et al., 2017; Pertsev et al., 2012). The core complex consists of a mixture of serpentinized peridotite, dolerite, gabbro, plagiogranite and occasional pillow basalts and flows that exhibit variable degrees of hydrothermal alteration (Escartín et al., 2017). Basalt flows on the detachment surface are interpreted as recent features post-dating the formation of the fault structure, and provide evidence of mafic magmatism occurring at depth below the seafloor (Escartín et al., 2017; MacLeod et al., 2009). Widely, basalt breccias cover the detachment fault surface and are interpreted as representing dismembered hanging wall lava flows and dike material that has been dragged up along the detachment fault surface (e.g., Escartín et al., 2017; Martin et al., 2024). The OCC is considered to be tectonically inactive owing to the propagation of volcanic ridges to the north, and consequent termination of the detachment fault as evidenced by the extensive rifting of the base of the core complex (Escartín et al., 2017; MacLeod et al., 2009). The OCC is estimated to have initiated 470,000 ka (Escartín et al., 2017), with U-Th dating of the sulfide mineralization on the OCC indicating a minimum age of ~124,000 years for mineralizing events (Kuznetsov et al., 2011).

Hydrothermal venting

The13°30'N OCC hosts five sites of hydrothermal mineral accumulation, collectively termed the Semenov vent field cluster (Cherkashev et al., 2013; Melekestseva et al., 2014; Pertsev et al., 2012). Only Semenov-2 is hydrothermally active, whilst Semenov-1, -3, -4 and -5 are inactive (Fig. 1B). The total sulfide endowment of the Semenov cluster is estimated at ~40 Mt (Cherkashev et al., 2013). The active Semenov-2 deposit is basalt-hosted, venting clear-whitish fluid at a maximum recorded temperature of 317 °C (Escartín et al., 2017). Semenov-3 and 5 are located on the surface of the core complex and consist of sulfide crusts and rubble with oxidation occurring extensively at the seafloor producing Fe(oxy)hydroxides. Semenov-4 is located at the eastern termination of the OCC and straddles both the hanging wall (basalt hosted) and footwall (ultramafic hosted) and consists of both large conical mounds as well as extensive areas of sulfide rubble.

This study focuses on the inactive Semenov-1 deposit, the furthest west deposit in the vent field cluster (Fig. 1B and C). The mound measures approximately 175 m high and 200 m wide and is located at water depth of ~2600 m. The surface of the mound consists of sub-angular sulfide rubble and sediments that are deep orange to red in color, indicating that extensive oxidation of sulfide material has occurred.

Methods

The data reported in this study were collected as part of project ULTRA on expedition JC224 aboard the RRS *James Cook* in 2021. The surface geology of the Semenov-1 hydrothermal mound was studied using videography using the remote underwater vehicle *HyBIS*. Drilling was conducted using the British Geological Survey, Rock Drill II (RD2). Drilling utilized core barrels that were 1.72 m in length and 61 mm in diameter. Each completed core run was then latched, recovered and stored at the seafloor during operation. A steel sleeve remained in the hole during drill core recovery. The steel tube ensured hole stability and that debris from higher up in the hole did not contaminate deeper samples. Several holes were drilled at Semenov-1 with varying degrees of core recovery. Here we present data from hole 52_RD_A, located at the sedimented base of the Semenov-1 mound (Fig. 1), and penetrating to a maximum depth of 20.7 mbsf. Note that depth below the seafloor is estimated based on core recovery, and when core recovery is low, samples may have an error of +/- 1.72 m, the length of a core barrel. A summary of the recovered core can be found in Table 1.

Sample selection

Pyrite, pyrrhotite, marcasite and chalcopyrite/isocubanite grains were picked from individual core sections (e.g., core A2, A3; Table 1) providing a composite record of the downhole mineralization. In order to understand depth variations in lithology, alteration, and sulfide petrology, 2-3 representative samples were selected from each core section for mineralogical characterization and X-ray diffraction analysis. We also present initial shipboard geochemical data analyzed via portable X-ray fluorescence (pXRF) for all drill core samples.

Sulfide petrography

For petrographic analysis, sulfide minerals were mounted in epoxy resin in 1" aluminum rounds. Mineral assemblages were identified using reflected light microscopy. Microtextural characterization was performed using etching with 1 M NaOCl for 90 s to tarnish the mineral surface and reveal mineral grain-scale zonations (Martin et al., 2023a; Tanner et al., 2013). The tarnish was later easily removed with a diamond polishing solution.

Alteration mineralogy

All recovered core was described and photographed aboard the RRS *James Cook*. X-ray diffraction analysis was carried out to identify different minerals on representative bulk samples from each core section. Samples were first crushed using an agate pestle and mortar. X-ray diffraction analysis was carried out at Cardiff University (UK) using a Philips PW1710 Automated Powder Diffractometer with Cu Kα radiation at a voltage of 35 kV and current of 40 mA. The scans were conducted between 2° and 70° at a scan speed of 0.04° 2θ/s. Mineral phases were identified using Philips PC Identify software. From the diffractogram peak area, semi-quantitative analysis was performed by measuring the area of the main peak of each mineral, and then a percentage of each mineral present was estimated.

Portable X-ray florescence analysis

Portable X-ray Fluorescence (pXRF) analysis was carried out aboard the RRS *James Cook*. Three-hundred point analyses were determined across all core samples using an Olympus Delta Professional pXRF analyzed in Geochem mode. Analysis lasted for 60 s to determine Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Se and Pb (Appendix A). Data quality was monitored through the repeat analysis of a silica blank, NIST1710a and two in house standards GY01 (seafloor mud) and HY02 (massive pyrite) analyzed every 20 samples (Appendix A). These data provide initial insights into geochemical trends downhole and provide the basis for future lab-based studies.

Sulfide mineral chemistry

The trace metal content of pyrite (*n=99 spots*), pyrrhotite (*n=10*) and marcasite (*n=12*) was determined using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) on six representative polished mounts containing numerous individual sulfide mineral grains. Laser ablation-ICP-MS analysis was performed at Memorial University of Newfoundland (Canada) using a GeoLas 193 nm laser coupled to a Thermo-Finnigan Element XR ICP-MS. Analysis employed a spot diameter of 50 μm at a frequency of 5 Hz and a fluence of 3 J/cm^2. Each analysis lasted 50 s and a gas blank was measured for 30 s prior to each analysis. Analyte masses measured included: ^{51}V, ^{53}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{69}Ga, ^{72}Ge, ^{75}As, ^{77}Se, ^{95}Mo, ^{109}Ag, ^{111}Cd, ^{115}In, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{197}Au, ^{205}Tl, ^{206}Pb and ^{209}Bi. Iron-57 was used as an internal standard for all analyses and a stoichiometric Fe content of 46.5% was assumed for pyrite and marcasite, and 62.3% for pyrrhotite. External calibration was performed using USGS MASS-1 and NIST 610. Precision was monitored through the repeat analysis of MASS-1 (*n= 26*) that yielded a relative standard deviation (RSD) for Mn, Ge, As, Sn, Au, Tl and Bi of <10%, and <13% for V, Cr, Ni, Ga, Se, Mo, Ag, Cd, In, Sn, Te and Au. Only Sb and Co showed a higher RSD, reaching 16% (see Appendix B). The subtraction of gas blanks and calculation of detection limits was performed using Iolite software.

Qualitative geochemical mapping

Wavelength dispersive spectroscopy on an electron probe microanalyzer (EPMA) was used to qualitatively map compositional zonations of Co and Mn in pyrite that showed zonations during etching (*n=2* mounts). Data was collected using a JEOL JXA-8230 SuperProbe equipped with five wavelength dispersive spectrometers at Memorial University of Newfoundland. Cobalt and Mn were collected on separate spectrometers using an accelerating voltage of 20 kV, a beam current of 250 nA and a dwell time of 500 ms. Map resolution was typically 1-3 μm per pixel. Element concentrations were not quantified during mapping, hence only relative changes in metal content can be assessed.

Sulfur isotope analysis

The sulfur isotopic ratio of spot analyses within pyrite (*n=86*), chalcopyrite (*n=15*), pyrrhotite (*n=8*) and marcasite (*n=5*) was determined using secondary ion mass spectrometry (SIMS) microanalysis in six polished mounts. Samples were mounted in epoxy resin with aluminum retaining rings, polished, and then coated with 300Å of Au to mitigate charging of the sample during ion bombardment. Analyses were performed using a Cameca IMS 4f SIMS instrument at the Microanalysis Facility at Memorial University of Newfoundland following the procedure detailed in Brueckner et al. (2015). Each sample was bombarded with a primary ion beam of 500-750 pA of Cs^+ accelerated through a potential voltage of 10 KeV and focused into a 10 μm rastered spot. Negatively charged secondary ions were accelerated into the mass spectrometer using a potential of +4.5 KeV. Each spot was pre-sputtered for 120-180 s prior to analysis with a 10-15 μm rastered beam to exclude sulfur contamination from the sample surface. Reproducibility of results was calculated based on the repeat analysis of standard reference materials UL9 (pyrite; $\delta^{34}S$= 16.3‰), KH87 (pyrite; $\delta^{34}S$= 0.4‰), USGS Norilsk (chalcopyrite; $\delta^{34}S$= 8.3) and PoW1 (pyrrhotite; $\delta^{34}S$= 3.6‰) (Appendix C). All analyses are reported in standard delta notation ($\delta^{34}S = 1000\times(R_{Sample}/R_{V\text{-}CDT}\text{-}1)$; where $R = {}^{34}S/{}^{32}S$), ‰) relative to Vienna Canyon Diablo Troilite (V-CDT).

Results

Visual core descriptions

Core recovered from the seafloor to a depth of 0.33 mbsf consists of poorly consolidated beige-colored pelagic sediment containing shell fragments. Underlying the sediment horizon is a 20 cm thick section of massive pyrite with a vuggy texture and orange veins of Fe-oxyhydroxide (Fig. 2A). Rare basaltic clasts occur intercalated within this massive sulfide. At a depth of 1.8 mbsf is a black sandy layer, approximately 15 cm thick, containing subangular to angular granular textured pyrite (~60%), chalcopyrite (~30%) and sphalerite (~10%) grains; hereafter referred to as sulfide sand (Fig. 2B). The sulfide sand is underlain by a

1.7 m thick section of bleached and silicified altered basalt. Within this section, below 3.8 mbsf, massive sulfide or sulfide rubble are absent and sulfide minerals occur only as fine (<2 mm; ~5% modal abundance) disseminations in the altered host rock. Vuggy calcite veins were common in some core samples (Fig. 2C). From 5 to 7 mbsf the core samples have a prominent brecciated texture with relict clay-rich clasts commonly showing a visible gradation in alteration mineralogy from the rim to core (Fig. 2D, E and F). Pyrite and marcasite occur as euhedral grains disseminated in the matrix. At 7.1 to 7.8 mbsf, core samples have a sub-vertical ultramylonitic fabric (Fig. 2G) with disseminated marcasite being common within the matrix (Fig. 2H, inset).

At 7.7 mbsf a distinct change in the color and texture of the core is observed. Samples above 7.7 mbsf contain clear and numerous clasts and are light-gray in color, below, samples become green-grey in color, generally lack brecciation, and contain visibly altered pyroxene phenocrysts (Fig. 2I, K and N). Samples are commonly cross-cut by an anastomosing network of mm-scale white-beige veins of carbonaceous material (Fig. 2I and K) and samples contain some disseminated pyrite (<2% modal abundance). At 9.3 mbsf a red, hematite-bearing dolomite horizon occurs (Fig. 2J). At 13.8 mbsf, a 20 cm wide zone of brecciation is intersected where clay gouge cements green-grey peridotite clasts (Fig. 2L). Below 14 mbsf the color of core becomes lighter and greener (Fig. 2M to O). Core samples at this depth generally have a massive texture containing pyroxene phenocrysts that are altered to a dark green mineral (Fig. 2N). Pyrite occurs disseminated throughout the samples in low concentrations (<1% modal abundance). At 15.5 to 16 mbsf a second mylonite zone is intersected; the zone is characterized by shallowly dipping foliation with clasts of green-grey serpentinized peridotite. Below 16 mbsf to the end of the recovered core at 19.1 mbsf, the core is white-green in color and contains chrome spinel (Fig. 2O) with traces of low angle foliation dipping at ~30°.

Alteration mineralogy

Pyrite and marcasite are the dominant sulfide minerals throughout the core, occurring as either disseminations, sulfide sand and rubble or massive pieces. Chalcopyrite is the third most abundant sulfide

mineral and is notably enriched in the rubble horizon at 1.8 mbsf (>40 vol.%). In brecciated samples, montmorillonite and kaolinite with chlinochlore are the dominant alteration minerals. Ultramylonite samples at 7.1 mbsf contain dolomite with disseminated pyrite and kaolinite. From 7.1 to 14.5 mbsf, dolomite is a major phase comprising >70 vol.% of some samples. From a depth of 10.9 mbsf, magnesite occurs in variable amounts. At 12.1 mbsf, serpentinite minerals occur with detectable antigorite, chrysotile, clinochrysotile and lizardite. Talc first occurs at 15.6 mbsf and is present sporadically until the end of the hole. A summary of the key alteration minerals present in each core section is provided in Table 2 and a complete photographic section off all recovered core is available in Appendix D.

Sulfide mineralogy

In the sulfide sand and rubble at 1.8 mbsf, marcasite is overgrown by euhedral pyrite (Fig. 3A). In some samples, framboidal pyrite aggregates are overgrown by marcasite and then by later euhedral pyrite (Fig. 3B). In other grains, marcasite was absent and pyrite with concentric growth zonations was present (Fig. 3C). Rarely, complex intergrowths of pyrite and marcasite occurred forming atoll structures (Fig. 4D). Elongate laths of pyrrhotite are spatially associated with isocubanite (Fig. 3E). Chalcopyrite exsolution lamella are a common feature in all isocubanite grains (Fig. 3F). Native Au grains 1-5 μm in diameter occur in pyrrhotite and are spatially associated with the grain boundary between isocubanite and pyrrhotite (Fig. 3G and H). Native Au was only found in pyrrhotite and was not observed in pyrite, marcasite or chalcopyrite. In core section A4, within altered basalt, marcasite is the dominant sulfide mineral forming euhedral elongate laths that overgrow framboidal pyrite (Fig. 3I and J). Laths commonly formed rosette shaped aggregates (Fig. 3K). Unlike in core samples located closer to the seafloor, pyrite here is overgrown by later euhedral marcasite (Fig. 3L). At the transition to ultramafic-dominated lithologies (core A5), only pyrite occurs, it is coarse-grained (> 2mm) and euhedral (Fig. 3M and N). In core A7, pyrite is coarse-grained and subhedral (Fig. 3O and P). Some pyrite grains from core A9, within altered peridotite, contain mesh-textured breccias of chrome spinel (Fig. 3 Q). Chalcopyrite forms discrete porous regions that are pyrite-poor and massive areas containing euhedral pyrite grains (Fig. 3R). Core A10, which is talc-rich,

239 contains pyrite, chalcopyrite and sphalerite (Fig. 3S and T). Chalcopyrite is overgrown by pyrite (Fig. 3S)
240 and sphalerite (Fig. 3T).

241 Microtextural analysis of pyrite and marcasite

242 Etching of pyrite in the massive sulfide piece (core section A2) reveals three distinct sulfide mineral
243 generations (Fig. 4A). Fine-grained pyrite aggregates with concentrically zoned pyrites are overgrown by
244 a rim of marcasite followed by coarse-grained euhedral pyrite (Fig. 4A). Coarse-grained pyrite exhibits
245 preferred growth orientation growing outwards (arrow in Fig. 4B). Framboidal pyrite is surrounded by
246 zones of colloform textured pyrite (dark purple; Fig. 4C), that is then overgrown by euhedral pyrite with
247 pronounced oscillatory zonations indicating outward growth (Fig. 4C). Marcasite randomly overprints
248 pyrite in several areas (Fig. 4C). In some samples, framboidal pyrite is absent and marcasite is overgrown
249 by pyrite (Fig. 4D).

250 Marcasite grains from the bleached and silicified basalt (core A4) exhibit variable internal morphologies
251 when etched. Some grains appear homogenous, some have a striped appearance and others have concentric
252 growth zonations (Fig. 4E, F and G). The complexity of internal zonation across individual grains is also
253 variable, some have relatively simple concentric zonations with only a few sub-domains that are parallel to
254 the present grain margins (Fig. 4F), whereas others contain complex oscillatory and sector zonations (Fig.
255 4G and H). In core sample A5 and A7, euhedral pyrite grains show pronounced sectoral zonations with
256 distinct patterns identified in several grains (Fig. 4I to L), some grains transition from sectoral zonation in
257 the grain core to oscillatory zonation at the grain rim (Fig. 4J to L).

258 In altered peridotite (core A8), pyrite contains random shapes with no clear zonation pattern (Fig. 4M). In
259 the talc-rich core, sample A9, early euhedral pyrite generations have been overgrown by later pyrite (Fig.
260 4N, O and P). The ultramafic mylonite (core A10) contained many different textures of pyrite with some
261 grains containing evidence of multiple pyrite generations with no clear zonation pattern (Fig. 4Q). In other
262 grains that are anhedral, sectoral zonations occur (Fig. 4R), whereas in other anhedral grains, radial

zonations perpendicular to the grain margin occurred (Fig. 4S). In coarse-grained pyrite, zones of bright oscillatory zonation delineate relict grain cores (Fig. 4T).

Sulfur isotope analysis

For all data, $\delta^{34}S$ values ranged from -20.6‰ to 13.6‰ with an average of 0.0±5‰ (1σ, *n=114*) (Fig. 5). Pyrite averaged -1.0±5.0‰ (1σ, *n=86*), marcasite -0.6±0.4‰ (1σ, *n=5*), pyrrhotite 5.4±1.5‰ (1σ, *n=8*) and chalcopyrite 3.0±4.0‰ (1σ, *n=15*). Framboidal pyrite from sample A4 ranged from -3.2 to -3.5‰ and was not notably different from later marcasite in the same samples that averaged -0.6±0.4‰ (1σ, *n=5*). There are no clear trends in pyrite $\delta^{34}S$ values with depth below the seafloor (Fig. 5). Pyrite in sample A10 shows the greatest amount of variation with a range from -20.6 to 4.7‰ (Fig. 5). Chalcopyrite in core A2 has a lower average $\delta^{34}S$ value of -0.4±0.7‰ (1σ, *n=5*) compared with chalcopyrite in deeper samples that average 5.2±3.7‰ (1σ, *n=8*).

To investigate intragrain variation in $\delta^{34}S$ values, detailed analytical transects were performed across individual pyrite grains. At the mineral scale $\delta^{34}S$ values are highly variable (Fig. 6A-L). In sample A7, an aggregate of pyrite grains, $\delta^{34}S$ values range from -14.3 to 1.9‰ (Fig. 6I). In other grains from the same sample the sulfur isotopic composition is more homogenous ranging from -0.3 to 3.1‰ (Fig. 6G). In core sample A8 a transition from low (-8.2‰) to high (6.9‰) $\delta^{34}S$ values is observed across an individual pyrite grain (Fig. 6I). The largest across-grain variation occurs in sample A10 where $\delta^{34}S$ values range from -20.6‰ to 4.6‰, with analytical points within 100 microns of one another ranging from -10.9‰ to 4.6‰ (Fig. 6L).

Bulk-rock core geochemistry

The initial geochemical data presented here provides qualitative evidence that the chemical composition of samples is highly variable with depth below the seafloor (Fig. 7). All analyzed elements are available in the supplementary information (Appendix A). We present downhole plots for Si, Ca, Al, Ni and Cr (Fig. 7). Silica and aluminum show the inverse relationship to Ca and are enriched in mafic lithologies (Fig. 7A, B

and C). The relative amount of Si increases toward the bottom of the drilled intersection corresponding to an increase in the abundance of talc (Fig. 7 and Table 2; core A10 and A11). Both Ni and Cr content increase at the mafic-ultramafic contact, as observed in pyrite geochemical data (7.5 mbsf; Fig 7 D, E, and 8). Nickel and Cr content are elevated in ultramafic lithologies relative to mafic lithologies (Fig. 7 D and E).

Sulfide mineral chemistry

Differences in trace metal content exist between pyrite, pyrrhotite and marcasite (Fig. 8A). The median content of Mn and Tl in marcasite is notably higher relative to pyrrhotite and pyrite (Fig. 8A). Marcasite is relatively depleted in all other measured elements, most notably Co, Ni, Cu, and As (Fig. 8A). The trace metal contents in pyrrhotite and pyrite are comparable, with pyrite containing slightly higher contents of Mo, Pb and Co relative to pyrrhotite (Fig. 8A).

Discernible differences in the metal content of pyrite occur with depth below the seafloor. A strong enrichment in V, Mn, Cu, Zn, Au, and Tl occurs in pyrite near the seafloor in samples hosted within the sulfide sediment (core A2; Fig. 8B). For example, the median Mn concentration in pyrite is 446 ppm (*n=12*) near the seafloor, whereas all other pyrite from deeper samples contain <10 ppm. Copper and Zn show similar trends, with an order of magnitude higher contents in pyrite close to the seafloor compared with all other samples (Fig. 8B). By contrast, the Ni content of pyrite is extremely low near the seafloor with a median of 1.5 ppm (*n=12*), compared with deeper samples that have median contents ranging from 363 to 1021 ppm (Fig. 8C). Selenium is highly enriched only in the deepest samples (Fig. 8C). Overall, the total measured trace metal content of pyrite is low, ranging from 1109 ppm in the mafic core section A4 to 428 ppm in ultramafic core A10. There is not notable correlation between the elements measured.

Discussion

Fluid conditions during alteration

Fluids responsible for the formation of SMS deposits are typically high-temperature (>300 °C), reducing (log fO_2 ~ -33 to -38; Kawasumi and Chiba, 2017) with a variable H_2 and H_2S content (e.g., Humphris and Klein, 2018). Fluids generated during serpentinization are geochemically distinct having variable but commonly elevated H_2 contents (0.25-13 mM), a variable fluid pH (2.8-8.0), and temperature (~40 to ~400 °C; Mével, 2003), relative to fluids typical for SMS formation. Thus, the alteration mineral assemblage generated by high-temperature SMS-related fluids and serpentinization will be distinct. In a typical high-temperature (>300 °C) hydrothermal system, such as that hypothesized to have formed the Semenov-1 SMS deposit, chlorite and epidote-rich alteration forms proximal to the massive sulfide mound (Alt et al., 1986; Humphris and Thompson, 1978). Ultramafic-hosted vent sites are different still and are dominated by serpentine minerals (antigorite, lizardite, chrysotile) with talc, magnetite, calcium carbonate and magnesium hydroxide minerals that are produced during serpentinization of mantle peridotites (Alt and Shanks, 2003; Bjerga et al., 2015; Ding et al., 2023; Lowell and Rona, 2002). Both chlorite-rich and serpentinite-rich alteration occur in the drill hole adjacent to the Semenov-1 mound indicating variable fluid sources and protolith material within the sub-surface.

The alteration mineral assemblage of core proximal to the Semenov-1 deposit can be divided into two distinct assemblages occurring at different depths below the seafloor indicating different protoliths, fluid conditions and ultimately fluid sources. At 7.5 mbsf the alteration mineralogy changes from chlinochlore, illite, and kaolinite-rich to an assemblage containing dolomite, talc and magnesite with chrysotile, antigorite and lizardite (Fig. 2 and Table 2). The occurrence of chlorite indicates fluid temperatures of ~300 °C with a near neutral pH (Alt and Jiang, 1991; Reyes, 1990). Chlorite is common in seafloor hydrothermal systems forming during the alteration of mafic host rocks by seawater derived hydrothermal fluids (Humphris and Thompson, 1978). The occurrence of illite indicates slightly lower fluid temperatures down to ~220 °C, that marks the minimum stability field for illite (Alt and Jiang, 1991). Thus, the alteration mineral

assemblage of chlinochlore with illite and kaolinite in the upper 7.5 mbsf indicate that fluids were of high-temperature >220 °C and near neutral to slightly acidic. The similarity between this alteration assemblage and that commonly observed in mafic-hosted SMS deposits (Humphris et al., 1995) and lack of obvious ultramafic influence (e.g., serpentinite) suggests the alteration of a mafic protolith. Similar chloritic alteration has been sampled at the toe of the detachment fault in an exposed scarp surface several km to the E of Semenov-1. In the detachment toe, the alteration is interpreted to represent fluid flow that occurred at deeper crustal levels (~3-5 km) that was subsequently exhumed and exposed at the seafloor (Martin et al., 2024).

Below 7.5 mbsf, and down to the end of the hole (20.7 mbsf) the inclusion of serpentinite minerals indicates that protolith material were of ultramafic origin (i.e., mantle peridotite) and were subsequently serpentinized and carbonized at or near the seafloor during exhumation along the detachment surface, however the depth of serpentinization remains unknown (e.g., Evans et al., 2013; Francis, 1981; Früh-Green et al., 2004; Rona et al., 1987). Serpentinization widely occurs on the seafloor where mantle peridotites are exhumed at fracture zones, oceanic core complexes and associated detachment faults, along slow- to ultra-slow spreading ridges (Cann et al., 1997; Cannat, 1993). The occurrence of serpentinites below the seafloor at Semenov-1 is in good agreement with previous studies that widely observed serpentinized ultramafic lithologies at the seafloor all over the core complex (Escartín et al., 2017).

Discerning the exact conditions of serpentinization near Semenov-1, specifically the temperature range and mineral paragenesis will require further study as pervasive serpentinization can occur at ~400 °C down to ambient seawater temperatures (Früh-Green et al., 2004). However, the persistence of disseminated euhedral pyrite throughout the drilled section indicates that temperatures were above ambient seawater (i.e., a few °C), at least for some period of time. In addition to serpentinization, carbonation, through the addition of CO_2 (and silica)-rich fluids forms talc-carbonate alteration containing magnesite, dolomite and talc; a common mineral assemblage in some ophiolite terrains (Barnes et al., 2009; Bjerga et al., 2015; Coltat et al., 2021a). Below 7.5 mbsf near Semenov-1, the alteration mineral assemblage contains evidence of both

serpentinization and extensive carbonation, owing to the large amount of dolomite and magnesite. Based on the presence of relict igneous phases (Fig. 2K) and occurrence of serpentinite (Table 2) in dolomite-rich samples, we exclude a sedimentary origin for the dolomite (Baker and Kastner, 1981).

Bjerga et al. (2015) note that the alteration of peridotites during serpentinization varies both as a function of temperature and CO_2 content. Two distinct mineral assemblages are noted to occur: an initial assemblage of olivine-clinopyroxene-serpentinite-magnetite-brucite that formed early and a later serpentinite-magnesite-magnetite-dolomite assemblage that formed during more pervasive serpentinization. The large quantities of dolomite relative to serpentinite and absence of primary igneous phases such as olivine show that serpentinization was pervasive in our samples. The CO_2 and silica content of the fluids can further influence the mineral assemblage formed, with lower CO_2 and high silica contents leading to the stabilization of talc-bearing mineral assemblages (Wang et al., 2017), such as those observed below 15.6 mbsf. Visually, talc-carbonate rocks near Semenov-1 are comparable to those described on land at the Leka Ophiolite (Bjerga et al., 2015), where the original peridotite texture has been completely obliterated in talc-rich rocks.

How serpentinization related temporally and spatially to the formation of Semenov-1 remains enigmatic. Two scenarios are possible: i) serpentinization occurred during seafloor exhumation at near ambient seawater temperatures or, ii) serpentinization occurred during high-temperature fluid circulation above ambient seawater temperature related to the formation of Semenov-1. Delineating between these two processes is challenging and ultimately the alteration observed in core samples most likely reflects both ambient seawater and high-temperature serpentinization related to Semenov-1 formation. Evidence of the "bi-modal" formation temperatures, such as those hypothesized here, where the temperature of serpentinization varies spatially (i.e., across mylonite zones) and temporally, have been observed at the Venma Fracture Zone (Atlantic) and the Izu-Bonin Forearc (Früh-Green et al., 2004). The inclusion of chalcopyrite which is typically considered a high-temperature mineral phase in SMS deposits (>250 °C; e.g., Humphris et al., 1995) in core A9 indicates a high-temperature origin. However, alteration in the same

core consists of clinochrysotile (Table 2) that forms at temperatures of ~30-80 °C (Bonatti et al., 1984), hence the occurrence of these two minerals in the same core samples suggests temperature variation over time. To further investigate the relationship between serpentinization and Semenov-1 deposit formation, oxygen and boron isotopes on serpentinite minerals (e.g., Bonatti et al., 1984) could be utilized. These data would constrain formation temperature variation; however, this remains outside the scope of our initial investigation.

At the seafloor, similar alteration minerals derived from ultramafic protoliths have also been documented at the Tianzuo (Southwest Indian Ridge; Ding et al., 2023), Lost City (Mid-Atlantic Ridge; Allen and Seyfried, 2004; Kelley et al., 2005) and Rainbow (Mid-Atlantic Ridge; Marques et al., 2007) vent fields. Moreover, similar mineral assemblages have also been sampled on land in ophiolite terrains and associated ultramafic-hosted VMS deposits (Bjerga et al., 2015; Coltat et al., 2021b; Fouquet et al., 2010; Martin et al., 2023b; Patten et al., 2022).

Serpentinization is known to have occurred within the 13°30'N OCC and Semenov vent field cluster (Escartín et al., 2017; Firstova et al., 2022). In the wider OCC, Escartín et al. (2017) note that peridotites are largely serpentinized, with most rocks showing evidence of static hydration (i.e., in situ, low-strain environments), containing prominent mesh textures. Talc-bearing lithologies were also observed at igneous contacts along with localized talc and serpentinite schists (Escartín et al., 2017). Finally, serpentine-rich clasts are also reported in fault breccias where they occur intercalated with basaltic clasts. Serpentinites have also been described at the inactive Semenov-5 SMS deposit, veins of sphalerite and pyrite occur in serpentinite occurring as a stockwork in "highly permeable" serpentinites (Firstova et al., 2022). In addition to serpentinite, Cr-spinel occurs as an accessory phase (Firstova et al., 2022), and is also observed in drill core samples from this study (Fig. 3Q). Thus, serpentinization is shown to be widespread at 13°30'N and does not appear to be spatially associated with only areas of high-temperature fluid discharge and sulfide accumulation.

Variation in sulfide mineralogy with depth below the seafloor

The sulfide minerals present in the subsurface adjacent to Semenov-1 vary with depth below the seafloor indicating variable fluid redox, sulfur fugacity, temperature and fluid pH. Sections taken near the seafloor (section A2) are characterized by blocks of massive sulfide ranging from ~10 cm down to the micron-scale and occur in a poorly-cemented sulfide layers as angular to sub-rounded clasts, hosted within brecciated mafic lithologies. The sulfide boulder and rubble horizons are unique, as all other sulfide minerals occur as disseminations and in a much lower abundance (<2 modal %). Within the sulfide sediment, in close proximity to the seafloor, Mn, Zn, Cu, Co and Tl are strongly enriched in pyrite (Fig. 8B) and isocubanite occurred readily (Fig. 3E).

Within the sulfide sediment, the occurrence of pyrrhotite and isocubanite suggests that the mineralizing fluids were highly reducing with a low sulfur fugacity compared to fluids responsible for pyrite formation and were high-temperature (>350 °C). Similar fluids and mineral assemblages are common in mafic-hosted seafloor hydrothermal systems (Monecke et al., 2016), but have also been observed in ultramafic-influenced sites such as Rainbow and Kairei (Marques et al., 2007; Wang et al., 2014). Pyrrhotite, chalcopyrite and isocubanite have also been documented in samples collected from the Semenov-1 mound and were interpreted to represent a pulse of late, high-temperature, reduced fluid to the mound (Melekestseva et al., 2014). Based on the mineralogy and morphology of the sulfide samples, we interpret the sulfide sediment as representing an apron of sulfide talus that was derived from the upper mound and likely formed from chimney collapse events. Chimney collapse is further supported by the presence of pipe-like structures that were once fluid conduits (Fig. 3D). Chimney collapse explains the abundance chalcopyrite and isocubanite, common in active chimneys (Hannington and Scott, 1989), and the rubbly and sandy morphology of the layer that indicates that gravity-driven remobilization and transport has occurred.

Pyrite occurs in all samples throughout the drilled section, whereas marcasite occurs only from the seafloor to ~7.5 mbsf (core A4). In core A4, marcasite is the dominant sulfide mineral, and occurs as rosettes of euhedral bladed crystals (Fig. 3I-L). Pyrite in this sample is rare and formed early in the paragenesis as

either framboids (Fig. 3I) or anhedral grains (Fig. 3L), both of which are overgrown by later euhedral marcasite. The transition from pyrite (FeS_2, cubic) to marcasite (FeS_2, orthorhombic) indicates changes in fluid temperature and pH over time. Pyrite is stable up to ~400 °C, whereas marcasite forms at temperatures of <240 °C. Moreover, marcasite is only stable at a pH <5 (Murowchick and Barnes, 1986). Therefore, the area around 7.5 mbsf has experienced multiple fluid flow events, one with low-pH, low-temperature fluids that occurred after an initial period of higher temperature fluid flow that precipitated pyrite. We relate this variability to the location of core A5 directly above the mafic-ultramafic transition that is marked by a downhole transition from basaltic breccias to serpentinite-bearing rocks, an area which is also enriched in Ni and Cr in bulk-core samples (Fig. 7D and E). The area, which most likely represents the detachment fault surface, is a site of increased permeability which would have experienced a periodic influx of geochemically diverse fluids (i.e., seawater, serpentinizing and hydrothermal fluid) during fault movement leading to fluctuations in fluid temperature and pH (Liao et al., 2022; Martin et al., 2024). The occurrence of pulsed fluid flow events is further supported by complex radial zonations in many marcasite grains (Fig. 3F-H) (Martin et al., 2023a) with similar complex zonations observed in pyrite from the toe of the detachment indicating temporal variation in fluid temperature and pH (Martin et al., 2024).

Evidence for variations in fluid conditions preserved in pyrite

The trace metal content and enrichment profile of pyrite can be used to assess variations in the temperature and chemical composition (e.g., pH) of hydrothermal fluids (Butler and Nesbitt, 1999; Grant et al., 2018; Keith et al., 2016; Wang et al., 2022). Additionally, internal zonation patterns can be used to determine how frequently these conditions changed (Martin et al., 2024, 2023a). Distinct changes in pyrite trace metal content are discernable with depth below the seafloor near Semenov-1 (Fig. 8B and C). Manganese, Zn, Cu, Co, Tl, V and, to a lesser extent, Au are enriched in pyrite near the seafloor versus deeper pyrite. The enrichment of these different metals, some of which are interpreted to represent high-temperature (e.g., Co and Cu) or low-temperature (e.g., Zn) hydrothermal fluid flow, or elements such as Mn and V that are adsorbed from seawater (Butler and Nesbitt, 1999; Grant et al., 2018; Keith et al., 2016; Melekestseva et

al., 2014) provides a mixed geochemical signature. We attribute this diverse geochemical signature to the origin of pyrite in core A2. During chimney collapse, both the high-temperature inner chimney lining and outer wall will become disaggregated and homogenized during collapse and transport down the mound, hence explaining the chaotic geochemical signature in pyrite from the upper sulfide layer.

The pyrite located directly above the transition from mafic to ultramafic lithologies (at ~7.5 mbsf; section A5) is enriched in Ni (Fig. 8C), relative to the pyrite closer to the seafloor. The enrichment in Ni (and Cr) is further supported by peaks in these metals in bulk-rock pXRF data (Fig. 8D and E). In combination with the alteration mineralogy that shows a transition to ultramafic rocks, we attribute the enrichment of Ni to an increased ultramafic source component, where fluids migrated along the detachment fault surface rising to the seafloor in areas of increased permeability. The boundary from mylonitic deformation within the detachment surface to brecciation above 7.5 mbsf probably promoted fluid mixing between hydrothermal or serpentinization-related fluids and seawater enhancing the precipitation of Ni, hence providing a mechanism of enrichment at this boundary. Cobalt/Ni ratios support that pyrite is influenced by an ultramafic fluid component, with Co/Ni ratios of pyrite hosted in ultramafic-derived lithologies (below 7.5 mbsf) averaging 0.1 ± 0.3 (1σ, *n=87*), comparable to the Co/Ni ratios of serpentinized peridotites at 0.06 (Marques et al., 2006). By contrast, pyrite from near the seafloor is relatively enriched in Co with a Co/Ni ratio of 46 ± 29 (1σ, *n=12*) indicating a more mixed mafic-ultramafic fluid signature for the sulfide minerals, likely derived from Semenov-1 and/or that near seafloor fluid mixing significantly biases these ratios.

Etching reveals subtle differences in internal zonation patterns in pyrite with depth below the seafloor (Fig. 4). In addition to being chemically distinct, pyrite from the mass-wasted sulfide layer in core A2 exhibits complex radial growth zonations (Fig. 4A and B), with zonations correlating to increased Mn content (Fig. 4B*). The complex zonations coupled with Mn enrichment indicates pulses of hydrothermal fluid flow punctuated by periods with relatively higher seawater influx precipitating Mn-rich zones (e.g., Grant et al.,

2018). Such a dynamic environment with large amounts of seawater influx is expected in chimney structures due to the thin chimney walls and frequent collapse and regrowth events.

Zoning is more complex in euhedral pyrite grains from deeper core samples (A5 and A7), consisting of both sectoral and radial zonation patterns (Fig. 4I-L). Sectoral zonation, which is comparatively rare compared with radial zonations, has been reported in pyrite from the Pascua high sulfidation epithermal Au deposit (Chouinard et al., 2005). At Pascua, similar zonations occur in response to the preferential incorporation of elements on different crystal faces. For sectoral zonation, the growth morphology of the pyrite is dominated by {111} octahedron, with metals preferentially incorporated in the sectors of {110} dodecahedron (Chouinard et al., 2005), hence explaining the visible difference in colors in etched images which correspond to different trace metal enrichment signatures (Fig. 4I-L). In some pyrite crystals, sectoral zonation is overprinted by radial zonations indicating a change in pyrite growth conditions and structure over time. In fluorite, which also has an isometric crystal system, temperature is suggested to strongly influence changes in growth from octahedral at lower temperature, to cubic at higher temperatures (Nadoll et al., 2018). We suggest that sectoral zonation formed under relatively stable fluid conditions whereas concentric zonations indicate transient fluctuations in fluid chemistry (e.g., pH and redox) and temperature.

Radial zonations are uncommon in pyrite from core samples taken at greater depth and within the ultramafic protolith (sections A9 and A10). Instead, the zonations are chaotic, irregular, and do not occur parallel to the current grain margin (Fig. 4M to T). Clear euhedral faces are visible within some of the etched grains (e.g., Fig. 4N and O). Similar euhedral faces were noted deep below the seafloor at the NW Caldera hydrothermal site at Brothers volcano (Kermadec Arc). Here, these textures were interpreted to indicate recrystallization and amalgamation of early pyrite generations, leading to random zonations (Martin et al., 2022). Co-rich pyrite cores (Fig. 4T*) similar to those described here were also found at Brothers volcano, and were attributed to brine dilution below the seafloor. The occurrence of such grains in the subseafloor near Semenov-1 may indicate similar complex processes (Fig. 4T).

Magmatic volatile influx as a source of sulfur and metals

Sulfur in SMS deposits hosted in unsedimented environments is derived from three main isotopically distinct reservoirs: i) seawater sulfate, with a composition of $\delta^{34}S$ = ~21‰ (Rees et al., 1978); ii) oceanic crust and contained magmatic sulfide minerals ($\delta^{34}S$ = ~0‰ in mid-ocean ridge basalts; Sakai et al., 1984); and iii) the addition of an SO_2-rich volatile phase which undergoes disproportionation, although this source is thought to be less important at mid-ocean ridges, and more common in volatile-rich arc environments (Kusakabe et al., 2000). Given that alteration mineralogy (i.e., chlorite and chalcopyrite) indicate temperatures in excess of ~250 °C, we discount bacterial sulfate reduction (BSR) as a potential major source of sulfur at Semenov-1, as BSR only occurs at low temperatures <<100 °C (e.g., Nozaki et al., 2020). Typically, varying proportions of seawater sulfate, which is thermochemically reduced at temperatures >160 °C in the presence of Fe-bearing minerals (Machel et al., 1995), and reduced sulfur leached from the oceanic crust produces sulfide minerals with $\delta^{34}S$ values of between 0-5‰ (e.g., Hannington et al., 2005; Fig. 9). During disproportionation, sulfur isotopes undergo fractionation, the amount of which is largely dependent on temperature (Kusakabe et al., 2000). At temperatures of ~300 °C, sulfide minerals formed during disproportionation will exhibit low $\delta^{34}S$ values that are less than the magmatic host rocks (~0‰), typically around -5‰ (Fig. 9; e.g., de Ronde and Stucker, 2015; Hannington et al., 2005).

Previous studies at Semenov-1 documented $\delta^{34}S$ values in sulfide minerals as low as -3.3‰, that in addition to CO_2 and SO_2 in barite-hosted fluid inclusions, indicate a possible magmatic volatile source of sulfur, and by association, metals (Fig. 6) (Melekestseva et al., 2014). The contribution of a magmatic volatile phase at the active Semenov-2 deposit is also suggested, due to the high overall Au and Cu contents and abundance of telluride minerals (Melekestseva et al., 2017a,b). The subseafloor sulfide minerals near Semenov-1 analyzed in this study range from -20.6 to 13.6‰ with an average of 0±5‰ (*1σ, n=114*) (Fig. 5 and 6). There is no correlation between depth below the seafloor and $\delta^{34}S$ values (Fig. 5). The lack of variation in $\delta^{34}S$ values with depth below the seafloor or lithology at Semenov-1 supports a well-mixed fluid source.

The average $\delta^{34}S$ value of 0.0±5‰ (1σ, *n=114*) indicates that sulfur at Semenov-1 was largely derived from the leaching of oceanic lithosphere (~0‰; Sakai, 1968), producing an average $\delta^{34}S$ value indistinguishable from that of MORB. What is clearly evident at the mineral scale is that the source of sulfur fluctuated during the growth of different sulfide minerals, producing highly heterogenous $\delta^{34}S$ values across individual mineral grains (Fig. 6). Mineral-scale heterogeneity is shown in Figure 6L, where analytical spots that are located within ~100 μm of one another range from -10.9 to 4.6‰, indicating temporal variation in the source of sulfur or processes that affect sulfur isotope fractionation, in and below the Semenov-1 mound. Such sources could include shifts in the relative amount of sulfur sourced from thermochemical sulfate reduction of seawater during fault slip events along the detachment (Martin et al., 2024) or variations in magmatic volatile degassing (e.g., de Ronde et al., 2005) or fluid phase separation (Gemmell et al., 2004). Similarly, such variation at the scale of individual mineral grains has been observed widely in arc-related SMS deposits (e.g., Martin et al., 2023a) and in sedimented environments (Nozaki et al., 2020), and now in pyrite from a detachment hosted setting.

Implications from exploring the third-dimension

Deep-sea drilling near the Semenov-1 deposit provides insights into the relationship between detachment faulting, fluid flow and sulfide mineralization (Fig. 10). We interpret the drilled intersection near the base of the Semenov-1 mound as representing the transition from a thin veneer, approximately 7.5 m in thickness, of brecciated altered basalt into the ultramafic-dominated detachment fault surface (Fig. 10). Our observations confirm earlier interpretations that depict a thin rubble layer overlying and burying the corrugated detachment surface with increasing distance from the toe of the detachment (Escartín et al., 2017). Moreover, the occurrence of multiple discrete mylonite zones within the ultramafic portion of the drill core confirms the presence of anastomosing fault networks delineating a broad zone of ductile deformation, as described by Escartín et al. (2017).

With the available data, the economic viability of subsurface mineralization at Semenov-1 cannot be determined as the drill core did not penetrate beneath the mound where stockwork mineralization is thought

553 to occur (Fig. 10). The absence of sulfide veins shows that the fluid up flow zone and stockwork
554 mineralization are highly localized features and our observations confirm that the stockwork does not
555 extend to the margin of the mound. Similar observations were made at the Brothers volcano NW Caldera
556 site where any potentially economic mineralization (e.g., sphalerite veins) occurred within 1-2 m of the
557 seafloor, below this disseminated pyrite with a low trace metal content dominated, similar to that observed
558 in the drill core here (Martin et al., 2022). Thus, seafloor drilling remains an integral part in understanding
559 the 3D architecture of sub-seafloor fluid flow and allows the spatial relationship between faulting, alteration
560 and mineralization to be assessed.

561 Summary and Conclusion

562 We present a glimpse into the sub-seafloor architecture of a detachment fault system. The drilled interval
563 that penetrated to 20.7 mbsf is highly heterogenous. Above ~7.5 mbsf, alteration is dominated by clay
564 minerals and chlorite and rocks have a brecciated texture. Below 7.5 mbsf, alteration consists of serpentinite
565 minerals, talc, magnesite and dolomite and rocks commonly contain sub-vertical to sub-horizontal mylonite
566 zones with associated fault gouge. The boundary between these texturally and mineralogically distinct
567 zones represents the transition from a mafic rubble zone through the upper surface of the detachment fault.

568 Sulfide sediment contains isocubanite, pyrrhotite and native Au, and in combination with the gravely
569 texture, indicates it originated from chimney collapse followed by local reworking next to the mound. By
570 contrast, disseminated mineralization is dominated by pyrite with lesser amounts of marcasite, chalcopyrite
571 and sphalerite (<1 vol %). Pyrite located directly above the detachment fault surface is enriched in Ni
572 reflecting the contribution of metals from the leaching of underlying ultramafic host rocks. However, most
573 economically significant metals (e.g., Au and Cu) are enriched in the talus layer near the seafloor, reflecting
574 the strong physicochemical gradients that are present in chimney structures favoring and enhancing metal
575 precipitation. Sulfur isotope ratios of sulfide minerals within the fault zone indicate that leaching of
576 magmatic sulfur from host rocks is the main source of sulfur, however notable variations exist at the mineral

scale indicating the source of sulfur or processes that affect fractionation fluctuated over time. Our data indicates that minimal economic potential exists immediately outside the stockwork zone due to the lack of base metal-rich sulfide mineralization and the low trace metal content of pyrite and marcasite.

This initial investigation into drill core from near Semenov-1 highlights the heterogenous nature of alteration mineral assemblages below the seafloor. Further investigation into the relationship between serpentinization, carbonation and sulfide mineralization and its temporal relationship to the formation of the Semenov-1 massive sulfide mound is needed to further understand fluid evolution and mineral deposit formation on and within an oceanic core complex detachment fault.

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Data Statement

All data and standard reference material analyses pertaining to this study are available in the four supplementary data files (Appendix A-D).

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838 Figure Captions

839 Figure 1: Location map of 13°30’N and Semenov-1. A) Location of 13°30’N on the Mid-Atlantic Ridge.
840 B) Bathymetric map of the13°30’N oceanic core complex with location of Semenov (Sem.) hydrothermal
841 fields. C) Location map of Semenov-1 mound showing location of drill hole 52_RD_A (mbsl = meters
842 below sea level) (Data: Escartin and Petersen, 2017).

843 Figure 2: Core samples recovered from deep-sea drilling operations. Core number and sample depth is
844 indicated in the figure. A) Massive pyrite with a porous texture and vein of iron oxide (FeOx). B) Massive
845 pyrite with chalcopyrite from the gravelly sulfide horizon. C) Calcite vein in brecciated amorphous and
846 clay-rich wall rock with disseminated pyrite and chalcopyrite. D) Brecciated sub-angular clay-rich clasts
847 and matrix containing disseminated pyrite. E) Brecciated sub-angular to sub-rounded clasts in a clay-

chlinochlore matrix containing disseminated pyrite. F) Matrix supported breccia with distinct sub-rounded clasts and coarse-grained disseminated pyrite (inset image). G) Mylonitic zone (fabric direction indicated by arrow) containing coarse-grained pyrite in a dolomite matrix (inset image). H) Brecciated fault gouge zone with angular to sub-rounded clasts containing dolomite and disseminated marcasite (Mrc). I) Altered peridotite containing a mesh of fine-scale (1-2 mm) dolomite veins and partially altered pyroxene crystals (Px). J) Dolomite with iron impurities, no pyrite was visible. K) Altered peridotite containing dolomite, magnesite and relict pyroxene crystals. L) Serpentinized peridotite containing dolomite and serpentine. M) Chrysotile and dolomite-rich rocks with sparse disseminated pyrite. N) Serpentinized talc and quartz-rich peridotite with relict pyroxene crystals visible. O) Talc-rich rock with a mottled appearance. The scale in all images is 1cm.

Figure 3: Photomicrographs in plane-polarized reflected light of mineral grain separates. A) Marcasite overgrown by pyrite. B) Framboidal pyrite overgrown by marcasite. C) Aggregates of pyrite with concentric layers. D) An atoll structure with concentric layers of pyrite and marcasite. E) Isocubanite with pyrrhotite. Isocubanite overgrows pyrrhotite. F) Chalcopyrite exsolution lamella in isocubanite. G) Native Au grains associated with the contact between pyrrhotite and isocubanite. H) Native Au grain in pyrrhotite associated with isocubanite (and chalcopyrite). I) Framboidal pyrite overgrown by bladed marcasite. J) Euhedral marcasite. K) Rosettes of euhedral marcasite. L) Pyrite overgrown by euhedral marcasite. M) Two intergrown euhedral pyrite grains. N) Euhedral pyrite. O) Subhedral pyrite. P) Intergrowth of two subhedral pyrite grains. Q) Mesh textured pyrite with chrome spinel. R) Chalcopyrite with both a porous and massive texture with euhedral pyrite. S) Pyrite aggregate with chalcopyrite inclusions. T) Chalcopyrite overgrown by sphalerite and pyrite. Py = pyrite, F-Py = framboidal pyrite, Mrc = marcasite, Cp = chalcopyrite, Crs = chrome spinel, Sph = sphalerite, Au = native gold. Blue outline = sulfide sediment-hosted, orange outline = mafic-hosted, green outline = ultramafic-hosted.

Figure 4: Photomicrographs in plane-polarized reflected light of etched mineral grains. A) Fine-grained pyrite is overgrown by later coarse-grained pyrite containing radial zonations. B) Close-up image (shown

873 in panel A) showing growth direction (arrow) and intergrowth between marcasite and pyrite. *Inset images
874 shows Mn distribution, red is high content (arrow = growth direction). C) Framboidal pyrite that is
875 overgrown by a generation of fine-grained pyrite that is intergrown with marcasite, then overgrown by
876 colloform pyrite and euhedral pyrite that exhibits radial zonations. D) Marcasite overgrown by pyrite
877 containing radial zonations. E) Euhedral marcasite with either radial or "licorice" zonations. F) Close up
878 image of a euhedral marcasite crystal showing oscillatory zonations. G) Complex sectoral and radial
879 zonation in a marcasite grain. Chaotic fine-scale radial zonations occur in addition to sectoral zonation. H)
880 Closeup image (shown in panel G) of zonations. I) Etching delineates four discrete pyrite grains with
881 sectoral zonations. J) Pyrite with sectoral zonations overgrown by a later pyrite generation with radial
882 zonations. K) Pyrite with sectoral zonations. L) Sectorally zoned pyrite overgrown by radially zoned pyrite
883 and later marcasite. M) Chaotic zonation in pyrite indicating recrystallization. N) Euhedral pyrite that has
884 been overgrown by later pyrite generations and undergone recrystallization. O) Closeup image (shown in
885 panel N) of euhedral pyrite. P) Recrystallized pyrite. Q) Recrystallized pyrite with random zonations. R)
886 Anhedral pyrite with a radial pattern and apparent sectoral zonation. Chalcopyrite occurs as inclusions. S)
887 Anhedral pyrite with weak radial zonation and evidence or recrystallization in the grain center. T) Pyrite
888 with "relict cores" (RC) containing wispy and irregular concentric zonations. *Inset is a map of Co
889 distribution, red = high content. Py = pyrite, F-Py = framboidal pyrite, Mrc = marcasite, Cp = chalcopyrite.
890 Blue outline = sulfide sediment-hosted, orange outline = mafic-hosted, green outline = ultramafic-hosted.

891 Figure 5: Down hole sulfur isotope analysis data for drill core samples. A) Data for pyrite separated by core
892 number. B) Data for pyrrhotite, marcasite and chalcopyrite. The average $\delta^{34}S$ value for oceanic crust is
893 shown in the gray box (~0‰; Sakai, 1968). Av. = average, out. = outlier, med. = median. Sulf. Sed. =
894 sulfide sediment layer.

895 Figure 6: Spatial location of SIMS analytical points in sulfide minerals. A) Pyrrhotite with isocubanite. B)
896 Pyrrhotite with isocubanite. C) Pyrite with zones of porous and massive textures. D) Euhedral marcasite
897 with framboidal pyrite (circles). E) Euhedral pyrite with $\delta^{34}S$ values ranging from -6.7 to 0.1‰ in a single

grain. F) Anhedral pyrite. G) Anhedral pyrite. H) Porous pyrite containing only $\delta^{34}S$ values >0‰. I) Transect of points across an aggregate of pyrite – $\delta^{34}S$ values are highly heterogenous. J) Anhedral pyrite. K) Porous chalcopyrite. L) Transect of analytical points showing a large range in inter-grain $\delta^{34}S$ values ranging from -10.9 to 4.6‰ over ~100µm.

Figure 7: Down hole bulk-rock geochemical data analyzed via pXRF (n=300). Blue = sulfide sediment, orange = mafic, green = ultramafic-dominated. Gray represents core recovery. A) Silica is enriched in mafic lithologies and in talc-rich cores A10 and A11. B) Calcium is enriched in ultramafic relative to mafic rocks and correlates with dolomite and magnesite abundance (Table 2). C) Aluminum is enriched only in mafic lithologies. D) Nickel content peaks at the mafic-ultramafic transition and is relatively enriched in ultramafic lithologies. E) Chromium shows the same trend as Ni (full data; Appendix A).

Figure 8: Laser ablation ICP-MS data for sulfide minerals in drill core samples. A) Comparison of the measured trace metal content between pyrite, pyrrhotite and marcasite. Marcasite is strongly enriched in Tl and Mn relative to pyrite and pyrrhotite. Pyrite is enriched in Ni and Ag, Cd and Cr, whereas pyrrhotite is enriched in Mo, Sb and Co. B) Downhole geochemical plots for pyrite divided by core number for Mn, Zn, Cu, Co, Tl, V, Au and Ag. C) Downhole geochemical plots for pyrite divided by core number for Ni, As, Se, Pb, Sb and Mo. Column to the right indicates, sulfide sediment, mafic or ultra-mafic core classification.

Figure 9: Sulfur isotope summary for SMS deposits categorized by broad tectonic setting (other), for ultramafic-hosted sites (ultramafic), the Semenov vent field cluster and data from this study. Gray fields indicate primary magmatic sulfur for MORB and arc settings (Sakai, 1968; Sakai et al., 1984). Data: Choi et al., 2023; de Ronde and Stucker, 2015; Ding et al., 2021; Dubinina et al., 2020; Hannington et al., 2005; Martin et al., 2024; Melekestseva et al., 2017, 2014; Meng et al., 2020.

Figure 10: Schematic representation of the subseafloor architecture of area adjacent to Semenov-1 based on observation from drill core 52RD_A. A thin veneer of calcareous sediment overlies a gravel-sand sulfide horizon that is enriched in chalcopyrite. Beneath this horizon rocks have a brecciated texture with visible

922 clasts that are clay and clinochlore-rich. Pyrite and marcasite occur as disseminations in the rock matrix.
923 Near seafloor pyrite is relatively enriched in Mn, Zn, Cu, Co, Tl and V, reflecting higher degrees of shallow
924 seawater mixing. At 7.5 mbsf a mylonite zone is intersected and rocks change to an ultramafic composition,
925 containing serpentinite minerals, magnesite and dolomite with relict pyroxenes. This represents the
926 transition from a thin basaltic breccia/talus veneer through the detachment fault surface. At deeper levels
927 still, alteration becomes more talc-rich. As with upper levels, pyrite occurs as disseminated grains in the
928 rock matrix. At the bottom the hole pyrite is notably enriched in Se.

929 Table 1: Summary of drill core from hole 52_RD_A.

930 Table 2: Summary of alteration mineralogy of recovered core samples analyzed by XRD.