

Spontaneous combustion of metal sulfide minerals and implications for seafloor massive sulfide mining

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Abstract

Metal sulfide minerals are abundant phases in many environments on earth, including seafloor massive sulfide (SMS) deposits, which occur at hydrothermal vents throughout the global ocean. These deep-sea settings are currently undergoing exploration for potential future mining. Here, we describe rocks from Escanaba Trough on the southern Gorda Ridge that underwent spontaneous combustion during laboratory processing. We compared the mineralogy, composition, and thermogravimetric behavior of the combusting samples to rocks from the same location that did not combust. We then used thermodynamic analyses to evaluate the exothermic nature of different metal sulfide oxidation reactions. The combusting rocks are primarily composed of nanocrystalline marcasite pseudomorphing blades of primary pyrrhotite. These altered, nanocrystalline rocks are less stable than their primary predecessors. Typically, recrystallization decreases reactivity as minerals trend towards steady state; however, both of the combusting samples we characterized are secondary, and demonstrate the instability of this metastable intermediate phase. Further, thermodynamic calculations indicate that metal sulfide oxidation is more exothermic when oxygen serves as the oxidant, as occurs in seawater or air. The distinct mineralogy, texture, and setting of SMS deposits in the modern oceans thus suggests a greater potential for self-heating in comparison to their ancient analogues.

Introduction

Metal sulfide minerals precipitate at hydrothermal vents throughout the global ocean, sometimes accumulating into seafloor massive sulfide (SMS) deposits¹. SMS deposits are modern analogs of terrestrial volcanogenic massive sulfide deposits (VMS), which have supplied significant amounts of global copper, zinc, lead, gold and silver². Since the discovery of SMS deposits, there has been interest in understanding whether they may constitute a viable metal resource. However, the distribution, size, and environmental setting of SMS deposits is still not well constrained³. As of 2026, contracts have been granted for exploration of SMS through the International Seabed Authority (ISA) on the Northern Mid Atlantic Ridge and Southwest Indian Ridge⁴ and a mining license has been granted for Solwara 1 in Papua New Guinea⁵, but mining has not yet taken place.

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The mining of sulfide-rich deposits, whether VMS or other deposit types, can encourage metal sulfide mineral oxidation which results in two major hazards: acid mine drainage, and self-heating, which may lead to combustion. Acid mine draining has been extensively studied in terrestrial settings^{6,7}. Exothermic oxidation associated with mining of VMS deposits leading to spontaneous combustion of sulfide-rich material has been documented, however the mechanisms by which it occurs are not well constrained⁸. Of the commonly occurring metal sulfide minerals, pyrrhotite is most often cited as an unstable and hazardous mineral in matrices as varied as coal, concrete, and massive sulfide, due to its propensity for rapid oxidation⁹. This instability has been attributed to the variable stoichiometry e.g.¹⁰, a high relative surface area, or surface roughness and extended fractures¹¹. Marcasite is less frequently cited as a combustion hazard, and it is also a less commonly occurring mineral in sulfide-rich ore deposits and industrial materials^{12,13}.

The production of heat through exothermic reactions has not been investigated in SMS deposits but has the potential to cause rapid onset fires on ships. There are several recent studies of oxidation reactions in SMS material^{14–18}, although SMS deposits are much less studied than VMS deposits. Specifically, textural and mineralogical differences between SMS and VMS rocks, and differences in oxidative environment such as the availability of oxidants and increased corrosivity of seawater compared to freshwater are still undergoing investigation and description, and potential mining procedures for SMS deposits are still being developed.

In 2022, during expedition TN-403 onboard the R/V Thomas G. Thompson we collected metal sulfide rocks from hydrothermal mounds and chimneys throughout the hydrothermally active Escanaba Trough, an oceanic spreading center, that forms the southernmost section of the Gorda Ridge in the northeast Pacific Ocean. The Escanaba Trough is buried in terrestrially-derived sediments¹⁹. Heavy sedimentation promotes the formation of hydrothermally derived petroleum, which can occur with the metal sulfide minerals, and, like sulfide minerals, has the capacity to self-heat and combust^{20,21}. Here we investigate the mineralogy and composition of the metal sulfide dominated samples collected on this expedition to Escanaba Trough, and evaluate risk factors for exothermic oxidation of metal sulfide minerals, especially as they occur in SMS and VMS deposits.

Results

Fifty-seven hydrothermal rock samples were collected from four regions of Escanaba Trough using a remotely-operated vehicle. Forty-one of these samples contained metal sulfides as a major mineral. Two of these metal sulfide-dominant samples combusted upon crushing in the laboratory under normal atmospheric conditions after freeze-drying, resulting in temperatures greater than 100 °C and complete oxidation of the original sample (Movie S1, S2).

Detailed mineralogical and geochemical analyses were focused on the two combusting rocks and other metal sulfide rocks in which combustion was not observed. The metal sulfide-rich rocks were dominated by pyrrhotite, marcasite, pyrite, or sphalerite. Moderate and minor minerals included barite, chalcopyrite/isocubanite, galena, wurtzite, goethite, lepidocrocite and akageneite (Table S1, ref²²). Many of these rocks exhibited millimeter-scale bladed textures, which were identified as either primarily pyrrhotite (14 samples) or marcasite (12 samples; Table S1, ref²²). The two combusting rocks were originally dominated by marcasite and were composed of maghemite after combustion²², Supporting Information.

Rocks consisting of metal sulfide minerals were sampled from a broad north-south distribution of mineralized locations within Escanaba Trough (Fig. 1). Rocks were collected from two hills exhibiting active hydrothermal fluid flow, a “high temperature” location with a maximum measured fluid temperature of 210 °C (Central Hill) and a “low temperature” location with a maximum measured fluid temperature of 22 °C (Southern Escanaba), as well as five locations where there was no evidence of current hydrothermal activity. (Edifice Rex, North Hill, East Hill, 3170 Hill, and Middle Escanaba region; hill names are given in ref. 24). The 12 marcasite-dominated samples were collected from geographically diverse regions of the trough, including the northernmost and southernmost locations investigated on this expedition. All sites containing marcasite were either inactive or

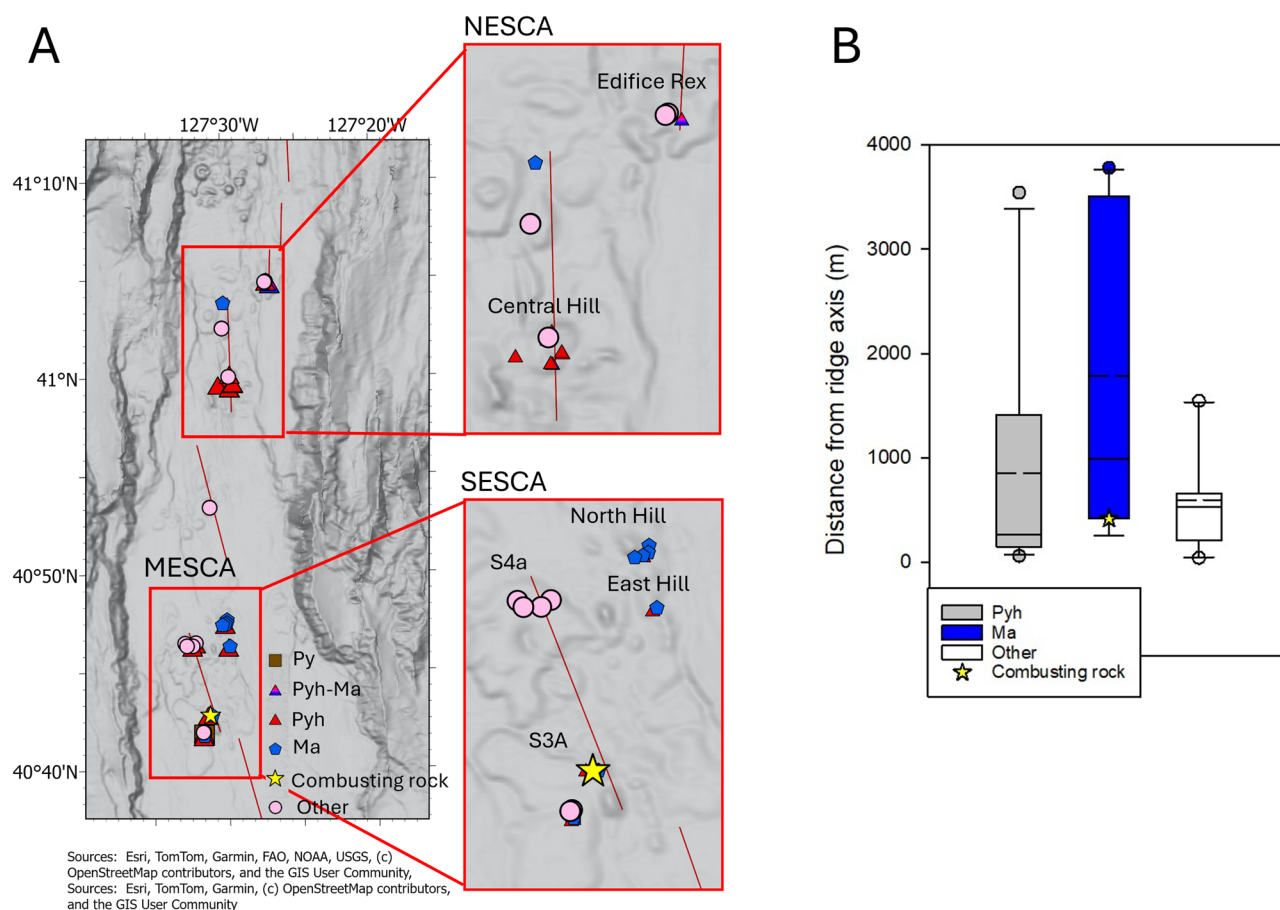


Fig. 1 A. Map of the Escanaba Trough, with popouts for the NESCA (Northern Escanaba) and SESCA (Southern Escanaba) regions. B. The box plot shows the difference from the ridge axis for pyrrhotite, marcasite, or “other” sulfide mineral dominated rocks; generally, marcasite dominated rocks occur farther from the ridge axes than pyrrhotite dominated rocks. Ridge axes are from¹. The solid horizontal line indicates the median value, and the dashed horizontal line is the average. Abbreviations: Py, pyrite; Ma, marcasite, Pyh, pyrrhotite. The “other” category includes all rocks where the dominant metal sulfide mineral was not an iron sulfide.

low-temperature locations (Fig. 1), and included chimneys and mounds with variable levels of iron oxyhydroxides coating the sulfide minerals. In this study, marcasite-rich samples generally occurred farther from the ridge axis compared to other metal sulfide dominated samples (Fig. 1). The two combusting rocks were both collected from the Southern Escanaba Region.

Bladed pyrrhotite and marcasite were imaged using a reflected light petrographic microscope, and micrographs were collected using scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) (Fig. 2). In reflected light, the marcasite shows textures consistent with increasing mass loss and replacement toward the interior of the blades (Fig. 2A). Under SEM and STEM, the color change was linked to fracturing and void spaces which increased towards the center of each blade (Fig. 2B and C). Raman analyses indicated that Fe-S and S-S stretching energies decreased moving toward the center of each blade (Fig. S1).

Results of bulk chemical analyses indicate that the rock samples dominated by pyrrhotite contained significantly higher Ba, Ga, Ge, Zn, Pb, Cd, Y and rare earth elements, than the rock samples in which the primary iron sulfide mineral is marcasite (Fig. 3, Fig. S2, ref²²). Results of X-ray diffraction (XRD) analyses indicate that these compositional differences are due to lower abundances of accessory minerals in the marcasite-rich rocks, predominantly sphalerite, isocubanite, chalcopyrite and galena (Table S1, ref²²). Electron microprobe analyses, used to determine the composition of either monomineralic pyrrhotite or marcasite (in comparison to the bulk

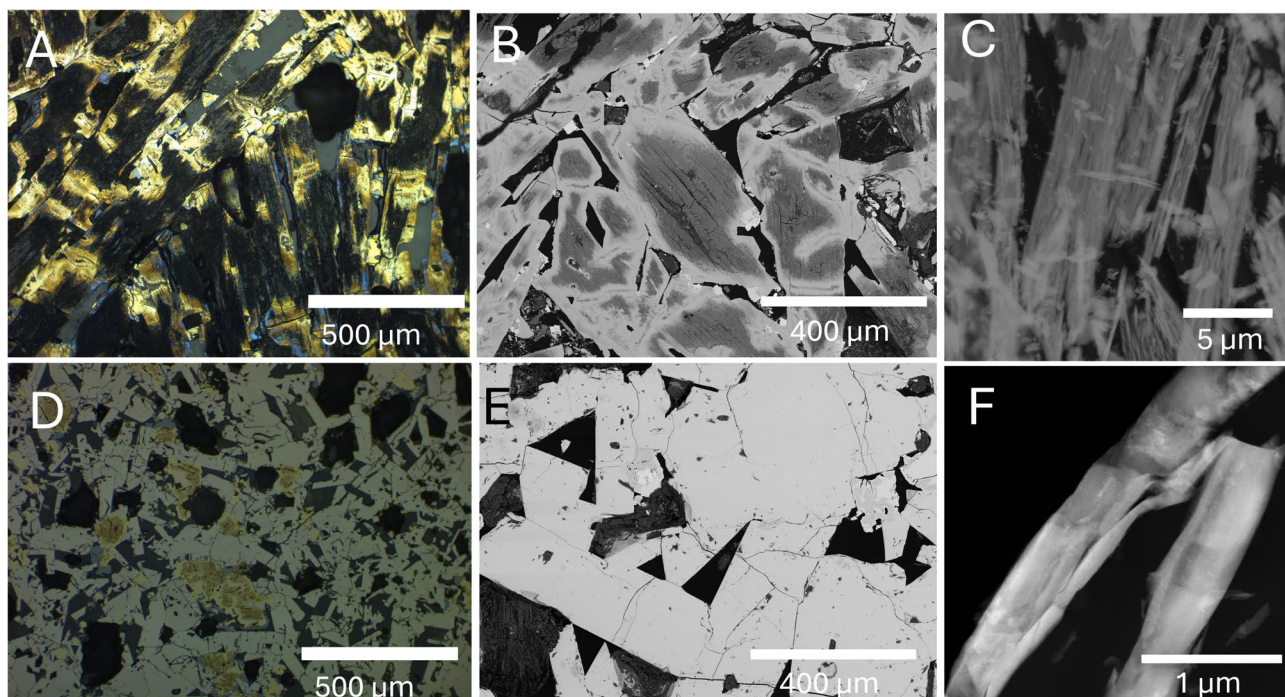


Fig. 2 Petrographic (A, D) SEM (B, E) and STEM (C, F) images of bladed marcasite (A, B,C) and bladed pyrrhotite (D, E,F). The petrographic images are reflected light under plane polarization. The brassy minerals in D are Iso being replaced by Ccp.

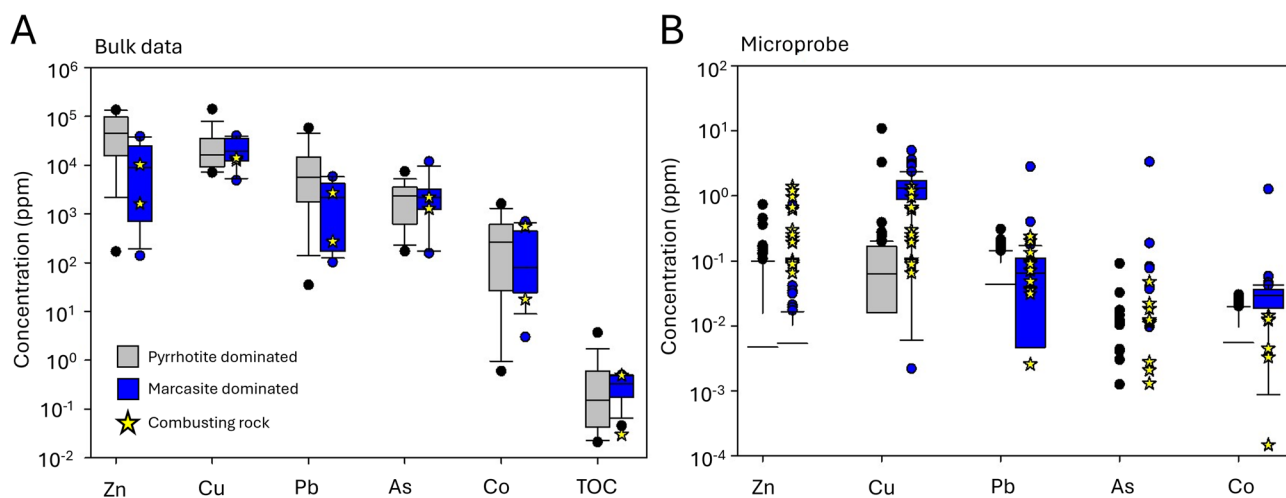


Fig. 3 Bulk rock compositional data (left) and electron microprobe compositional data (right) collected on either rock samples dominated by pyrrhotite (gray) or marcasite (blue, bulk plot) or pyrrhotite (gray) or marcasite (blue) blades (microprobe plot). The bulk rock composition includes minor and trace minerals occurring with the dominant metal sulfide mineral in each rock, whereas the microprobe data are specific to the pyrrhotite or marcasite minerals. The data points for the two combusting rocks are plotted on top of the marcasite boxes with yellow stars. The combusting rocks are not compositionally different from the other rocks dominated by marcasite, either for the five elements shown or the other elements measured.

analyses which contain major, minor and trace minerals) indicate that marcasite blades contain higher Co, and comparable concentrations of Zn, Cu, As and Pb relative to pyrrhotite blades (Fig. 2, ref²⁵). The two combusting rocks were within a standard deviation of the concentration of other marcasite containing rocks for all measured parameters, including total organic carbon, which would encompass any hydrocarbons present (Fig. 3).

Thermogravimetric analysis (TGA) was used to evaluate self-heating of the samples. TGA was conducted on 17 rock subsamples and three sediment subsamples. Self-heating was observed in the two samples (J2-1423-R03 and J2-1423-R04(parts A and B)). These results are consistent with the two rocks observed to combust (J2-1423-R03 and J2-1423-R04 B) as well as an additional subsample of one of the same rocks (J2-1423-R04 part A). The onset temperature of self-heating was between 185 and 224 °C (Table S3, ref²⁶). Mass loss corresponding with self-heating was as high as 1.3% of the total sample weight (Table S4). Self-heating rocks did not correspond to total organic content (TOC), nor was an “oily” aspect, interpreted as petroleum content, observed upon sampling (Table S3, Fig. S3). For two of the three rocks with TGA confirmed heating, the mass loss after self-heating exceeded TOC. For two of the three rock samples that exhibited self-heating, apparent activation energies obtained were 79 and 107 kJ/mol (Fig. S3, ref²⁶). To further check if self-heating was linked to the presence of hydrocarbons, three sediment samples with elevated hydrocarbon concentrations (ref²⁷) were analyzed with TGA. None of these samples exhibited evidence of self-heating (Table S3, ref²⁶).

Discussion

Pyrrhotite to marcasite transformation – stealth marcasite?

The alteration of pyrrhotite to marcasite and/or pyrite produces a reduction in volume and a loss of iron atoms^{28,29}. Yao et al. (2021) concluded that pyrrhotite-marcasite-pyrite conversions occur via solid-state transformations under dry conditions, and a dissolution-reprecipitation pathway under hydrothermal conditions³⁰. Qian et al. (2011) likewise concluded that pyrrhotite conversion to marcasite or pyrite proceeds via dissolution-reprecipitation, and that pyrite formation is dominated by crystal growth and marcasite formation is dominated by nucleation, with oriented marcasite crystals consistent with formation under low pH of conditions³¹. The Escanaba Trough dataset, in which bulk-crystalline pyrrhotite is replaced by nanocrystalline marcasite is consistent with dissolution-reprecipitation reactions (e.g.³²). The loss of mass observed towards the center of blades (Fig. 2B) is consistent with the mass loss associated with the pyrrhotite-marcasite conversion. There is significant uncertainty as to the timescales over which such transformations take place in situ and the in situ stability of these minerals over longer timescales. Our work raises the question of whether, in cases where mineralogy is determined via visual inspection, reports of highly unstable pyrrhotite may actually be due to secondary marcasite that has retained the original pyrrhotite morphology.

Geology and geochemistry; Implications for SMS preservation

The primary iron sulfide mineral at Escanaba Trough is hexagonal pyrrhotite with an approximate formula $\text{Fe}_{11}\text{S}_{12}$ and corresponds to pyrrhotite subtype 6 C³³. In 40% of our samples, pyrrhotite was replaced by nanocrystalline marcasite. In powder XRD results, application of the Scherrer Eq. (34), indicated crystallite domain sizes in the range of 5–16 nm (Fig. S4). Except for three samples (Table S1) in which remnant pyrrhotite was found together with marcasite, the replacement was complete.

Marcasite-containing rocks are generally further from the ridge axis than pyrrhotite dominated rocks (Fig. 1). This extra distance suggests that the marcasite containing rocks may be older than the pyrrhotite-dominated rocks, consistent with alteration under ambient conditions. Conversely, the greater distance from active venting may allow for higher oxidation rates than for rocks that are closer to low-oxygen hydrothermal fluids. Less abundant sphalerite and galena in rocks containing marcasite is consistent with prior observations of preferential loss of sphalerite relative to pyrite during oxidation^{16,17} and loss of Zn and Pb relative to Fe in sulfide mineral containing sediment cores in oxygenated seawater^{35,36}. Despite experimental results indicating that chalcopyrite is also lost preferentially to pyrite¹⁷, Cu concentrations do not exhibit significant differences between primary and secondary rocks in our collection, perhaps due to low overall Cu concentrations (Fig. 3.81 ppm in bulk pyrrhotite

vs. 2.18 ppm in bulk marcasite, $t^{20}=2.09$, $p=0.492$; ref 22). Although the pyrrhotite and marcasite-containing rocks differ compositionally, the combusting rocks do not exhibit significant compositional differences from other marcasite-containing rocks (Fig. 3), and analysis of this dataset does not indicate a direct connection between trace metal composition and the propensity for combustion. The only element for which the concentration within the combusting rocks fell outside the range of the non-combusting marcasite is Rb (2.64 ppm vs. 4.9 ppm in combusting marcasite, $t^5=2.57$, $p=0.003$; ref 22).

Oxygen concentrations and temperature are two of the factors that control the rate of oxidation of sulfide minerals in seawater. Oxygen concentrations in ambient seawater occurring around vent fields vary by approximately a factor of four due to global thermohaline circulation patterns, from near saturation, $\sim 330 \mu\text{M}$, in Arctic waters, to $\sim 70 \mu\text{M}$ at the Juan de Fuca Ridge. At $90 \mu\text{M}$, Escanaba Trough is close to the minimum oxygen found at hydrothermal vents globally. Locally, oxygen concentrations are lower in the immediate vicinity of active hydrothermal fluid flow^{37,38}. Ambient temperature in seawater surrounding hydrothermal vents ranges globally from approximately -0.7°C to as high as 15°C in shallow water arcs³⁹, and was approximately 2°C at Escanaba Trough. The low temperatures and low oxygen concentrations at Escanaba Trough result in slower in situ oxidation rates and may help preserve the seafloor persistence of unstable phases such as the nanocrystalline marcasite observed here, and such unstable minerals may be less prevalent in systems with higher ambient oxygen and temperatures.

The samples in which self-heating was observed via TGA correspond directly to the samples which spontaneously combusted on the laboratory bench when crushed. In these samples, the sulfur in marcasite combusts and volatilizes, resulting in the precipitation of maghemite and mass loss of sulfur (refer to Supporting Information). Although hydrocarbons including tar and petroleum can self-heat and have been reported at Escanaba Trough^{20,21}, total organic carbon (TOC) had an average concentration of 0.69 wt % (range 0.02–3.75 wt %) in the pyrrhotite dominated rocks and 0.32 wt % (range 0.05–0.50 wt %) in the marcasite dominated rocks. The combusting rocks had TOC concentrations that were within the range of other samples collected from Escanaba (Fig. 3) and mass loss on self-heating that exceeded the sample TOC by up to an order of magnitude (Table S3 and S4). Further evidence that the heating events were not due to organic carbon is based on the analysis of sediments with elevated hydrocarbon concentrations. These samples had %TOC concentrations at least three times greater than the combusting rocks, with TOC composed of up to 25% lipids, yet did not exhibit self-heating peaks (Table S3, ref^{26,27}).

Risk of spontaneous combustion

Metal sulfide minerals are thermodynamically unstable in oxygenated environments, but the rates and processes by which they oxidize may vary considerably. To consider exothermic oxidation and its potential to result in spontaneous combustion from a thermodynamic perspective we conducted simple calculations of enthalpy for a range of possible oxidation reactions reported in Plumlee, 1999 (6, Fig. 4, Table S2). These calculations indicate highly variable exothermic values, ranging between -20 and -1554 kJ/mol for pyrite, marcasite, and pyrrhotite in aqueous conditions, with marcasite exhibiting both the highest and lowest possible values based on products and reactants considered. Interestingly, reactions with Fe^{3+} as the oxidant, which occur at lower pH, are more likely to result in less negative (less exothermic) enthalpy values than reactions with O_2 as the oxidant. This suggests that the hazards of acid mine drainage and spontaneous combustion may be inversely related; a low pH will ensure Fe^{3+} as the oxidant, which may be one way to reduce energy release upon oxidation. For anhydrous conditions, reactions involving marcasite are also more exothermic than pyrrhotite (Table S2).

The activation energy for the onset of oxidation of pyrite, marcasite, and pyrrhotite ranges from 15 to 92 kJ/mol, with most values between 29 and 88 kJ/mol, which are typical of mineral solution interfaces (40; values compiled in ref. 16). The addition of heat and mechanochemical forcing (e.g., crushing, breaking, grinding) can supply energy to overcome the activation energy and initiate oxidation⁴¹. Mechanochemistry may be an especially important factor in spontaneous combustion because it can result in the onset of oxidation to multiple

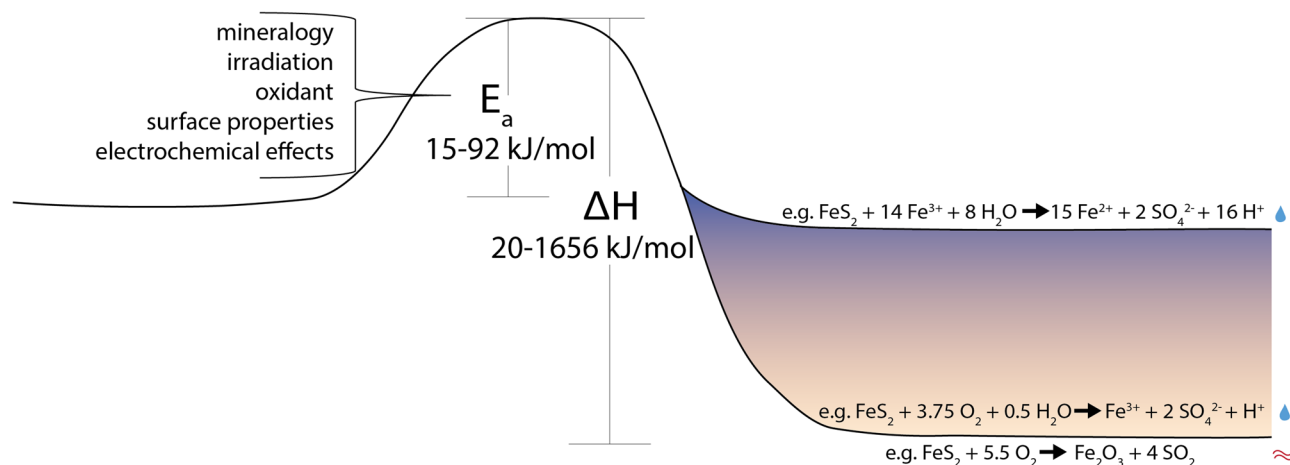


Fig. 4 Diagram indicating previously established ranges of activation energies (E_a) for metal sulfide minerals and associated parameters, and calculated enthalpy ranges (ΔH) after equations in Plumlee, 1999, given in Table S2. An example equation for marcasite oxidized by Fe^{3+} compared to marcasite oxidized by O_2 . Calculations consistently indicate larger enthalpy values when oxygen is the primary oxidant (Table S2), indicating that the hazards posed by exothermic oxidation and acid mine drainage may be inversely related. Thermodynamic data are from Stumm and Morgan (2013), Robie and Hemingway (1995), or Majzlan et al., (2003 a, b) and are at 25 °C and 1 bar.

molecules simultaneously, resulting in the accumulation of heat, which can continue the reaction, consistent with our observations of combustion triggered by breaking (Movie S1, S2).

Light and galvanic effects may lower the activation energy¹⁶. Increased oxidation rate due to the input of light is unlikely in the deep sea, but is relevant once rocks are brought shipboard. The pH provides a fundamental control on the reaction mechanism, through the availability of the oxidant. The removal of oxygen and/or water can prevent the reaction; if water cannot be removed, the addition of excess water to absorb heat generated from the reaction can prevent burning.

Relevance to SMS mining

The ignition of metal sulfide minerals via self-heating in existing VMS mines has been reported as “rare” and “easily avoided by proper blasting techniques”⁴². All fires reported in several compilations of anecdotes have onsets more than 40 years ago, although some were extinguished more recently (e.g. the 1968–2005 fire at Brunswick No. 6 and No. 12 VMS deposits in the Bathurst Mining Camp; ref. 43). Several recent compilations of environmental hazards associated with mining in the United States do not include fires caused by self-heating, indicating that self-heating is not a commonly occurring hazard^{44,45}. However, sulfide ore catching fire has been reported to occur “often” as recently as the 2000s in the Dongguashan Cu skarn mine in China⁴⁶, and may pose a particular hazard when it is not anticipated and engineering controls such as ventilation and fire suppression systems are lacking.

Given that SMS mining has yet to occur, there are currently no established engineering controls for mining sulfide deposits from the modern seafloor, nor has a risk assessment considering the risk of combustion for SMS been conducted. Little work has been done to compare the geochemical and physical properties of SMS and VMS deposits, which are the closest terrestrial analogue of SMS deposits and have been successfully mined and processed for decades. We suggest that for purposes of comparison there are three broad physicochemical categories of massive sulfide minerals: (1) surface chimney samples, which represent most SMS samples collected to date; (2) subsurface SMS material, which represents most of the material to be collected in a theoretical mine but has been minimally sampled from modern systems, and (3) massive sulfide material from VMS deposits (Fig. 5). SMS deposits are categorically younger than VMS deposits, and range in age from rocks actively precipitating

At-sea activities and physicochemical differences between (potential) SMS and (current) VMS mining

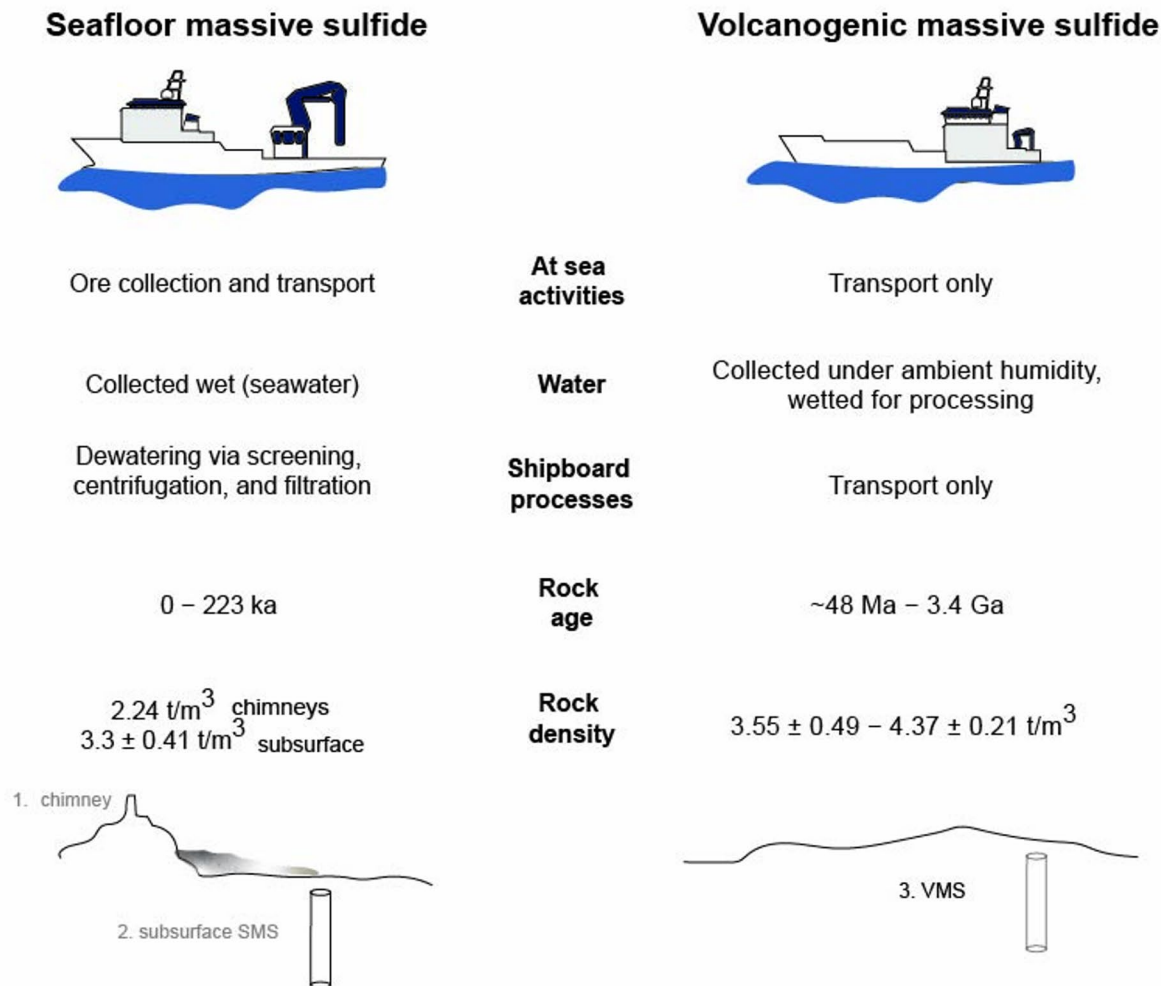


Fig. 5 Comparison between the at-sea activities occurring for potential SMS mining, compared to terrestrial VMS mining, an existing activity, as well as broad physicochemical parameters. Should SMS mining occur, activities at sea will broaden from mineral transport to also include mineral collection. Hydrothermal chimneys on the modern seafloor are less dense than massive sulfide material found below the seafloor surface, and both are less dense than typical VMS ore mined terrestrially. This may be related to the mineral ages. SMS density values are from Lipton et al., 2012; VMS values are from Thomas, 2003; SMS ages are from Jamieson et al., 2023, and VMS ages are from Nozaki et al., 2024 and Galley et al., 2007.

from black smokers (zero-age) through at least 223 ka, the oldest sample dated so far using radioisotopes (47, 48; compiled in ref. 49). Older SMS deposits likely exist although the probability of finding deposits older than a few Ma is unlikely due to burial under sediments or lava. In contrast, VMS deposits range in age from ~48 Ma to 3.4 Ga^{50,51}. This broad age difference is likely to result in a number of physicochemical differences, such as mineralogy, texture, density, and porosity, that are poorly constrained. To date, rocks from chimneys have been found to be less dense than subsurface sulfide minerals and samples from VMS deposits. For instance, data from the Solwara 1 deposit indicate chimney samples have an average density of 2.24 t/m³, compared to subsurface SMS material, or “sulfide dominant rock” with an average density of 3.3 ± 0.41 t/m³³⁵. These SMS values from Solwara 1 are lower than drill core from a number of deposits from Bathurst VMS camp, New Brunswick, which have mean values ranging from 3.55 to 4.37 t/m³³². These data follow logically from the fact that compared

to VMS deposits, SMS deposits are much younger, and, as a result, have undergone little to no compaction or metamorphism.

In addition to mineralogical and textural differences, there are differences in proposed mineral collection and shipboard activities that could be evaluated further, as VMS activities are generally limited to shipping and SMS related activities would also include collection (Fig. 5). The breaking of rocks underwater during a potential SMS mining operation presents the opportunity to dissipate heat and could reduce the risk of mechanochemically induced self-heating. In contrast, further shipboard crushing or excessive dewatering could create novel opportunities for self-heating, especially if moisture levels fall between 3 and 8%⁵³.

Although fires generated by self-heating may currently be rare, the possibility that a given sulfide mineral-containing rock may have the potential to self-heat is not well constrained. In a study focused on mines located in China, Liu et al., (2015) suggest that 1 in 10 mines producing iron, copper, lead, zinc or gold may be capable of self-heating, although the source of these data are not clear; Wu and Li, (2005) tested 19 ore samples from two mines, and found 12 out of 19 had the potential to combust, and Zhao et al. (2024) note that spontaneous combustion from sulfide minerals is a risk at one of three of metal mines in China^{46,54,55}. In samples from the Red Dog Mine, Alaska, Paley and Pickett (2020) found that less than 10% of rocks samples could react based on geochemical constraints, and reported one heating-induced fire in 25 years of operation⁵⁶. In a 2001 study, Rosenblum et al. noted that “most” sulfide concentrates had some potential to self-heat, although “in most cases the level is low enough to pose little or no risk”⁵⁷.

Previous studies of mineral self-heating have focused on empirical parameters, including percent hydration and the presence or absence of accessory minerals and H₂S gas^{57–59}. Our study results indicate that secondary minerals, with nanocrystalline mineralogy and porous morphology formed during replacement reactions in situ may also result in a higher risk of spontaneous combustion, consistent with the idea that a smaller grain size and resultant higher surface area can lead to greater reactivity⁵⁹. We suggest that minerals occurring in SMS deposits may exhibit a greater propensity for heating and ignition than long-mined VMS deposits, because they are younger by orders of magnitude, leading to important physicochemical differences including broadly smaller particle size, reduced crystallinity, and lower density^{5,16,52}. The smaller grain size, and space within mineral grains allows for increased contact between the mineral surface and the oxidizing environment, whether the oxidizing environment is an immersive liquid (seawater or freshwater) or the atmosphere, with variable humidity (Fig. 5). Further, given the circumneutral pH of seawater, there is a greater likelihood that O₂ will be the oxidant (as opposed to Fe³⁺), resulting in more exothermic oxidation reactions (Fig. 4, Table S2). Limited seawater remaining in pore spaces, as well as a more pronounced contact with the atmosphere and any ambient humidity would also result in oxygen as the oxidant. The results obtained in our study indicate that recrystallization does not always lead to increased mineral stability nor increased particle size, complicating straightforward conclusions based on broad physicochemical parameters. Rather, we observe smaller crystal size, more pore space, and accompanying decreased stability in the secondary minerals collected. Our study results indicate that, if mining of SMS deposits occurs, these minerals and their environmental and potential extraction conditions are significantly different enough from mining of terrestrial VMS deposits that a dedicated risk assessment and unique engineering controls to reduce the potential for spontaneous combustion as a result of self-heating could help inform hazard management⁶⁰.

Materials and methods

Samples were collected on expedition TN-403 using the ROV Jason and photographed upon shipboard recovery. Subsamples for mineralogical analysis were frozen at −20 °C, while additional subsamples were described shipboard. Upon return to shore samples were defrosted and described under flowing nitrogen in a glove box prior to freeze drying in a FreeZone 4.5 freeze dryer by Labconco (Kansas City, MO, USA). After drying samples were crushed in a shatterbox (SPEX industries, Industries, Metuchen, NJ, USA) using an alumina ceramic vessel (Cole-Palmer, Vernon Hills, IL, USA). The laboratory temperature was 23.3 °C and humidity was approximately

70%. When dried subsamples were too large to fit into the ceramic vessel in their entirety, the subsamples were broken by hand into chunks of a size appropriate for the vessel. The two combusting rocks began to noticeably generate heat and smoke as new faces were exposed, prior to the vessel being sealed and the shutterbox started. As can be seen in movie S1 and S2, the pieces of rock were several cm in each dimension at this stage.

Bulk powders prepared as described above were analyzed in a X'Pert3 powder diffractometer by Malvern Panalytical (Malvern, Worcestershire, England). Samples were scanned from 5 to 70° 2 theta at a 0, −1, and +1° wobble, with final scans a sum between the three. Phase identification and semi-quantitative analysis was performed by HighScore Plus (Malvern Panalytical). Major minerals are defined to represent approximately >25% of the sample, intermediate minerals 5–25%, and minor minerals <5% via semi-quantitative analysis. Bulk powders were also sent to Actlabs (Ancaster, Ontario, Canada) for analysis (details in ref²²). Total organic and inorganic carbon was analyzed using colorimetric titration after⁶¹ and are reported as percent dry weight.

TGA was conducted at the U.S. Geological Survey in Santa Cruz, California using a Pyris TGA9 (PerkinElmer, Shelton, CT, USA). Samples were size fractioned into the 75–150 µm range then run in triplicate under Ultra High Purity Nitrogen or air from 30 to 600 °C at a rate of 10 °C/minute and then normalized to starting weight. The presented data (Fig. S3) are an average of the three trials plotted against the program temperature. Samples that exhibited self-heating peaks were rerun at 5 °C/minute and 15 °C/minute to obtain Arrhenius plots and calculate apparent activation energies. Self-heating peaks were confirmed if they exceeded a standard deviation of the triplicate analyses. Full TGA data are available at²⁶.

SEM and Microprobe analyses were conducted at the USGS in Moffett Field using a Tescan (Brno, Czech Republic) VP-SEM Vega3 in high vacuum mode (SEM) and JEOL (Akishima, Tokyo, Japan) JXA 8530 F+ Electron Probe Microanalyzer (microprobe). For SEM, imaging and element analyses were performed at 20 kV and 15-mm working distance and images were acquired using secondary electron and backscatter detectors. Samples were sputter coated with carbon prior to analyses.

STEM imaging was conducted at the Molecular Foundry at Lawrence Berkeley National Laboratory using a FEI TitanX TEM (Thermo Fisher Scientific, Waltham, MA, USA). Images were acquired using a Gatan Ultra-Scan 1000 camera and diffraction patterns using a Gatan, Inc. (Pleasanton, CA, USA) Orius 830 CCD camera at 300 kV. Samples for STEM were prepared by selecting small aliquots of mineral blades using an optical loupe and embedding the blades according to manufacturer's instructions in Embed-812 Resin in BEEM tubes (Electron Microscopy Sciences, Morgantown, PA, USA). After curing, blocks were trimmed using DiATOME (Nidau, Switzerland) trim 45 and sectioned into using RMC Products PowerTome XL microtome (Boeckeler Instruments, Tucson, AZ, USA) with a DiATOME ultra Diamond Knife 1.5 mm 45° into 150 nm sections.

Raman analyses performed using a Thermo Scientific DXR3xi Raman Imaging Microscope, a 785 nm laser and a high-resolution grating, with 1800 lines per mm and a 50-µm pinhole were used. OMNIC software (version 9, www.thermoscientific.com/pm_molspec) was used to run the instrument.

All data discussed in this study are available in USGS data releases and are cited in the manuscript refs^{22,25,26}.

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Author contributions A.G. planned the study, conducted the work and wrote the manuscript with contributions from all authors J.F. and K.B.A. conducted rock sampling A.P. contributed microtome expertise J.J., R.Z., and I.Y. planned the study and conducted shipboard work K.B. performed STEM analyses I.S. and K.P. conducted thermogravimetric analysis H.I. contributed organic geochemistry expertise.

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Declarations

Competing interests The authors declare no competing interests.

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