

Supporting Information for

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

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Other supporting materials for this manuscript include the following:

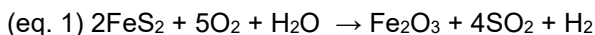
Movies S1 to S2

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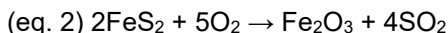
Supporting Information Text

Combustion mass balance

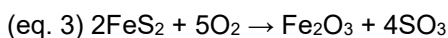
The oxidation of marcasite to maghemite can take place via the following reaction, which results in a solid phase weight loss of approximately 33%.



An anhydrous version of the reaction may be represented by:



Or



Mineral composition

For the samples grouped into the pyrite dominant, pyrrhotite dominant, pyrrhotite-marcasite, and marcasite dominant categories, the sum of iron plus sulfur ranged between 40.1 and 96.1 wt % (mean 78.4 wt %, median 84 wt %). Aside from Cu and Zn, all other elements had average and median values of one weight percent or less. Cu ranged from 0.5 to 14.1 wt % (mean 2.4, median 1.8 wt %); Zn ranged from 0.01 to 13.6 wt % (mean 3.5 wt %, median 2.3 wt %) and Si ranged from 0.01 to 9.6 wt % (mean 1.0 wt %, median 0.1 wt %). Other mineral forming elements in appreciable abundances included Mg (0.02 to 2.2 wt % (mean 0.12, median 0.04 wt %), Pb, which from 0.004 to 5.8 wt % (mean 0.7 wt %, median 0.3 wt, and As, ranged from 0.02 to 1.2 wt % (mean 0.3 wt %, median 0.2 wt).

Total weight percent barite ranged from 0.01 to 1.3 wt % (mean 0.5, median 0.4 wt %); total organic carbon ranged from 0.02 to 3.67 wt % (mean 0.44 wt %, median 0.25 wt %); and total inorganic carbon ranged from below detection limit to 0.10 wt % (mean 0.006 wt %, median 0.002 wt %). The sum of the elements Ag, Al, Au, B, Bi, Cd, Co, Cr, Ga, Ge, Hf, Hg, In, Li, Mn, Mo, Nb, Ni, Rb, Sb, Sc, Se, Sn, Ta, Te, Th, Ti, Tl, U, V, W, Zr, and REY, plus total TIC and TOC measured in samples always totaled less than 1 wt %.

Figures S1 to S4

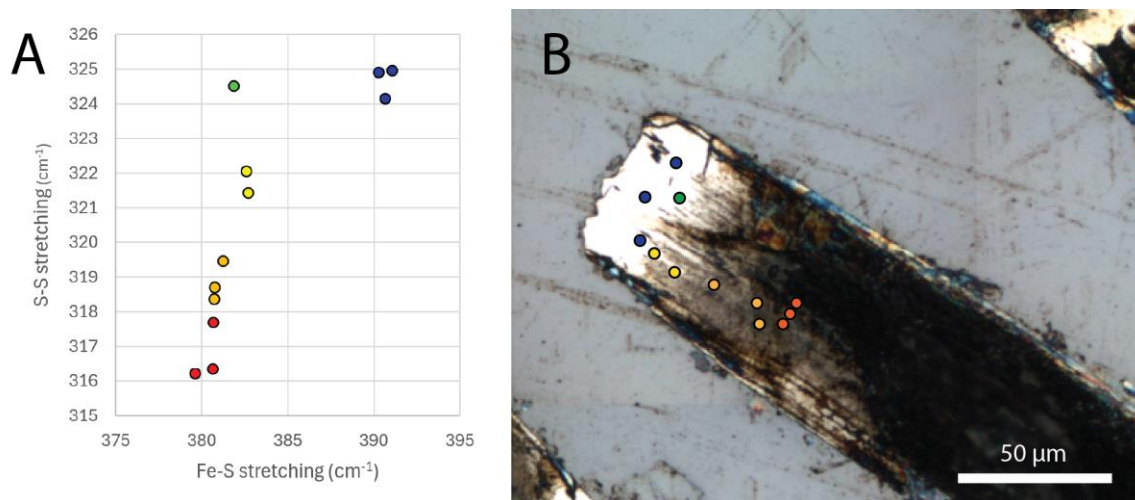


Fig. S1. Raman data (A) and location of spectra collection (B) across a marcasite blade. The decrease in both Fe-S and S-S bond energies moving away from the edge of the blade and towards the center, where there is void space. In the thin section, the void space is infilled with resin. The sample in this figure is J2-1423-R04 (Table S1, Table S3). Energies on the x and y axes are in cm^{-1} . The different colors are arbitrary, and are used to connect the plot (A) with the micrograph (B) and indicate the location on the mineral blade where each Raman spectra was collected.

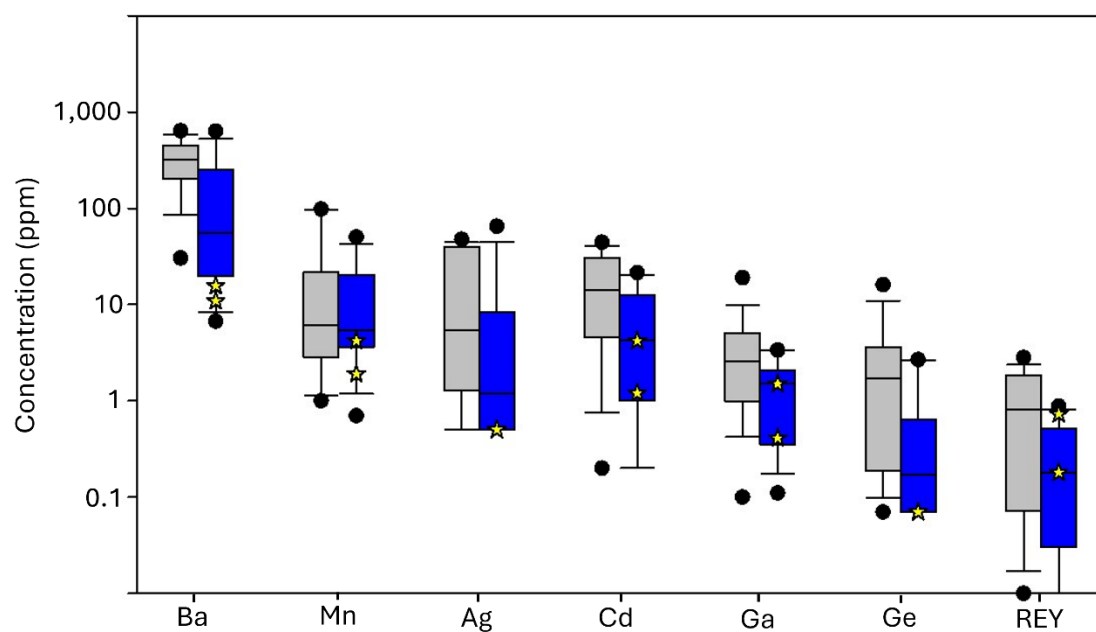


Fig. S2. Bulk rocks. Rock samples dominated by pyrrhotite (grey) are compared to rock samples dominated by marcasite (blue). Combusting rocks are indicated by yellow stars.

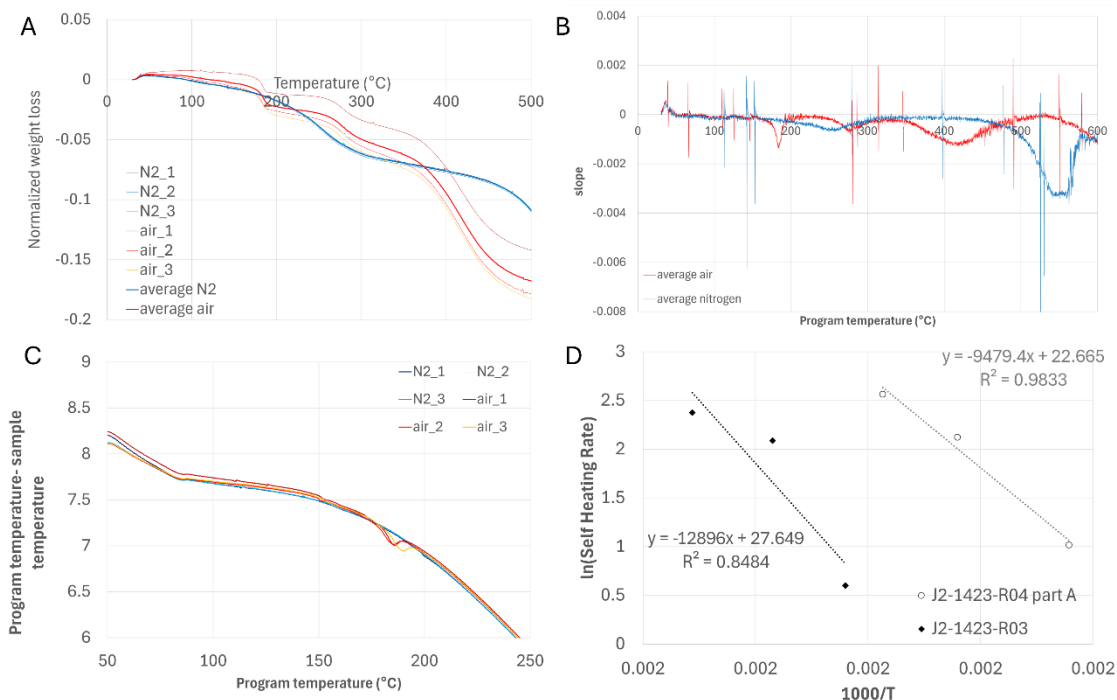


Fig. S3. Plots from TGA analyses (1) showing: A. the normalized weight loss versus program temperature for, sample J2-1423-R04 part A (Table S1, Table S3, 1,2). B. the difference in slope for samples run under air (in red) and samples run under nitrogen (in blue), with an arrow indicating the accelerated mass loss associate with the self-heating event in sample J2-1423-R04 part A C. the self-heating event (plotted as the difference between the program and sample temperature, vs program temperature) which occurs as a peak in the sample replicates run under air, and does not occur for the sample replicates run under nitrogen for sample J2-1423-R04 part A, indicated by an arrow; D. and the Arrhenius plots for samples J2-1423-R03 and J2-1423-R04 part A.

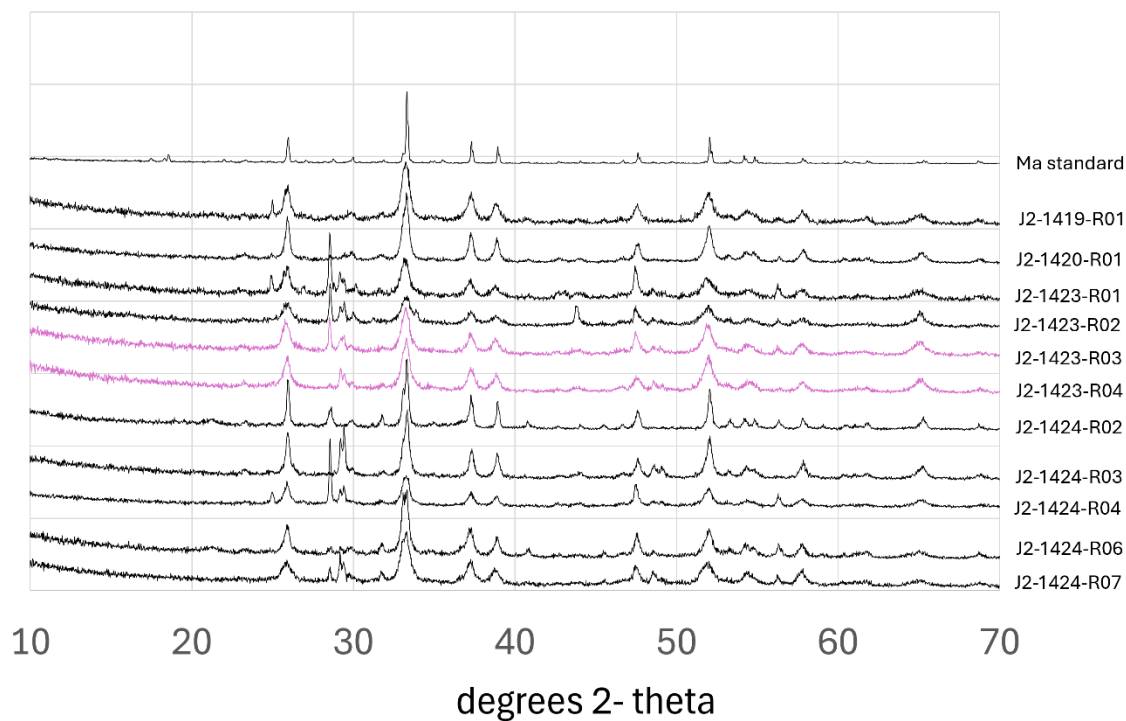


Fig. S4. X-ray diffractograms of a marcasite standard (top) and samples that are dominated by nanocrystalline marcasite, including the two which underwent exothermic oxidation in pink. The nanocrystalline nature of the marcasite is apparent in the significant peak broadening occurring in the marcasite samples from Escanaba Trough. Data provided in (2).

Tables S1 to S4

Table S1. Powder XRD table with semiquantitative analysis grouping minerals into major, moderate, and minor categories. Py, pyrite, Ma, marcasite, Pyh, pyrrhotite, Ccp/Iso, chalcopyrite/isocubanite, Wur, wurtzite, Qz, quartz, Gth, goethite, Ba, barite, Gn, galena, Opl, opal, S, sulfur, Cer, cerrusite, Akg, akageneite, Sp, sphalerite, Szo, szomolnokite Beav, beaverite, Jrs, jarosite, Cv, covellite, Ms, muscovite. XRD diffraction data are provided in (2). * indicates a combusting rock.

Rock ID	Major (> 25%)	Moderate (5-25%)	Minor (< 5%)
Pyrite dominant			
J2-1421-R05	Py	Ccp/Iso	Wur, Qz, Ba, Gth
Pyrrhotite dominant			
J2-1418-R02	Pyh	Iso/Ccp	Sp/ Wur, Ba, Ma
J2-1418-R03	Pyh	Iso/Ccp	Sp, Ba, lepidocrocite, Py
J2-1418-R04	Pyh	Iso/Ccp, Sp/ Wur	Gn
J2-1420-R04	Pyh	Iso/Ccp, Sp	Gn, Ba
J2-1421-R02	Pyh	Sp, Opl	Iso/Ccp, Gn, Ba, Py
J2-1422-R01	Pyh		Iso/Ccp, Ba, Ma
J2-1422-R05	Pyh	Opl, Sp	Ba, Gn, Ccp, S
J2-1423-R06 bulk 2	Pyh		Iso/Ccp, Sp, Cer Ba, Gn
J2-1424-R01	Pyh	Iso/Ccp	Sp, Ba
J2-1425-R01	Pyh	Sp	Gn, Ccp/Iso, Gth
J2-1425-R02	Pyh	Sp, Gn	Iso/Ccp, Ba, Gth, Akg
J2-1425-R04	Pyh	Iso/ Ccp	Sp, Gn, Ba, S
J2-1425-R05	Pyh	Sp	Iso/Ccp, Py, Gn, Ba
J2-1425-R06	Pyh	Sp	Py, Ccp/Iso, Ba, Gn
Pyrrhotite- Marcasite			
J2-1420-R06	Pyh	Ma, Ccp/Iso	Wur/Sp, Ba
J2-1425-R03	Pyh, Ma	Sp, Py	Iso/Ccp Gn, Ba
Marcasite dominant			
J2-1419-R01	Ma	Ccp/Iso	Ba, Sp, Gth
J2-1420-R01	Ma	Ccp/Iso	Sp, Gth,
J2-1423-R01	Ma	Iso/Ccp, Sp	Gn, Ba, Gth,
J2-1423-R02	Ma		Sp, Ccp/Iso
J2-1423-R03*	Ma		Iso/Ccp, Sp, Gn, Ms
J2-1423-R04-PartA	Ma		Iso/Ccp, Sp,
J2-1423-R04-PartB*	Ma		Iso/Ccp, Sp, Gn, Ba
J2-1424-R02	Ma		Sp, Gth, Fer, Ccp/Iso
J2-1424-R03	Ma		Ccp/Iso, Gth, Akg
J2-1424-R04	Ma	Ccp/Iso, Cv	Sp, Ba, Gth
J2-1424-R06	Ma	Ccp/Iso	Gth, Sp, Akg
J2-1424-R07	Ma	Ccp/Iso	Sp
Marcasite-pyrite			
J2-1421-R04	Ma, Py	Wur, Sp, Gth	Gn, Iso/Ccp, Pyh
Other			
J2-1417-R02	Sp	Pyh	Ba, Ccp/Iso, Gn
J2-1420-R02	Sp	Pyh	Gn, Ba
J2-1421-R01	Sp	Gn	Ba, Ccp/Iso
J2-1421-R03	Pyh	Sp	Gn, Ba
J2-1421-R06	Iso/Ccp	Sp, Pyh	Gn, Ba, Szo
J2-1422-R02		Sp, Pyh, Ba, Gn	
J2-1422-R04	Pyh	Sp	Iso/Ccp, Gn, Ba
J2-1422-R06		Iso, Sp, Pyh	Gn, Ba
J2-1422-R07		Sp, Pyh	Gn, Ba
J2-1423-R06 bulk 1		Sp, Pyh, Ma	Ba, Gn
J2-1424-R05	Pyh	Sp, Ccp/Iso	Py, Ba, Beav, Jrs, Gth

Table S2. Thermodynamic calculations after equations listed in Table 3.2 in ref. 3.
Thermodynamic data is from ref 4, 5, or 6 and 7. All data is standard state, 25°C and 1 bar.

		Acid generated	delta G	Reactants	Products
Native sulfur	$S^{\circ} + H_2O + 1.5 O_2 \rightarrow 2 H^{+} + SO_4^{2-}$	2	-623.4	-285.83	-909.2
Chalcopyrite	$CuFeS_2 + 4 O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2 SO_4^{2-}$	0	-1647.8	-194.9	-1842.7
Chalcopyrite	$CuFeS_2 + 16 Fe^{3+} + 8 H_2O \rightarrow Cu^{2+} + 17 Fe^{2+} + 2 SO_4^{2-} + 16 H^{+}$	16	-44.8	-3257.54	-3302.3
Pyrite	$FeS_2 + 3.5 O_2 + H_2O \rightarrow Fe^{2+} + 2 SO_4^{2-} + 2 H^{+}$	2	-1452.2	-457.33	-1909.5
Pyrite	$FeS_2 + 3.75 O_2 + 0.5 H_2O \rightarrow Fe^{3+} + H^{+} + 2 SO_4^{2-}$	1	-1552.5	-314.415	-1866.9
Pyrite	$FeS_2 + 3.75 O_2 + 3.5 H_2O \rightarrow 2 SO_4^{2-} + 4 H^{+} + Fe(OH)_3 (s)$	4	-646.5	-1171.91	-1818.4
Pyrite	$FeS_2 + 14 Fe^{3+} + 8 H_2O \rightarrow 15 Fe^{2+} + 2 SO_4^{2-} + 16 H^{+}$	16	-47.8	-3137.14	-3184.9
Sphalerite (Covellite, Galena)	$MS + 2 O_2 \rightarrow M^{2+} + SO_4^{2-}$	0	-859.0	-204.1	-1063.1
Sphalerite (Covellite, Galena)	$MS + 8 Fe^{3+} + 4 H_2O \rightarrow M^{2+} + 8 Fe^{2+} + SO_4^{2-} + 8 H^{+}$	8	-56.5	-1735.42	-1791.9
Pyrrhotite	$Fe_{0.9}S + 1.95 O_2 + 0.1 H_2O \rightarrow 0.9 Fe^{2+} + SO_4^{2-} + 0.2 H^{+}$	0.2	-863.2	-126.183	-989.39
Pyrrhotite	$Fe_{0.9}S + 2.175 O_2 + 0.7 H^{+} \rightarrow 0.9 Fe^{3+} + SO_4^{2-} + 0.35 H_2O$	-0.7	-955.3	-97.6	-1052.89
Pyrrhotite	$Fe_{0.9}S + 2.175 O_2 + 2.35 H_2O \rightarrow SO_4^{2-} + 2 H^{+} + 0.9 Fe(OH)_3 (s)$	2	-139.9	-769.301	-909.2
Pyrrhotite	$Fe_{0.9}S + 7.8 Fe^{3+} + 4 H_2O \rightarrow 8.7 Fe^{2+} + SO_4^{2-} + 8 H^{+}$	8	-65.2	-1619.22	-1684.37
Pyrrhotite (anhydrous)	$Fe_{0.9}S + 1.675 O_2 \rightarrow 0.9 Fe_2O_3 + 4 SO_2$	0	-926.5	-97.6	-1684.37
Pyrrhotite (anhydrous)	$Fe_{0.9}S + 2.175 O_2 \rightarrow 0.9 Fe_2O_3 + 4 SO_3$	0	-1025.4	-97.6	-1024.09
Marcasite	$FeS_2 + 3.75 O_2 + 0.5 H_2O \rightarrow Fe^{3+} + H^{+} + 2 SO_4^{2-}$	1	-1554.5	-312.415	-1866.9
Marcasite	$FeS_2 + 14 Fe^{3+} + 8 H_2O \rightarrow 15 Fe^{2+} + 2 SO_4^{2-} + 16 H^{+}$	16	-19.8	-3135.14	-3154.9
Marcasite	$2FeS_2 + 5 O_2 + H_2O \rightarrow Fe_2O_3 + 4 SO_2 + 2 H^{+}$	2	-1370.5	-624.83	-1995.3
Marcasite (anhydrous)	$2FeS_2 + 5.5 O_2 \rightarrow Fe_2O_3 + 4 SO_2$	0	-1656.3	-339	-1995.3
Marcasite (anhydrous)	$2FeS_2 + 7.5 O_2 \rightarrow Fe_2O_3 + 4 SO_3$	0	-2051.9	-339	-2390.9
Galena	$PbS + 2 O_2 \rightarrow PbSO_4 (anglesite)$	0	-819.6	-100.4	-920
Galena	$PbS + 0.5 O_2 + 2 H^{+} \rightarrow Pb^{2+} + H_2O + S^{\circ} (native sulfur)$	-2	-187.1	-100.4	-287.5

Table S3. Summary TGA data for all samples run at 30- 600°C at a rate of 10°C/ minute (1). Samples which did not exhibit peaks in excess of the standard deviation of the triplicate run are listed as "--". Also noted is the percent of organic carbon that was attributable to lipids (sediments only, published in ref. 8 and 9) and whether an "oily aspect" was noted when describing the sample.

Sample	Sample type	Temp. of self-heating peak	% mass loss at self-heating peak	% OC	% OC_lipid	oily aspect?
J2-1420-PC15-18-20	sediment	--		1.26	0.021	
J2-1421-PC03-0_2 cm	sediment	--		1.43	0.35	Y
J2-1421-PC06-0-2 cm	sediment	--		1.48	0.163	
J2-1418-R03	rock-pyrrhotite dominant	--		0.06	N/A	
J2-1418-R04	rock-pyrrhotite dominant	--		0.05	N/A	
J2-1422-R01	rock-pyrrhotite dominant	--		0.19	N/A	
J2-1424-R01	rock-pyrrhotite dominant	--		0.02	N/A	
J2-1425-R01	rock-pyrrhotite dominant	--		0.85	N/A	
J2-1425-R02	rock-pyrrhotite dominant	--		3.67	N/A	
J2-1420-R06	rock-pyrrhotite- marcasite dominant	--			N/A	
J2-1420-R01	rock- marcasite dominant	--		0.17	N/A	
J2-1423-R02	rock- marcasite dominant	--		0.26	N/A	
J2-1423-R03	rock- marcasite dominant	223	0.30	0.49	N/A	
J2-1423-R04 part A	rock- marcasite dominant	186	0.90	0.10	N/A	Y
J2-1423-R04 part B	rock- marcasite dominant	224	0.45	0.03	N/A	
J2-1424-R03	rock- marcasite dominant	--		0.05	N/A	
J2-1421-R03	rock- other	--		0.42	N/A	Y
J2-1422-R07	rock- other	--		0.17	N/A	
J2-1423-R06	rock- other	--		2.24	N/A	
J2-1418-R01	rock- other	--		0.22	N/A	

Table S4. Details of TGA results (1) for samples which exhibited self-heating peaks, including the temperature of the self-heating peak at different heating rates (either 5, 10, or 15°C/ minute) and the percent of sample mass loss that occurred coincident with that peak.

Sample	Sample type	% OC	oily aspect?	Temperature of self heating peak			Mass loss of self heating peak		
				5C/minute	10C/minute	15C/minute	5C/minute	10C/minute	15C/minute
J2-1423-R03	rock- marcasite dominant	0.49		207.63	223.07	241.28	0.664	0.303	0.379
J2-1423-R04 part A	rock- marcasite dominant	0.10	Y	165.70	185.65	200.08	1.295	0.902	1.099
J2-1423-R04 part B	rock- marcasite dominant	0.03			224.07			0.445	

Movie S1 (separate file). Movie showing rock combusting upon breaking in shatter box.

Movie S1 (separate file). Movie showing rock temperature is over the 100°C limit of our thermocouple.

Supporting references

1. Shapiro, I.M., Phan, K.C., and Gartman, A., 2026, Thermogravimetric Analysis of rock samples from the Escanaba Trough (Gorda Ridge): U.S. Geological Survey data release, <https://doi.org/10.5066/P13WN2F7>.
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9. Ianiri, H.L., Prouty, N.G., Campbell, P., Gartman, A., Adamczyk, K.B., and Favela, J.J., 2025, Lipid biomarker data from Escanaba Trough sediments, off the coast of Northern California, USA, from May-June 2022: U.S. Geological Survey data release, <https://doi.org/10.5066/P13XVXQC>.