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Pyrite: an authigenic host phase for tungsten in sulfidic sediments

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Supplementary Information

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Materials and Methods

Materials

These piston cores (Q6 and QDN-MS6) were collected in the Haima Cold Seep area of the Qiongdongnan Basin at a water depth of ca. 1400 m (Fig. 1b). After retrieving the core samples to the surface deck, they were cut into 60cm lengths, labeled, and subsequently stored in a cold storage at 4 °C. The Haima Cold Seep area was found to have a high methane flux and strong sulfate-driven anaerobic oxidation of methane (SD-AOM), resulting in a shallow sulfate-methane transition zone (SMTZ) within the sediment, i.e., only a few tens of centimeters below the sediment-water interface (Feng *et al.*, 2018; Hu *et al.*, 2023).

W element in sediment analyses

The samples were ground using natural agate mortar and pestle after being dried at low temperature (60 °C). They were then incinerated at 600 °C for 2 h to remove the organic matter. The samples were treated with a mixed-acid solution of 30 M HF + 14 M HNO_3. W in the sediments were analyzed using inductively coupled plasma mass spectrometry (ICP-MS, Thermo fisher VG-X7). For W testing, 10 ppb Rh element was used as an internal standard to monitor the instrument stability. Analytical performance was monitored by repeatedly analyzing certified reference materials (BHVO-2, W-2a, GSP-2, GSD-9) and blank samples. The pretreatment of the samples and measurement for major/trace elements were completed at the State Key Laboratory of Marine Geology, Tongji University. The results showed that the relative standard deviations of the W elements were less than 10%. It should be noted that the samples were not in contact with the metal apparatus during the sampling and experiment.

Trace elements in pyrite analyses

A proper amount of the original sediment was taken and immersed in distilled water for 24 h. Sediment particles larger than 0.063 μm were dried, bottled, and weighed. Selected sediments were examined using a stereoscope to identify and measure the weight of pyrite particles. Pyrite in sediments is selected and then the trace element content of pyrite is measured by laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS, New Wave UP-213 laser system; Agilent 7900 mass spectromete). For a detailed analysis, see Miao *et al.* (2022).

Enrichment factors (EF) were employed to assess authigenic enrichment of trace metals. X_{EF} = (X/Al)sample / $(X/Al)_{UCC}$ is the weight ratio of element X to Al in the sample divided by that for UCC (Rudnick and Gao, 2014).

The pyrite content and clay content in sediments analyses

The pyrite content of sediments were converted to Ag_2S(s) using the method described by Canfield *et al*. (1986) at NO.203 Research Institute of Nuclear Industry. To extract chromium reduction sulfur, sediment powder (50−200 mg) was mixed with a solution of 1.0 M $CrCl_2$-0.5 M HCl and 3 N HCl. The resulting mixture was then subjected to continuous nitrogen flow at 200-250 °C for 2 hours. The released H_2S was captured in an $AgNO_3$-NH_4OH solution and converted to Ag_2S precipitate. The amount of Ag_2S extracted was used to calculate the pyrite content.

We conducted tests on the grain size composition of sediments, with the content of the fraction less than 0.063 μm taken as an approximation of the clay content. Grain size composition was determined at a 1–4 cm depth resolution along studied sediment cores in the Key Laboratory of Submarine Geosciences and Prospecting (Ministry of Education), using a Mastersizer 3000 laser grain size analyzer with a measurement range of 0.02–2000 μm and grain size resolution of 0.01 φ. Carbonates and organic matter were removed from the test samples. The relative error between repeated measurements was less than 3%.

Supplementary Tables

Table S-1 Element content in sediments of QDN-MS6.

Depth (cm)	W (ppm)	Al (%)	Mo (ppm)	U (ppm)
21	3.05	6.47	0.50	2.02
41	2.87	6.39	0.32	2.55
61	2.85	6.40	0.40	2.59
81	2.83	6.56	0.41	2.72
101	2.74	6.44	0.39	2.89
121	2.95	6.79	0.45	2.99
141	3.10	7.14	0.39	3.55
161	3.39	7.07	0.40	3.38
181	2.76	6.72	0.42	2.70
201	2.76	6.19	0.47	3.54
221	2.83	6.19	0.57	3.85
241	3.66	6.96	0.71	4.05
261	3.52	7.74	0.79	4.53
281	3.64	7.49	0.75	3.98
301	3.74	7.68	1.07	4.12
321	2.87	5.92	0.67	3.65
341	3.09	4.76	0.49	3.02
361	3.13	6.68	1.44	3.95
363	2.76	8.12	1.73	4.74
369	2.31	6.71	1.91	4.75

Table S-1 continued.

Depth (cm)	W (ppm)	Al (%)	Mo (ppm)	U (ppm)
371	2.53	5.36	1.76	4.47
373	1.05	3.99	2.11	4.70
377	1.75	3.73	3.38	3.79
379	1.38	3.43	2.87	2.60
381	1.15	2.28	3.93	2.57
383	1.43	3.36	4.31	3.33
389	1.45	3.67	3.29	2.93
391	1.91	2.87	3.31	2.67
397	1.90	2.98	2.67	2.40
399	1.24	3.36	3.66	2.19
401	1.28	2.72	4.80	2.09
403	0.91	3.17	3.21	2.27
410	2.58	8.60	1.03	4.23
421	3.18	7.13	0.86	3.75
423	2.74	8.79	1.29	4.75
441	3.17	7.16	0.98	3.53
461	3.29	7.06	0.94	3.58
481	3.48	7.21	0.93	3.68
483	2.85	8.71	1.03	4.60
501	3.92	7.49	0.94	3.66
521	3.55	7.38	0.87	3.54
541	3.54	7.32	0.85	3.28
543	2.91	8.88	1.23	5.52
561	3.40	7.26	0.69	3.78
581	3.25	7.09	0.85	3.75
601	3.13	6.78	0.77	3.02
621	2.97	6.75	0.78	4.07
623	2.60	8.13	0.84	5.37
641	2.88	6.73	0.84	3.63
661	2.93	6.56	0.80	3.10
681	2.96	6.76	0.94	3.46
701	2.96	6.95	0.81	3.40
703	2.69	8.11	0.80	3.90

Table S-2 Element content in sediments of Q6.

Depth (cm)	W (ppm)	Al (%)	Mo (ppm)	U (ppm)
2	1.77	6.33	0.32	1.89
4	1.99	6.22	0.25	1.95
6	1.78	6.20	0.22	2.02
8	1.74	6.38	0.30	2.12
10	2.04	6.53	0.24	2.02
12	1.71	6.47	0.32	2.07
14	1.71	6.47	0.26	2.05
16	1.77	6.56	0.26	2.17
18	1.75	6.43	0.26	2.25
20	1.84	6.21	0.28	2.14
22	1.73	6.21	0.30	2.25
24	1.73	6.36	0.27	2.32
26	1.66	5.93	0.36	2.32
28	1.73	6.35	0.39	2.76
30	1.83	6.40	0.39	2.76
32	1.70	6.18	0.42	2.81
34	1.71	6.43	0.32	3.07
36	1.74	6.41	0.30	2.79
38	1.69	6.39	0.28	2.71
40	1.67	6.25	0.28	2.79
42	1.66	6.35	0.28	2.93
44	1.69	6.38	0.31	2.73
46	1.78	6.49	0.36	2.84
50	1.75	6.54	0.46	2.83
52	1.77	6.52	0.43	2.85
54	1.74	6.44	0.46	3.11
56	1.83	6.47	0.51	3.19
58	1.70	6.36	0.56	3.17
60	1.80	6.62	0.52	3.17
62	1.72	6.31	0.59	3.59
64	1.71	6.44	0.42	3.87
66	1.90	6.81	0.46	3.56
68	1.79	6.76	0.33	3.48
70	1.74	6.65	0.37	3.45
72	1.78	6.43	0.55	3.35
74	1.97	6.50	0.39	3.46
76	1.76	6.70	0.33	3.90
78	1.84	6.38	0.48	3.87
80	1.75	6.43	0.39	3.76
82	1.76	6.52	0.42	4.01
84	1.76	6.31	0.86	4.40
86	1.73	6.13	0.56	4.26
88	1.78	5.96	0.62	4.05
89	1.66	5.66	0.66	4.04
90	1.51	3.92	0.98	3.36

Table S-2 continued.

Depth (cm)	W (ppm)	Al (%)	Mo (ppm)	U (ppm)
91	1.24	3.83	0.94	3.42
92	1.15	3.26	1.11	3.04
93	1.08	3.04	1.23	2.81
94	1.10	2.88	1.72	2.77
95	1.21	3.66	1.29	2.84
96	1.33	3.85	1.19	2.79
98	1.82	6.74	0.68	3.66
100	1.82	7.24	0.75	3.50
102	1.83	7.07	0.93	3.27
104	1.78	6.83	1.26	3.05
106	2.01	6.97	0.79	3.09
108	1.87	6.94	0.93	3.31
110	1.77	6.33	0.88	3.03
112	1.80	6.51	1.04	3.35
114	1.80	6.68	0.89	3.39
116	1.60	5.57	0.79	3.04
117	1.39	4.65	0.85	2.73
118	1.32	4.07	0.96	2.57
119	1.38	3.74	0.93	2.42
120	1.45	3.81	0.94	2.71
121	1.51	4.23	0.91	2.85
122	1.38	3.99	0.98	2.55
123	0.90	3.09	1.36	2.04
128	1.72	6.81	0.56	3.02
130	1.76	6.94	0.67	2.90
132	1.96	7.01	0.68	2.97
138	1.72	6.86	1.11	3.05
140	1.90	6.87	1.35	3.12
142	1.86	6.97	1.41	3.05
144	1.97	6.89	1.96	3.16
146	1.88	6.93	2.48	3.17
148	1.92	6.98	2.80	3.22
150	1.79	6.90	2.90	3.13
152	2.01	6.85	2.46	3.04
154	2.00	6.92	2.41	3.04
156	2.22	7.61	2.75	3.44
158	2.11	7.82	2.24	3.61
160	2.08	5.92	1.28	3.05
162	1.94	5.78	3.31	3.36
168	2.02	6.36	0.84	3.32
170	1.71	6.41	0.73	3.39
172	1.76	6.24	0.68	3.38
174	1.68	6.02	0.76	3.62
176	1.67	6.06	0.83	4.01
178	1.62	6.19	0.66	4.20

Table S-2 continued.

Depth (cm)	W (ppm)	Al (%)	Mo (ppm)	U (ppm)
180	1.64	6.02	0.61	4.32
184	2.24	6.05	0.67	3.89
186	1.78	6.13	0.64	4.04
188	1.82	6.36	0.63	3.85
190	1.91	6.20	0.59	4.01
192	1.88	6.44	0.70	3.87
194	1.93	6.56	0.75	3.70
196	1.97	6.73	1.24	4.38
198	2.00	6.90	1.85	4.52
200	1.94	6.97	1.59	4.28
201	1.93	6.97	0.99	4.35
202	1.97	7.12	0.75	4.42
206	2.31	7.13	0.74	4.19
208	2.19	7.36	0.61	4.01
210	2.22	7.44	0.56	4.14
212	2.10	7.46	0.55	3.29
214	1.85	6.19	0.57	3.61
218	1.93	6.89	0.48	4.73
220	3.34	7.81	0.63	5.05
224	2.26	8.05	0.69	4.88
226	2.30	7.97	0.70	4.69
228	2.34	8.17	0.69	4.56
230	2.51	6.15	0.67	3.73
232	2.23	8.04	0.61	4.52
234	2.23	7.97	0.72	4.39
236	2.40	7.96	0.60	4.37
238	2.29	7.73	0.57	4.24
240	2.21	7.06	0.63	4.08
242	2.73	8.04	0.68	4.75
246	3.46	8.06	0.77	4.74
248	2.18	8.06	0.75	4.61
250	2.79	7.91	0.92	5.10
252	2.32	8.48	0.96	4.47
254	2.27	8.08	0.77	3.34
258	1.88	5.12	0.61	4.33
281	1.73	5.29	1.89	4.37
282	1.83	5.52	1.26	4.15

Table S-3 Trace elements (ppm) of authigenic pyrite of QDN-MS6.

Depth (cm)	Al (ppm)	W (ppm)	W_{EF}	Fe (ppm)	FeS_2 (%)
223	6.40	0.12	753.75	444357	95.21
223	45.11	0.16	142.58	443892	95.11
223	14.70	0.16	437.55	438672	93.99
223	13.94	0.17	490.24	451744	96.80
223	11.40	0.15	528.95	433788	92.95
223	17.37	0.13	300.86	451234	96.69
333	11.81	0.12	408.47	437652	93.78
333	21.25	0.19	359.44	422367	90.50
333	22.13	0.14	254.32	444761	95.30
333	25.69	0.19	297.31	455310	97.56
363	10.43	0.14	539.60	429800	92.09
363	5.36	0.07	525.00	447921	95.98
363	6.61	0.08	486.54	460233	98.61
363	12.26	0.13	426.26	450325	96.49
363	9.53	0.15	632.74	433250	92.83
363	1.19	0.15	5067.23	432988	92.78
389	2.47	0.07	1139.27	429754	92.08
389	3.99	0.06	604.51	435989	93.42
389	7.12	0.13	733.99	460911	98.76
399	0.98	0.14	5742.86	446582	95.69
399	0.85	0.04	1891.76	436672	93.57
399	3.03	0.07	928.71	437352	93.71
399	14.80	0.09	244.46	447170	95.82
399	8.31	0.07	338.63	446810	95.74
399	1.30	0.14	4329.23	451140	96.67
503	2.70	0.06	893.33	448260	96.05
503	5.34	0.10	752.81	447223	95.83
503	2.67	0.05	752.81	436807	93.59
503	6.94	0.11	637.18	434912	93.19
583	3.94	0.04	408.12	439256	94.12
583	19.96	0.36	725.05	430650	92.28
583	5.49	0.07	512.57	432347	92.64
663	36.09	0.16	178.22	450071	96.44
663	13.43	0.24	718.39	426617	91.41
663	7.40	0.11	597.57	421843	90.39
663	8.41	0.10	478.00	458410	98.22
663	28.49	0.18	253.98	435923	93.41
663	95.64	0.19	79.86	446827	95.74

Table S-4 Trace elements (ppm) of authigenic pyrite of Q6.

Depth (cm)	Al (ppm)	W (ppm)	W_{EF}	Fe (ppm)	FeS_2 (%)
62	38.29	0.19	199.48	432365	92.64
62	7.82	0.12	616.88	453861	97.25
62	35.22	0.17	194.04	445667	95.49
62	24.14	0.16	266.45	438752	94.01
74	79.98	0.13	65.34	460058	98.58
94	1.24	0.13	4214.52	441523	94.61
94	2.41	0.12	2001.66	435731	93.36
94	19.10	0.35	736.65	446737	95.72
94	1.33	0.18	5440.60	424962	91.06
94	20.90	0.05	96.17	452319	96.92
94	0.23	0.07	12234.78	456740	97.87
94	4.58	0.23	2018.78	457025	97.93
94	0.43	0.07	6544.19	430692	92.28
94	28.50	0.39	550.11	439402	94.15
94	28.50	0.53	747.58	447251	95.83
96	7.61	0.16	845.20	435974	93.42
96	23.00	0.31	541.83	449155	96.24
96	23.48	0.52	890.29	432749	92.73
96	25.35	0.34	539.17	460003	98.57
96	15.77	0.15	382.37	436781	93.59
96	59.48	0.33	223.03	446570	95.69
96	31.22	0.13	167.39	457390	98.01
121	38.37	0.38	398.12	438239	93.90
121	31.01	0.42	544.47	445400	95.44
121	12.08	0.07	232.95	443872	95.11
121	25.41	0.14	221.49	446984	95.78
121	31.88	0.17	214.37	453692	97.21
121	59.70	0.30	202.01	438035	93.86
121	24.97	0.23	370.28	435590	93.33
121	12.52	0.14	449.52	434473	93.09
121	86.28	0.91	423.99	434270	93.05
123	0.97	0.20	8288.66	429805	92.09
123	8.82	0.13	592.52	460367	98.64
123	1.73	0.07	1626.59	456680	97.85
123	5.02	0.72	5765.74	449914	96.40
123	9.11	1.87	8251.81	450238	96.47
123	62.10	0.19	123.00	460147	98.60
123	0.52	0.08	6184.62	458834	98.31
123	3.38	0.70	8325.44	457910	98.12
123	4.44	2.98	26981.08	432601	92.69
123	4.43	0.03	272.23	450169	96.46
123	3.00	0.14	1876.00	445552	95.47
123	7.66	0.25	1312.01	441505	94.60
140	53.80	0.05	37.36	436639	93.56
140	165.00	0.16	38.98	430192	92.18

Table S-4 continued.

Depth (cm)	Al (ppm)	W (ppm)	W_{EF}	Fe (ppm)	FeS_2 (%)
140	3.53	0.01	113.88	441472	94.59
140	12.50	1.08	3473.28	449513	96.32
140	2.22	0.25	4527.03	446293	95.63
140	46.33	0.08	69.42	430375	92.22
140	28.30	0.02	28.41	463720	99.36
140	0.98	0.02	820.41	440247	94.33
140	3.29	0.04	488.75	429831	92.10
140	1.51	0.16	4259.60	447930	95.98
140	18.80	0.30	641.49	426629	91.41
152	7.05	0.05	285.11	432503	92.67
152	5.85	0.04	274.87	431597	92.48
152	2.31	0.06	1044.16	446598	95.69
152	8.82	0.20	911.56	447042	95.79
152	3.73	0.05	538.87	430723	92.29
152	7.75	0.14	726.19	439635	94.20
152	3.21	0.07	876.64	438642	93.99
160	33.2	0.25	302.71	437560	93.76
160	7.1	0.27	1528.73	436825	93.60
160	15	0.45	1206.00	442964	94.91
160	27.1	0.56	830.70	459019	98.35
160	34.1	0.33	389.03	448429	96.09
160	44.83	0.15	134.51	435482	93.31
160	18.03	0.24	535.11	446218	95.61
160	13.76	0.44	1285.47	435038	93.22
160	70.22	0.04	22.90	440219	94.33
160	51.3	0.31	242.92	456320	97.78
160	18.7	0.48	1031.87	429735	92.08
160	34.8	0.57	658.45	460925	98.76
160	7.95	0.24	1213.58	437651	93.78
160	3.58	0.18	2021.23	443276	94.98
160	0.77	0.07	3654.55	442864	94.89
160	1.87	0.27	5804.28	449230	96.26
160	1.52	0.09	2380.26	444528	95.25
160	0.92	0.47	20536.96	463890	99.40
160	0.79	0.11	5597.47	436744	93.58
160	11.8	0.21	715.42	435529	93.32
160	3.43	0.25	2930.03	434458	93.09
160	4.64	0.14	1212.93	432375	92.65
202	28.02	0.08	114.78	434589	93.12
202	11.94	0.04	134.67	432290	92.63
202	112.50	0.26	92.91	436198	93.46
202	202.90	0.42	83.21	445759	95.51
202	32.14	0.09	112.57	453280	97.12
202	52.77	0.13	99.03	429467	92.02
202	77.80	0.12	62.01	462691	99.14

Table S-4 continued.

Depth (cm)	Al (ppm)	W (ppm)	W_{EF}	Fe (ppm)	FeS_2 (%)
202	15.94	0.27	680.93	440258	94.33
202	184.30	0.62	135.24	421480	90.31
202	73.46	0.21	114.92	432988	92.78
202	173.80	0.22	50.89	436042	93.43
202	21.05	0.37	706.60	436304	93.49
212	33.60	0.06	71.79	458002	98.14
212	84.24	0.61	291.10	437764	93.80
212	87.00	0.13	60.07	445439	95.44
212	79.44	0.10	50.60	441025	94.50
212	38.89	0.40	413.47	452294	96.91
212	33.61	0.25	299.02	446328	95.63
212	92.75	0.14	60.68	440351	94.35
212	141.30	0.09	25.61	447294	95.84
212	88.19	0.16	72.93	448201	96.04
212	68.89	0.54	315.11	436258	93.48
212	52.09	0.34	262.39	449084	96.23
212	63.89	0.25	157.30	458203	98.18
212	41.77	0.43	413.84	460276	98.62
260	59.89	0.46	308.77	443672	95.07
260	193.40	0.79	164.21	449036	96.22
260	36.14	0.44	489.43	441704	94.64
260	30.26	0.30	398.55	442740	94.87
260	46.17	0.58	505.00	440326	94.35
277	195.20	0.57	117.39	431985	92.56
277	40.23	0.28	279.79	430853	92.32
277	74.01	1.14	619.21	439042	94.07
277	76.86	0.34	177.83	439841	94.24
277	59.77	0.32	215.23	447283	95.84
277	66.21	0.41	248.94	429740	92.08
277	69.20	0.43	249.80	453901	97.26
277	53.09	0.26	196.87	438524	93.96
277	60.14	3.95	2640.34	435819	93.38
277	98.46	4.53	1849.54	448920	96.19
277	40.66	0.78	771.18	436856	93.61
277	49.89	0.47	378.71	448325	96.06
277	68.45	0.28	164.44	444361	95.21

Supplementary Figure

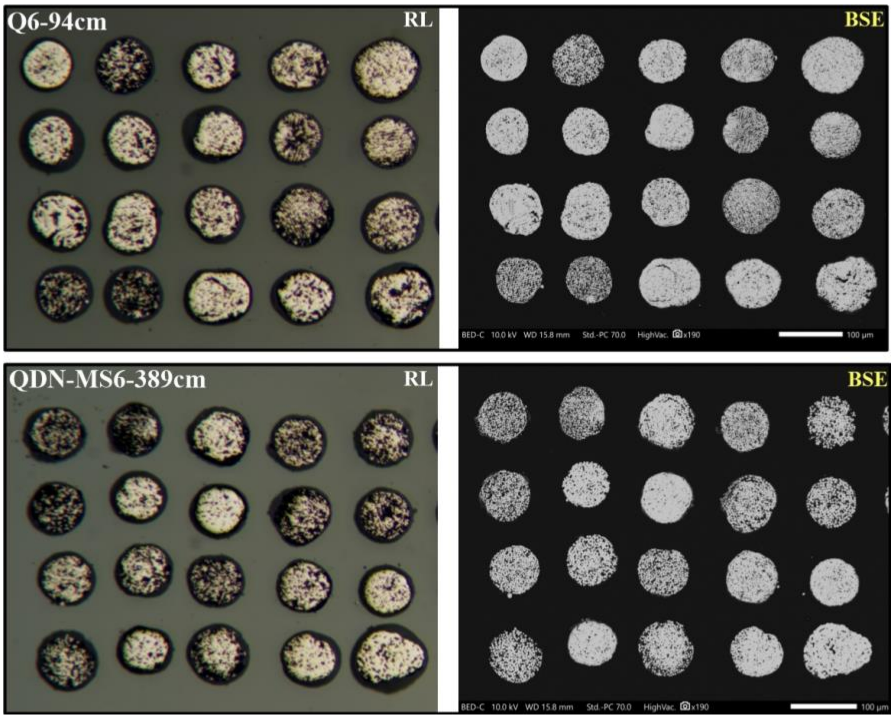

Figure S-1 Partial reflected light (RL) and backscattered electron (BSE) images of pyrite.

Supplementary Information References

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