

Supplementary Materials

# Petrographical and Geochemical Signatures Linked to Fe/Mn Reduction in Subsurface Marine Sediments from the Hydrate-Bearing Area, Dongsha, the South China Sea

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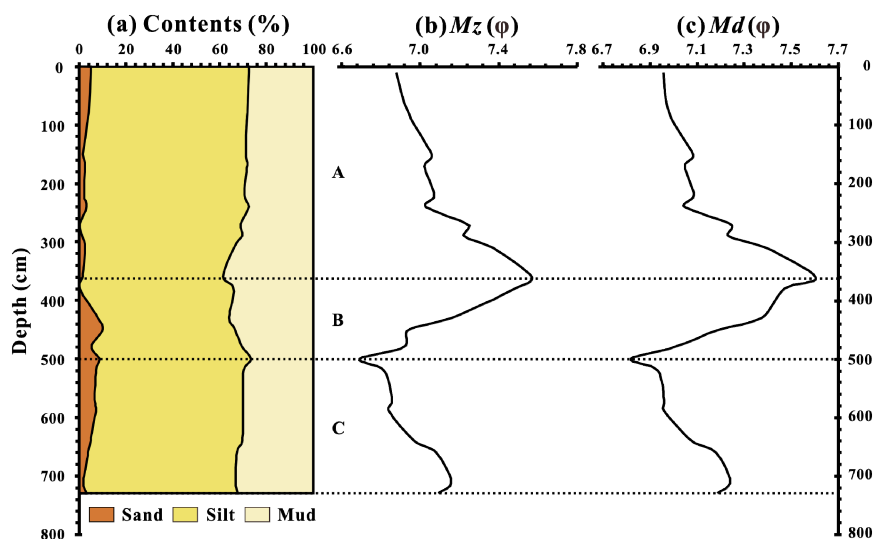
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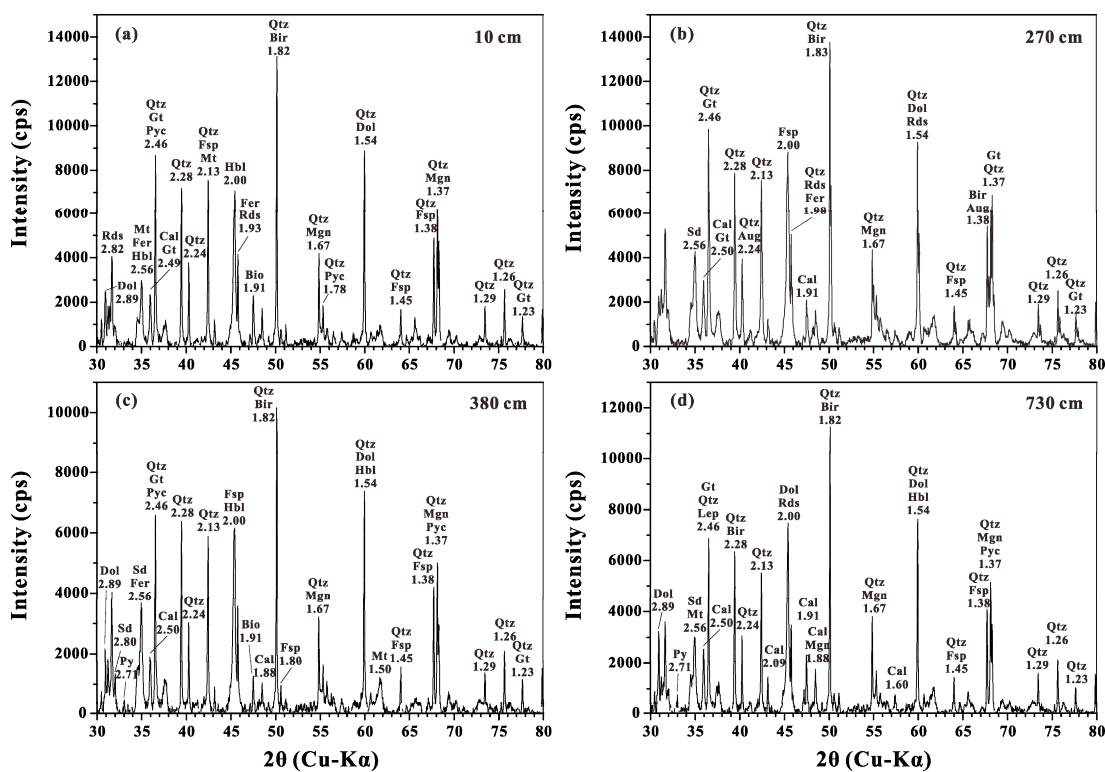
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The catalogs of 3 supplementary figures and 4 supplementary tables are shown as below.

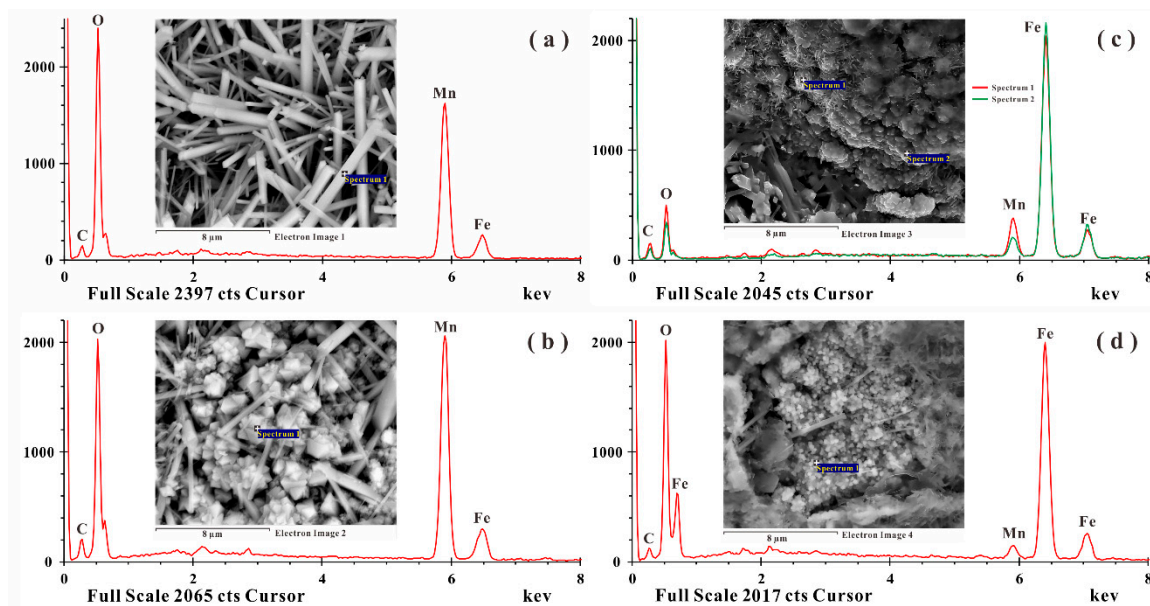
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**Figure S1.** Variations of (a) grain compositions, (b) mean grain size ( $Mz$ ), and (c) median grain size ( $Md$ ) for core DH-CL14. This core may be roughly divided into zones A-C by dashed lines.



**Figure S2.** X-ray diffraction patterns of sediment samples at the depths of 10 cm (a), 270 cm (b), 380 cm (c), and 730 cm (d) in core DH-CL14, respectively. Abbreviations: Qtz, quartz; Mt, magnetite; Pyc, pyrochroite; Hem, hematite; Gt, goethite; Py, pyrite; Sd, siderite; Rds, Rhodochrosite; Cal, Calcite; Mgn, manganite; and Dol, dolomite. The numbers below every abbreviation represent their d-spacing values. Fsp, feldspar; Hbl, hornblende; Bt, biotite; Aug, augite; Fer, ferrihydrite; Lep, Lepidocrocite; Bir, birnessite; Arg, aragonite



**Figure S3.** Energy dispersive spectroscopy (EDS) analysis of a Fe-Mn microscopic concretion from core DH-CL14. Sections (a), (b), (c), and (d) were all coated with Au before analysis.

**Table S1.** Grain composition and parameters of core DH-CL14

<b>Depth (cm)</b>	<b>Sand (%)</b>	<b>Silt (%)</b>	<b>Mud (%)</b>	<b><i>Mz</i> (<math>\varphi</math>)</b>	<b><i>Md</i> (<math>\varphi</math>)</b>
10	5.24	67.79	27.00	6.88	6.96
80	4.13	68.11	27.73	6.94	6.98
150	1.77	69.82	28.45	7.06	7.08
170	2.65	69.57	27.77	7.02	7.05
220	2.12	68.79	29.11	7.07	7.09
240	3.34	69.49	27.17	7.03	7.05
270	0.41	69.10	30.52	7.25	7.25
290	1.46	68.51	30.00	7.23	7.23
310	2.57	63.93	33.49	7.37	7.39
360	1.54	60.39	38.09	7.57	7.60
380	0.34	66.10	33.58	7.49	7.47
430	8.12	56.46	35.42	7.16	7.37
450	10.16	56.80	33.06	6.94	7.19
480	5.34	64.73	29.94	6.92	7.01
500	8.78	65.02	26.16	6.69	6.82
520	7.34	63.40	29.25	6.82	6.93
570	6.77	63.69	29.50	6.86	6.96
590	7.24	63.07	29.69	6.84	6.96
640	4.98	65.14	29.88	6.97	7.08
660	3.94	63.84	32.20	7.08	7.18
710	1.88	65.26	32.87	7.16	7.24
730	3.31	64.99	31.74	7.09	7.19

*Mz* and *Md* represent mean grain size and median grain size, respectively.

Table S2. Geochemical parameters in core DH-CL14

Depth (cm)	CH <sub>4</sub> (mM)	SO <sub>4</sub> <sup>2-</sup> (mM)	δ <sup>13</sup> C <sub>DIC</sub> (‰)	ΣH <sub>2</sub> S (mM)	TOC (wt%)	TIC (wt%)	TA (mM)	PO <sub>4</sub> <sup>3-</sup> (μM)	NH <sub>4</sub> <sup>+</sup> (μM)	<i>apsA</i> (copies/g)	Mg <sup>2+</sup> (mM)	Ca <sup>2+</sup> (mM)
10	0.62	29	-4.42	0	0.46	0.86	2.82	11.6	49	76	50	11
80	0.66	30	-10.28	7.0 × 10 <sup>-6</sup>	0.40	0.88	3.95	14.2	173	78	56	11
130										56		
150	0.91	27	-14.05	2.0 × 10 <sup>-6</sup>	0.46	0.65	4.48	19.5	243	26	50	10
170					0.44	0.68				422		
220	1.06	21	-14.96	1.2 × 10 <sup>-5</sup>	0.48	0.80	5.31	19.6	348	2,896	51	10
240					0.50	0.65				4,039		
270					0.47	0.82				4,108		
290	1.16	26	-17.83	8.0 × 10 <sup>-6</sup>	0.54	0.66	6.27	26.4	437	4,709	51	10
310					0.54	0.70				4,604		
360	0.94	24	-22.67	2.0 × 10 <sup>-6</sup>	0.61	0.73	6.06	32.9	573	5,059	52	9
380					0.64	0.55				346		
430	1.34	22	-23.84	5.0 × 10 <sup>-6</sup>	0.66	0.83	7.79	60.4	686	317	51	9
450					0.67	1.39				301		
480					0.65	1.42				459		
500	0.22	24	-26.12	3.8 × 10 <sup>-4</sup>	0.65	1.43	7.34	35.7	651	12,320	49	8
520					0.63	1.37				9,146		
570	2.90	21	-32.56	8.0	0.63	1.21	8.68	40.7	740	14,852	51	8
590					0.63	1.19				26,577		
640	14.63	11	-46.24	61.8	0.60	1.18	14.54	55.7	983	30,536	47	6
660					0.63	1.10				29,127		
710					0.61	1.10				17,166		
730	24.06	10	-37.31	62.6	0.61	1.09	15.19	83.7	1137	16,282	47	6

CH<sub>4</sub>, methane; SO<sub>4</sub><sup>2-</sup>, sulfate; δ<sup>13</sup>C<sub>DIC</sub>, stable carbon isotope ratios of dissolved inorganic carbon (DIC); ΣH<sub>2</sub>S, total sulfide; TOC, total organic carbon; TIC, total inorganic carbon; TA, total alkalinity; PO<sub>4</sub><sup>3-</sup>, phosphate; and NH<sub>4</sub><sup>+</sup>, ammonium; *apsA*, the functional gene of sulfate-reducing bacteria (data referred from [32]); Mg<sup>2+</sup>, magnesium; Ca<sup>2+</sup>, calcium.

**Table S3.** Contents of major elements (wt%) in core DH-CL14

Depth (cm)	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	MgO	CaO	K <sub>2</sub> O	MnO	BaO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SrO	ZrO <sub>2</sub>	LOI
10	60.42	0.70	14.03	5.59	1.99	4.23	2.74	0.05	0.02	2.05	0.12	0.02	0.03	8.20
80	59.69	0.72	14.49	5.43	2.07	3.61	2.83	0.04	0.02	2.05	0.11	0.01	0.02	7.75
150	60.66	0.72	14.41	5.40	1.99	3.42	2.80	0.04	0.01	1.94	0.11	ND	0.01	7.35
170	60.76	0.72	14.31	5.45	2.01	3.25	2.79	0.03	0.01	1.98	0.11	0.02	0.03	7.39
220	61.80	0.73	14.60	5.47	2.03	3.30	2.86	0.04	0.02	1.78	0.11	0.02	0.03	7.18
240	59.48	0.72	14.49	5.79	2.09	3.22	2.85	0.03	0.01	2.16	0.10	ND	0.02	7.85
290	58.61	0.76	15.90	5.97	2.16	3.46	3.10	0.04	0.03	1.77	0.11	0.02	0.03	7.90
360	57.28	0.76	16.80	6.42	2.44	2.51	3.29	0.05	0.02	2.00	0.09	ND	0.01	8.08
380	56.54	0.75	16.64	6.35	2.41	2.61	3.24	0.05	0.02	2.13	0.10	0.01	0.02	8.40
430	53.46	0.68	14.91	5.55	2.19	6.06	2.92	0.04	0.01	2.07	0.09	0.01	0.01	10.88
480	57.77	0.68	13.55	4.80	2.12	5.84	2.72	0.04	0.02	2.05	0.10	0.02	0.03	9.74
500	57.60	0.69	13.62	4.90	2.15	6.24	2.70	0.04	0.03	1.96	0.10	0.03	0.03	9.80
590	56.03	0.65	13.06	4.86	2.14	6.75	2.64	0.04	0.02	2.10	0.10	0.03	0.03	10.59
710	56.09	0.69	14.24	5.37	2.36	5.40	2.89	0.04	0.03	2.02	0.11	0.02	0.02	9.44

The detection limit (DL) was 0.01%; and ND denotes below the DL.



**Table S4.** Spearman's correlation coefficients among the contents of major elements (wt%) and grain parameters in sediment core DH-CL14

Parameters	Sand (%)	Silt (%)	Mud (%)	Mz ( $\varphi$ )	Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup> (%)	CaO (%)	SiO <sub>2</sub> (%)	TiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	MgO (%)	SO <sub>3</sub> (%)
Sand (%)	1	-0.4022	-0.4374	-0.7855**	-0.6447*	0.7758**	-0.1956	-0.8317**	-0.6601*	-0.2266	0.2070
Silt (%)		1	-0.5165	-0.0264	0.1100	-0.4725	0.8374**	0.4482	0.0660	-0.6843**	-0.6828**
Mud (%)			1	0.7811**	0.4730	-0.1736	-0.5912*	0.1762	0.5325*	0.7415**	0.3700
Mz ( $\varphi$ )				1	0.8304**	-0.6271*	-0.1914	0.6585*	0.8744**	0.5705*	-0.0154
Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup> (%)					1	-0.7525**	-0.0440	0.7858**	0.9515**	0.4593	-0.1367
CaO (%)						1	-0.4110	-0.8607**	-0.7085**	-0.0308	0.3899
SiO <sub>2</sub> (%)							1	0.4125	-0.0088	-0.8185**	-0.8216**
TiO <sub>2</sub> (%)								1	0.7947**	0.1105	-0.4224
Al <sub>2</sub> O <sub>3</sub> (%)									1	0.4207	-0.2315
MgO (%)										1	0.7387**
SO <sub>3</sub> (%)											1

The significant correlations of  $p < 0.01$  and  $p < 0.05$  are highlighted by \*\* and \*, respectively.