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Pyritization of heavy metals in Lake Shihwa sediments, Korea

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The pyritization of heavy metals in Lake Shihwa sediments was investigated to determine sedimentary pyrite-heavy metal associations influenced by various metal fractions, organic carbon, and total reduced sulfur. Parameters indicating the degree of heavy metal pyritization (DTMP) and degree of pyritization (DOP) were used to study the incorporation of heavy metals into the pyrite phase. The DOP levels ranged from 3.28–39.45%, showing wide differences among sampling stations. The levels were greater near the water gate and the center of the lake than near the industrial complex. The spatial pattern of the DOP levels was similar to the S/C ratio and also to the salinity. Based on the measured relationships between DOP and DTMP, heavy metals can be divided into three groups. In the first group was As, which showed a high affinity for pyrite. In the second group were Ni, Co and Cu, which showed a gradual increase in DTMP with increasing DOP. In the final group were Pb, Zn, Mn and Cr, which all showed a low DTMP with constant values with respect to DOP.

INTRODUCTION

The man-made Shihwa lake was constructed for the purpose of supplying freshwater to the farm land, industrial complex and residential areas, and was developed by the Development Project of the Shihwa Area in Ansan. It is located on the western coast of Korea. With the construction of a seawall, the Lake was formed in January, 1994, when there was still a normal coastal environment. However, since the construction, the lake has become rapidly polluted by the input of non-treated industrial and municipal wastewaters.

In marine environments, pyrite formation results from the reaction of H_2S and from bacterial sulfate reduction with reactive detrital iron minerals (Berner, 1984). This procedure is one of the pathways for removing sulfate from oceans into sediments and is controlled by the amount of organic matter, reactive iron minerals, and dissolved sulfate (Berner, 1984; Vairavamurthy *et al.*, 1995). The degree of pyritization (DOP) is represented by

$$DOP(\%) = \frac{pyriteFe}{reactiveFe+pyriteFe}\times 100$$

where pyriteFe and reactiveFe represent the Fe concentrations of pyrite and reactive fractions, respectively (Berner, 1970). Since DOP is different for each depositional environment, the DOP level has been proposed as an indicator of depositional environments (Raiswell *et al.*, 1988; Donelly *et al.*, 1988; Raiswell and Al-Biatty, 1989; Calvert and Karlin, 1991; Middelburg, 1991). Also, the S/C ratio has been used as a diagnostic criterion for recognizing anoxic environments and an S/C ratio of 0.36 is generally accepted as the level that characterizes normal oxygenated sediments (Calvert and Karlin, 1991).

Heavy metals commonly undergo chemical diagenesis in anoxic sediments by association with metal oxides, organic matter, and other reactive components to coprecipitate with pyrite (Huerta-Diaz and Morse, 1990). Thus, pyrite can be an important sink for heavy metals and reduced sulfur (Boulegue *et al.*, 1982; Huerta-Diaz and Morse, 1990). In order to understand the incorporation of heavy metals into the pyrite phase, Huerta-Diaz and Morse (1990) introduced a term, the degree of trace metal pyritization (DTMP), defined by

$$DTMP(\%) = \frac{pyriteMetal}{reactiveMetal+pyriteMetal}\times 100$$

where pyriteMetal and reactiveMetal represent the concentrations of pyrite and reactive metal fractions, respectively. The relationship between DOP and DTMP can

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be regarded as a measure of the degree to which heavy metals have been incorporated into the pyrite phase with pyritization of Fe. The chemical behavior of heavy metals is strongly influenced by interaction with authigenic iron-sulfide minerals in anoxic marine environments (Huerta-Diaz and Morse, 1990). Lake Shihwa, an anoxic lake, is a suitable site for the study of the pyritization of heavy metals. Therefore, the objectives of this study are 1) to study the behavior of heavy metals with pyritization, 2) to interprete the DOP and S/C ratio as indicators of depositional environments.

MATERIALS AND METHODS

Surface sediments were collected with van Veen grab in June, 1997 (Fig. 1), packaged into zipper-bags and stored in a refrigerator. These samples were later freeze-dried, ground and stored at room temperature.

Heavy metals (Cr, Mn, Co, Ni, Zn, Cu, As, Pb and Fe) in the freeze-dried samples were sequentially extracted according to the procedure described by Huerta-Diaz and Morse (1990). This method is designed to extract sequentially three fractions: reactive fraction (1M HCl), silicate fraction (10M HF), and pyrite fraction (concentrated HNO_3). Since heavy metals associated with the silicate fraction can be considered essentially non-reactive towards pyrite formation (Huerta-Diaz and Morse, 1992), this fraction will not be discussed here. The total concentrations of heavy metals were obtained by summing the concentrations of the three fractions.

The concentrations of heavy metals were determined by ICP-MS(VG PQ II$^+$) or flame atomic absorption spectrophotometry (Perkin Elmer Analyst 300). Organic carbon and total reduced sulfur concentrations were determined by a carbon and sulfur analyzer (LECO-SC 444) after elimination of inorganic carbon with 10% HCl and no treatment with HCl, respectively.

RESULTS AND DISCUSSION

The DOP Levels and S/C ratio

As shown Fig. 2, stratification in the water column was formed by the density difference from spring to fall in 1997(KORDI, 1998). Dissolved oxygen was reduced, whereas H_2S increased rapidly at the 3 to 3.5 m depth.

The results for sediment samples extracted by a series of extractions are shown in Table 1. The DOP levels ranged from 3.28–39.45%, showing wide differences among the sampling stations. The DOP levels near the water gate and the center of lake were greater than near the industrial complex (Fig. 3). It was reported that normal marine sediments have DOP<42% and semi-euxinic and euxinic sediments have DOP values of 46–80% and 55–93%, respectively (Raiswell *et al.*, 1988).

Therefore, the Shihwa lake sediment results were within the range of normal marine sediments. The DOP levels from the Baltic Sea and Black Sea were 33–69% and 46–85%, respectively (Bosen and Postma,

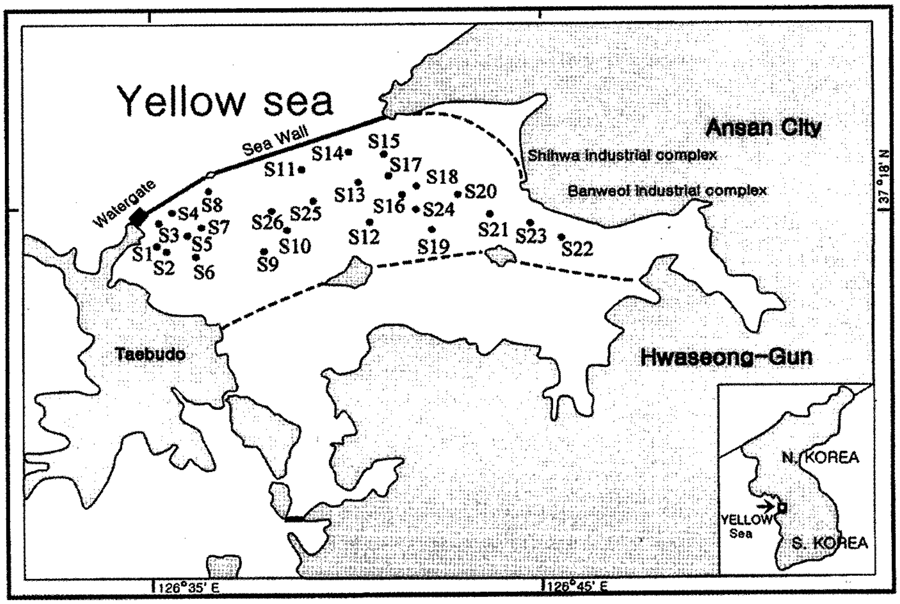

Fig. 1. Sampling stations in Lake Shihwa.

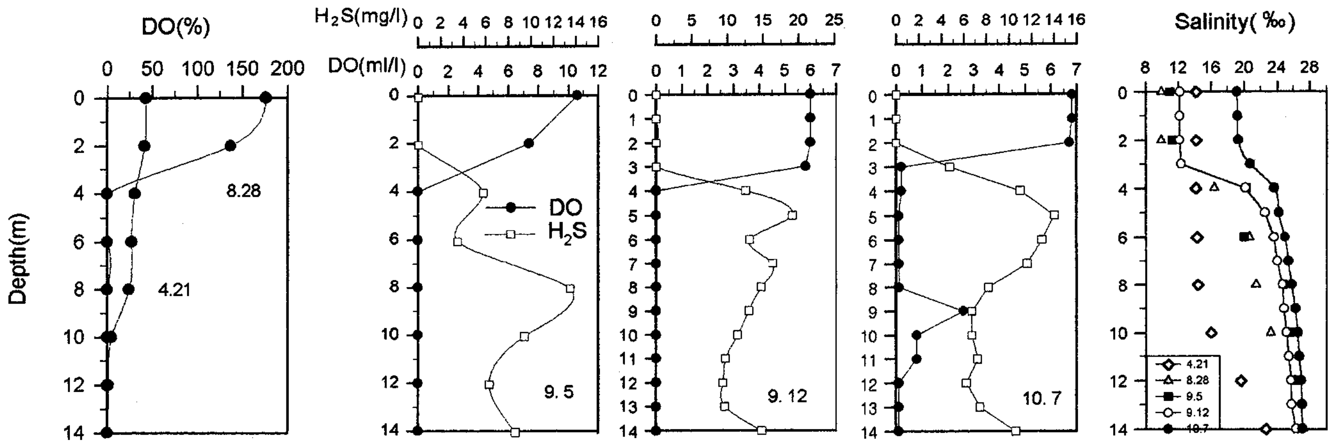

Fig. 2. Water column depth profiles of DO, H_2S and salinity at st. 13 nearby st. s8, replotted from the data of KORDI, 1998.

Table 1. The concentrations, DOP and DTMP of trace metals in surface sediments.

(heavy metal concentrations: ppm, DOP/DTMP: %)

St.	Fraction	Fe(%)	Cr	Mn	Co	Ni	Zn	Cu	As	Pb
S1	Reactive	0.31	3.6	389	2.61	5.39	19.7	3.79	0.77	5.38
	Pyrite	0.04	13.1	2.8	0.19	4.28	0.43	0.91	0.25	0.18
	Total	1.58	36.4	522	5.90	16.98	49.5	10.11	3.53	13.81
	DOP/DTMP	11.85	78.2	0.72	6.91	44.26	2.14	19.35	24.32	3.28
S2	Reactive	0.49	6.54	95.7	3.31	6.06	32.1	9.75	0.62	8.14
	Pyrite	0.12	–	3.68	0.48	0.56	0.96	3.10	1.25	0.54
	Total	1.64	33.37	208.9	8.01	17.9	66.5	18.81	3.07	15.21
	DOP/DTMP	19.54	0.00	3.70	12.59	8.52	2.91	24.13	66.67	6.23
S3	Reactive	0.77	8.93	181	4.30	7.32	37.8	13.2	0.97	15.1
	Pyrite	0.18	0.09	5.00	0.63	0.84	1.41	3.94	2.10	0.34
	Total	3.01	45.44	343	10.34	24.21	88.2	27.4	6.85	22.3
	DOP/DTMP	18.86	0.96	2.68	12.77	10.25	3.60	23.0	68.43	2.23
S4	Reactive	0.92	10.82	164	4.64	7.01	41.9	16.3	1.26	14.3
	Pyrite	0.08	0.02	0.94	0.49	0.37	0.88	4.03	1.43	0.38
	Total	3.55	47.46	334	10.31	23.97	93.8	32.1	6.92	24.9
	DOP/DTMP	8.09	0.17	0.57	9.50	5.05	2.05	19.9	53.16	2.60
S5	Reactive	0.69	11.4	162	5.24	13.7	71.9	32.4	1.30	16.9
	Pyrite	0.07	0.17	1.37	0.40	0.67	1.51	8.33	1.27	0.33
	Total	2.39	45.6	302	10.67	29.3	117.8	50.8	5.98	25.4
	DOP/DTMP	8.61	1.49	0.84	7.07	4.66	2.06	20.5	49.46	1.93
S6	Reactive	0.42	3.94	248	2.78	5.23	21.7	5.62	0.81	6.04
	Pyrite	0.02	–	0.60	0.16	0.14	0.53	1.50	0.52	0.24
	Total	1.40	24.00	349	6.16	13.45	50.2	11.68	3.06	11.78
	DOP/DTMP	4.33	0.00	0.21	5.43	2.52	2.39	21.1	39.06	3.90
S7	Reactive	0.58	8.43	165	4.34	9.52	47.6	19.7	0.79	12.0
	Pyrite	0.09	–	0.18	0.42	0.54	2.63	4.73	1.85	0.49
	Total	2.58	40.87	340	9.69	22.98	96.8	34.1	5.72	21.3
	DOP/DTMP	13.82	0.00	0.11	8.88	5.40	5.25	19.4	70.05	3.93
S8	Reactive	1.44	17.4	268	8.76	13.4	68.3	34.5	2.09	26.5
	Pyrite	0.09	0.07	4.57	0.73	0.61	1.29	8.33	1.28	0.25
	Total	5.29	66.1	448	16.26	42.6	141.9	65.8	15.45	35.9
	DOP/DTMP	5.64	0.40	1.67	7.70	4.33	1.86	19.5	38.05	0.95

Table 1. continued

St.	Fraction	Fe(%)	Cr	Mn	Co	Ni	Zn	Cu	As	Pb
S8	Reactive	1.44	17.4	268	8.76	13.4	68.3	34.5	2.09	26.5
	Pyrite	0.09	0.07	4.57	0.73	0.61	1.29	8.33	1.28	0.25
	Total	5.29	66.1	448	16.26	42.6	141.9	65.8	15.45	35.9
	DOP/DTMP	5.64	0.40	1.67	7.70	4.33	1.86	19.5	38.05	0.95
S9	Reactive	0.59	8.26	168	4.21	7.59	34.0	12.2	0.94	14.1
	Pyrite	0.02	–	0.33	0.20	0.08	0.41	1.47	0.48	0.38
	Total	1.71	29.70	339	7.86	15.71	70.2	19.9	2.94	20.2
	DOP/DTMP	3.28	0.00	0.20	4.50	1.02	1.19	10.8	33.69	2.66
S10	Reactive	0.33	4.71	360	2.92	6.91	25.7	7.02	0.77	6.02
	Pyrite	0.22	–	9.93	0.57	0.57	1.45	4.73	2.71	0.29
	Total	2.36	46.57	566	10.06	25.83	88.6	23.63	8.11	14.40
	DOP/DTMP	39.45	0.00	2.68	16.2	7.62	5.33	40.2	77.9	4.61
S11	Reactive	0.94	14.6	270	6.49	12.1	72.1	33.7	1.25	23.4
	Pyrite	0.14	0.18	6.78	0.56	0.75	1.73	8.60	2.04	0.36
	Total	3.88	60.9	455	14.11	33.3	136.9	56.2	8.18	31.6
	DOP/DTMP	13.0	1.24	2.45	7.94	5.82	2.35	20.4	61.90	1.53
S12	Reactive	0.55	8.71	285	4.32	9.42	49.2	20.3	0.87	11.8
	Pyrite	0.06	–	1.17	0.33	0.37	0.83	3.80	0.98	0.22
	Total	2.77	39.34	456	9.06	21.80	93.7	33.2	5.23	20.9
	DOP/DTMP	9.39	0.00	0.41	7.14	3.80	1.67	15.8	52.97	1.81
S13	Reactive	0.93	19.2	237	6.01	11.6	63.9	38.4	1.36	23.2
	Pyrite	0.21	0.30	14.1	0.73	0.97	1.58	8.61	2.78	0.31
	Total	4.44	71.6	446	15.09	37.0	141.5	63.8	9.27	29.7
	DOP/DTMP	18.64	1.56	5.61	10.80	7.76	2.42	18.3	67.13	1.30
S14	Reactive	0.61	12.1	359	4.49	9.74	56.6	36.3	0.97	14.4
	Pyrite	0.05	–	1.13	0.25	0.25	0.76	4.59	0.88	0.20
	Total	2.52	47.4	549	9.97	24.48	113.6	54.0	4.88	22.9
	DOP/DTMP	7.29	0.0	0.31	5.22	2.55	1.33	11.2	47.70	1.36
S15	Reactive	0.46	5.33	172	2.63	4.63	23.8	6.96	0.89	6.51
	Pyrite	0.02	–	–	0.14	–	0.31	1.24	0.42	0.20
	Total	1.43	25.03	295	5.94	12.79	53.5	13.40	2.77	11.95
	DOP/DTMP	3.56	0.00	0	4.94	0.00	1.26	15.09	32.16	2.96
S16	Reactive	0.61	11.1	167	4.27	9.40	61.1	29.5	1.13	15.4
	Pyrite	0.08	0.06	0.93	0.44	0.65	1.10	6.92	1.31	0.28
	Total	2.36	46.0	314	9.89	24.95	108.7	46.4	5.52	22.5
	DOP/DTMP	11.47	0.52	0.55	9.36	6.48	1.78	19.0	53.69	1.81
S17	Reactive	0.96	25.9	182	5.96	18.1	121	74.9	1.93	27.3
	Pyrite	0.13	1.12	4.88	0.43	1.11	3.10	23.6	2.19	0.38
	Total	3.04	76.9	352	13.70	41.1	192	117.1	7.86	33.8
	DOP/DTMP	11.85	4.15	2.61	6.70	5.78	2.49	23.9	53.19	1.38
S18	Reactive	0.29	4.29	197	2.08	4.34	30.0	12.3	0.46	5.78
	Pyrite	0.01	–	–	0.18	0.09	0.42	2.19	0.44	0.30
	Total	1.62	26.78	357	5.32	12.73	63.3	20.7	2.92	12.03
	DOP/DTMP	4.29	0.00	0	7.82	1.99	1.37	15.1	48.69	4.99
S19	Reactive	0.41	5.35	251	2.85	4.68	23.7	6.06	0.65	7.60
	Pyrite	0.05	8.94	2.09	0.43	5.28	0.78	1.51	0.88	0.26
	Total	2.17	55.84	424	7.60	30.68	66.3	15.06	3.83	15.85
	DOP/DTMP	10.48	62.6	0.83	13.0	53.0	3.20	19.9	57.48	3.35

Table 1. continued

St.	Fraction	Fe(%)	Cr	Mn	Co	Ni	Zn	Cu	As	Pb
S20	Reactive	0.34	5.95	823	2.80	5.73	40.1	11.7	0.90	7.49
	Pyrite	0.01	–	0.31	0.15	0.01	0.41	1.90	0.35	0.20
	Total	1.90	30.65	987	6.37	14.38	75.4	20.2	26.45	15.27
	DOP/DTMP	3.41	0.00	0.04	5.11	0.11	0.99	14.0	28.13	2.61
S21	Reactive	0.54	14.2	338	3.88	10.7	92.2	46.3	0.87	17.1
	Pyrite	0.03	–	1.07	0.17	0.27	0.64	5.26	0.63	0.27
	Total	1.89	44.8	492	8.30	22.2	133.9	60.8	3.54	23.9
	DOP/DTMP	5.59	0.0	0.32	4.20	2.46	0.69	10.2	41.90	1.55
S22	Reactive	0.98	26.0	206	6.06	14.3	118	61.9	1.21	29.8
	Pyrite	0.08	0.45	2.78	0.40	0.79	1.47	6.24	1.02	0.26
	Total	3.86	80.5	394	14.23	38.2	193	84.8	8.88	36.6
	DOP/DTMP	7.20	1.70	1.33	6.19	5.24	1.23	9.16	45.86	0.86
S23	Reactive	1.14	53.8	375	7.33	26.7	239	164	1.26	45.6
	Pyrite	0.09	1.20	0.34	0.36	1.03	2.37	15.1	1.48	0.37
	Total	4.42	115.7	564	14.95	51.1	317	202	9.19	54.0
	DOP/DTMP	7.09	2.19	0.09	4.64	3.71	0.98	8.44	54.03	0.81
S24	Reactive	0.46	9.16	145	3.76	7.50	41.3	18.7	0.81	8.90
	Pyrite	0.04	–	0.25	0.31	0.28	0.59	3.08	1.02	0.25
	Total	1.64	34.24	274	7.96	18.05	77.0	28.4	4.06	15.77
	DOP/DTMP	8.55	0.00	0.17	7.59	3.61	1.41	14.2	55.53	2.74
S25	Reactive	1.00	22.4	295	8.33	17.2	94.2	46.7	1.55	24.9
	Pyrite	0.15	0.28	12.2	0.49	0.83	1.93	11.4	2.52	0.41
	Total	3.29	72.8	460	16.30	41.4	158.3	71.2	7.65	31.0
	DOP/DTMP	13.34	1.25	3.98	5.59	4.58	2.06	19.6	61.97	1.62
S26	Reactive	0.76	13.5	206	5.97	10.1	50.6	18.6	1.16	18.8
	Pyrite	0.16	3.00	19.6	0.71	2.36	2.00	5.91	3.22	0.31
	Total	3.56	58.9	407	13.18	31.0	114.4	36.2	8.84	27.0
	DOP/DTMP	17.21	18.1	8.69	10.62	19.0	3.80	24.1	73.57	1.63

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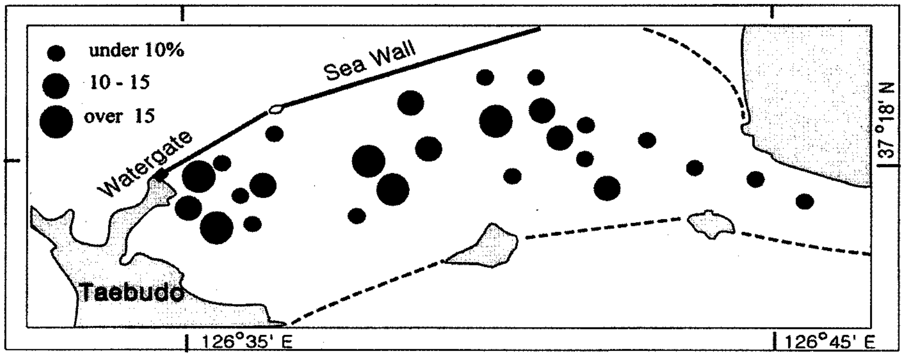


Fig. 3. DOPs in surface sediments.

1988; Calvert and Karlin, 1991). Although the overlying water of Lake Shihwa is anoxic, the DOP levels of this lake are lower than those of other anoxic areas.

The range for the S/C ratio was 0.17–0.88 (Table 2) and the spatial pattern of the S/C ratio was similar to that of DOP, as shown in Fig. 4. The mean S/C ratio was about 0.35, similar to 0.36, the mean ratio of normal marine sediments (Calvert and Karlin, 1991). In normal marine sediments, the relationship between organic carbon and reduced sulfur shows a positive correlation, whereas in freshwater sediments organic carbon shows a nonlinear relationship with reduced sulfur due to the absence of dissolved sul-

Table 2. The concentrations of organic carbon, total reduced sulfur and S/C ratio in surface sediments

(unit: %)

St.	Corg	Stot	S/C
S1	0.18	0.06	0.34
S2	0.40	0.17	0.43
S3	0.55	0.35	0.63
S4	0.47	0.39	0.83
S5	0.94	0.28	0.29
S6	0.23	0.08	0.34
S7	0.70	0.20	0.29
S8	0.95	0.83	0.88
S9	0.31	0.08	0.26
S10	0.70	0.33	0.47
S11	1.18	0.38	0.33
S12	0.59	0.11	0.19
S13	0.91	0.41	0.45
S14	0.49	0.09	0.19
S15	0.21	0.05	0.25
S16	0.73	0.15	0.20
S17	1.31	0.45	0.34
S18	0.22	0.05	0.24
S19	0.28	0.07	0.27
S20	0.32	0.05	0.17
S21	0.61	0.11	0.17
S22	0.91	0.26	0.29
S23	1.65	0.49	0.30
S24	0.37	0.07	0.20
S25	1.24	0.50	0.41
S26	0.88	0.38	0.43

fate. In this study, the total reduced sulfur showed a positive correlation with organic carbon (Fig. 5), whose characteristics were similar to those of normal marine sediments.

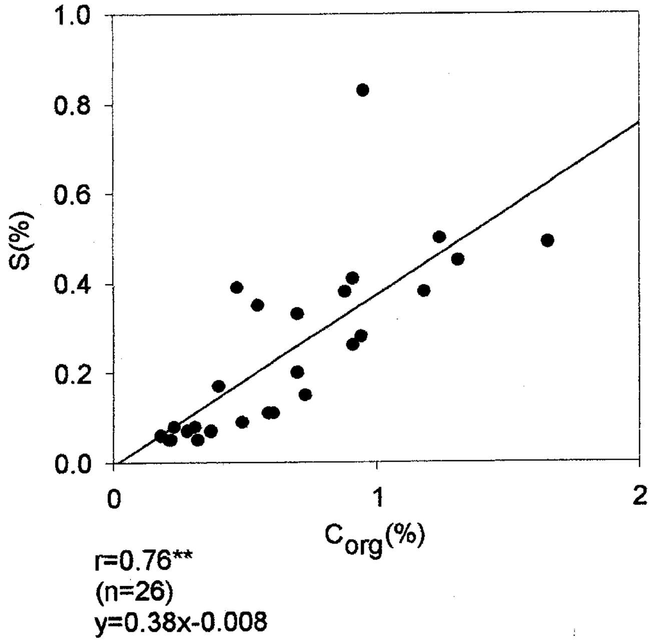


Fig. 5. Correlation between organic carbon and total reduced sulfur. **significant at the 99% level.

Since the influence of seawater near the industrial complex is lower than that near the water gate and the center of the lake, the salinity is low near the industrial complex in comparison to near the water gate and the center of the lake (KORDI, 1998). Therefore, the amount of total reduced sulfur was less near the industrial complex than the center of the lake. According to KORDI (1998), the salinity near the industrial complex is lower than that near the water gate and the center of the lake. This means that the characteristics of the spatial pattern of DOP may be associated with the salinity distribution in Lake Shihwa.

The behavior of heavy metals

Table 1 shows that the concentrations of reactive fractions were higher than those of pyrite fractions for all the analyzed heavy metals except As. Based on relationship between DOP and DTMP, heavy met-

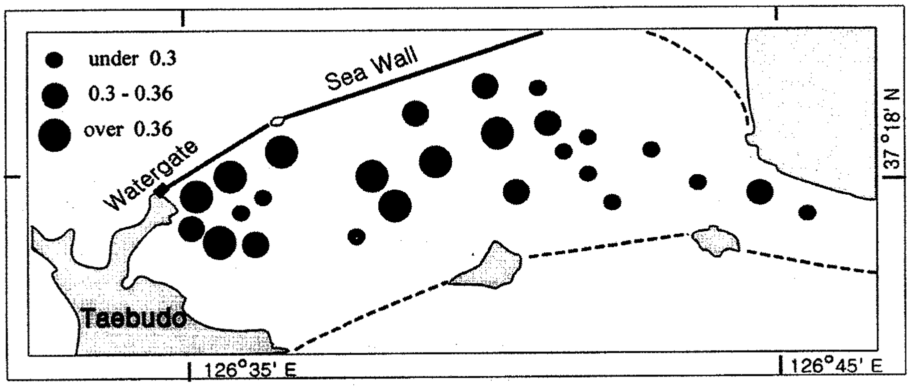


Fig. 4. The S/C ratios in surface sediments.

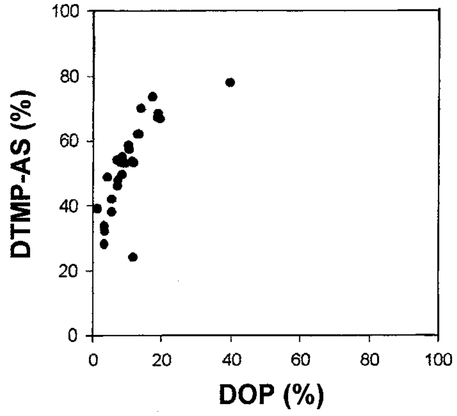


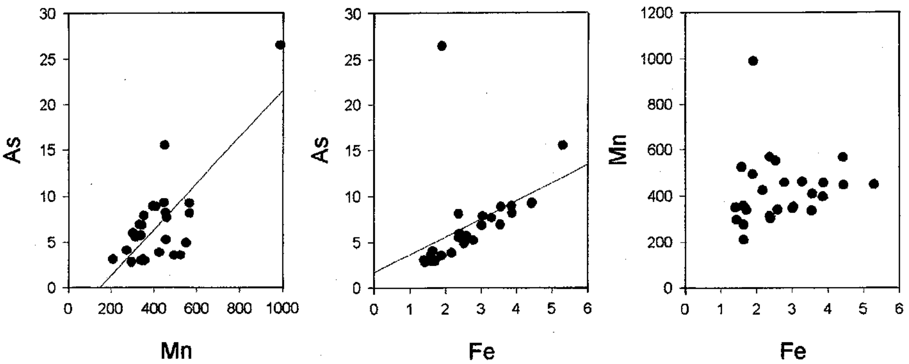
Fig. 6. Relationship between DOP and DTMP-As.

als can be divided into three main groups. The first group is As (Fig. 6). This metal showed high DTMP even at low DOP. This means that As showed complete transfer from the reactive to the pyrite phase and had a high affinity for pyrite (Huerta-Diaz and Morse, 1992). Correlations of the total concentrations of heavy metals versus organic carbons and the mean grain size are shown in Table 3. The total concentrations of heavy metals, except Mn and As, showed a high correlation with organic carbon and the mean grain size. Also, Table 3 shows that DTMP of heavy metals had no correlation with organic carbon and the mean grain size except for DTMP of Mn and As, although the correlation was weak in this case. To study the relationships for Mn, Fe and As in detail, the correlations among these metals are shown in Fig. 7. Arsenic had a positive correlation with Mn and Fe, and the relationship between Fe and Mn showed no correlation. It was reported that the positive correlation is a result of intense scavenging of As in the overlying waters by Mn or Fe-rich sediments, or dissolution of solid phase As at depth followed by upward diffusion and co-precipitation with Mn or Fe oxides at or near the sediment-water interface (Peterson and Carpenter, 1986). Therefore, it is suggested that the high affinity of As for pyrite could be dependent on the geochemical processes of Fe and As.

The second group comprised Ni, Co and Cu (Fig 8). These transition metals showed a gradual increase in DTMP with increasing DOP. Huerta-Diaz and Morse (1992) reported that these metals were approximately equally partitioned between the pyrite and

Table 3. Correlation coefficients(r) among organic carbon, mean grain size, total heavy metal concentrations and the DTMP of trace metals

	Total Cr	Total Mn	Total Co	Total Ni	Total Zn	Total Cu	Total As	Total Pb
Corg	0.88	0.07	0.89	0.91	0.90	0.86	0.27	0.90
Mz	0.78	0.08	0.86	0.81	0.70	0.63	0.27	0.72
	DTMP Cr	DTMP Mn	DTMP Co	DTMP Ni	DTMP Zn	DTMP Cu	DTMP As	DTMP Pb
Corg	−0.27	0.36	−0.08	−0.22	0.05	0.03	0.39	−0.63
Mz	−0.23	0.48	0.13	−0.16	−0.03	0.15	0.38	−0.60



r=0.76**
(n=26)
y=0.025x-3.69

r=0.42*
(n=26)
y=1.94x+1.68

Fig. 7. The correlation between Fe, Mn and As (total concentrations). **significant at the 99% level, *significant at the 95% level

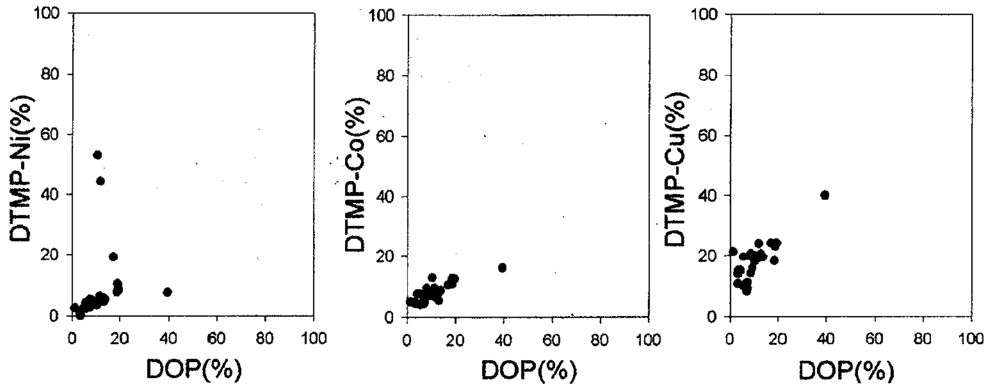


Fig. 8. DTMP plotted against DOP for Ni, Co, and Cu.

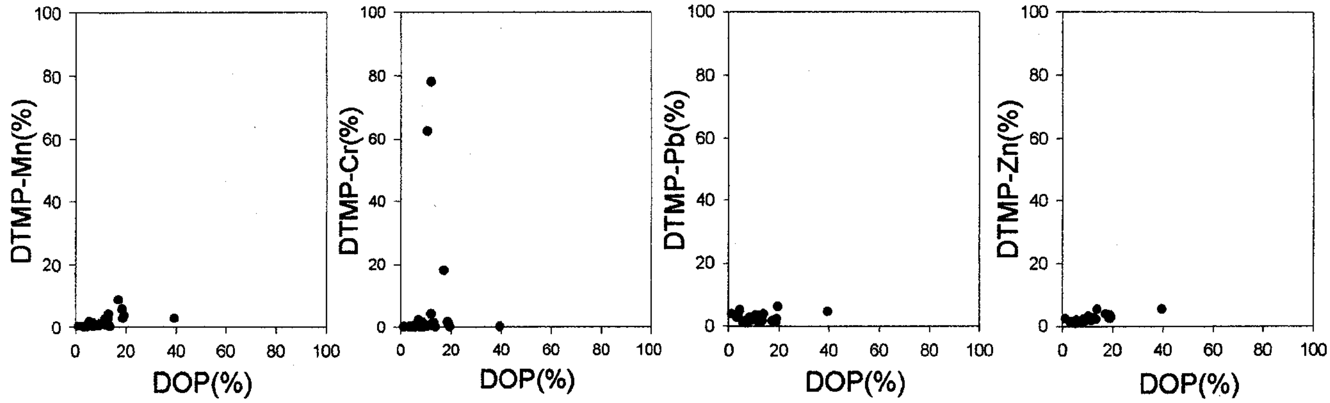


Fig. 9. DTMP plotted against DOP for Mn, Cr, Pb, and Zn.

reactive phases. However, the DTMP of Mn and Cr showed differences from other transition metals.

The final group of metals comprised Pb, Zn, Mn and Cr (Fig 9). These metals showed low DTMP constant with DOP. Class B metals, namely Pb and Zn, are preferentially coordinated with bases containing I, S, or N as donor atoms (Stumm and Morgan, 1981), and ions of Class B metals can form insoluble sulfide with reduced sulfur. However, if the concentration of reduced sulfur is increased, these ions show greater solubility with increasing sulfide concentration owing to strong complexation by reduced sulfide ligands (Emerson *et al.*, 1983). Hence, an increase in reduced sulfur concentration will result in an increased concentration of soluble Pb and Zn sulfide complexes, leaving less of these heavy metals available for solid heavy metal sulfide formation (Huerta-Diaz and Morse, 1992). The Cr behavior might be due to the fact that this metal is rapidly precipitated either with particulates or as $Cr(OH)_3$ and $(Cr, Fe)(OH)_3$ (Curl *et al.*, 1965; Schroeder and Lee, 1975; Lu and Chen, 1977; Eary and Rai, 1989). Thus, insoluble Cr hydroxides compete with pyrite for Cr under anoxic marine conditions (Huerta-Diaz, 1992).

CONCLUSION

The values of DOP and the S/C ratio near the water gate and the center of the lake were greater than those near the industrial complex. The measured values of surface sediments in Lake Shihwa are similar to those of normal marine sediments. Based on the relationship between DOP and DTMP, heavy metals could be divided into three groups. The first group, As, showed high DTMP even at low DOP. It is suggested that As has a high affinity for pyrite. The second group, Ni, Co and Cu, showed a gradual increase in DTMP with increasing DOP. The final group, Pb, Zn, Mn and Cr, showed low DTMP which was constant with DOP. This implies that the relationship between DOP and DTMP can be a useful parameter for studying the incorporation of reactive metals into the pyrite phase. Its importance lies in providing a basis for studying the mechanism of incorporation into heavy metal pyrites.

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REFERENCES

Berner, R.A., 1970. Sedimentary pyrite formation. *Amer. J. Sci.*, **268**: 1 – 23.

Berner, R.A., 1984. Sedimentary pyrite formation: An update. *Geochim. Cosmochim. Acta,* **48**: 605 – 615.

Bosen, C. and D. Postma, 1988. Pyrite formation in anoxic environments of Baltic. *Amer. J. Sci.*, **88**: 575 – 603.

Boulegue, J., G.J. Lord and T.M. Church, 1982. Sulfur speciation and associated trace Metals (Fe, Cu) in the porewaters of Great marsh, Delware. *Geochim. Cosmochim. Acta*, **46**: 453 – 464.

Calvert, S.E. and R.E. Karlin, 1991. Relationships between sulfur, organic carbon, and iron in the modern sediments of the Black Sea. *Geochim. Cosmochim. Acta*, **55**: 2483 – 2490.

Curl, H., M. Cutshall and C. Osterberg, 1965. Uptake of Cr (II) by particulates in sea water. *Nature*, **205**: 275 – 276.

Donelly, T.H., J.H. Shergold and P. N. Southgate, 1988. Pyrite and organic matter in normal marine sediments of middle cambrian age, southern Georgina Basin, Australia. *Geochim. Cosmochim. Acta*, **52**: 259 – 263.

Eary, L.E. and D. Rai, 1989. Kinetics of chromate reduction by ferrous ions. *Amer. J. Sci.*, **289**: 180 – 213.

Emerson, S., L. Jacobs and B. Tebo, 1983. The behavior of trace metals in marine anoxic waters: Solubilities at the oxygen-hydrogen sulfide interface. In trace metals in sea water, edited by Wong, C.S. *et al.*, Plenum Press, pp. 579 – 608.

Huerta-Diaz, M.A. and J.H. Morse, 1990. A quantitative method for determination of trace metal concentrations in sedimentary pyrite. *Mar. Chem.*, **29**: 119 – 144.

Huerta-Diaz, M.A. and J.H. Morse, 1992. Pyritization of trace metals in anoxic marine sediments. *Geochim. Cosmochim. Acta*, **56**: 2681 – 2702.

KORDI (Korea Oceanic Research & Development Institution), 1998. A study on environmental changes in Shihwa lake. Report of KORDI. (in Korean), BSPE 98705-01-34, 363pp.

Lu, C. and K. Chem, 1977. Migration of trace metal in interfaces of seawater and polluted surficial sediments. *Environ. Sci. Technol.*, **11**: 174 – 182.

Middelburg, J.J., 1991. Organic carbon, sulphur, and iron in recent semi-euxinic sediments of Kau Bay, Indonesia. *Geochim. Cosmochim. Acta*, **55**: 815 – 828.

Peterson, M.L. and R. Carpenter, 1986. Arsenic distributions in porewaters and sediments of Puget Sound, Lake Washigton, the Washigton coast and Saanich inlet, B.C. *Geochim. Cosmochim. Acta*, **50**: 353 – 369.

Raiswell, R.F., F. Buckley, R.A. Berner and T.F. Andersen, 1988. Degree of pyritization of iron as a paleoenvironmental indicator of bottom water oxygenation. *Jour. Sed. Petrology*, **53**: 660 – 663.

Schroeder, D.C. and G.F. Lee, 1975. Potential transformations of chromium in natural waters. *Water Air Soil Pollut.*, New York, **4**: 355 – 365.

Stumm, W. and J.J. Morgan, 1981. Aquatic chemistry. 2nd Edition. J. Wiley & Sons, 780 pp.

Vairavamurthy, M.A., W.L. Orr and B. Manowitz, 1995. Geochemical transformations of sedimentary sulfur:an introduction. In geochemical transformations of sedimentary sulfur, ed. by Vairavamurthy M.A. and M.A.A. Schoonen, *Amer. Chem. Soc.*, pp. 1 – 14.

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