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Source and depositional controls on heavy metal distribution in marine sediments of the Gulf of İskenderun, Eastern Mediterranean

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Abstract

The concentrations of major (Al, Mg, Fe, and Mn) and trace (Zn, Cr, Ni, Co, Cu, and Pb) elements as well as carbonate, organic carbon, and grain size distributions have been determined in surface sediments collected at 73 stations from the Gulf of İskenderun.

The shelf sediments of the Gulf of Iskenderun are largely muds but sediments with higher contents of sand and gravel also occur due to the presence of high biogenic $CaCO_3$ contents (up to 80%) in the samples.

The abundance and regional distributions of elements in the surface sediments of the Gulf are largely controlled by differences in grain size and in the level of dilution by skeletal/shell remains, and by the variation in composition of source materials. Mg, Ni, Cr, Co, and to a lesser extent Zn and Pb, are significantly enriched relative to their average crustal abundances. These metal enrichments are found especially in the eastern part along the SW–NEtrending areas of the Gulf and are mostly consistent with the chemical and mineralogical compositions of the major basic and ultrabasic source rocks present on the adjacent coast and hinterland. There is strong evidence that suggest that aluminosilicates, Fe and Mn compounds (possibly oxyhydroxides), and organic matter act as the most effective carriers for transfer of available metals (Zn, Cr, Ni, Co, and Cu) to the sediments.

1. Introduction

The Gulf of İskenderun is situated in the easternmost part of the Mediterranean Sea off southern Turkey (Fig. 1). The Gulf of İskenderun serves as an ideal natural laboratory to study the combined effects of various terrain sources on the sediment chemistry. To the south and east, the Gulf is bordered by narrow coastal plains usually flanked by a high topographic relief with abundant ophiolitic (i.e., basic and ultrabasic rocks) series and associated mineral deposits of Cretaceous to Quaternary age. In contrast, large fluvial plains flanked by Neogene calcareous rocks (mainly Miocene limestones and marls poor in heavy metals) occur in the north and west of the Gulf.

The very limited knowledge on marine sediment geochemistry of the Gulf of İskenderun (Ergin et al., 1988; Kapur et al., 1989) prompted the present study with as main purpose the investiga-

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Fig. 1. Map showing the bathymetry, sampling stations and surrounding-land geology of the study area, Gulf of İskenderun. Geologi is slightly modified from the Geological Map of Turkey (1989).

tion of the major geochemical characteristics of bottom sediments in respect to the geological specifics of the surrounding land. Particular emphasis here is placed on the dispersal and provenance of major (Al, Mg, Fe, Mn) and minor (Zn, Cr, Ni, Co, Cu, and Pb) elements, as well as grain size, organic carbon content, and carbonate distribution in the sediment. The results presented here show that the elemental distribution in marine sediments can be used as guidance in finding the source rocks, providing a useful tool for geochemical exploration of mineral deposits.

2. Geology, hydrography and potential sources of heavy metals to the Gulf of İskenderun

The geological evolution of the Gulf of Iskenderun is related to Neogene convergence and strike-slip displacements along the East Anatolian and Dead Sea Fault complexes (e.g., Şengör et al., 1985; Kelling et al., 1987). During the Plio-Quaternary period, this orogenic depocentre was filled with very thick sedimentary sequences from the prograding deltas (Tolun and Pamir, 1975).

The important geological formations (Fig. 1) outcropping in the coastal hinterland of the gulf have already been reported in Aslaner (1973) and Tolun and Pamir (1975). Of these formations, the Cretaceous ophiolitic succession (up to 3000 m thick) represented by various basic (mainly gabbro, amphibolite, diabase and basalt) and ultrabasic (mainly dunite, harzburgite, and serpentinite) rocks comprises a potentially important source of some heavy metals (i.e., Cr and Ni).

The Ceyhan River is the main supplier of siliciclastic sediments into the Gulf and has built a prominent delta complex with a large fluvial coastal plain, exhibiting several typical lagoons, marshes, abandoned channels, delta mouths, etc (Bal and Demirkol, 1987). Other rivers and streams entering the gulf are ephemeral and are found on the eastern and southern hinterland. These regions are characterized by narrow coastal plains (i.e., Fig. 1) usually flanked by high topography.

The general circulation current pattern in the Gulf of İskenderun is largely affected by the northwesterly flowing open-sea waters and local winds (Fig. 2; Iyiduvar, 1986). During the summer months, branches of open-sea waters enter in the gulf from the northwest and forms clockwise and anticlockwise gyres (Fig. 2). During this period, as a result of radiative heating of the surface, the water column is strongly stratified. During the winter, open-sea waters enter into the gulf from the south-southwest and move towards the inner gulf along the coast (Fig. 2). Due to northerly and northeasterly winds in winter, the water in the gulf becomes cooler and wind-induced mixing intensifies resulting in a homogenous vertical structure in the water column.

3. Material and methods

Seventy-three surface (5-6 cm of the top layer)sediment samples were taken during the 1988–1991 cruises of R.V. Bilim and R.V. Cubuklu in the Gulf of Iskenderun, in water depths ranging from 15 to 190 m (Fig. 1; Table 1). Samples were collected using a Dietz Lafonde grab and the bulk material was immediately placed in plastic bags and frozen onboard ship up until return to the laboratory. In the laboratory, sediment samples were oven-dried at 60°C and representative portions of the samples were separated for grain size analyses. Standard sieve and pipette analysis techniques (Folk, 1980) were used to determine the clay (< 0.002 mm), silt (0.002-0.063 mm), sand (0.063-2 mm), and gravel (>2 mm diameter) fractions of the sediments. The term "mud" used here defines a sediment mixture composed of the varying proportions of silt and clay, with neither sand nor gravel. The main lithogenic and biogenic components of the sedi-



Fig. 2. Surface circulation patterns (A. summer; B. winter) in the Gulf of İskenderun (after Iyiduvar, 1986).

Table 1													
Locations	of the	studied	surface	sediments	and	their	textures	obtained	in tl	he G	ulf of	f İskenc	lerun

Station	Long.	Lat.	Depth (m)	Gravel (%)	Sand (%)	Silt (%)	Clay(%)	Mud (%)	Texture
1	35.20	36.27	38	1	10	69	20	89	(g)M
2	35.23	36.15	190		1	52	47	99	Μ
3	35.31	36.20	117	1	2	55	42	97	(g)M
4	35.36	36.14	137	1	57	23	19	42	(g)sM
5	35.43	36.21	76	2	20	46	32	78	(g)sM
6	35.39	36.25	86		1	51	48	99	Μ
7	35.33	36.29	64		1	61	38	99	Μ
8	35.39	36.34	41		1	72	27	99	Z
9	35.42	36.32	78	1	1	53	45	98	(g)M
10	35.46	36.29	83	1	1	63	35	98	(g)M
11	35.50	36.26	65	12	13	37	38	75	gM
12	35.57	36.31	50	36	20	28	16	44	mG
13	35.53	36.35	76	1	2	45	52	97	(g)M
14	35.50	36.38	71		1	47	52	99	Μ
15	35.47	36.41	55		1	57	42	99	Μ
16	35.53	36.45	49		1	55	44	99	Μ
17	35.56	36.42	58	3	53	20	24	44	(g)mS
18	35.59	36.38	7	1	1	45	53	98	(g)M
19	36.03	36.35	58	1	1	59	39	98	(g)M
20	36.09	36.37	44		2	64	33	97	Μ
21	36.09	36.40	55	1	1	51	47	98	(g)M
22	36.06	36.43	55	1	6	55	38	92	(g)M
23	36.03	36.47	53	33	37	14	16	30	msG
24	36.00	36.50	45		1	56	43	99	М
25	36.02	36.49	51	1	1	63	35	98	(g)M
26	35.55	36.47	48	1	1	60	38	98	(g)M
27	35.52	36.47	28	1	12	65	22	87	(g)sM
28	35.58	36.46	56	1	2	74	23	97	(g)M
29	36.04	36.39	68	1	1	49	49	98	(g)M
30	35.58	36.29	25	3	55	34	8	42	(g)mS
31	35.56	36.51	61	6	46	33	15	48	gM
32	35.43	36.39	56		1	62	37	99	M
33	35.47	36.34	76		1	55	44	99	Μ
34	35.45	36.26	83	1	1	51	47	98	(g)M
35	35.48	36.23	57	5	29	48	18	66	(g)sM
36	35.38	36.20	96	1	4	57	38	95	(g)M
37	35.32	36.25	88	1	1	54	44	98	(g)M
38	35.29	36.32	16	1	48	47	4	51	(g)sM
39	35.23	36.30	19	1	24	70	5	75	(g)sM
40	35.26	36.25	90	7	5	52	36	88	gM
41	35.27	36.20	115		1	55	44	98	M
47	35.47	36.43	45		1	64	35	99	М
43	35.41	36 37	46		1	51	48	99	Μ
44	35.46	36.31	77		1	55	44	99	Μ
45	35.53	36.36	77	1	1	47	51	98	(g)M
46	35.52	36.46	35	-	1	65	34	99	M
47	35.52	36.26	35	31	43	17	9	26	msG
48	36.08	36 48	18	36	33	24	7	30	msG
49	36 10	36 38	58	1	1	52	47	99	(g)M
50	35.58	36.50	44	-	1	58	41	99	M
51	35.58	36.40	65	4	14	31	51	82	(g)sM
52	35.40	36.21	80	1	1	41	57	98	(g)M
53	35 37	36 30	71		1	56	43	99	M

Station	Long.	Lat.	Depth (m)	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Mud (%)	Texture
54	35.45	36.22	80	2	4	57	37	94	(g)M
55	35.58	36.31	38	12	31	39	18	57	gM
56	36.01	36.53	18	2	16	68	14	82	(g)sM
57	35.42	36.25	80	1	14	47	38	85	(g)sM
58	36.11	36.36	20	1	11	65	23	88	(g)sM
59	35.53	36.28	65	2	10	48	40	88	(g)sM
60	35.24	36.30	25	1	17	64	18	82	(g)sM
61	35.48	36.38	65	1	1	50	48	98	(g)M
62	35.34	36.33	15		11	69	20	89	sZ
63	36.00	36.42	70	1	80	10	10	20	(g)mS
64	35.29	36.21	94	1	2	54	43	97	(g)M
65	35.34	36.31	38		1	60	39	99	M
66	35.44	36.40	51		1	61	38	99	Μ
67	35.52	36.44	44		1	53	46	99	Μ
68	35.58	36.41	59	1	12	36	51	87	(g)sM
69	36.00	36.52	17	1	2	71	27	98	(g)M
70	36.09	36.47	22	12	29	41	18	59	gМ
71	36.08	36.38	54		1	52	47	99	M
72	35.50	36.26	69	1	4	49	46	95	(g)M
73	36.05	36.45	51	1	3	54	42	96	(g)M

M = mud; Z = silt; (g)M = slightly gravelly mud; msg = muddy sandy gravel; (g)sm: slightly gravelly sandy mud; (g) ms = slightly gravelly muddy sand; mG = muddy gravel.

ment samples were identified by standard microscopic examination techniques. A representative split of each bulk (whole) sediment sample was ground for chemical analyses to a fine powder using an agate mortar. Total carbonate contents were determined volumetrically in a modified Scheibler-apparatus through the release of CO_2 and the results are expressed as %CaCO₃. Total organic carbon contents were determined using the wet-combustion method of Gaudette et al. (1974). The analytical absolute precision for total carbonate and total organic carbon determinations were, $\pm 0.5\%$ and $\pm 0.2\%$ respectively. Total concentrations of Al, Mg, Fe, Mn, Ni, Zn, Cr, Co, Cu, and Pb were measured by flame atomic absorption spectrometer (Varian Techtron AA6 Model) after complete digestion of 0.3 g of the dry and ground bulk samples in a HF-HNO₃-HClO₄ mixture. Final solutions were made up in 1 M HCl acid. In the case of Al and Mg, an acetylene/nitrous oxide flame was used while other metals were analyzed using an acetylene/air flame. The accuracy of the analytical method was tested against standard material CRM 142 (light sandy soil from the

Community Bureau of Reference Materials BCR, Brussels) and the results were satisfactory (0.1-5.0% from the accepted values), except for Co (<%15) and Al (<%19). The analytical relative precision of triplicate analysis were; $\pm 2.8\%$ for Al, and for Mg $(\pm 14.5\%)$, Fe $(\pm 7\%)$, Mn $(\pm 1.1\%)$, Ni $(\pm 3\%)$, Cr $(\pm 2.5\%)$, Zn $(\pm 1\%)$, Co (+14%), Cu (+4%), and for Pb (+9%). The logtransformed correlation coefficients were calculated using a QPRO-Advanced Math Program. Correlation matrix has been used to clarify the relationships between the distribution of the elements and the textural and chemical characteristics of the sediments in the different parts of the gulf. The correlations in this study are considered statistically significant (r > 0.29; n = 73) at greater than the 99% confidence level (Student's t test; P < 0.01).

4. Results and discussion

The results obtained from the grain size and chemical analyses are presented in Fig. 3 and Table 1 as well as discussed below.



Fig. 3. Grain size distribution in surface sediments of the Gulf of İskenderun.

4.1. Grain-size, carbonate and organic carbon distribution

The grain-size distribution and related textural classification of the surface sediments in the Gulf of İskenderun are summarized in Table 1 and illustrated in Fig. 3. As shown, fine-grained sediments referred to as muds, with varying clay (4-71%) and silt (2-74%) fractions, dominate (up to 99% of the bulk sediment) in most parts of the Gulf (Fig. 3; Table 1). Low mud contents (30-75%) are present in patches off the southern, eastern and northwestern coasts where coarser-

grained sediments contained higher sand (5-80%)and gravel (12-36%; Table 1; Fig. 3) components due to the presence of benthic organisms. Otherwise, at most stations, sand and gravel fractions in the sediments constituted no more than 2% of the bulk sediment (Fig. 3).

Total carbonate content (expressed as % $CaCO_3$) in surface sediment of the Gulf of Iskenderun varies between 19-80% (Table 2; Fig. 4). The majority of sediment samples contain 20-25% $CaCO_3$ (Table 2). The carbonate contents, on the whole, show inverse correlation with the fine-grained (i.e., mud) sediment fractions

Table 2 Chemical analysis of surface sediments in the Gulf of İskenderun

Station	Fe (%)	Mn (ppm)	Ni (ppm)	Zn (ppm)	Cr (ppm)	Co (ppm)	Cu (ppm)	Pb (ppm)	Mg (%)	Al (%)	CaCO ₃ (%)	C _{org} (%)
1	3.94	609	316	75	156	68	20	28	3.4	4.5	27.6	0.43
2	4.42	663	283	87	174	6	26	22	3.5	4.9	28.8	0.59
3	4.38	591	279	77	170	67	26	50	3.6	4.7	30.7	0.61
4	3.20	404	179	52	107	36	15	28	2.7	2.4	59.5	0.40
5	3.59	498	571	67	241	52	19	33	5.4	4.0	41.4	0.49
6	4.29	613	354	97	196	21	26	33	3.9	5.4	28.4	0.56
7	4.56	648	333	104	170	31	32	17	3.5	5.9	23.6	0.75
8	4.51	613	338	92	182	6	30	22	3.4	5.6	24.1	0.65
9	4.47	661	337	96	179	6	26	28	3.8	5.6	23.6	0.73
10	4.42	634	404	97	189	57	29	39	4.2	5.2	24.5	0.65
11	3.28	463	446	59	207	36	17	17	4.5	3.1	40.2	0.59
12	3.85	637	271	82	200	36	26	44	3.5	2.2	26.7	0.57
13	4.56	648	450	90	237	16	28	22	5.1	5.0	24.1	0.67
14	4.60	650	425	103	211	6	30	22	4.6	5.1	23.3	0.59
15	4.60	665	367	93	204	63	30	38	4.4	5.4	21.5	0.68
16	4 47	674	438	97	237	31	30	22	4.9	5.0	22.4	0.69
17	2.98	543	271	61	219	41	17	33	3.9	3.0	34.1	0.33
18	4 60	648	500	99	252	73	24	28	5.1	5.2	23.3	0.68
19	4 25	606	575	82	267	57	20	11	6.2	2.1	25.8	0.63
20	4.91	639	604	89	315	93	28	17	5.9	4.5	20.7	0.76
20	4 56	615	583	96	259	83	24	16	5.7	4.2	21.5	0.78
21	2 67	641	542	81	256	47	20	11	5.7	4.1	30.5	0.61
22	473	661	188	36	82	68	9	16	2.3	1.1	79.6	0.28
22	4.15 A A7	646	624	73	341	83	26	33	6.8	4.3	21.5	0.77
24	4.87	661	625	78	274	84	28	11	6.6	4.5	23.9	0.69
25	4.82	704	517	86	274	67	30	56	54	5.5	21.5	0.75
20	4.02	276	222	20	110	24	14	30	3.6	2.5	59.6	4 45
27	4.96	655	535	83	256	63	24	39 44	5.5	5.0	23.6	0.67
20	4.00	620	503	80	200	00	24	77	5.5	5.0	23.0	0.07
27	4.00	550	742	42	215	57	16	22	79	2.1	23.0	0.00
21	2.05	476	212	42 61	119	57	10	11	/.0	13	56.9	0.47
22	3.20	4/0	202	00	167	26	25	29	2.6	6.0	21.4	0.77
32 22	4.99	670	203 116	00 95	107	27	20	20	3.0	1.0	21.4	0.77
33 24	4.80	617	440	85 87	190	57	30 26	11	4.4	5.0	24.1	0.64
24 25	4.70	407	430 500	02 19	270	12	12	29	4.J	2.0	20.3	0.05
33 26	5.20	407	367	40	174	42 63	15	30 44	3.2	4.5	49.J 34 1	0.4-
20 27	9.69	1120	506	117	604	03	20	- 11 61	5.0	۰.5 ۵.4	24.1	0.52
3/ 20	0.00	602	275	56	200	21	39 17	11	2.0	7.4 1 1	24.5	0.02
38	3.40	602	273	50	105	51 02	17	11	3.3	4.1	23.4	0.52
39	3.33	024 550	292	33 70	105	65 57	14	44	5.0	5.7	29.5	0.59
40	3.72	550	342	70	141	57	22	22	3.5	5.5	34.5	0.04
41	4.38	620	338	70	16/	68	24	38	3.7	5.7	27.6	0.58
42	4.78	65/	408	/8	245	03	29	27	4.6	5.1	22.4	0.68
43	4.86	648	36/	84	219	83	30	28	3.4	5.6	20.7	0.78
44	4.60	. 667	388	79 77	259	/8 72	24	16	4.3	5.4	25.0	0.67
45	4.56	657	407	11	322	15	20	39 22	4.8	4.7	23.0	0.71
46	9.03	570	388	80	203	4/	52	22	4.6	5.2	24.1	0.74
47	1.57	281	296	30 50	/0	51	11	22	4.3	4.0	/1.9	0.52
48	2.58	463	363	50	174	63	12	28	5.5	4.1	41.4	0.44
49	4.73	630	596	78	389	57	26	28	5.6	4.6	22.4	0.66
50	4.42	665	641	60	339	63	22	17	6.I	4.0	20.7	0.79
51	4.03	600	450	74	270	83	22	22	3.0	4.0	34.5	0.65
52	4.60	646	425	80	233	78	24	27	4.0	5.3	25.9	0.64

Table 2 (continued)

Station	Fe (%)	Mn (ppm)	Ni (ppm)	Zn (ppm)	Cr (ppm)	Co (ppm)	Cu (ppm)	Pb (ppm)	Mg (%)	A1 (%)	CaCO ₃ (%)	C _{org} (%)
53	5.04	670	416	85	211	83	33	28	3.8	5.5	18.9	0.83
54	4.42	584	542	69	348	42	20	11	4.8	4.8	31.3	0.69
55	3.02	498	404	51	256	58	15	28	4.8	2.8	50.0	0.54
56	3.77	622	654	57	555	78	15	17	7.6	4.2	25.0	0.57
57	3.99	585	808	65	237	57	22	11	4.1	4.0	32.1	0.59
58	4.34	565	808	115	245	42	26	33	6.2	2.7	19.3	0.63
59	4.16	531	537	64	326	78	20	17	4.9	3.6	35.3	0.60
60	3.55	611	200	60	278	36	15	11	3.3	3.9	34.5	0.53
61	4.82	685	487	82	85	6	24	22	4.6	5.4	23.8	0.63
62	3.94	657	362	60	300	72	18	16	3.3	4.8	23.6	0.58
63	2.54	537	258	40	278	26	9	16	3.8	2.6	35.9	0.33
64	4.25	666	404	76	67	73	21	22	3.8	5.0	31.9	0.59
65	4.64	630	333	82	222	78	24	33	3.3	4.9	24.8	0.79
66	4.69	648	334	82	219	78	28	10	3.6	5.8	21.5	0.63
67	4.42	635	429	71	311	78	22	27	5.0	4.6	22.4	0.59
68	4.07	602	500	65	259	89	22	22	4.9	3.8	30.2	0.60
69	4.16	628	621	64	666	83	22	17	6.3	3.8	20.2	0.82
70	2.58	454	446	48	185	42	13	16	4.3	1.9	53.4	0.66
71	4.69	611	563	73	348	83	26	16	5.8	4.1	22.9	0.70
72	4.29	556	492	66	96	63	17	27	5.4	3.8	31.9	0.50
73	4.25	626	596	64	345	68	20	38	5.6	3.8	28.9	0.58

(r=-0.72; Table 3). A significant and positive correlation is obtained between CaCO₃ and sand (r=0.65) and gravel (r=0.59) contents suggesting the predominance of carbonates in the coarsegrained sediment fractions. Microscopic examinations on sand and gravel fractions revealed that the higher carbonate contents in the sediments appear to have a predominantly biogenic origin, i.e., derived mainly from the calcareous remains of a variety of benthic organisms.

A gradual increase in carbonate content from about 20% in offshore to approximately 70% in nearshore areas is clearly evident particularly along the south-southeastern, eastern, and northeastern areas of the Gulf (Fig. 4). The narrow and carbonate-rich strip along the south-southeastern part of the Gulf tends to broaden towards the west, in the outer Gulf entrance, and follows the distribution of the surface circulation pattern in the Gulf (Fig. 4). On the other hand, higher carbonate content (41–80%) is also found in the eastern northeastern part of the Gulf (Fig. 4) due to both benthic production on the sea floor and to riverine input of Neogene calcareous rocks from the drainage basin.

The total organic carbon contents in the surface sediments of the Gulf of Iskenderun varies between 0.33 and 0.83% (avg. 0.60%; Table 2; Fig. 4). The high Corg contents found in sediments from the central part of the Gulf (0.71-0.83%; Fig. 4) roughly correspond to an area of intensive organic matter accumulation due to the presence of anticyclonic surface currents (Fig. 2). Substantial high concentrations of C_{org} are also observed in patches off the northeastern (0.77-0.82%) and eastern (0.76-0.78%) coasts in the inner Gulf (Fig. 4) where a higher terrestrial and anthropogenic input was expected due to the relative proximity of rivers and existing sewage outfalls. Otherwise, the majority of Corg contents in the sediments varied between 0.58 and 0.68% and are believed to define the primary production pattern in this Gulf. Comparison showed that these values are also typical for the Mediterranean Sea and reflect the marine production of organic matter in this sea (0.57–0.69; Emelyanov and Shimkus, 1986). The



Fig. 4. $CaCO_3$ and C_{org} distributions in surface sediments of the Gulf of İskenderun.

low C_{org} contents (0.28–0.44%; Fig. 4) also reflect variations in the degree of dilution by the coarsegrained biogenic components. This is further indicated by inverse relationships between C_{org} and sand (r = -0.76) and gravel (r = -0.35), as well as, between C_{org} and $CaCO_3$ (r = -0.63) contents (Table 3). The fine-grained (rich in clay) sediments show a reasonably good correlation (r = 0.67) with the C_{org} contents (Fig. 3), due to their large specific surface areas. Therefore, it appears that the distribution of organic carbon in the Gulf of İskenderun sediments is controlled by a complex interplay of hydrodynamic, biogenic, terrestrial, and anthropogenic factors.

4.2. Relative abundances and areal distribution of the elements

The total bulk concentrations of the studied elements Al, Mg, Fe, Mn, Ni, Cr, Zn, Co, Cu, and Pb in the surface sediments of the Gulf of İskenderun are presented in Table 2. In general, low element concentrations coincide with increases in CaCO₃ (predominantly of biogenic origin) contents of the sediments (negative and high "r" values; Table 3). Thus, the coarse-grained carbonate components act as a diluent to most of the measured element concentrations in the sediments. This explains the overall low element concentrations found in the sediments from the southsoutheastern, eastern, northern, and northwestern areas of the Gulf. To compensate for the dilution effect by carbonates, the measured total element concentrations in this study are also calculated on a carbonate-free ("non-biogenic") basis (CFB). In addition; as known, Al has commonly been used as a reference element, not only in order to minimize grain-size effects (Bruland et al., 1974; Pratt and Davis, 1992), but also to determine the primary source rocks and the accompanying soils and deposits in aquatic environments (Herron et al., 1977). Therefore, the possible enrichment relative to Al of other elements in the studied Gulf of İskenderun sediments has also been considered here.

4.2.1. Aluminium

The surface sediments of the Gulf of İskenderun contain from 2.4 to 14.2% Al (on CFB; Fig. 5); however, in most cases, Al ranges from 6-8%(Fig. 5). These values are comparable with the average compositions of crustal rocks (Table 4). The areal distribution pattern of Al shows, with the exception of two values obtained in the two westerly stations (14.2% at st. 47 and 12.5% at st. 37 on CFB), that the Al contents measured along the eastern peripheral areas of the Gulf are found to be generally lower (<6.0% on CFB) than those obtained in the easterly stations (>6.0% on CFB; Fig. 5). This is attributed to the differences in the

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	Gravel	Sand	Silt	Clay	Mud	CaCO ₃	Corg	Fe	Mn	ïŻ	Zn	Ŀ	c	Сц	Pb	Mg	AI
Gravel	1.00																
Sand	0.40	1.00															
Silt	-0.54	-0.62	1.00														
Clay	-0.46	-0.74	0.08	1.00													
Mud	-0.68	-0.93	0.74	0.72	1.00												
CaCO ₃	0.59	0.65	-0.52	-0.54	-0.72	1.00											
C _{ore}	-0.35	-0.76	0.38	0.67	0.71	-0.63	1.00										
Fe	-0.35	-0.56	0.39	0.46	0.58	-0.63	0.49	1.00									
Mn	-0.34	-0.52	0.34	4 .0	0.53	-0.63	0.39	0.72	1.00								
ïZ	-0.27	-0.30	0.17	0.29	0.31	-0.33	0.39	0.21	0.19	1.00							
Zn	-0.42	-0.49	0.46	0.58	0.71	-0.72	0.61	0.62	0.66	0.20	1.00						
Ç	-0.28	-0.22	0.01	0.32	0.21	-0.40	0.29	0.35	0.51	0.60	0.13	1.00					
ථ	-0.05	-0.24	0.07	0.20	0.19	-0.20	0.25	0.23	0.26	0.34	-0.04	0.41	1.00				
Cu	-0.43	-0.71	0.46	0.60	0.73	-0.70	0.71	0.74	0.66	0.16	0.87	0.15	0.06	1.00			
Pb	-0.01	-0.12	0.15	0.01	0.11	-0.08	0.02	0.23	0.24	0.05	0.20	0.04	0.12	0.28	1.00		
Mg	-0.14	-0.16	0.07	0.15	0.15	-0.26	0.28	0.17	0.17	0.83	0.10	0.66	0.30	0.84	0.02	1.00	
AI	-0.38	-0.59	0.46	0.43	0.61	-0.60	0.47	0.58	0.65	0.01	0.61	0.25	0.22	0.66	0.25	- 550.02	1.00

Table 3 Correlation coefficient matrix for the chemical and textural parameters of the surface sediments in the Gulf of Iskenderun. Based on bulk (natural) data. Significant correlations (P < 0.01; r > 0.29; n = 73) at greater than 99% confidence level are shown in bold type



Fig. 5. Al contents (carbonate-free data) of the surface sediments in the Gulf of İskenderun.

lithogenic source areas on the coast and hinterland. For example, the sediments with lower Al contents receive significant input from the ophiolite-associated rocks or their weathering products which are widespread on the eastern coasts and are relatively low in Al. By contrast, the higher Al contents (6–8% on CFB; Fig. 5) generally occur in sediments which have received substantial input from the Holocene alluvial soils through run-off by the Ceyhan River and from the nearby Gölovasi clayey deposits (Kapur et al., 1989). The ophiolitic source rocks which have been drained by the northwesterly Ceyhan River are approximately 100 km away from the mouth of this river.

4.2.2. Magnesium, chromium, nickel, and cobalt

The concentrations of Mg (4.2–15.3% on CFB), Cr (212–919 ppm on CFB), Ni (305–1337 ppm on CFB) and Co (30–150 ppm on CFB; Fig. 6) measured in surface sediments of the Gulf of Iskenderun are noticably high when compared with the relative abundances of these elements in average crustal rocks (Table 4), even given our possible underestimation of Co by 15>. However, the levels of Mg, Cr, Ni, and Co concentrations obtained in this study broadly conform to an intermediate compositions between ultrabasic and basic rocks occurring on the south- to northeastern coasts of the Gulf (Table 4). This is further indicated by noteworthy zonations of the Mg, Cr, Ni, and Co concentration values within the Gulf (Fig. 6). Here, with the exception of two stations, the majority of the concentrations of Mg (5.9–10.3% on CFB), Cr (258–568 ppm on CFB), Ni (370-1190 ppm on CFB) and Co (61-203 ppm on CFB) obtained in sediments from the eastern part of the Gulf was considerably higher than those found in the western part (4.2-6.1% Mg; 212-424 ppm Cr; 305-593 ppm Ni;40-128 ppm Co) of the Gulf (Fig. 6). The enrichment of Mg, Cr, Ni and Co in the eastern part (especially along the SW-NE-trending peripheral areas) of the Gulf is also evident from the presence of higher element to Al ratios (Mg/Al>1; Cr/Al>50; Ni/Al>100; Co/Al > 15; Fig. 6), values comparable to those found in the ultrabasic-basic rocks (Table 4) on the adjacent land. Thus, the overall high Mg, Cr, Ni and Co contents appear to be confined to the eastern peripheral areas of the Gulf where there is important terrigenous input from the basic-ultrabasic rock sources close to the coast. By contrast, the generally lower concentrations of Mg, Cr, Ni and Co obtained in the western part of the Gulf (Fig. 6) rather reflect long distances (approx. 100 km) between the easterly ophiolitic source rocks and westerly marine depositional sites. Nevertheless, the fluvial input (i.e., suspended solids) of the northerly Ceyhan River contained relatively high Cr (275 ppm), Ni (338 ppm) and Co (40 ppm) compared to their crustal abundances (Table 4; Fig. 7).

Regional comparisons showed similar Mg, Cr, Ni and Co enrichments in the surface sediments in other parts of the Mediterranean (Shaw and Bush, 1978; Emelyanov and Shimkus, 1986; Bodur and Ergin, 1988), Aegean (e.g., Ergin et al., 1993), and Black Seas (Yücesoy and Ergin, 1992), as a result of the seaward dispersal of detrital minerals from nearby ultrabasic rocks. Mg, Cr, and Ni are commonly known to be guide elements of most ultrabasic–basic rocks or their ferromagnesian minerals such as olivine, pyroxene, chromite (Rose et al., 1979; Mason and Moore, 1982).

4.2.3. Iron and manganese

Most of the total concentrations of Fe (3.8-7.9%) on CFB) and Mn (700-1104 ppm on CFB) fall in



Fig. 6. Fe, Mn, Co, Mg, Cr, and Ni contents and their ratios to Al in the surface sediments of the Gulf of İskenderun. Note the overall increased Fe, Mn, Co, Mg, Cr, and Ni contents in the eastern part of the Gulf.

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	Al(%)	Mg(%)	Fe(%)	(mqq)nM	Ni(ppm)	Cr(ppm)	Zn(ppm)	Co(ppm)	Cu(ppm)	Pb(ppm)
(1) This study ^a	1.1-9.4	2.3-7.8	1.5-9.0	281-1130	179-808	70-694	30-117	66-9	9–39	1061
This study ^b	2.4-14.2	4.2-15.3	3.8-23.2	700-3240	305-1337	212-919	62-176	8–333	14–52	13-97
This study ^c	5.4-8.1*	4.2-6.1*	4.5-7.9*	751-978*	305-593*	212-424*	73-155*	40 - 177	20-45*	14-81*
This study ^d	$2.2 - 7.0^{+}$	$5.9 - 10.3^{+}$	3.8-7.6+	$700 - 1000^{+}$	370-1190+	258 - 568 +	76 - 178 +	$41 - 130^{+}$	14-44+	14-97 +
(2) Mersin Bay	7.5	3.2	5.3	1103	326	551	107	n.d.	42	n.d.
(3) Eastern Aegean Shelf	n.d.	n.d.	0.5-5.7	103-2625	11-406	9-312	19-162	2-41	3-77	n.d.
(4) Marmara Sea Shelf	n.d.	n.d.	1.7-5.1	307-2059	42-173	89-186	50-169	13–33	14-04	31-306
(5) Golden Horn Estuary	n.d.	n.d.	2.6-3.8	333-565	98-167	242-485	450-8750	17 - 31	333–3900	124-702
(6) Southern Black Sea Shelf	n.d.	n.d.	0.2 - 4.9	112-1064	11-202	13-224	24-138	< 1-20	15-82	12-66
(7) Crustal average	8.1	5.	5.0	950	75	100	70	25	55	13
(8) Shales	8.0	2.1	4.7	850	68	90	90	6	45	20
(9) Ultrabasic rocks	0.4 - 1.6	18.9–23.7	5.0-7.6	700-2600	1700-2900	500-7000	n.a.	75-101	46–62	n.a.
(10) Basic	1.1 - 9.1	2.3-19.3	1.5-8.5	500-4900	200-3200	400 - 3000	n.a.	25-112	39–87	n.a.
(11) Ceyhan River	n.d.	n.d.	3.2-5.9	285-2159	115-1066	124-683	121–318	25–95	4084	2-110

This Study^d (eastern samples); (2) Shaw and Bush (1978); (3) Ergin et al. (1993); (4) Bodur and Ergin (1994); (5) Ergin et al. (1991); (6) Yucesoy and Ergin (1992); Numbers in bold indicate CaCO₃ free values. Sources: (1) This study^a (all samples); This study^b (CaCO₃-free data for all samples); This study^c (western samples); (7) Mason and Moore (1982); (8) Turekian and Wedepohl (1961); (9, 10) Analysis of rocks surrounding the Gulf of Iskenderun (Aslaner, 1973). Values from two stations (*), (⁺) are excluded; (11) Clay sediment, Sevim (1991).

n.a. = not available.

n.d. = not determined.



Fig. 7. Relationships among the Mg, Cr, and Ni contents of the surface sediments of the Gulf of İskenderun.

the range of the average composition of crustal rocks (Table 4). The maximum concentrations of Fe (23.2% on CFB) and Mn (3240 ppm on CFB) are found in the northeastern part of the Gulf (St.23), a region which seems to receive waste materials from the iron and steel works on the nearby coast. This is confirmed by the microscopic studies of the coarse grain fractions of sediment samples. High Fe/Al (270) and Mn/Al (373) ratios found in the central part of the gulf (St. 33; Fig. 6) possibly indicate that intense redox chemistry may occur in these sediments. As shown (Fig. 6), Fe/Al and Mn/Al ratios suggest some zonal peculiarities. For example, Fe/Al and Mn/Al ratios obtained in sediments especially from the southern, eastern, and northeastern peripheries of the Gulf (Fig. 6), are generally greater than 0.96 and 140 (10^{-4}) , respectively. The enrichment of these sediments in Fe and Mn relative to Al must largely be caused by their proximity to the ultrabasic-basic source rocks (Fig. 1) which contain higher Fe (up to 9%) and Mn (up to 4900 ppm; Table 4).

4.2.4. Zinc and lead

The larger part of the total concentrations measurements of Zn (62-176 ppm on CFB) and Pb (13-97 ppm) of the Gulf of İskenderun surface sediments was considerably high when compared to those found in average crustal rocks (Table 4). Furthermore, Zn appears to be enriched relative to Al in sediments from the eastern part of the Gulf where Zn/Al ratios are usually greater than 19 (Fig. 8). Thus, it can be inferred that the ultrabasic-basic source rocks on the eastern coasts of the Gulf seem to play a considerable role in the relative abundance of Zn in the Gulf sediments. Higher Zn contents (121-318 ppm; Table 4) are also known from the fluvial fine sediments of the Ceyhan River (Sevim, 1991), suggesting an influence from the weathering products of ultrabasic-basic source rocks (Fig. 1). Sediment with the highest Zn (143-178 ppm on CFB) content measured in the east-northeastern part of the Gulf (St.23) are most likely due to the contamination effect from the nearby iron and steel complexes.

It is not clear whether the presence of generally higher Pb/Al ratios, especially in the southern part of the Gulf (Fig. 8), can be linked to the presence of ultrabasic-basic rocks or/and associated mineral deposits on the adjacent land, because no data on Pb content of the surrounding major source rocks are available. The other higher Pb contents are measured in sediments from the northeastern part of Gulf, close to the discharge areas of industrial and domestic effluents. The overall high Pb contents (2–110 ppm; Table 4) of fluvial sediments of the Ceyhan River, on the other hand, could be, in part, due to anthropogenic activities.

4.2.5. Copper

The Cu contents of surface sediments in the Gulf of İskenderun varied between 14 and 52 ppm (on CFB), where most sediments in the area contained 30–45 ppm Cu. These values are roughly similar to those found in average crustal rocks



Fig. 8. Zn, Pb, and Cu contents and their ratios to Al in the surface sediments of the Gulf of İskenderun.

(Table 4). The ultrabasic and basic rocks in the surrounding regions, as well as the fluvial sediments of the Ceyhan River (Sevim, 1991) however, contain, on average, notably higher Cu levels (39–87 ppm; Table 4); however, the studied sediments do not show any significant regional trend in the distribution of Cu within the Gulf (Fig. 8).

4.3. Relationships between the geochemical and textural characteristics of the sediments

The general element distribution pattern reflects their close relationship to sediment texture with high concentrations preferentially occurring in fine-grained sediments. For example, the significant increases in the concentrations of Cu, Zn, Fe, and Mn is indicated by decreasing grain-size toward clay or mud (Table 3). This observation is found to be in good agreement with the findings from a number of investigations (e.g., Brannon et al., 1977; Oakley et al., 1981; Cauwet, 1987) that the finer-grained (mainly clay and silt) sediments show relatively high metal content due to the large specific surface area and thus strong adsorptive properties of the fine-sized particles. On the other hand, significant correlation of Al with increasing clay (r=0.43) and silt (r=0.46) or mud (r=0.61;Table 3) content in sediments reflects that aluminosilicates such as clay minerals, micas, feldspars are the main form of Al in these sediments.

The correlation between C_{org} and Cu, Zn, Fe, Al, Mn, and Ni contents (r=0.71-0.39; Table 3) imply either a primary association or a secondary relationship to grain size (i.e., complexation, adsorption on clay minerals) in which the organic carbon content increases with increasing mud content in the sediments (e.g., Stumm and Morgan, 1981; Loring, 1984; Calvert et al., 1985).

4.4. Correlation between the elements

The distribution of Mg, Cr, Ni, Co, Fe, and Mn in the Gulf sediments seem to be generally related to each other (r=0.34-0.83; P>0.99; Table 3; Fig. 7) which attest to a similarity in their geochemical source, i.e., the weathering products from the nearby basic and ultrabasic rocks (Fig. 1). The significant correlation between Mg and Cu (r=0.84; Table 3) can be interpreted as reflecting interferences or competitions between Cu²⁺ and Mg²⁺ during the adsorption/replacement processes in clays, as has also been observed by O'Connor and Kester (1975).

Significant correlation of Fe with Mn (r=0.72) and Cu (r=0.74), and of Mn with Zn (r=0.66)and Cr (r=0.51; Table 3) suggest important associations between the oxide-oxyhydroxides of Fe-Mn and other elements (Tessier et al., 1979; Wallace et al., 1988; Pruysers et al., 1991). On the other hand, the covariance of Al with Cu, Mn, Zn and Fe (r=0.66-0.58; Table 3) found in the İskenderun Gulf sediments can be interpreted in terms of common detrital and non-detrital associations of this element mainly with the fine-grained aluminosilicates (i.e., clay minerals; Brannon et al., 1977; Oakley et al., 1981). The significant correlation of Cu with Zn (r=0.87) is probably primarily due to uptake by microorganisms since these elements also behave as micronutrients for plankton growth (e.g., Pratt and Davis, 1992; Calvert and Pedersen, 1993).

5. Conclusions

Mud with locally high biogenic sand and gravel contents is the major sediment type of the sea floor of the Gulf of Iskenderun. A biogenic carbonate belt extends from the western to southwestern to northeastern peripheral areas of the gulf. This indicates the possible influence of prevailing currents (i.e., calm, nutrient-rich and clear offshore waters) on benthic carbonate production (benthic algae) in this part of the gulf. Organic carbon contents mostly reflect normal marine production and hydrographically-related deposition.

It appears that the source of the Al, Fe, Mn, and partially Cu, in the sediments of the Gulf of Iskenderun is primarily weathering of average crustal rocks. Higher anomalies of Mg, Cr, Ni, Co, and Zn however, occurring in the eastern part of the area, along the SW–NE-trending peripheral areas of the gulf, most likely result from seaward dispersal of detrital minerals from the nearby basic and ultrabasic source rocks.

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