Possible sources and mechanisms of manganese enrichment in the deep-sea sediments of the Marmara Trough depressions (NE-Mediterranean, Turkey)

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ABSTRACT

Enrichment of Mn in deep-water relative to shallow-water sediments in the Marmara Basin was investigated using earlier metal data and some geochemical information from other similar marine regions on a comparative basis. Deep-water (1152-1276 m) sediments from the three depressions located along the Marmara Trough of the seismically-active North Anatolian Fault Zone contained much higher Mn concentrations (< 6355 ppm; over 10 600 ppm in some core horizons; on a carbonate-free basis) than those from the surrounding shallow-water (54-855 m) sediments (307-2059 ppm Mn on a carbonate-free basis). Cu and Ni showed the same trend although their concentrations were small. On the other hand, the sediments were not enriched in other metals (Fe, Co). The low variations of Ni, Cu and Co content in both shallow- and deep-water sediments would suggest that there is no significant hydrogenous contribution of Mn to the deep Marmara sediments. While diagenetic Mn enrichment was inferred from typical downcore colour changes, upward-increasing Mn content in the upper core sections and the correlation between Mn and CaCO₃ contents in sediments from the lower core sections, the generally high Mn concentrations are believed to reflect, in part, the presence of possible hydrothermal activities along fault planes in the Marmara Basin and external Mn-input from the so-called "manganese pump zone" prevailing close to the oxic/anoxic interface (chemocline) in the near-surface waters of the Black Sea.

RÉSUMÉ

Sources de manganèse et enrichissement des sédiments dans les dépressions de la mer de Marmara (NE-Méditerranée).

L'enrichissement en manganèse des sédiments profonds du bassin de Marmara a été étudié à l'aide de données antérieures de métaux et de données géochimiques d'autres régions marines comparables. Les sédiments profonds (1152-1276 m) des trois dépressions situées le long de la fosse de Marmara, dans la zone sismique active de la faille nord-anatolienne, présentent des teneurs en Mn (jusqu'à 6355 ppm ; plus de 10600 ppm dans certaines carottes, en l'absence de carbonates) très supérieures à celles des sédiments peu profonds (54-855 m) environnants (307-2059 ppm Mn en l'absence de carbonates). Le cuivre et le nickel montrent la même tendance malgré leurs faibles concentrations. En revanche, il n'y a pas d'enrichissement en d'autres métaux (Fe, Co), les faibles variations des teneurs en Ni, Cu et Co avec la profondeur des sédiments suggèrent l'absence de contribution hydrogène significative au Mn des sédiments profonds. L'enrichissement en Mn par diagenèse est déduit des variations caractéristiques de la cou-
INTRODUCTION

A considerable number of investigations have shown the occurrence of high Mn concentrations to be a common characteristic of many deep-sea sediments, as reported from a wide variety of depositional environments; Mn is thus considered to be one of the few major elements which are concentrated in deep-sea relative to near-shore sediments (e.g., Chester and Aston, 1976; Glasby, 1977; EmilianI, 1981 and many references therein). This has been interpreted mostly as a consequence of hydrogenous (e.g., Chester and Hughes, 1967; Elderfield, 1976), hydrothermal-volcanogenic (e.g., Hoffert et al., 1978; Varnavas and Cronan, 1991) diagenetic (e.g., Sevast'yanov and Volkov, 1967; Pruyssers et al., 1991), and biogenous (e.g., Bowen et al., 1971) processes prevailing near or above the sediment-water interface.

The Sea of Marmara is a marine environment where all the above processes are expected to exist with greater or lesser intensity, and possibly in combination with each other. More particularly, recent investigations have further confirmed the presence of a fine particle layer of manganese in the oxic-anoxic interface zone of Black Sea waters (Kempe et al., 1991) which seems to attract more attention to the southeasterly Sea of Marmara because this adjacent sea receives a quite significant input from the Black Sea (Ergin et al., 1991; 1993, 1994a). However, very little has been reported on the sedimentary Mn anomalies in the Sea of Marmara (Ergin and Bodur, 1992). Consequently, the aim of this paper is to analyse metal data obtained during the present study and to compare them to results reached earlier by other authors. It also discusses the possibility of an external Mn input through the surface or near-surface waters from the adjacent Black Sea.

General characteristics of the Sea of Marmara

The Sea of Marmara forms a transitional zone between the Black Sea in the northeast and the Aegean Sea in the southwest and connected to these adjacent seas through the narrow and shallow Straits of Istanbul ("Bosphorus") and Çanakkale ("Dardanelles"), respectively (Fig.1A). Another prominent feature of the Sea of Marmara is its tectonics-related basin morphology (Wong et al., 1990; Fig.1B). An east-west trending Marmara Trough in the centre consists of three small depressions ("fault-bounded pull-apart-basins") with maximum depths of between 1152 and 1276 metres, separating the narrower northern shelf from the much broader southern shelf (Fig.1A). The Marmara Trough is a continuation of the seismically active North Anatolian Fault (NAF) zone (Fig.1B) along which relative motions between the Anatolian and Black Sea blocks have occurred (Sengör et al., 1985), mostly in the form of earthquakes.

The hydrography of this sea is characterized by a two-layer flow consisting of low-salinity (18-22 ppt) surface waters inflowing from the Black Sea (Oguz et al., 1990; Fig. 2) and high-salinity (38.5 ppt) subsurface waters inflowing from the Aegean Sea (Oguz and Sur, 1989). A permanent pycnocline exists between these two layers, at depths of approximately 50 m at the Black Sea approach (Fig. 2).

MATERIAL AND METHODS

A large number of sediment samples were collected during the 1984 and 1988-1990 cruises of R.V. *Bilim* and 1989 cruise of R.V. *Knorr*, by a wide variety of sampling techniques (grab sampler, boomerang corer, box corer). Sediment samples obtained at water depths between 10 and 1226 metres were then analysed for their petrology and chemistry. Some of the results have already been presented in Bodur and Ergin (1994), and Ergin et al. (1993, 1994a). The total concentrations of Fe, Mn, Ni, Cu and Co were determined with flame-AAS after the sediment samples were digested using HF-HNO$_3$-HCl acid mixture. Details of analytical procedures including tests with reference materials and the reproducibility of the method are given elsewhere (Bodur and Ergin, 1994).

RESULTS AND DISCUSSIONS

The bulk metal concentrations for Fe, Mn, Ni, Cu and Co calculated on a carbonate-free basis are illustrated in Figs. 3-5. Except for Mn, all other metal concentrations measured appear to be nearly within the same range in the both shallow- and deep-water sediments; the results are comparable with those for average crustal rocks in general, and sedimentary rocks in particular (Fig. 6). This suggests that the contents of Fe, Ni, Cu and Co in the sediments have their origin mainly in the weathering of the lithosphere. In contrast, Mn concentrations show important regional variations within the Sea of Marmara, those obtained among the shallow (0-6 cm) sediment samples being much higher in deep waters of the easterly Istanbul Basin (4498 ppm), central Marmara Basin (6355 ppm) and westerly Tekirdag Basin (4798 ppm) in comparison with those from the surrounding shallower waters (Fig. 3). Sedimentary Mn
enrichment was found not only in surface sediments (Fig. 3) but also throughout the core profiles from all the three deep basins (Fig. 7). The enrichment of Mn in deep-sea sediments relative to that in shallow waters was also inferred from the Fe/Mn ratios, which are much lower (1-10) in deep-water sediments than in shallow-water sediments (20-88; Fig. 4). In general, it seems that iron increases relative to manganese in sediments with increasing continental influence; this trend is reflected in the greater amount of Mn relative to Fe available in sediments far distant from the continent or land-based sources. The two high Mn values obtained in the Gemlik Bay (2059 ppm) to the southeast, and in the Çanakkale Strait approach (1040 ppm) to the west, in the Sea of Marmara (Fig. 3) obviously
reflect post depositional processes (diagenesis, etc.) of only local importance.

The mechanisms responsible for this enrichment are still obscure; however, an external supply of Mn and diagenetic processes leading to the Mn accumulation in the sediments are required. Diagenetic Mn enrichment, particularly in deep-sea sediment cores, can be inferred from two observations: downcore colour changes within the sediment column (from reddish-brown at the surface to greenish-gray at the subsurface (>5 cm)); and the presence of surface Mn enrichment in the uppermost core sections (Fig. 7). The role of diagenesis in the redistribution of manganese in the sediment column is well established (e.g., Bonatti et al., 1971; Calvert and Price, 1972); surface enrichment of manganese is caused by the upward migration of Mn\(^{2+}\) ions due to a diffusive gradient into the oxic zone where precipitation occurs. Moreover, the higher Mn concentrations observed in the lower sections of cores BC3 (20-24 cm: 6473-8981 ppm; 34-38 cm: 8427-9127 ppm), BC4 (36-40 cm: 6683-8235 ppm; 52-56 cm: 4487-7428 ppm) and BGC3 (22-24 cm: 3940 ppm; 50-54 cm: 6854 ppm) reflect post depositional processes (diagenesis, etc.) of only local importance.

Total concentrations (CaCO\(_3\)-free) of Fe and Mn in the surface (top 6 cm of sea floor) sediments of the Sea of Marmara. Note the relatively high Mn concentrations in the deep relative to shallower water sediments. Filled circles indicate grab samples; filled squares denote box coring sites; filled triangle shows boomerang coring site.
4001-4667 ppm; 64-66 cm: 4336 ppm; Fig. 7) appear be associated, to some degree, with the total carbonate (CaCO₃) content present in the samples (12-16% in core BC3, mostly 10%; 10-13% in core BC4, mostly 8-9%; 11-12% in core BGC3, mostly 9-10%; Fig. 8). Such a correlation between elevated Mn and CaCO₃ contents is known to exist in sediments from the southwestern Black Sea (Sites 380-381 of Leg 42; close to the Strait of Bosphorus) due to the diagenetic formation of carbonates of the manganoan siderite-type (Emelyanov et al., 1978).

There is therefore no doubt that diagenesis affects the Mn chemistry of the surface Marmara sediments (Ergin, 1988), although it cannot be solely responsible for the presence of overall high Mn concentrations throughout the cores. It is obvious that the litholog (i.e., grain size) of the cores (Fig. 8) has no significant influence on the Mn fluctuations at some subsurface horizons (Fig. 7). On the basis of ²¹⁰Pb-dating, these fluctuations of the Mn concentrations within the cores would correspond to a time period of the last 500 years BP (Fig. 7). This 500-year span of time in and around the study area bears a record of changing climatic conditions, such as the Little Ice Age and colder and wetter periods (Lamb, 1977; Ergin, 1978), which could have affected the water and sediment chemistry of the Sea of Marmara. For instance, these climatic events include floating of ice masses on this sea (Ergin, 1978); precipitation and Black Sea level changes (Lamb, 1977); peak bloom of coccolithophorid species of Emiliania huxleyi (Hay et al., 1991); and agitation of the water column, bringing deeper water to the surface in the adjacent Black Sea (Hay et al., 1991). However, it is not clear whether or not one or a combination of the above changing climatic conditions could have led to abrupt changes in the water or land sediment chemistry, and hence to increased Mn precipitation. But this remains a possibility.

Another possible explanation, besides diagenetic enrichment, for the presence of anomalously high Mn contents in the deep-sea Marmara sediments could be the effects of hydrogenous processes (slow precipitation or scavenging of trace elements from the normal sea water). Along with the possible formation of chemogenic-diagenetic Mn-side­rites (Emelyanov et al., 1978), the oxides and hydroxides of manganese and iron could, both quantitatively and geochemically, be the most important hydrogenous precipitates (i.e., ferromanganese nodules) in deep-sea sediments, which usually contain relatively high concentrations of Mn, Fe, Ni, Co, Cu, etc. (e.g., Bonatti et al., 1972; Calvert and Price, 1977; Cronan, 1977; Emelyanov et al., 1978; Fig. 9). This means that for a hydrogenous hypothesis to be advanced in explanation of Mn enrichment in the deep Marmara sediments, the concentrations of Ni, Co (as they are in recent sediments of Sites 380-381 of the Black Sea; Emelyanov et al., 1978), and Cu must be considerably higher than those found in the shallow-water sediments of

![Figure 4](image-url)

Total concentrations (CaCO₃-free) of Co and the calculated Fe/Mn ratios Mn in the surface (top 6 cm of sea floor) sediments of the Sea of Marmara. Note the relatively high Fe/Mn values in the deep-sea relative to shallower water sediments. Filled circles indicate grab samples; filled squares denote box coring sites; filled triangle shows boomerang coring site.
this sea. But this is not the case (Figs. 4-5). Moreover, the non-hydrogenous character of these Mn enrichments in the deep Marmara sediments is further demonstrated by the \((\text{Ni}+\text{Cu}+\text{Co})/10\)-Fe-Mn diagram (after Bonatti et al., 1972) where it plots out of the hydrogenous field (Fig. 9). Moreover, the 210Pb-based and overall high sediment accumulation rates in the Sea of Marmara do not show any significant differences between the deep-water (100-260 cm/1000 yrs) and shallow-water (190-280 cm/1000 yrs) depositional environments of this sea (Ergin et al., 1994a).

In the present case, because the sediments were not enriched in other metals (Co, Zn, Pb), besides Mn and perhaps Cu and Ni, it is likely that hydrogenetic Mn enrichment plays only a minor role in the deep Marmara basins.

The presence of increased Mn concentrations in the deep Marmara sediments might also be explained by the influence of hydrothermal activities possibly occurring in this basin, although this remains to be confirmed. As already mentioned, the Marmara Basin is located on the highly tectonized and active North Anatolian Fault zone associated with several strike-slip and transform faults (Fig. 1b). Similar tectonics-related depositional environments have been described from many parts of the world oceans (e.g. the Agua Blanca Fault system of San Andreas, in California, the transform Fault zones of Mid-Atlantic Ridge, etc.) where hydrothermal solutions cause considerable amounts of metal enrichment (mainly in the form of iron and manganese oxides) relative to the surrounding sea water and sediments (Hoffert et al., 1978; Vidal et al., 1978). Boström (1975) suggested a convenient means of detecting hydrothermally-derived metal anomalies by calculating the ratio of Al (a relatively immobile element in hydrothermal systems) versus enrichment elements such as Fe, Mn, etc. He found \([\text{Al}]/(\text{Al}+\text{Fe}+\text{Mn})\) ratios to be generally below 0.4 for hydrothermal metal enrichment and above 0.4 for normal deep-sea sediment with only slight hydrothermal supply. On the basis of \([\text{Al}]/(\text{Al}+\text{Fe}+\text{Mn})\) values calculated from Evans et al. (1989) and Ergin and Evans (1988) for deep-sea sediments from the eastern Marmara basin (0.58-0.60), a hydrothermal contribution to the Marmara sea floor may be discounted, because these values are those or close to those of detrital sediments derived from the weathering of average crustal rocks. On the other hand, Fig. 6, which compares the concentrations of Fe, Mn, Ni, Co and Cu obtained in the present study with results from other sediments from adjacent waters, average crustal rocks and some selected hydrothermally-influenced sediments worldwide, shows that hydrothermally-derived sedimentary metals demonstrate a wide range of concentration values and that the metal levels of this study fall into the same range as the hydrothermal deposits. Despite the absence of proof, therefore, it is not unreasonable to expect the Mn concentrations, at least in part, to have been

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**Figure 5**

Total concentrations (CaCO3-free) of Ni and Cu in the surface (top 6 cm of sea floor) sediments of the Sea of Marmara. Filled circles indicate grab samples; filled squares denote box coring sites; filled triangle shows boomerang coring site.
MANGANESE ENRICHMENT IN DEEP-SEA SEDIMENTS

Comparison of Mn concentrations obtained in Marmara sediments with those from various other sources: Ts: This study (shallow-water sediments); Td: This study (deep-water sediments); SBS: Southern Black Sea sediments (Yücesoy and Ergin, 1992); AS: Aegean Sea sediments (Ergin et al., 1994); MS: Mediterranean Sea sediments (Emelyanov and Shimkus, 1986); DBS: Diagenetic Black Sea sediments (Sevast’yanov and Volkov, 1967); Hy: Hydrothermally-influenced deposits (compiled from various sources; in Bodur and Ergin, 1994); Crs: Crustal average (Mason and Moore, 1982)

derived from possible local hydrothermal sources within the tectonically-active deep Marmara Trough zone. Unfortunately, no data are available on the chemistry of bottom waters at or close to the presumed faults within the deep basins of this sea. Some deep-sea sediments which are affected by hydrothermal solutions may also have high concentrations of Fe, Cu, Ni, Co, etc. which are not comparable with those found in this work (Fig. 9). This is probably because fractionation of Fe and some other elements from Mn occur during the sub sea floor hydrothermal circulation due to their different solubilities; for instance, Fe is oxidized in sea water more readily than

Downcore Mn concentration profiles obtained from the three deep depressions of the Marmara Trough. See Fig.1A for location of coring sites. Note the distinct Mn fluctuations during the last 500 years BP, possibly affected by changing climatic conditions or/and diagenetic manganosiderite formation (See Fig.8). Arrows indicate CaCO3-rich horizons associated with higher Mn contents, possibly due to diagenetic formation of manganosiderite. See text for details.
Mn (e.g. Bonatti, 1981), and hence the residence time of Mn in sea water (1 × 10^4) is much higher than that of Fe (2 × 10^2; Murray and Brewer, 1977). As an example, at the Galapagos Rift Spreading Centre of Pacific, Fe/Mn ratios decreased from 229 near the hydrothermal vent to 6 at some distance from the vent (Marchig et al., 1987).

Although this also remains to be proved, input from the Black Sea surface or near-surface waters seems to play a significant role in the accumulation of Mn in the deep Marmara sediments. This hypothesis is based mainly on the fact that the boundary zone between the oxygenated surface waters and H_2S-containing deep waters in the Black Sea is relatively enriched in concentrations of particulate Mn (Fig. 10) and some other metals, and the circulation of these surficial waters is normally directed towards the Sea of Marmara (Fig. 2). Also, in the Black Sea sediments (i.e. sites 380-381 of Leg 42), diagenetic carbonates, besides oxides, hydroxides and sulphides are important carriers of Fe and Mn (e.g. Emelyanov et al., 1978). The former process of particulate metal enrichment (i.e. Mn-oxides precipitation) is known to occur in or near the oxic-anoxic interface zone (the so-called “manganese pump zone” of Black Sea waters (e.g. Kempe et al., 1991)}
as a result of various adsorption-desorption-substitution processes (Haraldsson and Westerlund, 1988; Lewis and Landing, 1991; 1992). In this model, it is proposed that upward advective and diffusive processes transfer the already reduced metal species to the overlying oxidized zone (Lewis and Landing, 1992). Therefore, the transportation of surface/nearsurface water towards the Sea of Marmara (Fig. 2) should also be involved in the transportation of a considerable amount of Mn from the surficial waters of the Black Sea in association with organic carbon fluxes (Ergin et al., 1993). An example of offshore Mn transport has been reported from the deep waters of the Gulf of Mexico (Trefry and Presley, 1982). Here, in the rapidly accumulating Mississippi delta sediments, diagenetic processes induce a 45% loss of Mn from the sediments to the overlying seawater; released Mn is then adsorbed and oxidized on particles that are being actively transported away from the shallower delta to the deep waters of the gulf.

CONCLUSIONS

It can be concluded that the generally high Mn content of the deep-sea sediments obtained in the Marmara Trough depressions cannot be explained solely in terms of lithogenic input from land-based geological sources. It may be a function of several factors which include: external Mn input from the Black Sea; possible hydrothermal supply along the submarine fault planes of the Marmara basin; and postdepositional redistribution of Mn within the sediment column with very little or no hydrogenous contribution. In contrast with Mn, the concentrations of Fe, Cu, Ni and Co mostly remain within the range of average crustal rocks. Thus, a hydrogenetic supply of Mn to the deep Marmara sediments seems to be only of minor importance. Fe/Al and Fe/Mn ratios in the sediments all confirm the enrichment of Mn in deep relative to shallower waters of this sea. Diagenetic processes of Mn enrichment in surface or near-surface sediment horizons in the cores were evident in typical downcore colour changes, from reddish-brown at the surface to greenish-gray at the subsurface. On the other hand, the correlation between the higher Mn and carbonate contents found in some subsurface core sections may be evidence of the diagenetic manganan carbonate (i.e. manganosiderite) which is well known from the sediments of the southwestern Black Sea, close to the Bospho-
rus Strait of the northeastern Sea of Marmara. The occurrence of particulate Mn-rich water layers in the surficial waters of the adjacent Black Sea and the prevailing outflowing current system directed towards the Sea of Marmara at the surface would also suggest a possible external Mn input from the Black Sea. Because the Sea of Marmara is situated on the tectonically-active North Anatolian Fault Zone and the Marmara Trough depressions are products of pull-apart and strike-slip movements within this zone, it seems that Mn enrichment in the deep-water Marmara sediments could have also been derived, at least in part, from possible submarine hydrothermal activities at or near these faults.

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