Some peculiarities of Mn distribution in the Adriatic Sea

T. Dolenec

Department of Geology, University of Ljubljana, Aškerčeva 12, Ljubljana, Slovenia and Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, Slovenia

The Adriatic as a modern epicontinental sea is situated between the eastern Italian coast and the western coast of Slovenia, Croatia, Jugoslavia and Albania. The results of a regional geochemical study indicate that major, minor and several trace elements are closely related to the catchment geology, following the type of sediment and prevalent currents. Their distribution pattern is affected by the morphological characteristics of the sea-bottom, anthropogenic impact and local hydrological and physicochemical conditions (Dolenec *et al.*, 1998, in press).

The present study deals with some peculiarities of Mn distribution in surficial sea bottom sediments from the Adriatic Sea, especially in the Jabuka Pit, which represents the deepest (up to 275 m deep) part of the central Adriatic (Fig. 1).

Results and discussion

The concentrations of Mn in surficial sediments range from 242 to 3760 ppm. The areal distribution pattern of Mn concentrations shows a general tendency to increase in the deepest part of the central and southern Adriatic (Fig. 2). The peak values up to 3760 ppm were measured in the Jabuka Pit (central Adriatic) and in the southern Adriatic (572–2050 ppm) which represents a more than 1200 m deep subcircular bathyal basin. The lowest concentrations (242–681 ppm) are restricted to the northern Adriatic, with average depth of about 30 m.

As rock-forming ferromagnesian minerals contain a considerable amount of Mn (1000–4000 ppm, see Wedepohl, 1978), much of the Mn accumulation in the southern Adriatic can be derived from the detrital material from the Albanian ophiolite hinterland. The suspected main source of Mn concentrations in the Jabuka Pit is supposed to be the submarine weathering of basaltic rocks of the islands Jabuka and Svetac, as well as pyroclastic material from these areas. Contamination from the manganese processing

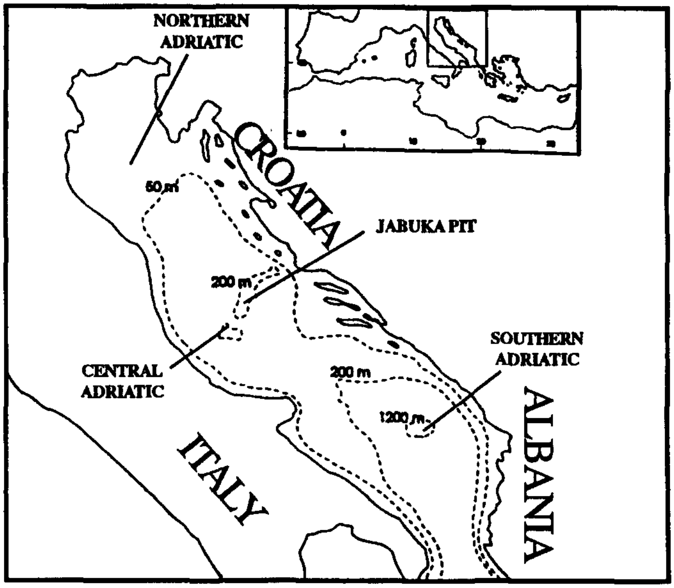

FIG. 1. Map of the Adriatic Sea indicating the position of the Jabuka Pit.

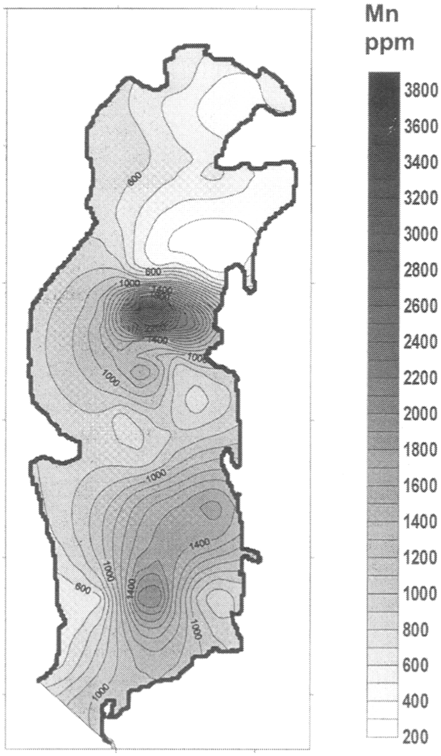

FIG. 2. Regional distribution of Mn in the surficial bottom-sea sediments of the Adriatic Sea.

plant located in ibenik Bay may also result in very high concentrations of Mn in this basin. The Mn concentrations in the northern Adriatic are in general consistent with the average abundance in crustal and/ or sedimentary rocks.

The finding of ferromanganese incrustations and coatings on deep water mollusk shells and shell fragments from a depth of about 200 to 270 m in the Jabuka Pit suggests a diagenetic redistribution of Mn in the surficial sediment, as already discussed by Paul and Meischner (1976). They suggested that Mn solution, diffusion and reprecipitation is active over the whole Adriatic. Mineralogically, ferromanganese incrustations and coatings consist of sodium manganese oxide hydrate (todorokite) and amorphous iron oxyhydroxides (Fe $OOH{\cdot}xH_2O$). The main mineral phase is todorokite which seems to be the most important trace metal bearing phase, following by Fe oxyhydroxides. The results of geochemical studies show that the incrustations and coatings contain a considerable concentration of Ni (1210 ppm), Co (405 ppm), Mo (124 ppm), As (53 ppm), W (18 ppm), Zn (148 ppm) and Sb (8 ppm). This enrichment can be explained by sorbtive scavenging of dissolved heavy metal seawater compounds on the surface of Mn and Fe oxyhydroxide phases.

The ferromanganese incrustations and crusts were also found to have *REE* concentrations of about an order of magnitude less relative to the sediment. The shale-normalized pattern of *REE* exhibits a pronounced positive Ce anomaly of 1.45 and slight depletion of La and Yb relative to Sm. The source of *REE* in the ferromanganese coatings seems to be the surficial sediment and/or the bottom seawater. *REE* are adsorbed or co-precipitated onto Mn-Fe oxyhydroxide phases. The release of *REE* to the upper pore water and bottom water is accompanied by fractionation across the trivalent *REE* series and by the preferential imput of Ce relative to its *REE* neighbours. Ce removal occurs faster than it neighbours *REE* (III), indicating a rapid oxidation of Ce (III) to Ce (IV) (Sholkovitz *et al.*, 1992, and references therein). Prominent expressions of its oxidation thus led to the positive anomaly observed in ferromanganese coatings.

The exact mechanism of precipitation of ferromanganese coatings in the Jabuka Pit is still unknown. However, in our model we assumed a hydrogenous precipitation, meaning direct precipitation or accumulation of colloidal metal oxides from seawater, as well as oxic diagenesis (Dymond *et al.*, 1984, and references therein). Hydrogenous precipitation could explain the formation of ferromanganese incrustations and crusts on mollusk shells and fragments which are exposed to seawater, while oxic diagensis involving reactions in the oxidized upper part of sediments is hypothesized to provide much higher fluxes of Mn and trace elements to the precipitating coatings. The release of Mn from the topmost surface sediment during oxic diagenesis is supported by the Mn enrichment within the upper 2 cm of the sediment and its decrease in the deeper parts, as noted by Paul and Meischner (1976).

References

Dolenec, T., Faganeli, J. and Pirc, S. (1998) *Geologia Croatica* - in press.

Dymond, J., Lyle, M., Finney, B., Piper, D. Z., Murphy, K., Conrad, R. and Pisias, N. (1984) *Geochim. Cosmochim. Acta*, **48**, 931–49.

Paul, J. and Meischner, D. (1976) Schenkenbergiana marit., **8**, 91–102.

Sholkovitz, E. R., Shaw, T. J. and Schneider, D. L. (1992) *Geochim. Cosmochim. Acta*, **56**, 3389–402.

Wedepohl, K. H. (1978) *Handbook of Geochemistry*, 2/3.