

A manganese deposit from the South Tyrrhenian region

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Received 17/4/79, in revised form 27/8/79, accepted 1/9/79.

ABSTRACT

Specimens dredged from within the summit of a volcanic seamount during an oceanographic cruise in the Eolian Island Arc (South Tyrrhenian Sea) were examined. Mineralization, which forms veins and pockets within a silty-clayey material, consists mainly of todorokite with scarce birnessite. The chemistry (Mn 48%, Fe 0.26%, Ni 249 ppm, Co 223 ppm) and the mineralogy of the deposit are discussed; the findings, compared with data from some of the literature, suggest a hydrothermal genesis with extreme fractionations of Mn from Fe. A process explaining the anomalous Cu content (8 200 ppm) of the deposit is also suggested.

Oceanol. Acta, 1980, 3, 1, 107-113.

RÉSUMÉ

Dépôt manganésifère de l'aire Sud Tyrrhénienne

On caractérise du point de vue minéralogique et chimique un dépôt manganésifère dragué sur un seamount de la région des Iles Éoliennes (Tyrrhénienne Sud). Dans cette minéralisation, composée de veines et poches dans un matériel sédimentaire argileux-cinérétique, on a reconnu comme phases cristallines de la todorokite et, en quantité minime, de la birnessite. On donne et on discute la composition chimique (Mn 48%, Fe 0,28%, Ni 249 ppm, Co 223 ppm) en comparant à d'autres dépôts similaires de la littérature. Les données obtenues permettent d'attribuer au dépôt manganésifère une genèse hydrothermale avec fractionnement extrême du Mn du Fe. Enfin, on propose un mécanisme pour expliquer l'enrichissement anomal en Cu (8 200 ppm).

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INTRODUCTION

The study of the deep-sea ferromanganese oxide deposits has been considerably encouraged in recent years by the development of oceanographic research and by the realization that metalliferous deposits may constitute a potential ore resource.

Many geological, geochemical and environmental investigations have been made with the aim of determining the origin of such deposits and relating their composition to their origin. The suggestion that submarine volcanism may provide the conditions for metal segregation and ore formation has stimulated a wide programme of

oceanographic research in the South Tyrrhenian region, particularly on the volcanic submarine seamounts of the Eolian Islands area.

During cruises T76 and T78 of the R/V "Bannock", a large number of samples were dredged on the volcanic seamounts Enarete and Eolo (T76), which are located in the submerged western portion of the Eolian Arc, and on top of Mt. Lametino (T78), situated at a distance of approximately 70 sea miles from these seamounts, in the submerged eastern portion of the Eolian Arc.

The samples from Mts. Enarete and Eolo comprise Fe-Mn crusts characterized by an elevated Fe/Mn ratio (Morten *et al.*, in press), while those from Mt. Lametino



Figure 1
Silty-clayey block crossed by veins of Mn-minerals.

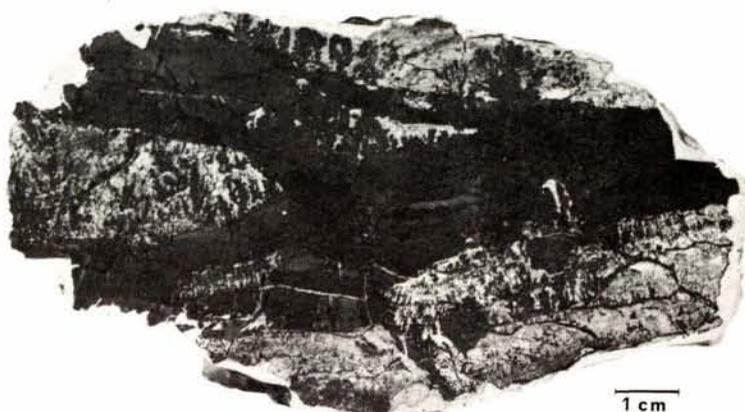


Figure 3
Lengthwise cut of a block, showing Mn-mineralization inside the sediment.

show a very low Fe/Mn ratio. This paper, which concerns the latter samples, constitutes the first report of a remarkable Mn deposit in the South Tyrrhenian region.

GEOLOGICAL SETTING AND SAMPLING

Mt. Lametino is a volcanic seamount located in the South Tyrrhenian Sea 20 sea miles north of the island of Stromboli. Situated on the continental slope, it is characterized by two summits, which reach -1330 m and -862 m depths respectively.

The full chemistry and radiometric age of the volcanic structure of Mt. Lametino are not available at present, but we believe it to have a calcalkaline-shoshonitic affinity, and an emplacement age lower than 1 my, in agreement with the Eolian Island volcanism (Barberi *et al.*, 1974).

The dredging T78L, carried out on the main top (-862 m), yielded over one hundred fragments of variable sizes including sediments with dark intercalations (Mn-minerals) and volcanic rocks.

The Mn mineralization, dark brown and black, forms veins and pockets within blocks of light grey silty-clayey

material. Several of these veins occur in each single specimen, with sizes varying from less than 1 mm to 4-5 cm (Figs. 1-2).

One of these blocks (Fig. 3) has a lengthwise cut which indicates that one part of the deposit is constituted by a main block vein which branches off, and by a thick network of small veins within the sedimentary material. The mineralization appears also as a diffused dendritic growth that impregnates the enclosing material.

Mn ore is soft and porous, showing in its small fragments a laminated structure, and in some cases a fibrous structure with slightly diverging fibres. The fracture is opaque and conchoidal, while the espholiation lamina has a submetallic brightness. We observed bothrioidal concretions of variable size (from about 1 to 3-4 mm) along the surface of contact with the enclosing sediment.

Figure 2
Silty-clayey block crossed by veins of Mn-minerals.



Figure 4
Accretionary cylinders in the Mn-mineralization (SEM 50x).





Figure 5
Accretionary cylinders perpendicular to the deposition laminae seen through a fracture parallel to the laminae (SEM 50 ×).



Figure 7
External surface of an accretionary cylinder (SEM 150 ×).

On the same surface, we almost invariably noticed a very thin patina of orange-yellow material. This material, which is also present inside the vacuoles of the deposit, is an amorphous iron hydroxide. In some instances, the ore fragments show frequent laminations parallel to the vein attitude. Careful SEM examination revealed that the laminae grow through cylinders which are perpendicular to the same laminae. The accretionary structures are pronounced on the external surfaces (Fig. 4), and on a fracture parallel to the laminae (Fig. 5). The cylinders show a radial structure on the

fracture surfaces (Fig. 6) and a coralline aspect on the external surface – grater-like – (Fig. 7).

MINERALOGY

Diffraction investigation of some of the ore fragments, employing both the CuK_α and the FeK_α radiations, permitted identification of todorokite as the predominant crystalline phase, associated to very scarce birnessite. The average data established for the Tyrrhenian specimens are reported in Table 1, together with data taken for comparison from the literature.

Figure 6
Fracture surface of an accretionary cylinder showing the radial structure (SEM 150 ×).



Table 1
Interplanar *d* spacings and intensities of the lines relative to samples from Mn submarine deposits.

T78L		1		2		3	
<i>d</i> (Å)	I						
9.80	100	9.80	100	–	–	9.70	100
7.17	5	–	–	7.18	100	7.20	80
4.90	50	4.81	75	–	–	4.80	50
–	–	4.45	50	–	–	4.45	20
–	–	–	–	3.57	30	3.57	20
2.44	20	2.45	55	2.44	20	2.44	30
2.40	10	2.40	50	–	–	2.39	25
2.33	10	2.36	30	–	–	2.35	15
–	–	2.23	40	–	–	2.25	20
–	–	2.13	25	–	–	–	–
–	–	1.97	25	–	–	–	–
–	–	1.91	10	–	–	–	–
–	–	1.77	15	–	–	–	–
–	–	1.53	35	–	–	–	–
–	–	1.42	35	1.41	15	1.42	30
–	–	1.40	10	–	–	1.39	10

T78L. This work.
1, Cronan and Tooms, 1969. Todorokite.
2, Cronan and Tooms, 1969. Birnessite.
3, Cronan and Tooms, 1969. Todorokite and Birnessite.

Thermal gravimetric analysis was also carried out on this material by a Du Pont termobalance in nitrogen atmosphere. The thermal gravimetry and derivative thermal gravimetric curves (Fig. 8) show that the total loss amounts to some 25%, and occurs in three main stages. The main loss (H₂O) of about 16% occurs within the first 300°C; subsequent loss (about 9%) occurs in two stages, the former between 400 and 700°C and the latter between 850 and 1000°C. These two last losses are referable to todorokite, as pointed out by Frondel *et al.* (1960).

The enclosing sedimentary material was subjected to optical and diffractometric analysis. It is composed by a silty and by a clayey part. In the former, quartz, feldspar, and biotite were recognized in angular fragments; they probably derive from a pyroclastic source. Chlorite, kaolinite, calcite, and perhaps illite are present in the latter.

Chemical analyses were carried out on different bulk parts of the mineralization, using different methods. Si, Al, Ti, Fe, Mg, Ca, Co, Cu, Ni, Mo, Rb, Sr, V and Zn were determined both by emission spectrography and XRF: for both methods, calibration curves have been drawn for the different elements through suitably prepared standards. Na and K were determined by spectrophotometry, and Ba by the gravimetric method, Mn was determined by the volumetric method (Ingamells, 1958), by colorimetric analysis and by XRF. The data obtained with the different techniques showed good agreement (2% precision), permitting us to average

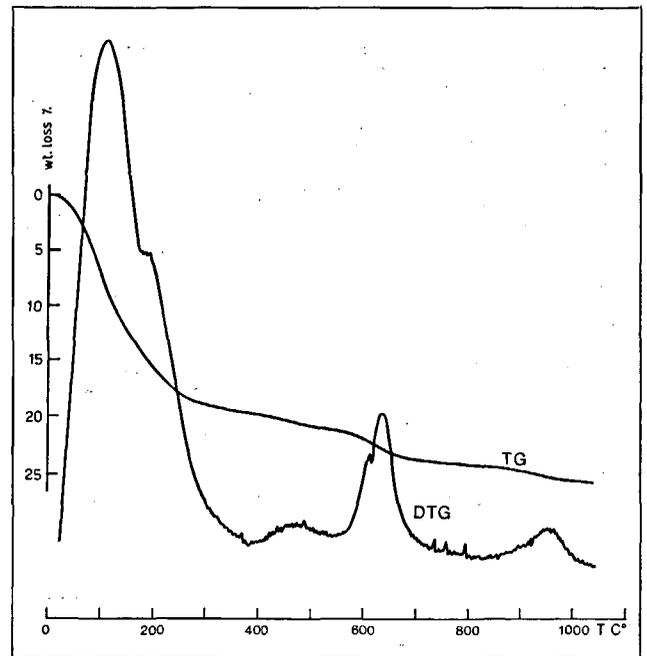


Figure 8
Thermal gravimetric (TG) and derivative thermal gravimetric (DTG) curves of the T78L Sample.

Table 2
Chemical analyses of samples from Tyrrhenian Sea (T78L and T76E) and from literature.

	South Tyrrhenian		Hydrothermal						Diagenetic	
	T78L	T76E	1	2	3	4	5	6	7	8
Wt (%):										
Mn	48.02	0.19 ÷ 8.29	54.20	50.02	44.64	27.60	0.77	0.15	40.50	27.85
Fe	0.26	6.99 ÷ 44.06	0.15	0.26	0.09	10.49	26.51	29.00	4.60	4.19
Na	2.61	-	1.55	2.99	0.11	1.46	1.27	0.75	-	-
Mg	1.52	0.30 ÷ 1.93	0.06	1.36	0.06	1.92	1.75	0.90	-	1.87
Al	0.41	0.53 ÷ 7.94	-	0.36	0.21	0.64	0.11	3.70	-	2.22
Si	0.87	6.08 ÷ 11.68	0.20	5.98	13.30	5.94	21.27	14.00	-	6.32
K	0.80	-	0.35	0.60	0.10	0.52	2.68	0.60	-	1.03
Ca	2.33	0.43 ÷ 2.14	0.70	1.54	1.50	3.43	0.43	1.36	-	5.57
Ti	0.02	0.02 ÷ 0.19	0.05	-	tr	0.04	0.01	0.56	0.05	0.21
L.O.I.	24.78	13.00 ÷ 22.00	-	-	-	18.02	6.22	-	-	-
ppm:										
V	84	50 ÷ 400	-	-	-	215	5	160	240	-
Co	223	tr ÷ 800	< 5	5	65	82	2	17	170	121
Ni	249	15 ÷ 3000	< 10	469	70	271	2	18	470	69
Cu	8200	40 ÷ 900	< 5	103	305	206	46	11	110	18
Zn	83	tr ÷ 1000	-	378	70	83	126	-	-	77
Rb	22	-	-	-	-	-	-	-	-	39
Sr	600	-	-	-	-	484	59	-	-	729
Mo	557	-	-	-	-	-	-	-	330	51
Ba	3200	-	58,000	1706	2500	646	43	135	-	3958
Si/Al	2.12	-	-	16.61	63.33	9.28	193.36	3.78	-	2.85
Fe/Mn	0.005	-	0.003	0.005	0.002	0.38	34.43	193.33	0.11	0.15

tr, trace; dash, not quoted.

T78L, representative composition of Mt. Lametino mineralization.

T76E, range of ten analyses from Mts. Eolo and Enarete mineralization (Morten *et al.*, in press).

1, Afar-Mn-rich (Bonatti *et al.*, 1972 a). En Kaf 9 ab; 2, Galapagos Rift (Corliss *et al.*, 1978). Average of TB samples; 3, Apennine ophiolites (Bonatti *et al.*, 1976 c). Sample Z14; 4, Famous (Hoffert *et al.*, 1978). Average of two analyses: cyp 74-23-12 and cyp 74-26-15-2; 5, Famous (Hoffert *et al.*, 1978). Cyp. 74-26-15-1 c; 6, Afar Fe-rich (Bonatti *et al.*, 1972 a). En Kaf 6; 7, Jervis Inlet (Ku and Glasby, 1972); 8, Loch Fyne (Calvert and Price, 1970). Average of five samples (analyses 2-6, Table 2).

the results. The Th determination, performed by XRF, is only semi-quantitative, since the concentration of this element is close to the detectability limit.

The data pertaining to the mineralization studied in this work are reported in Table 2, together with the range of ten analyses of Fe-Mn crusts from seamounts Enarete and Eolo (Morten *et al.*, in press) and other analyses from the literature.

The specimens studied here show a high Mn (48%) and a very low Fe (0.26%) content, with Fe/Mn ratio 0.05. Among minor and trace elements we call attention to the high concentrations of Ba (3200 ppm) and Cu (8200 ppm), and the low concentrations of Ni (249 ppm), Co (223 ppm) and Th (< 2 ppm).

DISCUSSION

Both mineralogy and chemistry, together with geological setting, may provide information concerning the origin of a submarine metalliferous deposit.

A genetic classification based on the prevalent source of metals was suggested by Bonatti *et al.* (1972c), and four main types of deposits were recognized: hydrogenous, diagenetic, hydrothermal and halmyrolitic.

The Mn deposit dredged from the top of Mt. Lametino is mainly formed by todorokite in combination with very scarce birnessite. Todorokite and birnessite are the main minerals present in nodules and ferromanganesiferous concretions. Different data taken from the literature show pelagic oceanic areas to be the genetic setting of todorokite, while birnessite is present in areas with very shallow waters, and particularly on the tops of seamounts (Barnes, 1967; Cronan, Tooms, 1969; Cronan, 1972). This is not in agreement, however, with our own finding of todorokite, and only scarce birnessite, on the top of a seamount. The chemical composition of the Mt. Lametino deposit is different from that of the classical oceanic ferromanganesiferous nodules (Fig. 9). The high Mn and low Fe content, and the extremely low content of Ni and Co indicate a high deposition rate typical of hydrothermal deposits, as pointed out for the MAR Median Valley hydro-

thermal field (Scott *et al.*, 1974); or may possibly be due to Mn remobilization from reduced sediments in a diagenetic environment (Manheim, 1965; Ku, Glasby, 1972). Comparison of the different elements of hydrothermal manganesiferous concretions and diagenetic deposits (Table 2), does not permit recognition of significant differences between the two groups of mineralizations. In fact, both groups are characterized by a great variability of the Si/Al ratio and by very low Fe/Mn ratio, which appears steadily lower in hydrothermal manganesiferous deposits. Moreover both groups show low contents of trace elements (particularly Ni, Co, Cu) in comparison with the well-known nodules of hydrogenous origin (Bonatti *et al.*, 1972c, Table 2).

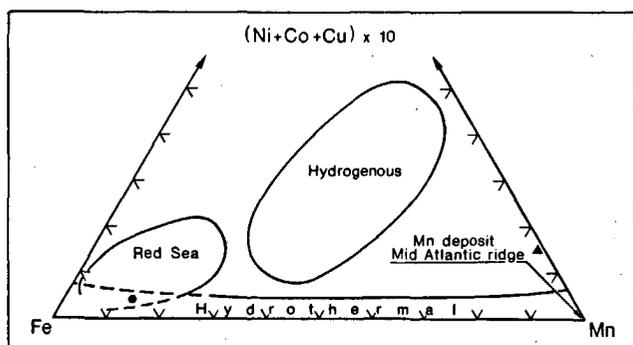
As far as Ba is concerned, this element always appears enriched in deposits which are rich in Mn, showing a negative correlation between Ba and Fe/Mn ratio in hydrothermal deposits (Bonatti *et al.*, 1972a, c; Hoffert *et al.*, 1978). This fact is explained by Ba precipitating with Mn rather than Fe, both giving origin to barite and entering the Mn-phases lattices. A rough positive intercorrelation between Ba and Mn is also evident in deposits of diagenetic or even of hydrogenous origin, according to the literature (Calvert, Price, 1970; Lyle *et al.*, 1977). All the above suggests that the correlation between Ba and Mn is independent of the genetic setting, and that only particular enrichments of Ba (e.g. sample 1, Table 2) are surely recoverable in hydrothermal environments, where this element may give place to barite; Ba contents such as those found in the Mt. Lametino samples, which are similar to both diagenetic and hydrothermal samples (Table 2), are consistent with Ba hosted within the lattice of todorokite (Burns, Burns, 1977; Corliss *et al.*, 1978) and are not a proof of genetic setting.

The strong enrichment of Cu in our samples poses problems which are difficult to elucidate at the present time. The geochemistry of Cu is always considered close to that of Ni in iron-manganese deposits, where Cu, Ni and Zn substitute for Mn^{2+} in both birnessite and todorokite (Burns, Burns, 1977; Corliss *et al.*, 1978). Copper abundance (8200 ppm) in the T78L samples is about 100 times higher in comparison with that of diagenetic and hydrothermal deposits, approaching only the content of some deposits of hydrogenous nodules; the latter, however, show a particular enrichment of Ni and Co, not noticed here. This fact lies outside normal schemas, and calls for a particular genetic picture, which we shall suggest in the following section.

MODEL OF GENESIS OF THE Mt. LAMETINO DEPOSIT

The forgoing discussion on mineralogy and chemistry did not permit a sure conclusion with regard to the genesis of the Mt. Lametino deposit. However, such data, associated with the characteristics of emplacement (deposit of vein and pockets) and of environment (top a volcanic seamount) lead us to suggest that the mineralization was deposited from a hydrothermal spring, rather

Figure 9
Fe-Mn-(Ni+Co+Cu) × 10 diagram (Bonatti, 1975); triangle: sample T78L of Table 2; dot: sample T76E of Table 2.



than by a diagenetic process. This hypothesis is also supported by the low content of Th (less than 2 ppm), which rules out a diagenetic origin and—even more firmly—a hydrogenic one (Bonatti *et al.*, 1972 *c*).

The construction of a model explaining the extreme fractionation of Mn from Fe remains an important question.

Such fractionation may derive from two main processes, one of which occurs during ascent of the thermal solutions, the other during precipitation of metals after discharge on the sea floor. In the latter process, the fractionation of Mn from Fe results from the different solubility of the two elements during the oxidation caused by the sea water (Kranskopf, 1957; Scott *et al.*, 1974). This causes a chemical zonation of hydrothermal fields, with Fe enrichment close to the vent of thermal solutions and Mn enrichment far from the discharge. In the former process, recently proposed by Bonatti (1975), Fe-Mn fractionation occurs during sub-bottom hydrothermal circulation, leading to iron sulphide formation below Mn deposits. In fact, if circulation is deep, the reactions between marine water and volcanic rocks, occurring in the 200-500°C temperature range, produce an acidic, reducing solution, highly enriched in Fe, Mn and Cu, leading to the deposition of iron and copper sulphides, while Mn is kept preferentially in solution, as verified in the laboratory by Hajash (1975). This model of fractionation well explains copper-iron sulphide mineralization found inside basalts dredged from oceanic ridges (Bonatti *et al.*, 1976 *a*), and the mineralizations associated with Appennine ophiolites (Bonatti *et al.*, 1976 *b*) and with Cyprus ophiolites (Parmentier, Spooner, 1978).

In the literature on hydrothermal springs from the South Tyrrhenian region, both these processes are reported. Discharges of hydrothermal solutions on the sea floor explain the submarine iron-rich deposits close to Stromboli Island (Bonatti *et al.*, 1972 *b*) and those of seamounts Enarete and Eolo (Morten *et al.*, in press), while a Fe fractionation in sulphides (pyrite and marcassite) is found in submarine deposits within volcanoclastic rocks from the Volcano Island area (Honnorez *et al.*, 1973).

At Mt. Lametino, the emplacement of the mineralization in veins and pockets, the constancy of the Fe/Mn ratio in the deposit and the low Fe contents (Fe_2O_3 tot. 4.8-5%) in the sediments crossed by the Mn veins all seem to indicate that the Fe present in the hydrothermal vent was deposited in deeper areas, during sub-bottom circulation, probably in form of sulphides.

The hypothesis explaining the existence of both processes in the South Tyrrhenian region is thus that a more superficial and/or rapid circulation could be responsible for the discharge of hydrothermal solutions in the sea floor, causing high Fe/Mn ratio deposits; while a longer and/or deeper circulation of the same hydrothermal solutions within the rocks of a volcanic apparatus develops reducing conditions which lead Fe to deposit in sulphide phases; Mn would deposit higher in oxidation areas, probably due to the contact with sea water oxygen.

This last would be the case of Mt. Lametino deposit.

With regard to the high content of Cu, about 100 times greater than other similar deposits of rapid accumulation, we would advance the hypothesis that this element has been supplied by reaction between phases containing Cu and the warm solution rising within the highest portions of the apparatus. These phases could, for example, be produced within late dikes connected with the last phases of calcalkaline-shoshonitic volcanism in the Eolian Islands area.

Acknowledgements

We are grateful to Prof. E. Bonatti for critically reading the manuscript and making a number of helpful suggestions, to Dr. R. Sartori for useful discussions, and to Prof. R. Pirani, Dr. L. Poppi and Mr. V. Landuzzi for their laboratory assistance. This work was supported by the National Research Council of Italy (CNR) Contribution no. 78.01074.88 P.F. Oceanography.

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