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GEOCHEMISTRY OF MESSINIAN CLAY SEDIMENTS: METAL DISTRIBUTION

RIASSUNTO. — È stata studiata la distribuzione di Fe, Mn, Ni, Co, Cu, Zn, V, B, K, Ca, Mg, Sr in campioni di marne pre- e intra-evaporitiche di età messiniana appartenenti a due bacini della Sicilia Orientale (Ciminna ed Eraclea Minoa). Tale studio è stato effettuato allo scopo di ricavare informazioni utili per la ricostruzione dell'ambiente di deposizione.

I tenori di Fe e di Mn suggeriscono differenze nelle caratteristiche ambientali fra i due bacini. Tutti gli altri metalli pesanti presentano concentrazioni dello stesso ordine di grandezza di sedimenti privi o con poca sostanza organica, non è stato trovato perciò alcun arricchimento.

I tenori di K sono direttamente correlati con la frazione argillosa; quelli di Ca con la frazione carbonatica.

Le coppie Ni-Co, Cu-Zn, V-B, sono correlate con la frazione argillosa e fra loro; Mn appare invece correlato con la frazione carbonatica.

Si ipotizzano condizioni ossidanti per il bacino di Ciminna, riducenti per quello di Eraclea Minoa, con assenza però di condizioni totalmente anossiche durante la deposizione delle marne.

ABSTRACT. — Pre- and intra-evaporitic marls of Messinian age from two basins in western Sicily (Ciminna and Eraclea Minoa) were studied for Fe, Mn, Ni, Co, Cu, Zn, V, B, K, Ca, Mg, and Sr distribution in the attempt to obtain information on the depositional environment.

Fe and Mn contents suggest differences of environmental features between the two basins. All other heavy metals show concentrations comparable with similar sediments with little or none organic matter; in spite of many evidences for euxinic deposition conditions, no significant metal enrichment was found.

K concentration is directly correlated with the clay fraction; Ca wholly correlates with the carbonate fraction.

The couples Ni-Co, Cu-Zn, V-B correlate with the clay fraction and with each other; Mn instead correlations with the carbonate fraction.

For the basin of Cimina conditions more oxidizing than for Eraclea Minoa are inferred, as well as the absence of fully anoxic conditions during deposition of marls.

Introduction

The depositional features of Messinian sediments from Ciminna and Eraclea Minoa basins (western Sicily) have been recently investigated by a number of researches. The papers are related to the general problem on the « Significato Geodinamico della crisi di salinità del Miocene terminale nel Mediterraneo » (1).

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Theoretical (EUGSTER and HARDIE, 1976), geochemical (CORADOSSI and CORAZZA, 1976; DECIMA, 1976), isotopic (PIERRE and CATALANO, 1976; LONGINELLI and RICCHIUTO, 1977; LONGINELLI et al., 1978), petrographical (Lo CICERO and CATALANO, 1976; NESTEROFF and GLAÇON, 1977), sedimentological (CATALANO et al., 1976; SCHREIBER and DECIMA, 1976; SCHREIBER et al., 1976), palaeontologic (DI STEFANO and CATALANO, 1976) and geological studies (MASCLE and HEIMAN, 1976) were focused on the causes and effects of the « salinity crisis ».

In order to obtain further informations on the depositional environment of

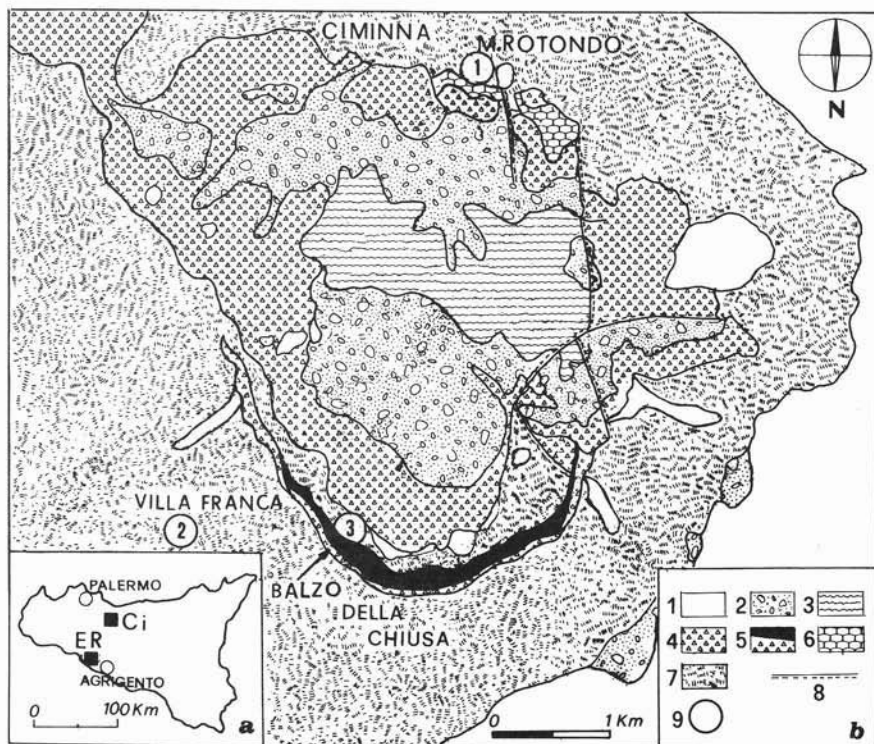


Fig. 1. — Geological sketch map of the Ciminna area (from DI STEFANO and CATALANO, 1976). - a) Index map of the samples basins: Ci = Ciminna; ER = Eraclea Minoa. b) Geological map of the Ciminna basin: 1 = Landslides; 2 = Alluvial deposits; 3 = Marls and limestones (Trubi) and biocalcarenes (Pliocene); 4 = Upper evaporitic level; 5 = Lower evaporitic level, 6 = Reef limestones (Baucina formation); 7 = Basal and intraevaporitic sandy marls; 8 = Faults; 9 = Sampling sites.

evaporites the present paper deals with the distribution of K, Ca, Mg, Sr, Fe, Mn, Cu, Zn, Co, Ni, V and B in some clay sediments sampled from two basins (Ciminna and Eraclea Minoa, Sicily).

In a previous paper (CORADOSSI and CORAZZA, 1976) the same sediments were studied for boron distribution and ions in leachate solutions.

The relationship between trace elements and between them and clay minerals

is considered very important in order to infer the depositional environment. In fact in particular basins where circulation is restricted the clay sediments exhibit high concentrations of a number of trace elements, like Mo, Ni, Co, Cu, Zn, Pb, V (KEITH and DEGENS, 1967). In the Ciminna and Eraclea Minoa basins depositional and erosional periods probably were alternated, owing to intermittent communications with the open sea. For this reason the knowledge of the distribution of the above elements, known as geochemical indicators is considered of a particular interest.

Sample collection

Twenty-four samples of pre- and intra-evaporitic marls were analyzed. These are part of a group of samples collected during a previous work, to which the reader is invited to refer (CORADOSSI and CORAZZA, 1976). Of the 24 samples, 14 were collected in the basin of Ciminna (9 at Monte Rotondo, 5 at Villa Franca, 2 at Balzo della Chiusa, fig. 1), and 10 in the basin of Eraclea Minoa. The samples from the Ciminna basin are both pre-evaporitic (Monte Rotondo and Villa Franca) and intra-evaporitic marls (Balzo della Chiusa). The fossil content of these marls shows that faunal associations are autochthonous and were deposited in a marine environment (DI STEFANO and CATALANO, 1976), even though they were influenced by continental waters (PIERRE and CATALANO, 1976).

The marls from Eraclea Minoa are intra-evaporitic and belong to the upper evaporitic series where seven sedimentation cycles at least are present (DECIMA and WEZEL, 1971; NESTEROFF, 1973; PIERRE, 1974). The marls were deposited in a marine basin with a moderate depth (PIERRE, 1974; NESTEROFF and GLAÇON, 1977).

Analytical procedures

A) CHEMICAL ANALYSIS

Two types of analysis were followed to elicit the major element and trace element distribution, either in the whole rock and in the acid-leaching solution.

1. *Total extractable metals*: K, Ca, Mg, Fe, Mn, Cu, Zn, Co, Ni, and V determination.

The procedure given by SCHWEIZER (1975) was followed starting from 1 g of sample. All the above elements were determined by means of the atomic absorption method, using Perkin Elmer 303 and 503 spectrophotometers equipped both with flame and graphite furnace atomizers; the latter device was used for V determination, using the procedure set up by CIONI et al. (1972). For the other elements the standard instrumental methods given in Perkin Elmer's literature were followed.

2. *Non-detrital extractable metal*: K, Ca, Mg, Sr, Fe, Mn, Cu, Zn, determination.

Samples were dried at 110° C; 500 mg were acidified with 40 ml 0.1 N HCl at room temperature for 30 min. using a magnetic stirrer according to the procedure suggested by OSTROM (1961). The suspensions were filtered through fritted glass filtrating funnels, size 5, and repeatedly rinsed with demineralized water. Finally

the volume was adjusted to 50 ml and appropriate dilutions were made for standard atomic absorption spectroscopy.

B) MINERALOGICAL ANALYSIS

The samples were analyzed by X-Ray powder diffraction. The clay mineral content is given as difference, complementary to all other minerals. The fraction lesser than 2 μm in size was separated by the conventional sedimentation method based upon the velocity of settling particles. This fraction was analyzed for individual clay minerals by X-Ray diffraction on the oriented and untreated sample, on the ethylene glycol treated sample, and after heating to 450 and 600° C.

Analytical results

The results of the chemical analysis for metals are shown in Table 1.

Potassium. Concentrations of total K do not vary significantly in the samples from Ciminna and Eraclea Minoa; they are 1.41 and 1.35 % respectively in the average. The amount of potassium removed by 0.1 N HCl leaching is approximately constant in all samples and corresponds to about 10 % of the total K.

Calcium. No difference is shown between concentrations of total calcium and obtained by 0.1 N HCl leaching. This is an indication that Ca belongs entirely to the carbonate fraction or any other fully soluble fraction, not to silicates. The concentrations of total Ca vary between 2.5 and 6.1 % in the samples from Ciminna (average 3.6 %), the highest values being in the lowermost part of the series (Ci 1, Ci 2, Ci 5); at Eraclea Minoa the amount of total Ca ranges from 8.9 to 28.6 % (average 13.84 %).

Magnesium. Total Mg varies between 0.62 and 1.73 % at Ciminna (average 1.1 %), between 0.63 and 1.67 % at Eraclea Minoa (average 1.31 %). Concentrations of Mg leachable in 0.1 N HCl are very similar in either basin and correspond to 18 % of the total Mg.

Strontium. Sr has been determined only in the fraction soluble in 0.1 N HCl. Strontium differences in the two basins are five times greater than Ca, 161 ppm in the average at Ciminna and 814 ppm at Eraclea Minoa.

Iron. The mean content of total Fe is 4.07 % at Ciminna and 3.03 % at Eraclea Minoa. The lowest values for ER 81 and ER 89 samples (1.75 and 1.25 % respectively) are related to a low concentration of the clay fraction (fig. 2 d). The amount of Fe removed by 0.1 N HCl is low and some differences between Ciminna and Eraclea Minoa are evident: 5.9 and 2.31 % of total Fe respectively.

Manganese. The mean concentration of total Mn at Eraclea Minoa is twofold greater than at Ciminna, 657 and 296 ppm respectively. But it is important to point out that the fraction leached in 0.1 N HCl is more than 50 % of total Mn (64 % at Ciminna and 72 % Eraclea Minoa). Unlike Fe, Mn is present mainly in the carbonate fraction (tab. 1 and fig. 3).

Copper. Concentrations of total Cu are of the same order of magnitude in

TABLE 1
Metal content in the bulk sediment (T) and in 0.1 N HCl (L)
from Ciminna and Eraclea Minoa basins

Sample	K		Ca		Mg		Sr		Fe		Mn		Cu		Zn		Co		Ni		V		B				
	(T)	(L)	(T)	(L)	(T)	(L)	(T)	(L)	(T)	(L)	(T)	(L)	(T)	(L)	(T)	(L)	(T)	(L)	(T)	(L)	(T)	(L)	(T)	(L)			
CI 12	1.52	0.11	2.55	2.20	1.13	0.18	70	4.33	0.27	260	70	19	6.5	110	16	25	39	70	71								
CI 10	1.45	0.14	2.60	2.50	1.08	0.22	98	4.30	0.32	330	196	17	6.5	100	16	26	36	66	65								
CI 9	1.38	0.12	3.32	3.30	1.16	0.19	160	4.33	0.47	270	175	7	107	27	28	45	68	78									
CI 6	1.26	0.08	2.60	2.60	0.92	0.17	105	4.03	0.26	260	160	13	5	95	16	22	30	58	52								
CI 5	1.01	0.07	4.95	4.85	0.86	0.20	220	3.45	0.54	280	220	10	5.2	87	25	21	30	43	46								
CI 2	0.84	0.04	6.10	5.95	0.62	0.18	175	3.15	0.10	460	340	8.5	1.2	73	4.5	14	18	33	30								
CI 1	1.02	0.06	5.55	5.71	0.68	0.23	175	3.15	0.16	430	427	8.5	1.2	65	5.5	14	29	38	38								
CI 31	1.38	0.13	3.21	2.60	1.30	0.18	125	4.50	0.08	280	160	20	4.8	120	9.6	26	49	66	79								
CI 27	1.38	0.13	2.84	2.79	1.25	0.08	122	4.18	0.25	260	130	21	9.5	112	31	43	66	69	104								
CI 22	1.71	0.19	3.00	2.59	1.26	0.10	139	4.50	0.32	325	130	20	7.2	101	24	24	46	78	73								
CI 20	1.68	0.16	2.89	2.61	1.26	0.25	105	4.41	0.11	300	210	20	4.6	112	11	34	51	69	83								
CI 19	1.48	0.15	2.82	2.79	1.30	0.18	125	4.55	0.21	290	155	20	7.5	120	23	23	45	77	92								
BDC 450	1.54	0.17	5.56	5.50	1.30	0.30	462	3.75	0.20	195	114	19	6	100	14	20	36	58	74								
BDC 4	1.63	0.19	2.53	2.30	1.37	0.26	147	4.35	0.10	197	80	21	5.2	113	7.3	39	50	74	57								
Average:	1.41	0.13	3.60	3.47	1.10	0.20	161	4.07	0.24	296	190	17	5.5	101	16	26	41	62	67								
ER 98 VII	1.68	0.22	9.50	9.50	1.56	0.19	550	3.25	0.11	670	474	22	7.2	108	14	28	58	65	82								
ER 97 VII	1.73	0.16	8.91	8.61	1.62	0.40	812	3.95	0.03	330	202	8	7.1	100	5	61	22	57	111								
ER 95 VI	1.40	0.13	10.84	10.79	1.56	0.44	360	3.50	0.07	380	206	22	5.2	175	27	25	52	64	79								
ER 93 VI	1.82	0.18	9.21	8.71	1.38	0.29	623	3.83	0.09	440	306	16	4.5	80	6	28	50	63	103								
ER 90 VI	1.61	0.18	10.57	10.49	1.42	0.17	500	3.25	0.08	700	500	20	9	125	31	25	61	64	168								
ER 89 VI	0.33	0.05	28.59	22.38	0.63	0.23	2720	1.25	0.05	1880	1775	12	1.2	33	1	20	54	37	31								
ER 88 V	1.48	0.17	13.01	12.97	1.07	0.01	750	2.63	0.06	605	405	16	4.8	75	8	23	42	46	137								
ER 85 V	1.57	0.13	12.01	11.79	1.32	0.18	548	3.25	0.07	450	274	19	5.2	204	32	27	51	54	93								
ER 81 IV	0.51	0.05	24.39	22.41	0.90	0.17	740	1.75	0.03	730	380	30	12	79	18	21	45	33	31								
ER 78 III	1.40	0.13	11.32	11.20	1.67	0.31	540	3.63	0.12	375	233	19	6	80	5.5	25	49	59	69								
Average:	1.35	0.14	13.84	12.88	1.31	0.24	814	3.03	0.07	657	474	18	5.6	106	19	28	48	54	90								

Concentrations of K, Ca, Mg, Fe as %; concentrations of Sr, Mn, Cu, Zn, Co, Ni, V, B as ppm.

both series examined: 17 ppm at Ciminna and 18 ppm at Eraclea Minoa. The amount of Cu in the fraction leached by 0.1 N HCl is in the average 30 % of the total, an indication that a significant fraction of Cu is present in carbonates.

Zinc. In the same way as Cu, even total Zn has the same average concentration in both series (101 and 106 ppm respectively at Ciminna and Eraclea Minoa); at

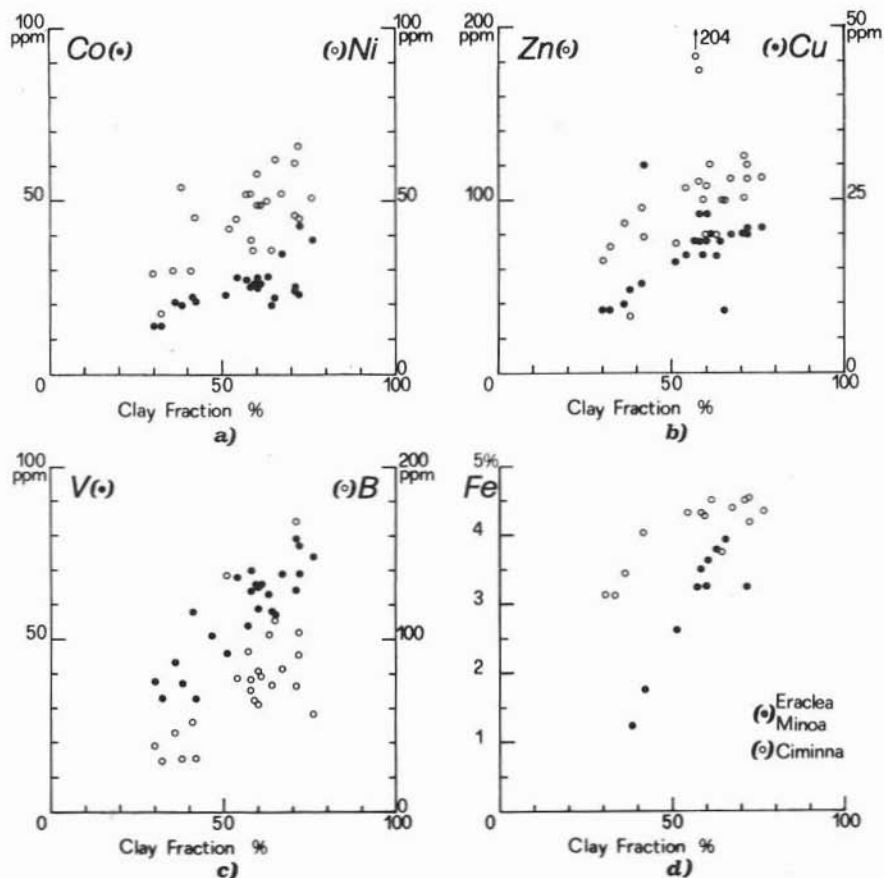


Fig. 2. — Concentration compared to the of trace elements versus clay fraction in Ciminna and Eraclea Minoa clay sediments.

Eraclea Minoa anyway variations range from 33 to 204 ppm. The average concentration of leached Zn is approximately the same in either series, 16 % at Ciminna and 15 % at Eraclea Minoa, with wide variations. Generally Zn appears to be related with Cu and with the clay fraction, rather than with the carbonate fraction.

Nickel. Ni varies between 18 and 66 ppm (average 41 ppm) at Ciminna and it does not show variations at Eraclea Minoa, where the average is 48 ppm.

Cobalt. Concentrations of Co do not vary in either series, where the mean contents are 26 and 28 ppm (Ciminna and Eraclea Minoa respectively). Like Ni, Co shows to be correlated with the clay fraction (fig. 2 a)).

Vanadium. No variations in V concentrations are evident in either series where the average values are 62 and 54 ppm (Ciminna and Eraclea Minoa respectively). Vanadium is strongly correlated with boron, and either one with the clay fraction (fig. 2c); boron was determined in a previous work by CORADOSSI and CORAZZA (1976).

Mineral composition. Quartz and calcite are the most abundant components in all samples, with the general feature that sediments with a higher fraction of quartz contain less calcite and the contrary: at Ciminna 27 % quartz and 11 % calcite; at Eraclea Minoa 8.5 % quartz and 25 % calcite. It is noteworthy that the lowermost part of the series from Monte Rotondo (Ci 1, Ci 2, Ci 5) shows high quartz content (44 % in the average). Actually these samples are made up of sandstones and greyish sandy clays (DI STEFANO and CATALANO, 1976).

All other components like feldspars, dolomite and gypsum are generally absent or less than 5 %.

Fraction lesser than 2 μ m. The total clay fraction is given as difference, complementary to all other minerals; it varies between 25 and 78 % at Ciminna (average 51 %), and between 38 and 70 % at Eraclea Minoa (average 57 %).

Discussion

The results in table 1 and figs. 2, 3, 4, suggest that distribution of the metals analyzed is significantly different between the basins of Ciminna and Eraclea Minoa.

This is true for some major elements, like Ca and Fe as well as for Mn, Sr, and to a lesser major elements, like Ca and Fe as well as for Mn, Sr, and to a lesser extent for V, B and Ni; Cu, Zn and Co instead result of the same order of magnitude. These differences give an indication of the sedimentation environment to have been different for the two basins. The common feature is the evaporitic event which took place in the same moment, as the common sedimentary facies witness.

Potassium and calcium are bound to clay minerals and to carbonates (and to gypsum whenever present) respectively; all other metals determined which are bound to either one of the above mi-

neralological fraction, can give indications on the sedimentation environment. In fact their concentrations are influenced to a greater or lesser extent by the chemical and physical conditions of the environment. In the two basins the Fe-Mn couple has significantly different average values and distributions. At Ciminna

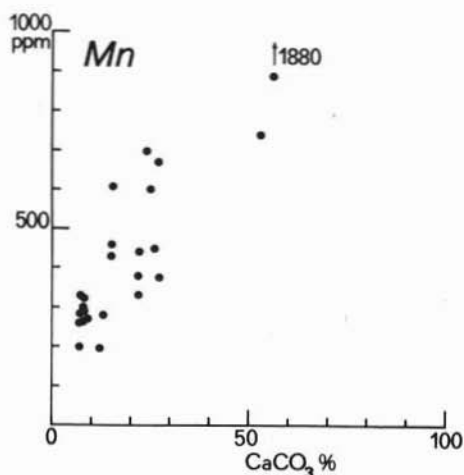


Fig. 3. — Mn-CaCO₃ relationship in Ciminna and Eraclea Minoa clay sediments.

the average concentration of total Fe is 26% greater than at Eraclea Minoa. This difference in concentration can be ascribed to the different mineralogical composition of the clay fraction; at Ciminna in fact such minerals as illite-montmorillonite, chlorite and chlorite-vermiculite are prevailing on kaolinite which is instead the most abundant clay mineral at Eraclea Minoa.

Another interesting observation is that treatment with 0.1 N HCl dissolves a small fraction of total Fe, but the Fe content in the 0.1 N HCl solution from the Ciminna samples is two times greater than Fe extracted from the Eraclea Minoa samples; such a difference can be an indication that clay sediments from Ciminna

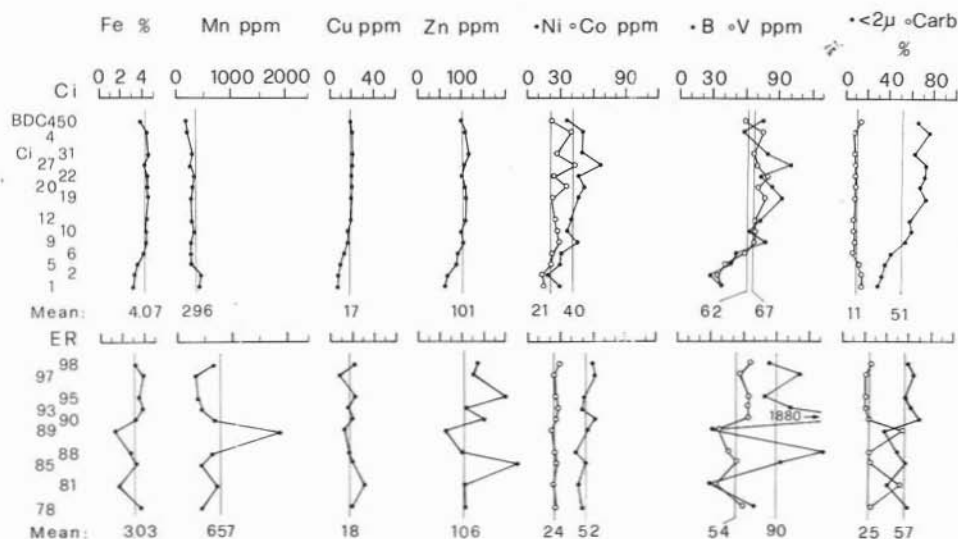


Fig. 4. — Metal content and mineralogical composition of CaCO_3 and $< 2 \mu$ fraction in Ciminna and Eraclea Minoa clay sediments.

contain a significant fraction of iron in a soluble form. In the positive correlation between Fe and clay fraction (fig. 2d and fig. 4) some differences are evident between two basins: the trend for Eraclea Minoa is toward a 30% approximately of iron-free clay with decreasing Fe concentration (fig. 2d); besides, the Fe pattern in fig. 4 exactly follows the clay fraction pattern, an indication that all iron belongs to the crystal lattice of clay minerals. For Ciminna instead the trend shown in fig. 2d, though less clear, is for a fraction of Fe (2-3%) not related to the clay minerals; in fig. 4 the Fe pattern does not follow but dampens the clay fraction pattern, especially for low-clay sediments. The reason for this can be the presence of non-clay iron minerals, such as hydroxides, which are easily soluble.

Further informations on the environment conditions in the two basins are given by Mn distribution. The difference in concentrations, even 50% on the average, is almost certainly a consequence of the higher carbonate content in the sediments

from Eraclea Minoa. In fact Mn closely correlates calcium carbonate in the Eraclea Minoa sediments (fig. 3) which contain calcite more than twice as much as the ones from Ciminna. This difference in content can be attributed to the different origin of calcite: mainly detritic at Ciminna and mainly organogenic at Eraclea Minoa; this accounts for the high Mn concentration in the latter series. In fact it is well known that Mn accumulates in deep sea sediments through an organogenic extraction, as much as 100,000 times (as MnO). Mn undergoes enrichment in carbonates with respect to Fe because of its ionic radius, closer to Ca^{2+} radius than Fe^{2+} . This enrichment can take place even without the intervention of such organisms as diatoms and foraminifera, just for chemical precipitation under reducing conditions once carbonates saturation is reached.

Concentration of Cu, Zn, Ni, Co, V and B are all of the same order of magnitude as the ones found in marine sediments with none or little organic matter. Examination of couples Cu-Zn, Ni-Co, and V-B confirms their geochemical correlation as well as the correlation of all them with the clay fraction (figs. 2a, b, c). For Cu the arithmetic mean of 2,000 samples from various sites is 39 ppm, while higher mean values and a higher scattering are found in pelagic sediments (WEDEPOHL, 1970). Zn has a behaviour similar to Cu, and even its distribution is similar, yet greater variations are evident for Eraclea Minoa, where two samples (ER 85 and ER 95) are twice the average value. More than Cu, Zn in either basin approaches the values found for deep sea sediments.

Ni and Co have similar concentrations in both series. Ni concentrations, in turn, are of the same order as the ones observed in recent marine clays (LANDERGRÉN, 1948; POTTER et al., 1963; YOUNG, 1968); Co concentrations instead are 40% higher than the ones found in shales (world-wide) (RONOV et al., 1955; CARR and TUREKIAN, 1961).

For V there are slight differences between the two basins; its concentrations too are lesser than in recent marine clays (TUREKIAN and WEDEPOHL, 1961).

Conclusions

The observed trace element distribution appears to be independent of the evaporitic events which affected the basins studied. No significant differences can be pointed out for Cu, Zn, Ni, Co, V and B between pre-evaporitic sediments (environment with an active exchange) and intra-evaporitic ones (reduced exchange); as a consequence an euxinic environment, though likely to have occurred, is not reflected by any metal enrichment.

Instead the Mn concentration differences between the two basins give informations on different sedimentation environments. The higher total (as well as leachable) Mn content associated to a higher CaCO_3 content in the sediments from Eraclea Minoa suggests a Mn accumulation owed to organisms during precipitation of their calcareous tests. Besides, in a basin with restricted circulation, with salinity variation, and subjected to an evaporitic climate the predominant biota are

mollusks, foraminifera, ostracods and some type of algae, all of them contributing in an essential way to the formation of calcareous deposits.

The high carbonate content (25 %) observed at Eraclea Minoa, with reference to Ciminna, can be ascribed to two factors governing its concentrations: one is the CaCO_3 supersaturation in anoxic waters during CO_2 generation; as a consequence calcareous microfossils are preserved together with authigenic carbonates (Suess, 1979). The second reason can be the partial dissolution of CaCO_3 either because of fresh water or because of a CO_2 -rich oxic environment, where solid CaCO_3 is undersaturated. At Ciminna the evidence is of frequent fresh water inputs, as confirmed also by the abundant detrital minerals and by the deltaic clastic character of sediments. The presently observed carbonate contents can therefore be ascribed to different origins in the two basins: at Ciminna mainly detrital and/or partially dissolved carbonates which reflect an oxic and possible hypersaline environment; an anoxic (hypersaline) environment at Eraclea Minoa.

The greater fraction of leachable Fe at Ciminna is a further indication of different environment where an important fraction of Fe could be «trapped» in the sediment in an acid-soluble form. This did not take place in sediments at Eraclea Minoa, where all Fe results to be bound into the clay mineral crystal lattice. So, even the presence of «free» iron at Ciminna and its absence at Eraclea Minoa is an indication of some particular environmental conditions which controlled the water-sediment equilibrium.

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