

Trace element distributions in the Strait of Sicily (Central Mediterranean Sea). I. Evidence of rock-water interactions and pollution

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ABSTRACT. — Distributions of V, Cr, Fe, Co, Ni, Cu, Zn, Y, Cd, Ba, La, Ce, Nd, Eu, Pb were determined in seawater samples collected at different depths in the Strait of Sicily (Central Mediterranean) during the oceanographic cruise BANSIC 98. Sampling sites were selected in order to study mechanisms of water-rock interactions and anthropic inputs.

Application of Principal Component Analysis (PCA) carried out on the whole dataset allowed us to recognize different behaviours of the studied elements along the water column. In particular:

– Water-rock interactions probably take place at the bottom of the stations around Pantelleria Island and can be invoked as responsible of some observed elemental distributions. Distribution patterns of Ce and Nd behaviours reflect recycling phenomena at the presence of iron oxyhydroxides. Barium and Eu distributions could be related to the effects of alteration of feldspar bearing rocks similar to those outcropping in the Pantelleria area.

– Distribution patterns of V, Cr, Ni, Cu, Zn and Cd are probably of atmospheric origin and their concentration are also driven by biological cycling processes mediated by organic particulate. Distribution of Co and Pb could be explained as result of surface absorption processes on calcite particulate. Vanadium and Ni contents in seawater

seem also strongly related to petroleum pollution mainly present in the Strait of Sicily close to the Gulf of Gela.

RIASSUNTO. — La distribuzione di V, Cr, Fe, Co, Ni, Cu, Zn, Y, Cd, Ba, La, Ce, Nd, Eu, Pb è stata determinata in campioni di acqua marina raccolti a differenti profondità nello Stretto di Sicilia (Mediterraneo Centrale) durante la crociera oceanografica BANSIC 98. I siti di campionamento sono stati selezionati in modo tale da potere studiare meccanismi di interazione acqua-roccia ed esiti di apporti antropici.

L'applicazione dell'Analisi della Componente Principale (PCA) condotta sull'intero dataset ha permesso di riconoscere differenti comportamenti degli elementi in tracce studiati lungo la colonna d'acqua. In particolare:

– Interazioni acqua-roccia hanno avuto probabilmente luogo in stazioni circostanti Pantelleria e sembrano essere responsabili di alcune distribuzioni elementari osservate. Il comportamento di Ce e Nd riflettono fenomeni di *recycling* in presenza di ossidrossidi di Fe, mentre la distribuzione di Ba ed Eu potrebbero essere dovute ad effetti di alterazione di rocce feldspatiche affioranti nell'area di Pantelleria.

– Il comportamento di V, Cr, Ni, Cu, Zn e Cd lasciano intendere che tali elementi sono legati a fallout atmosferico e la loro distribuzione nella colonna d'acqua è governata da processi biologici

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mediati da particolato organico. La distribuzione di Co e Pb sembra essere legata a fenomeni di interazione superficiale su particolato carbonatico, mentre il contenuto di V e Ni nella colonna d'acqua sembra indicare esiti di inquinamento da prodotti petroliferi.

KEY WORDS: *Mediterranean Sea, Trace elements, Rare Earth Elements, Rock-water interaction*

INTRODUCTION

In the last years, an increasing number of data concerning concentrations of several trace metals was collected in the Mediterranean waters to better understand their distribution and interaction paths in seawater (Laumond *et al.*, 1984; Copin-Montegut *et al.*, 1986; Greaves *et al.*, 1991; Saager *et al.*, 1993; Grousset *et al.*, 1990; 1995; Schijfs and De Baar, 1995; Bau *et al.*, 1997; Morley *et al.*, 1997; Yoon *et al.*, 1999; Zeri *et al.*, 2000; Elbaz-Poulitchet *et al.*, 2001).

The Mediterranean basin represents an interesting «natural laboratory» for the study of the geochemical response of trace elements in seawater to river contributions, diffusion of continental shelf sediments, aeolian particulate fallout, antropogenic sources and water-rock interactions (e.g., results of the project EROS 2000; Martin and Milliman, 1997). Moreover several studies (e.g., Boyle *et al.*, 1985) identified trace metal anomalies in outflow core of Mediterranean waters into the Atlantic Ocean.

The present study concerns the analyses of selected trace elements in order to evidence the occurrence of rock-water interactions under hydrothermal conditions and anthropic inputs in areas possibly polluted by large chemical, mainly petrolchemical, wastes. Two different areas were selected in the Strait of Sicily: Gulf of Gela and Island of Pantelleria. The large geochemically «incompatible» elements as Ba, La, Ce, Nd, Eu and Y, were measured in order to define the possible occurrence of rock-water interactions, since these elements are enriched in alkaline and peralkaline magmatic products outcropping in the Pantelleria area, especially in sampling sites located very close to large

tectonic discontinuities (Civetta *et al.*, 1998). On the contrary, V, Cr, Fe, Co, Ni, Cu, Zn, Cd and Pb were studied because their occurrence in seawater could provide useful information of anthropic inputs in seawater (Grousset *et al.*, 1995).

MATERIALS AND METHODS

Samples were collected in the early summer of 1998 during the BANSIC 98 cruise, aboard of the RV «Urania». Location of sampling sites is given in Fig. 1.

Distribution of samples throughout the column water were selected to identify, from a geochemical point of view, the most important oceanographic discontinuities recorded by temperature and salinity profiles. In any case, one surface and one bottom water sample was collected. Along the water column each sample was collected in correspondence to identified salinity changes. For the deeper profile of the station S-945, four samples were collected to record trace metal variations below 200 m, at depths where the maximum of salinity was recorded. The Gulf of Gela and Pantelleria area were selected for trace metal analyses in order to identify the anthropic influence from the continental zone and to monitor the geochemical response of the seawater to interactions with alkaline-perialkaline rocks and hydrothermal fluids.

A statistical approach, mainly based on the Principal Component Analysis, was used to identify different groups of elements whose distribution was induced by different origin and/or water-rock interaction mechanisms and for a better comprehension of the behaviour of selected elements in the aqueous system.

The sampling system consisted in a Neil-Brown CTD rosette frame on which 24x12 l teflon-lined GoFlo bottles were mounted. Upon recovery of the GoFlo bottles, 1 liter of each water sample was immediately filtered using 0.4 mm Millipore® filters, using a teflon tubing apparatus, acidified with HNO₃ (Merck ULTRAPUR®) in order to obtain pH 1-2, and stored in hot-acid washed polyethylene bottle.

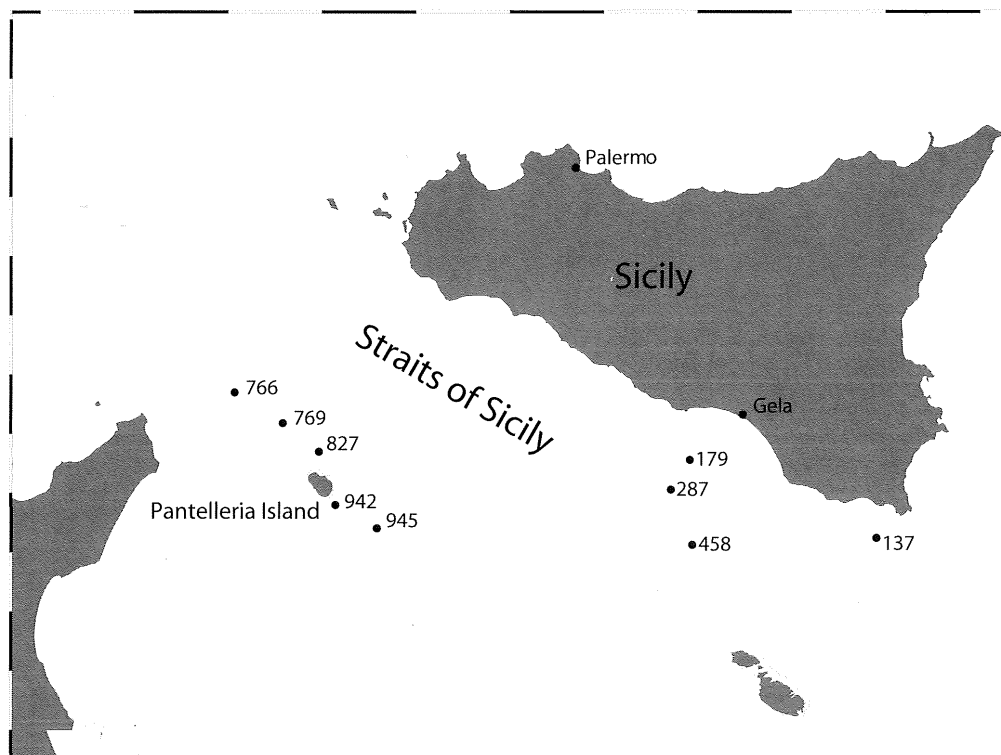


Fig. 1 – Stations location in the studied area.

In the clean room of DITHF chemical laboratory (University of Palermo) $\text{NH}_4\text{-CH}_3\text{COO}$ was added to the samples in order to adjust pH in the range from 6 to 7. Then samples were preconcentrated with CHELEX 100® (100-200 mesh) ion-exchange resin in a column according to Paulson (1986) and Möller *et. al.* (1992). Concentrated fractions were eluted adding 5 ml of 20% HNO_3 Merck ULTRAPUR® solution in ultrapure MILLIPORE® water, obtaining an enrichment factor of 200. Chemical analyses of V, Cr, Fe, Ni, Co, Cu, Zn, Y, Cd, La, Ce, Nd, Eu and Pb were carried out on this concentrated fraction with a Agilent HP 4500 inductively coupled plasma mass spectrometer (ICP-MS) equipped with autosampler and acid-resistant spray chamber. On the contrary Ba analyses were carried out directly on previously 10 times diluted seawater samples with a Finnigan MAT

Element 2 high resolution ICP-MS (HR-ICP-MS) being Ba is not well recovered onto CHELEX 100® resin. Moreover Ba intensity was also measured on the enriched fraction of each sample in order to evaluate the effective capability of CHELEX-100 to concentrate Ba ions whose presence in the eluted fraction can originate spectral interferences of $^{135}\text{BaO}^+$ and $^{137}\text{BaO}^+$ molecular ions on ^{151}Eu and ^{153}Eu , as reported by Möller *et al.* (1992).

The evaluation of the interferences due to spectral overlapping both of isotopes and MO^+ and MOH^+ molecular ions were carried out according to manufacturer's recommendations, monitoring several isotopes, where possible, for each element. Moreover the analytical results obtained measuring standard reference materials of National Research Council (NRC) of Canada SRM'S (CASS-4, NASS-5) confirm that analyses of first transition row elements using a

Quadrupole IPC-MS can be performed as reported by several authors (Willie *et al.*, 1998; Hirata *et al.*, 2001; Jiménez *et al.*, 2002) and allow us to evaluate instrumental repeatability of the measured values and accuracy of data.

Instrumental repeatability was evaluated from 10 consecutive measurements of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd in CASS-4 solution and of La, Ce, Nd, Eu and Y in an artificial

seawater standard that was prepared according to Hirata *et al.* (2001). The amount of recovery with CHELEX 100® resin for V, Cr, Fe, Co, Ni, Cu, Zn, and Cd were evaluated using CASS-4 and NASS-5 international seawater standards while for La, Ce, Nd, Eu and Y was used the above mentioned artificial seawater standard. These results are reported in Table 1. All samples were treated under a laminar air

TABLE 1

Investigated trace elements and their percent recovery with CHELEX 100® exchange resin calculated on CASS-4, NASS-5 Standard Reference Seawaters and artificially prepared seawater both with batch and column method approaches. Standard deviations (σ) and detection limits (D.L.) are also reported. Values are quoted in mg/Kg. For detailed informations see text.

Isotope	CASS-4 Batch	CASS-4 Column	σ	D.L.	Reference	Recovery % Batch	Recovery % Column
⁵⁰ Cr	0.12	0.14	± 0.060	0.180	0.144	83	97
⁵¹ V	0.99	1.13	± 0.050	0.150	1.18	84	95
⁵⁷ Fe	0.79	0.67	± 0.020	0.060	0.713	110	94
⁵⁹ Co	0.023	0.024	± 0.009	0.027	0.026	90	93
⁶⁰ Ni	0.33	0.30	± 0.030	0.090	0.314	107	96
⁶³ Cu	0.57	0.58	± 0.010	0.030	0.592	97	97
⁶⁵ Cu	0.545	0.510	± 0.015	0.045	0.592	92	86
⁶⁶ Zn	0.341	0.382	± 0.018	0.054	0.381	90	100
⁶⁸ Zn	0.39	0.38	± 0.020	0.060	0.381	103	99
¹¹¹ Cd	0.025	0.024	± 0.005	0.015	0.026	96	92
	NASS-5	NASS-5			Reference		
⁵⁰ Cr	0.09	0.11			0.11	82	96
⁵¹ V	1.01	1.16			1.2	84	97
⁵⁷ Fe	0.20	0.21			0.207	98	99
⁵⁹ Co	0.012	0.010			0.011	109	86
⁶⁰ Ni	0.25	0.26			0.253	98	103
⁶³ Cu	0.27	0.29			0.297	91	98
⁶⁵ Cu	0.261	0.281			0.297	88	95
⁶⁶ Zn	0.090	0.122			0.102	88	119
⁶⁸ Zn	0.11	0.10			0.102	105	96
¹¹¹ Cd	0.021	0.025			0.023	91	109
	SEAWATER*	SEAWATER*			Reference*		
⁸⁹ Y	4.61	4.63	± 0.06	0.180	5.00	92	93
¹³⁹ La	2.74	2.83	± 0.04	0.120	3.00	91	94
¹⁴⁰ Ce	1.32	1.55	± 0.02	0.060	1.50	88	104
¹⁴⁴ Nd	2.76	2.80	± 0.08	0.240	3.00	92	93
¹⁵¹ Eu	0.23	0.23	± 0.01	0.030	0.25	93	91

flow clean bench to minimize the contamination risks.

Analytical blanks were obtained with 50 ml of HNO₃ Merck Ultrapure in Millipore ultrapure waters and measured concentrations were negligible compared with those measured in the enriched eluted fractions. Five aliquots of this ultrapure solutions were analysed five times and the standard deviations calculated from the average values measured (Tab. 1).

A Principal Component Analysis (PCA) approach was adopted for statistical treatment of the available data. PCA is an analytic ordination technique commonly used to reduce the dimensionality (i.e., the number of variables) of the original dataset and to detect structure in the relationships among variables. It consists in the extraction of statistically independent linear combinations from the original variables, with the aim of obtaining a small set of components able to explain most of the total variance of data. All statistical analyses were carried out using the statistical software STATVIEW 5.0.1 for Mac OS.

RESULTS

Trace elements distribution

Trace element concentrations vs. depth, and sampling area are reported in Tab. 2 while temperature and salinity profiles are given in Fig. 2.

Trace element distributions in stations S-179, S-287 and S-458 generally show an increase of V, Cr, Fe, Ni, Co, Cu, Zn, Cd, and Pb concentrations at about 100 m (Fig. 3). Barium and Eu in S-287 site show minimum values around 100 m. Similar concentration values for all these elements can be observed down to about 400 m, except for Cr at site S-179 that reaches a minimum at the same depth similarly with Cr, Co, Cd and Pb in site S-287. Generally from 400 m down to the bottom of the S-179 and S-458 sites many trace elements show decreasing concentrations. Yttrium, Ce and Nd generally show a regular increase from the

surface down to the bottom of the water column. Below 400 m in S-287 site Cr, Co, Ni, Zn, Fe and Pb concentrations reach maximum values.

In the stations S-766 and S-769 the largest concentration values of V, Cr, Fe and Ni are reached in shallow water layer while in the S-827 station, elemental concentrations increase down to about 300 m (Fig. 4). At S-766 and S-769 sites the lowest contents of some trace elements are recorded at depths ranging from surface to 100 m, reflecting the lower salinity values (Fig. 2). Finally, the S-766 station shows the highest values of all the elements, except La, at the bottom of the water column.

Stations S-942 and S-945 show an abrupt increase of concentration from the surface to about 100 m for all the elements, which corresponds to a general increase of salinity values recorded in the two sites from 50 to 200 m of depth (Fig. 2 and 5). Furthermore, in the station S-945, V, Fe, Co, Cd and Ba show a further relative positive peak of concentration at about 600 m and a strong increase at the bottom.

Principal Component Analyses

Principal component analyses allowed us to identify three principal components (PCs) that represent 57% (PC1), 14% (PC2) and 11% (PC3) of the whole variance, respectively. Graphical plot of factor loadings (Fig. 6) shows that PC1 is not able to discriminate the contributions of different groups of elements. On the other hand, contributions of V, Cr, Fe, Co, Pb and those of Cd, Ba, La and Eu are enhanced by PC2 and PC3. Factor scores of PCA calculations are given in Table 3.

Plots of scores mainly discriminate samples coming from stations placed North-West from Pantelleria (S-766, S-768, S-827), samples from South-East from Pantelleria and other samples from stations near to the Gulf of Gela. This discrimination is shown in PC2 vs. PC1 space and in PC3 vs. PC1 space, while PC3 vs. PC2 plot allowed us to discriminate samples enriched in Ba and Eu from samples with higher Cd content.

TABLE 2
Location, sampling depth and trace elements compositions of the studied samples.

Location	Sample	depth (m)	V nmol/l	Cr nmol/l	Fe nmol/l	Co nmol/l	Ni nmol/l	Cu nmol/l	Zn nmol/l	Y nmol/l	Cd nmol/l	Ba nmol/l	La nmol/l	Ce nmol/l	Nd nmol/l	Eu nmol/l	Pb nmol/l
Strait of Sicily	179/4	5	4.71	0.53	270.5	0.362	4.3	7.4	37	0.049	0.115	74	0.028	0.014	0.009	0.009	0.004
Strait of Sicily	179/3	70	6.09	1.49	509.4	0.531	5.7	16.8	80	0.064	0.248	260	0.032	0.019	0.012	0.025	0.006
Strait of Sicily	179/2	400	6.28	0.56	404.7	0.500	8.0	27.2	67	0.074	0.274	208	0.059	0.022	0.017	0.030	0.007
Strait of Sicily	179/1	488	4.71	0.82	408.6	0.361	4.5	8.7	38	0.091	0.155	185	0.096	0.035	0.021	0.029	0.004
Strait of Sicily	287/4	1.5	6.48	1.74	402.9	0.456	6.4	15.7	70	0.054	0.451	196	0.041	0.018	0.012	0.020	0.007
Strait of Sicily	287/3	101	8.05	2.40	397.3	1.193	8.5	12.6	58	0.070	0.326	12	0.035	0.019	0.014	0.002	0.020
Strait of Sicily	287/2	339	9.23	1.76	441.0	0.663	10.2	14.9	60	0.073	0.169	89	0.056	0.026	0.018	0.010	0.005
Strait of Sicily	287/1	780	11.97	3.66	600.4	4.062	12.4	17.9	89	0.089	0.236	55	0.051	0.019	0.014	0.008	0.032
Strait of Sicily	137/3	1.5	5.30	0.83	422.0	0.424	5.3	9.0	49	0.053	0.167	18	0.032	0.017	0.013	0.002	0.005
Strait of Sicily	137/2	52	7.26	1.08	477.7	0.527	7.4	13.5	62	0.064	0.300	175	0.046	0.018	0.012	0.024	0.006
Strait of Sicily	137/1	86	5.69	0.53	379.8	0.522	7.3	11.2	68	0.077	0.238	75	0.044	0.027	0.021	0.011	0.007
Strait of Sicily	458/4	5	6.48	1.20	420.4	0.403	5.2	11.2	39	0.047	0.149	206	0.024	0.014	0.010	0.024	0.004
Strait of Sicily	458/3	110	10.40	1.67	527.8	0.753	14.1	16.7	70	0.076	0.293	273	0.043	0.018	0.012	0.033	0.006
Strait of Sicily	458/2	449	11.58	1.82	581.0	0.771	11.7	17.2	71	0.091	0.230	207	0.054	0.021	0.014	0.024	0.006
Strait of Sicily	458/1	600	8.44	1.23	409.0	0.700	10.8	16.2	83	0.081	0.204	177	0.057	0.024	0.018	0.018	0.006
N-E Pantelleria	766/5	0	4.12	0.35	207.0	0.366	10.3	6.8	37	0.044	0.130	89	0.027	0.015	0.010	0.010	0.004
N-E Pantelleria	766/4	74	1.96	0.08	67.3	0.142	1.2	3.3	24	0.011	0.087	34	0.015	0.004	0.004	0.003	0.003
N-E Pantelleria	766/3	200	4.12	0.28	276.5	0.276	3.3	6.9	34	0.033	0.126	73	0.070	0.008	0.007	0.010	0.003
N-E Pantelleria	766/2	320	4.71	0.85	229.2	0.430	6.6	11.3	56	0.030	0.171	146	0.168	0.012	0.008	0.018	0.006
N-E Pantelleria	766/1	530	6.48	0.99	391.6	0.559	9.2	29.2	85	0.069	0.374	147	0.106	0.023	0.016	0.018	0.007
N-E Pantelleria	769/7	5	3.73	0.14	120.0	0.283	4.0	11.3	35	0.033	0.052	10	0.038	0.021	0.014	0.002	0.003
N-E Pantelleria	769/6	12	1.18	0.18	77.2	0.072	1.2	1.3	6	0.002	0.006	52	0.004	0.001	0.001	0.009	0.001
N-E Pantelleria	769/5	47	6.28	0.47	263.2	0.449	6.8	11.2	62	0.053	0.081	32	0.046	0.026	0.017	0.005	0.004
N-E Pantelleria	769/4	81	5.10	0.79	297.2	0.348	4.3	10.2	43	0.024	0.155	169	0.027	0.011	0.007	0.016	0.004
N-E Pantelleria	769/3	148	5.30	0.99	336.6	0.352	4.2	9.3	47	0.040	0.162	135	0.070	0.013	0.007	0.014	0.004
N-E Pantelleria	769/2	300	6.87	1.28	384.1	0.487	6.3	9.3	48	0.051	0.142	161	0.056	0.016	0.012	0.015	0.004
N-E Pantelleria	769/1	458	6.28	1.07	411.6	0.454	5.9	11.2	50	0.049	0.286	229	0.031	0.015	0.009	0.020	0.005

TABLE 2: *Continued*

Location	Sample	depth (m)	V nmol/l	Cr nmol/l	Fe nmol/l	Co nmol/l	Ni nmol/l	Cu nmol/l	Zn nmol/l	Y nmol/l	Cd nmol/l	Ba nmol/l	La nmol/l	Ce nmol/l	Nd nmol/l	Eu nmol/l	Pb nmol/l
N-E Pantelleria	827/7	0	0.20	0.00	0.4	0.006	0.0	0.9	1	0.006	0.000	1	0.005	0.003	0.006	0.001	0.000
N-E Pantelleria	827/5	58	0.98	0.11	41.2	0.064	0.8	2.2	7	0.004	0.005	12	0.007	0.004	0.005	0.001	0.001
N-E Pantelleria	827/4	216	4.32	0.88	175.1	0.334	4.3	7.2	45	0.048	0.109	88	0.063	0.036	0.024	0.009	0.003
N-E Pantelleria	827/3	270	4.71	0.62	215.8	0.451	5.2	8.7	48	0.049	0.145	16	0.040	0.024	0.017	0.002	0.004
N-E Pantelleria	827/2	500	3.93	0.63	201.6	0.245	3.5	6.5	46	0.026	0.080	58	0.025	0.010	0.009	0.005	0.003
N-E Pantelleria	827/1	606	0.39	0.01	0.2	0.003	0.0	2.0	5	0.008	0.006	5	0.037	0.001	0.001	0.001	0.001
S-W Pantelleria	942/6	0	6.48	0.97	316.2	0.617	7.7	14.2	63	0.066	0.234	40	0.053	0.020	0.015	0.005	0.010
S-W Pantelleria	942/5	42	6.48	0.53	354.0	0.441	5.6	12.0	48	0.043	0.250	20	0.031	0.011	0.009	0.003	0.004
S-W Pantelleria	942/4	78	8.83	1.37	335.7	0.654	10.6	16.4	70	0.059	0.173	125	0.157	0.045	0.027	0.016	0.007
S-W Pantelleria	942/3	400	6.67	0.61	329.5	0.510	8.1	11.0	53	0.058	0.167	101	0.053	0.021	0.015	0.011	0.006
S-W Pantelleria	942/1	735	5.30	0.49	312.1	0.398	5.3	9.1	41	0.033	0.170	66	0.019	0.008	0.006	0.007	0.004
S-W Pantelleria	945/10	0	6.28	1.42	344.9	0.582	11.1	21.7	97	0.042	0.238	41	0.032	0.015	0.009	0.004	0.006
S-W Pantelleria	945/9	45	8.05	2.44	495.1	0.929	8.8	14.6	83	0.080	0.214	31	0.125	0.045	0.029	0.004	0.008
S-W Pantelleria	945/8	121	7.26	1.96	431.3	0.909	14.5	42.6	172	0.108	0.718	177	0.256	0.073	0.050	0.016	0.017
S-W Pantelleria	945/7	219	4.71	0.40	242.1	0.417	12.5	27.9	64	0.041	0.448	150	0.080	0.008	0.006	0.017	0.006
S-W Pantelleria	945/5	601	6.87	0.51	360.4	0.477	7.5	17.6	63	0.044	0.712	153	0.093	0.011	0.008	0.019	0.006
S-W Pantelleria	945/4	899	4.12	0.30	204.7	0.335	5.0	12.7	45	0.026	0.415	130	0.129	0.010	0.005	0.013	0.006
S-W Pantelleria	945/3	1200	0.79	0.00	1.8	0.040	1.0	1.7	10	0.000	0.011	94	0.003	0.001	0.000	0.005	0.002
S-W Pantelleria	945/1	1294	6.09	0.61	348.3	0.474	8.2	16.2	73	0.031	0.363	144	0.343	0.013	0.008	0.017	0.007

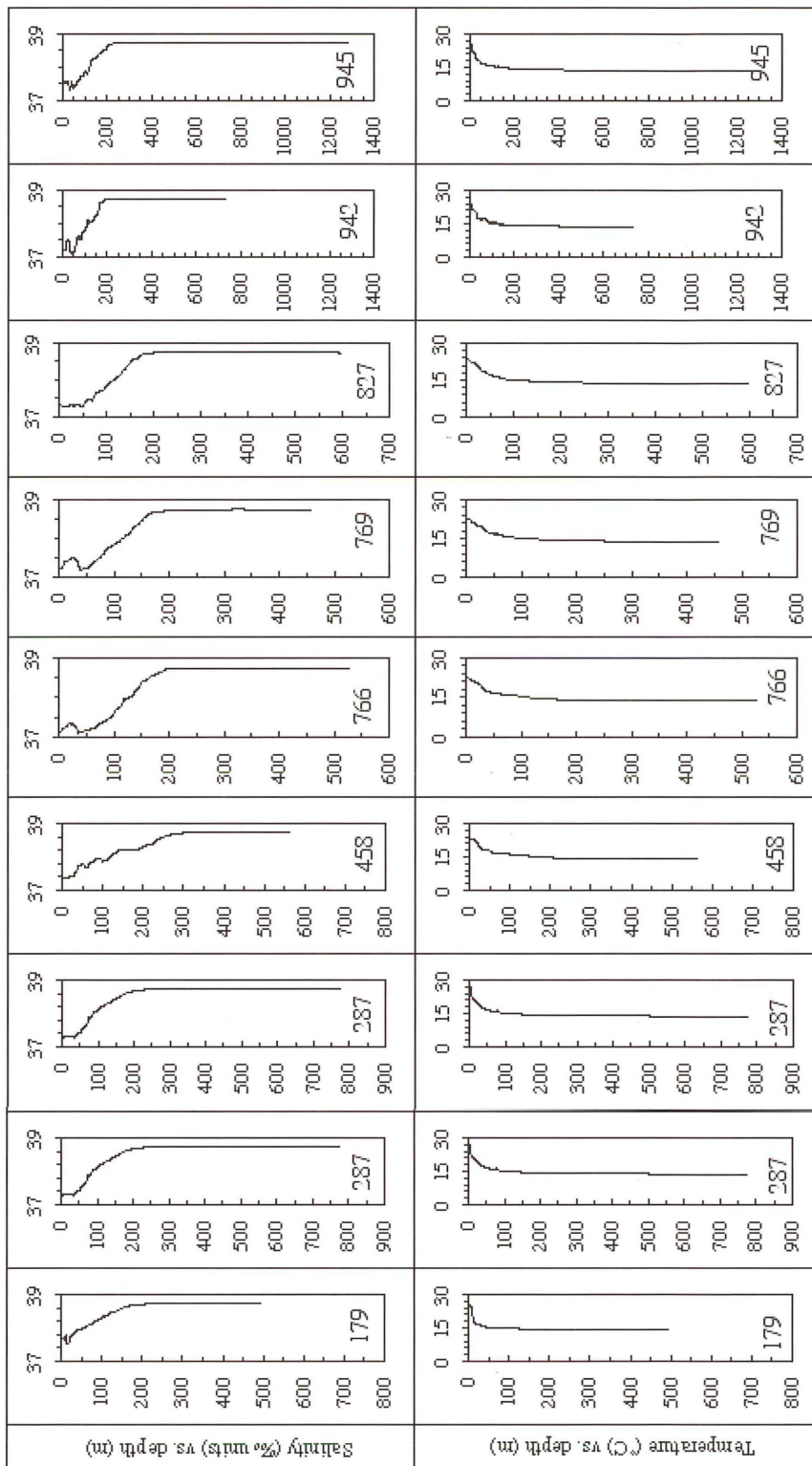


Fig. 2 – Water profiles illustrating salinity and temperature distributions in studied sites.

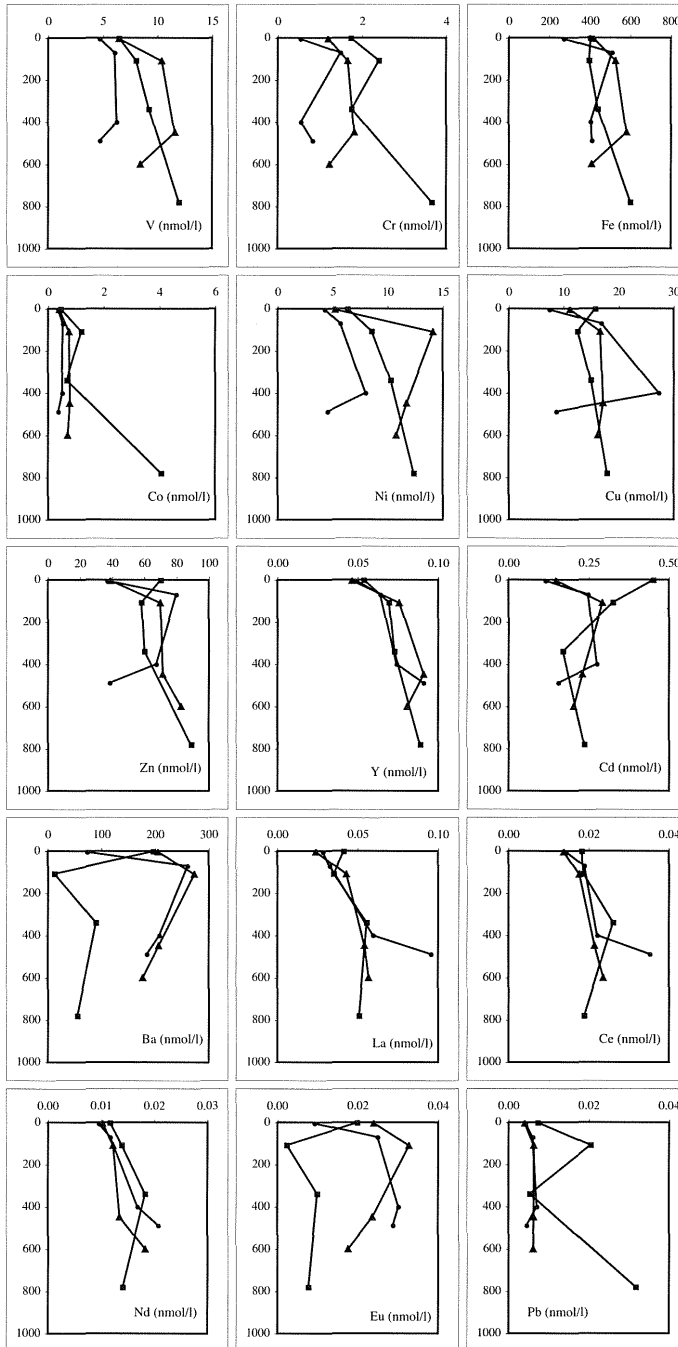


Fig. 3 – Water profiles illustrating trace elements distributions in station 179 (full circles), 287 (full squares) and 458 (full triangles).

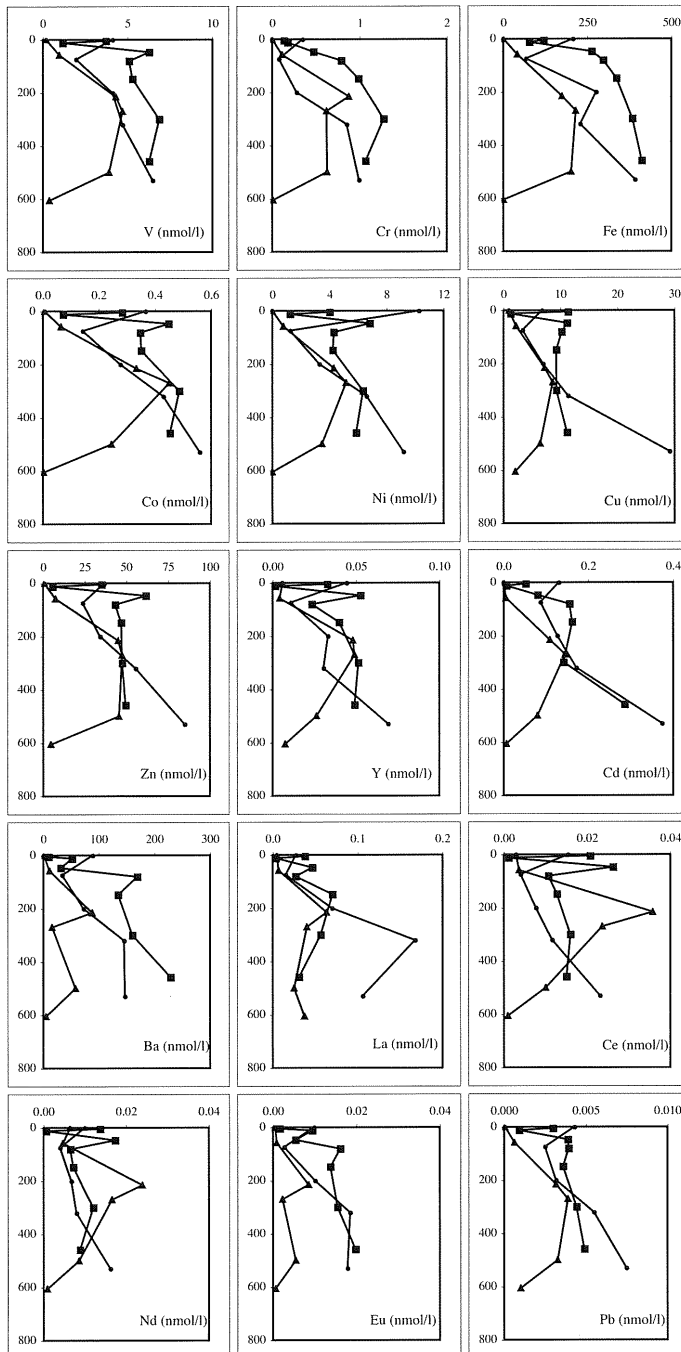


Fig. 4 – Water profiles illustrating trace elements distributions in station 766 (full circles), 769 (full squares) and 827 (full triangles).

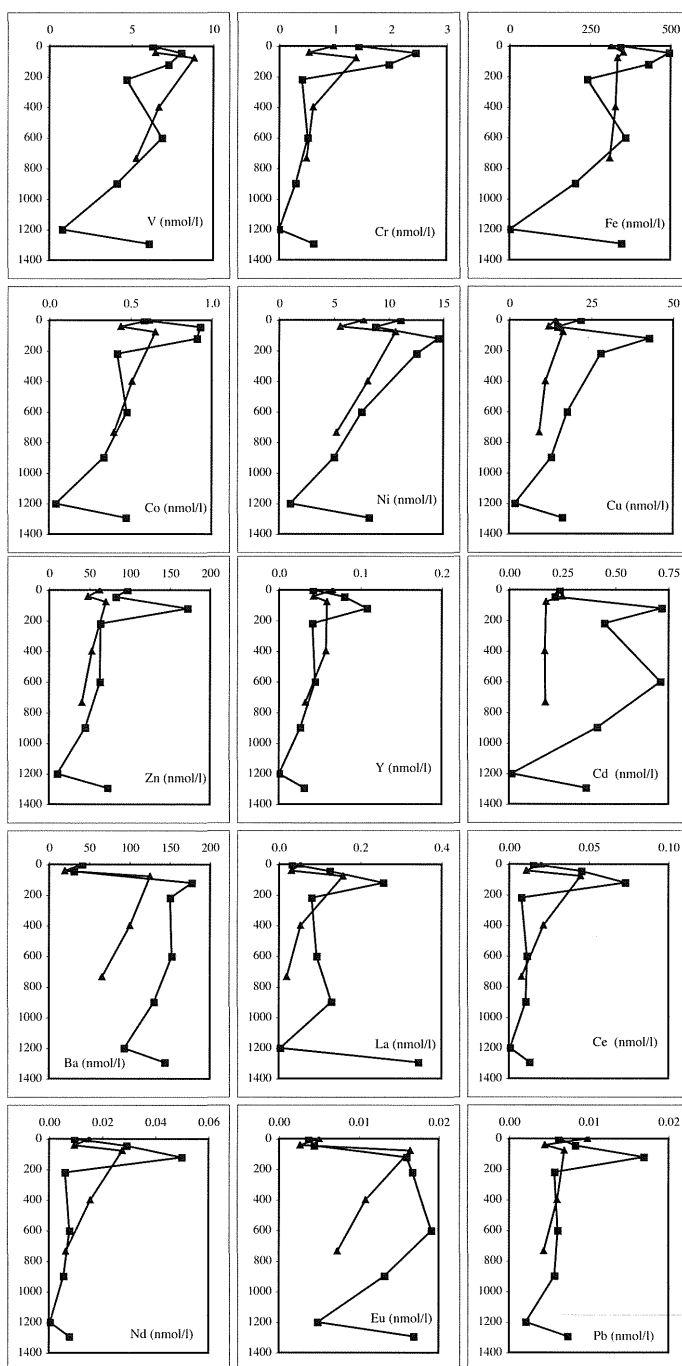


Fig. 5 – Water profiles illustrating trace elements distributions in station 942 (full triangles) and 945 (full squares).

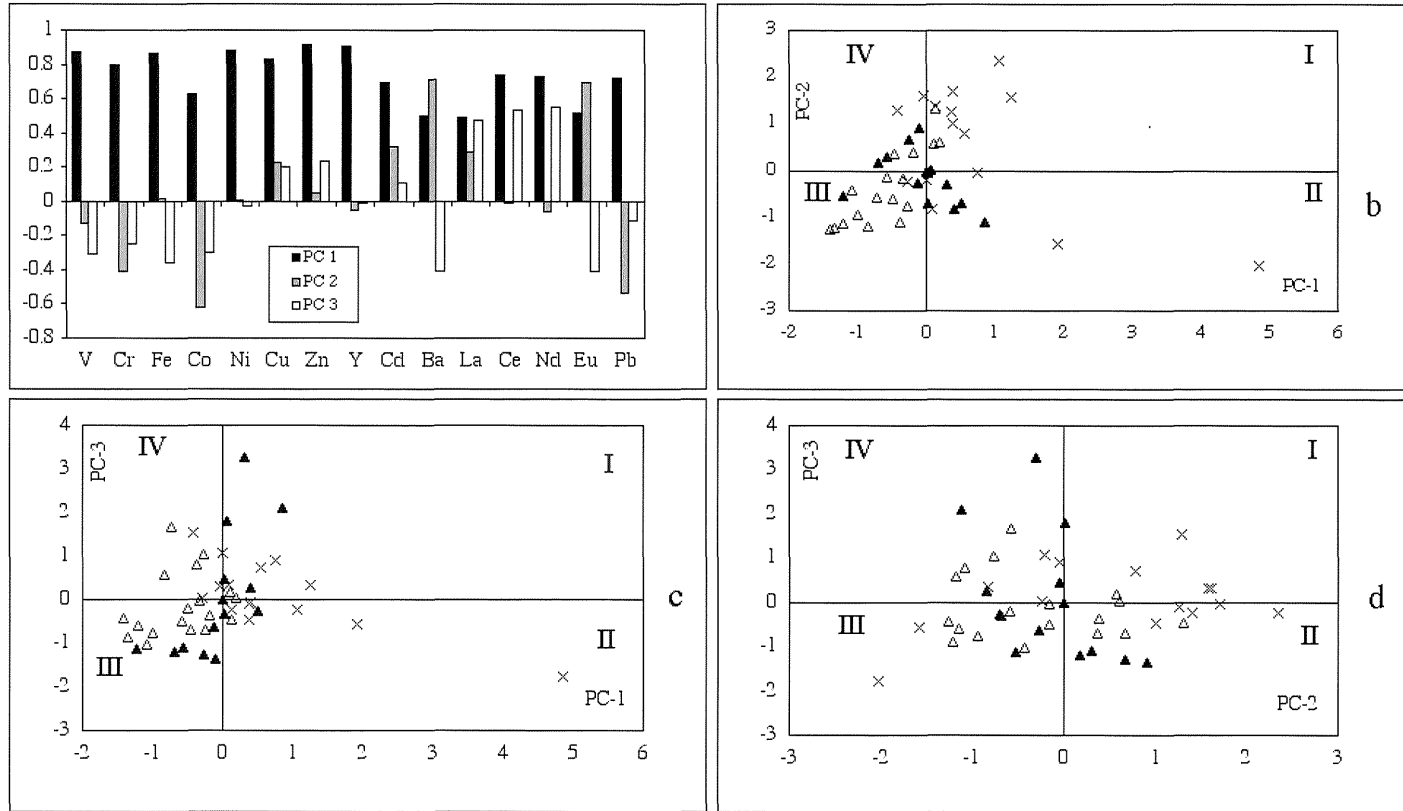


Fig. 6 – (a): Factors loadings of the three principal components; (b) Plotting of factor scores in PC2 vs. PC1 space; (c) Plotting of factor scores in PC3 vs. PC1 space; (d) Plotting of factor scores in PC3 vs. PC2 space. Crosses: samples from nearest zone of the Southern Sicilian Coast. Open Triangles: samples from stations located in the Northwestern of Pantelleria. Full Triangles: samples from stations located in the Southeastern of Pantelleria.

TABLE 3

Factor scores, sampling depth and proportion of explained variance of the three principal components in PCA calculations.

Sample	depth	PC1	PC2	PC3
179/4	5	-0.286	-0.238	0.034
179/3	70	0.387	1.703	-0.055
179/2	400	-0.049	1.605	0.308
179/1	488	-0.423	1.294	1.546
287/4	1.5	0.385	1	-0.454
287/3	101	1.916	-1.574	-0.564
287/2	339	0.748	-0.042	0.898
287/1	780	4.847	-2.034	-1.772
137/3	1.5	0.09	-0.829	0.34
137/2	52	0.365	1.254	-0.098
137/1	86	0.01	-0.213	1.075
458/4	5	0.119	1.398	-0.232
458/3	110	1.063	2.348	-0.232
458/2	449	1.243	1.58	0.323
458/1	600	0.544	0.783	0.73
766/5	0	-0.331	-0.166	-0.029
766/4	74	-1.001	-0.938	-0.778
766/3	200	-0.574	-0.155	-0.494
766/2	320	-0.459	0.369	-0.693
766/1	530	0.108	0.574	0.172
769/7	5	-0.843	-1.185	0.571
769/6	12	-1.092	-0.43	-1.034
769/5	47	-0.266	-0.767	1.048
769/4	81	-0.259	0.664	-0.686
769/3	148	-0.195	0.388	-0.38
769/2	300	0.189	0.612	0.039
769/1	458	0.124	1.313	-0.473
827/7	0	-1.408	-1.261	-0.449
827/5	58	-1.206	-1.148	-0.594
827/4	216	-0.732	-0.571	1.658
827/3	270	-0.378	-1.089	0.794
827/2	500	-0.494	-0.596	-0.215
827/1	606	-1.348	-1.218	-0.883
942/6	0	0.397	-0.838	0.264
942/5	42	0.023	-0.69	-0.319
942/4	78	0.057	0.011	1.794
942/3	400	0.025	-0.048	0.465
942/1	735	-0.12	-0.266	-0.627
945/10	0	0.504	-0.698	-0.282
945/9	45	0.856	-1.116	2.098
945/8	121	0.304	-0.309	3.262
945/7	219	-0.261	0.671	-1.282
945/5	601	-0.099	0.917	-1.37
945/4	899	-0.694	0.168	-1.197
945/3	1200	-1.22	-0.533	-1.132
945/1	1294	-0.566	0.299	-1.098

A detailed examination on PC2-PC1 plot shows that:

– PC1>0, PC2>0 (I quadrant): samples enriched in all traces. Only few samples close to the Gulf of Gela area fall here.

– PC1>0, PC2<0 (II quadrant): samples mainly enriched in V, Cr, Fe, Co, Pb. They are the other samples from the Gulf of Gela area and some samples from shallow waters SE to Pantelleria.

– PC1<0, PC2<0 (III quadrant): samples with lower values in trace elements except V, Cr, Fe, Co, Pb. Mainly shallow and intermediate samples of water columns located NW to Pantelleria fall here.

– PC1<0, PC2>0 (IV quadrant): Samples enriched in Ba, Eu and partially in Cd. They are deep samples from stations S-766, S-769 and S-945.

In the PC3-PC2 plot the same examination allows us to discriminate input of Ba and Eu from those of Cd, V, Cr, Fe, Co, Pb. It shows:

– PC2>0, PC3>0 (I quadrant): few samples enriched in Cu, Zn, Cd, La mainly coming from the shallow water masses of the Gulf of Gela.

– PC2>0, PC3<0 (II quadrant): deep samples coming from the stations NW of Pantelleria (S-766, S-769) and station S-945. In these samples the enrichment in Ba and Eu are discriminated from those in Cd, V, Cr, Fe, Co, Pb.

– PC2<0, PC3 <0 (III quadrant): samples enriched in Cd, V, Cr, Fe, Co, Pb. They are samples coming from stations S-827 and S-942, close to Pantelleria and deep samples from the Gulf of Gela.

– PC2<0, PC3>0 (IV quadrant): samples enriched in Ce and Nd. Samples from the stations S-827 and S-942; shallow waters from NW and SE from Pantelleria.

DISCUSSION

The grouping of studied trace elements derived from PCA allowed us to identify the behaviour of these elements in seawater in response to different driving natural and

anthropic inputs. In the following paragraph we will discuss the geochemical significance of each selected group of trace metals identified by means of statistical analysis and we will use them for tracing different behaviour of the seawater samples in response to different input mechanisms.

Ba and REY

As pointed out by statistical treatment of data and confirmed by the high correlation coefficients (Table 4), a strong covariance exists between Ba and Eu and between Ce and Nd pairs in the studied samples. Other significant linear correlations also occur among V, Cr, Fe and Ni, Cr, Co Fe and Pb, and Cu, Zn, and Ni.

Since Ba and Eu occupy crystal lattice sites in alkali feldspar, a strong interaction process between seawater and the alkali-feldspar bearing rocks outcropping in the Pantelleria area could explain the observed relationship and related Ba and Eu enrichments recorded in the aqueous system of the bottom waters close to the Pantelleria Island (stations S-766 and S-945). Such a process could be enhanced by means of a light hydrothermal system that could rise the effect of the water-rock interactions. The occurrence of a hydrothermal activity is well represented in the Island of Pantelleria with emission of geothermal fluids at different temperatures ranging from environment to higher than 100°C (Fulignati *et al.*, 1997), and easy related to the transtensional tectonics existing along the axial part of the Straits of Sicily (Boccaletti *et al.*, 1987; Civetta *et al.*, 1998). Under these conditions, at high temperature and in high ionic strength media, the mobility of the REY, especially LREE as chloride complexes increases (Wood, 1990; Gammonds *et al.*, 1996).

It is not reasonable to explain the observed distribution of La, Ce, Nd and Eu contents only with complexation processes and speciation in seawater. In fact, under these conditions seawater speciation of LREE is dominated by carbonate complexes and free ions, being

REE(CO₃)⁺ and REE³⁺ the most representative species (Guy *et al.*, 1999). Following Pearson (1963) the REE can be considered strong acids and form bonds with OH⁻ and with CO₃²⁻ (Brookins, 1989), which in alkaline environment are both extremely stable especially under high ionic strength conditions (Wood, 1990).

Moreover, the relationship between Ce and Nd distributions emphasised by PCA analysis seems to be driven largely by the recycling process of REEs under oxidizing conditions where REEs are scavenged together with iron oxyhydroxides as suspended particulate and precipitate along the water column (De Baar *et al.*, 1988; Bertine *et al.*, 1996). This is typical of alteration processes of basalts in hydrothermal plume vents under submarine conditions (Bau, 1999). Only local redox conditions could trigger increasing mobilisation of Ce and Nd being their turnover rate higher than the other REEs (De Baar *et al.*, 1988).

If REEs have a lithogenic origin, their distribution in examined samples should be very similar, except for Ce involved in redox processes. Therefore the observed discrepancies occurring among the behaviour of La and other REEs allowed us to suppose that La from different sources is present in the system, possibly related to anthropogenic waste (Olmez *et al.*, 1990).

Other trace elements

Distribution of trace elements in the Mediterranean Sea is usually considered strongly controlled by mixing processes of water masses with different origin or/and by atmospheric input (Boyle *et al.*, 1985; Saager *et al.*, 1993; Grousset *et al.*, 1995; Yoon *et al.*, 1999). Statistical treatment of trace element dataset allowed us to discriminate three different groups of elements:

- Cu, Zn and Cd with positive factor loadings in PC2 and PC3,
- V, Cr, Co and Pb with positive factor loadings in PC2 and negative in PC3,
- Fe and partially Ni with negative factor loadings in PC3.

TABLE 4
Correlation matrices for the studied trace elements.

depth	V	Cr	Fe	Co	Ni	Cu	Zn	Y	Cd	Ba	La	Ce	Nd	Eu	Pb	
depth	1.00	0.02	-0.05	-0.03	0.16	0.00	0.03	-0.01	-0.09	0.14	0.16	0.37	-0.18	-0.21	0.12	0.13
V		1.00	0.81	0.91	0.66	0.83	0.58	0.70	0.82	0.47	0.43	0.25	0.50	0.49	0.45	0.63
Cr			1.00	0.78	0.80	0.65	0.47	0.65	0.72	0.36	0.25	0.18	0.51	0.50	0.23	0.80
Fe				1.00	0.57	0.72	0.59	0.70	0.85	0.52	0.55	0.23	0.48	0.46	0.58	0.57
Co					1.00	0.54	0.35	0.47	0.54	0.25	0.02	0.11	0.27	0.29	0.05	0.91
Ni						1.00	0.79	0.83	0.77	0.62	0.41	0.41	0.57	0.56	0.42	0.60
Cu							1.00	0.89	0.66	0.79	0.46	0.52	0.60	0.61	0.45	0.51
Zn								1.00	0.77	0.73	0.39	0.55	0.74	0.74	0.35	0.61
Y									1.00	0.49	0.41	0.28	0.76	0.77	0.47	0.60
Cd										1.00	0.47	0.53	0.40	0.39	0.44	0.46
Ba											1.00	0.26	0.20	0.14	0.95	0.05
La												1.00	0.49	0.45	0.27	0.27
Ce													1.00	0.99	0.22	0.39
Nd														1.00	0.17	0.41
Eu															1.00	0.06
Pb																1.00

We supposed this discrimination to be induced by different mechanisms which drove the distribution of these elements.

Concentrations of Cu, Zn and Cd show a minimum at the surface and mainly increase with depth reflecting salinity peaks. Such behaviour is considered related to downward transport of biological particles and metal release in bottom waters for particles breakdown (Yoon *et al.*, 1999).

Vanadium could be trapped by biotic materials (Prange and Kremling, 1985) and released in bottom water. On the contrary the distribution of dissolved Cr could be influenced by bacterial/detrital organic fractions (Auger *et al.*, 1999). The affinity of V and Ni for organic phase could be related to their speciation as VO^{2+} and Ni^{2+} respectively. In this form these elements are enriched in metalloporphyrine and their covariance in seawater samples is usually considered a

signature of petroleum pollution phenomena (Manning and Gize, 1993).

High concentrations of Fe can be observed in bottom waters following salinity increases and could be related to the presence of Levantine Intermediate Waters flowing from the eastern to the western Mediterranean basin at the bottom waters of the Strait of Sicily. Maximum concentration of Ni recorded in the surface waters of some stations could reflect its origin from detrital silicate fraction of suspended particulate of aeolian origin.

The observed similarities of Co and Pb distributions are probably a signature of the adsorption processes onto calcite surfaces in which they are usually involved in the seawater environment (Kornicker *et al.*, 1985; Xu *et al.*, 1996; Sturchio *et al.*, 1997). Cobalt and Pb could be removed from the aqueous system thus accounting for interactions with the carbonatic particles driven from the runoff

system of continental origin or with newly formed biogenic carbonates, as suggested by Reeder (1983), Lorens (1981), Zachara *et al.* (1991) and Reeder (1996). But also other ions with ionic radius larger than Ca^{2+} , as Pb^{2+} (Reeder *et al.*; 1994; Qian *et al.*; 1994), can be absorbed from the aqueous solution both to occupy Ca^{2+} sites in calcite crystal lattice and in interstitial sites (Sturchio *et al.*, 1997).

CONCLUSIONS

The study of 15 trace elements was carried out on 9 stations in the Central Mediterranean area. A multivariate statistical approach allowed us to thoroughly understand modes and distribution systems for the studied elements.

Barium and Eu show very close distribution patterns, especially in the Pantelleria area being probably derived from water-rock interactions in the deepest water bodies. These conditions could be recognized in seafloor close to the Island of Pantelleria especially at the S-766 and S-945 sites, where increasing Ba and REEs contents in the bottom waters were recorded. Also Ce and Nd occurrences seem to be related to rock-water interactions, or to aeolian inputs, while La origin could be not only related to a «natural» inputs but strongly influenced by anthropogenic origin.

Cobalt and Lead distributions are in agreement with a biolimiting behaviour of these elements involved in adsorption processes on calcite surfaces. On the other hand analogous similarities observed for V and Ni distributions could be related to petroleum pollutions from the coast of the Gulf of Gela. The distributions of the latest two elements and Cr, Fe, Cu, Zn and Cd are probably driven by biological recycling processes related to complexation by organic particulate or to the presence of iron oxyhydroxide phases.

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