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ON THE METALLOGENESIS OF THE HERMIONI AREA, GREECE. MESOZOIC MID-OCEAN RIDGE DEPOSITS

(Figs. 7, Tabs. 3)

Abstract: Manganese, and ferromanganese deposits are studied from the Hermioni area, Greece. Their chemical and mineralogical features, their relative stratigraphic location and their association with layered mafic volcanic rocks suggest that they have been formed from hydrothermal exhalations in a similar process to that occurring presently on mid-ocean ridges. The Mn-deposits have high Mn/Fe ratios and low trace metal contents, features which are observed in modern submarine hydrothermal Mn-crust from various sections of the mid-ocean ridge system. The relatively high Al and Zn contents found, compared with other volcanogenic-sedimentary Mn-deposits, are considered to be of hydrothermal origin. Using the metal/Co ratios the relative degree of hydrothermal supply of the trace metals examined was determined as follows: Zn > > Ni > Cu > Cr > Pb.

The Fe-Mn deposits are similar to the modern metalliferous sediments found on mid-ocean ridges. Of the trace elements examined in these deposits Ni, Cu, Zn, As, Rb and Sr behave similarly, their incorporation being associated with the hydrothermal process, but it is more favourable away from the vents; Cr has rather similar behaviour, except that it is little affected by the changes of the physicochemical conditions; Zr is associated with detrital material.

Резюме: Месторождения марганца и ферромарганца изучаются из района Гермиони в Греции. Их химические и минералогические признаки, их относительное стратиграфическое местоположение и ассоциация с слоистыми мафическими вулканическими породами намечают, что они были образованы из гидротермальных эксгалаций во время процесса подобного тому, который происходит сейчас в среднеокеанических утесах. Месторождения марганца имеют высокие Mn/Fe отношения и низкое содержание рассеянных металлов, признаки которых наблюдаются в современных субмаринных гидротермальных Mn корах разных участков среднеокеанической системы утесов. Относительно высокие полученные содержания Al и Zn сравнены с другими вулканогенно-осадочными месторождениями Mn считают гидрогермального происхождения. Применяя отношения металл/Co была определена относительная степень гидротермального привноса исследованных рассеянных металлов следующим образом: Zn > Ni > Cu > Cr > Pb.

Fe-Mn месторождения похожи на современные металлоносные осадки находящиеся в среднеокеанических утесах. Из рассеянных элементов рассматриваемых в этих месторождениях Ni, Cu, Zn, As, Rb и Sr ведут себя подобным образом, их включение связано с гидротермальным процессом, но оно благоприятнее вдали от отверстий; Cr ведет себя подобным образом, кроме того, что на него немножко влияют изменения физикохимических условий; Zr связан с детритовым материалом.

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Introduction

Extensive oceanographic expeditions carried out during last decade, including diving for direct observations of the seafloor hydrothermal fields (see Cronan, 1980) and laboratory experiments (Bischoff — Dickson, 1975; Seyfried — Bischoff, 1977) showed that seawater-basalt interaction is the main process being responsible for the formation of mineral deposits encountered at mid-ocean ridges. Such deposits are metal sulfides, being accumulated within the basalt or on the seafloor near the hydrothermal vents (Hekinian et al., 1980), ferromanganese oxide sediments, being precipitated in a more widespread area and manganese deposits which may accumulate at some distance from the vents (Cronan, 1980). The results of recent studies on these deposits (Cronan, 1980) give us new criteria in the study of similar deposits found on land but formed under similar geological conditions. A number of such land based deposits have been described from the ophiolites of Cyprus (Constantinou — Govett, 1972; Robertson — Boyle, 1984), Italy (Bonatti et al., 1976), Oman (Fleet — Robertson, 1980), Turkey (Robertson, 1981), etc.

The aim of this paper is to study the ferromanganese, and manganese deposits occurring in the Hermioni area, Greece and to deduce the process of their formation using criteria proposed in recent studies of marine mineral deposits. The geological and stratigraphic setting of these deposits has been previously given by Aronis (1951), Mousoulos (1958) and Aranitis (1963) (see Fig. 1).

Manganese deposits

Manganese ore samples have been analysed by atomic absorption spectrophotometry for Mn, Fe, Ni, Co, Pb, Zn, Ca, Cr, Ti, Al, Ca and Mg and the results are given in Table 1. The Hermioni Mn-deposits are characterized by high Mn/Fe ratios and low trace metal contents, features which have been observed in modern submarine manganese crust associated with mid-ocean ridge hydrothermal activity (Scott, et al., 1974; Moore — Vogt, 1976; Cann et al., 1977; Hoffert et al., 1978; Varnavas — Cronan, 1981; Moorby — Cronan, 1983; Varnavas et al., 1983). Interestingly, the Hermioni Mn-deposits contain higher amounts of Fe, Zn and Al compared with all the subpelagonian and Pindos volcanogenic sedimentary Mn-deposits which are not in close association with sulfide mineralization (Varnavas — Panagos, 1982; Panagos — Varnavas, 1984). Zn and Al correlate positively with Fe.

Compared with modern submarine hydrothermal Mn-crusts the Hermioni Mn-deposits have higher Fe/Mn ratios, higher Al and Zn and lower Mg contents.

Mineralogically, the Hermioni Mn-deposits consist primary of pyrolusite, goethite, haematite and quartz (Spathi, 1964).

Ferromanganese deposits

Ferromanganese sediments are found in all localities where sulfide mineralization occurs but with greater volumes towards the Baroutospelia area.

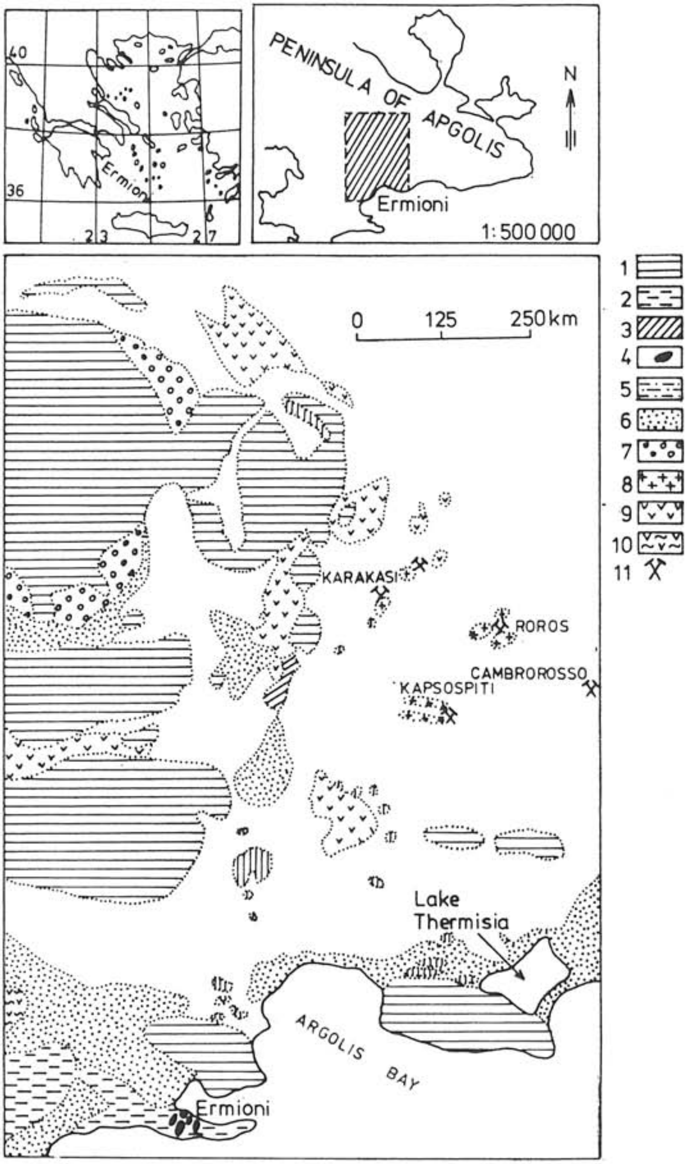

Fig. 1. Geological map of the Hermioni area (after Aronis, 1951) showing the location of the deposits studied.
Explanations: 1 — limestones with megalodon; 2 — limestones of Ermioni; 3 — limestones of Iliokastro; 4 — shale-sandstone formation with layers of limestones; 5 — Pliocene sediments; 6 — Quaternary deposits; 7 — Quaternary conglomerate; 8 — diabase; 9 — peridotites; 10 — shales-sandstones with peridotites; 11 — old mines of pyrites.

Table 1

Chemical composition of the manganese deposits

Sample No.	Mn %	Fe %	Ni ppm	Co ppm	Pb ppm	Zn ppm	Cu ppm	Cr ppm	Ti ppm	Al %	Ca %	Mg %	Fe/Mn	Co/Zn	Co+Ni+Cu ppm	Ni/Co	Pb/Co	Zn/Co	Cu/Co	Cr/Co
MP_1	48.00	1.04	170	50	40	282	113	30	700	2.60	1.80	0.44	0.0217	0.177	333	3.4	0.80	5.64	2.26	0.60
MP_2	55.00	.78	190	160	20	146	60	80	600	1.80	0.80	0.51	0.0142	1.096	410	1.19	0.13	0.91	0.38	0.50
MP_3	48.00	1.40	190	110	40	265	96	30	1000	2.60	1.60	0.61	0.0292	0.42	396	1.73	0.36	2.41	0.87	0.27
MP_4	39.00	6.70	370	90	50	410	174	30	800	3.10	1.90	0.72	0.1718	0.22	634	4.11	0.56	4.55	1.93	0.33
MP_5	55.00	.36	120	120	30	98	70	60	300	1.48	0.98	0.33	0.0065	1.22	310	1.00	0.25	0.82	0.58	0.50
MP_7	37.00	6.00	300	70	40	430	97	70	600	2.80	1.30	0.60	0.1622	0.16	440	4.29	0.57	6.14	1.36	1.00
MP_9	40.00	1.26	190	90	50	270	130	30	900	3.30	2.50	0.58	0.0315	0.33	410	2.11	0.56	3.00	1.44	0.33
MP_{10}	38.00	.63	80	90	20	62	36	40	200	.84	0.98	0.24	0.0166	1.45	206	0.89	0.22	0.69	0.40	0.44
MP_{12}	45.00	5.00	290	110	40	450	285	80	1000	3.00	2.10	0.54	0.1111	0.24	435	2.64	0.36	4.09	2.50	0.73
MP_{13}	41.00	2.10	170	60	20	310	175	30	500	1.70	1.10	0.33	0.0512	0.19	405	2.83	0.33	5.17	2.92	0.50
MP_{14}	38.00	2.00	180	60	20	300	168	30	600	1.60	1.10	0.36	0.0526	0.16	408	3.00	0.33	5.00	2.80	0.50
MP_{16}	51.00	.45	120	190	30	85	63	20	200	1.30	0.93	0.36	0.0088	2.24	373	0.63	0.16	0.45	0.33	0.11
MP_{17}	50.00	3.10	260	130	40	420	146	80	700	2.80	0.86	0.52	0.0620	0.31	536	2.00	0.31	3.23	1.12	0.62
MP_{18}	40.00	4.20	260	90	20	340	115	30	900	2.80	1.20	0.64	0.1050	0.26	465	2.89	0.22	3.78	1.28	0.33
MP_{19}	42.00	.54	100	80	20	100	46	30	400	1.60	1.30	0.20	0.0129	0.80	226	1.25	0.25	1.25	0.59	0.33

Table 2

Chemical composition of Baroutospelia ferromanganese sediments

Sample No.	Fe %	Mn %	Ni ppm	Pb ppm	Zn ppm	Cu ppm	Cr ppm	Sr ppm	Rb ppm	Zr ppm	As ppm	SiO_2 %	Al %	Ca %	K_2O %	Fe/Mn
B2	7.36	0.69	106	45	215	102	74	17	26	111	30	40.3	6.90	2.02	3.7	10.67
B3	15.15	2.82	146	81	257	102	55	94	105	64	122	33.9	5.67	4.58	1.4	6.64
B4	15.00	1.32	123	90	290	70	91	77	40	85			6.90	1.33	3.9	11.35
B6	8.84	0.96	109	45	257	91	86	124	37	105	47	31.2	7.78	0.95	4.1	9.21
B7	8.42	0.45	116	27	247	226	49	62	21	116	43	45.5	7.29	0.90	4.5	18.71
B/AB	8.96	0.83	113	63	268	70	85	80	50	103	24	41.8	7.39	1.06	4.5	10.80
BM	15.83	2.23	187	60	347	1.027	70				58	38.2	6.70	1.60		7.10
BD_1	5.82	0.41	102	20	210	64							9.30	1.10		14.20
BD_2	12.85	1.92	167	50	283	81	70						7.30	2.00		6.69
BD_3	10.50	2.06	129	36	268	97	87	193	45	97	52	47.1	6.92	1.95	2.9	5.10
BD_5	7.96	0.52	106	18	215	113	80	112	20	110	23	46.5	7.88	0.90	4.5	13.31
BD_6	7.29	0.72	123	0	215	86	87	101	25	114	29	45.5	7.48	0.84	3.9	10.13
BD_{11}	5.70	0.14	104	0	221	97							10.30	1.70		40.71
BD_{12}	6.33	0.15	98	10	214	21							9.40	1.30		42.2

A number of Fe-Mn sediment samples from the sulfide mineralization areas have been analysed by X-ray fluorescence for Fe, Mn, Ni, Pb, Zn, Cu, Cr, Sr, Rb, As, Si, Al, Ca and K.

The results are given in Tables 2 and 3. These data show that Hermioni Fe-Mn sediments have all the chemical features of modern metalliferous sediments found at mid-ocean ridges (Cronan, 1980; Cronan — Varnavas, 1981 and others), and especially of those associated with metal sulfides. The most marked characteristic of the latter deposits is that although they are enriched with Fe and/or Mn, they are depleted, or are not as enriched with trace metals as other sediments, this being due to the earlier incorporation of the metals in the sulfides. Haematite, quartz, calcite and smectites are the main minerals indentified by X-ray diffraction analysis in the Hermioni sediments, while no discrete Mn minerals have been detected. The ferromanganese sediments investigated are also chemically and mineralogically comparable with the Mesozoic Tethys ocean metalliferous sediments (Elderfield et al., 1972; Robertson — Hudson, 1973; Robertson, 1976, 1978, 1981; Varnavas, 1981; Robertson — Boyle, 1984).

Major elements

Iron and manganese behave similarly correlating positively with each other and thus suggesting co-precipitation in the sediments. Aluminium contents are higher than those reported for recent metalliferous sediments. Aluminium has generally been considered to be a detrital element although it has been shown recently (Seyfried — Bischoff, 1977; Dymond, 1981) that it may have also a hydrothermal origin. A negative correlation exist between Fe and Al suggesting that Al is derived from other than a hydrothermal source. Silica, like in other metalliferous sediments is enriched in the Hermioni Fe-Mn deposits. No clear relationship has been found between Si an Fe or between Si and Al confirming its presence in the form of quartz. Potassium correlates positively with Al and negatively with Fe showing its detrital origin.

Trace elements

The trace elements examined can be classified into the following groups:

a) Ni, Cu, Zn, As, Rb and Sr.

The elements of this group behave similarly, correlating positively with Fe and Mn and with one another (see Fig. 2) and thus suggesting that they are of hydrothermal origin or that the hydrothermal process played an important role in their incorporation in the sediments. They also all correlate negatively with K and with the Fe/Mn ratios (Fig. 3). It is well established that Fe/Mn ratios in marine metalliferous sediments is a measure of the physicochemical conditions (i.e. eh, ph temperature) which occurred in the hydrothermal field. Sediments with high Fe/Mn ratios precipitate first closed to the fumarolic outlets, whereas sediments with low Fe/Mn ratios precipitate from the residual solutions of the hydrothermal activity, away from the vents. The negative correlation found between the elements of this group and the Fe/Mn ratios

Table 3

Chemical composition of Kapsospiti and Roros ferromanganese sediments

Sample No.	Fe %	Mn %	Ni ppm	Pb ppm	Zn ppm	Cu ppm	Cr ppm	Sr ppm	Rb ppm	Zr ppm	As ppm	SiO_2 %	Al %	Ca %	K_2O %	Fe/Mn	
AO6	9.24	0.72	116	36	193	145	109	85	33	150	30	31.6	7.75	1.97	3.0	12.83	KAPSOSPITI
AO7	8.69	0.94	126	36	236	59	89	78	20	101	23	44.0	7.63	1.00	4.1	9.24	
KY1	8.62	0.43	94	40	192	36	180						8.40	6.60		20.05	
KY2	18.72	0.46	133	72	257	202	65	124	33	103	38	34.7	6.23	1.45	1.9	40.70	
KY4	14.61	1.57	126	27	279	134	80	128	39	103	45	32.6	7.68	1.68	2.9	9.31	
KY5	6.87	0.74	93	0	268	129	77	64	20	94	23	33.5	6.95	8.89	2.8	9.23	
KY6	7.10	0.53	133	80	241	43							8.80	1.00		13.40	
KY10	4.04	0.43	139	9	215	108	57	64	16	137	27	38.2	7.80	1.03	4.8	9.40	
KY11	11.59	1.00	194	40	232	173	90						7.80	3.20		11.59	
KY12	7.00	0.39	99	10	211	96	90						8.70	1.10		17.95	
KY14	9.32	0.51	123	63	193	269	76	67	43	129	50	37.2	7.80	1.00	4.6	18.27	
KY15	7.18	0.68	114	20	189	330							9.00	1.50		10.55	
KY18	5.62	0.36	106	45	215	108	60	268	19	147	22	40.9	7.93	1.53	4.1	15.61	
90/1A	9.14	1.30	170	40	267	71	80						8.90	1.30		7.03	ROROS
90/2	13.29	2.03	119	63	279	124	91	171	43	140	50	33.0	6.80	1.66	2.8	6.55	
90/3	13.23	1.61	146	36	322	97	92	212	38	120	44	35.2	7.14	1.34	3.1	8.22	
90/5	9.86	1.52	172	40	233	100	90						7.70	1.20		6.49	
90/6	19.85	2.01	139	45	236	48	92	96	51	91	59	31.0	6.46	1.48	2.3	9.88	
90/7	6.02	0.42	96	0	172	86	71	174	21	110	24	12.2	8.49	3.90	4.0	14.33	
90/11	6.33	0.36	109	0	236	26							9.70			17.58	
90/20	10.48	0.65	129	27	247	108	91	207	34	126	40	33.6	7.51	5.27	3.8	16.12	
90/22	6.32	0.10	94	20	214	70							10.80			63.20	
90/23	6.25	0.13	68	0	164	68	120						10.70	1.00		48.08	

shows that the conditions become more favourable for their incorporation away from the vents. This is consistent with recent geochemical investigations in the Santorini hydrothermal field, where it has been found that As increase away from the vents (V a r n a v a s — C r o n a n, in prep.).

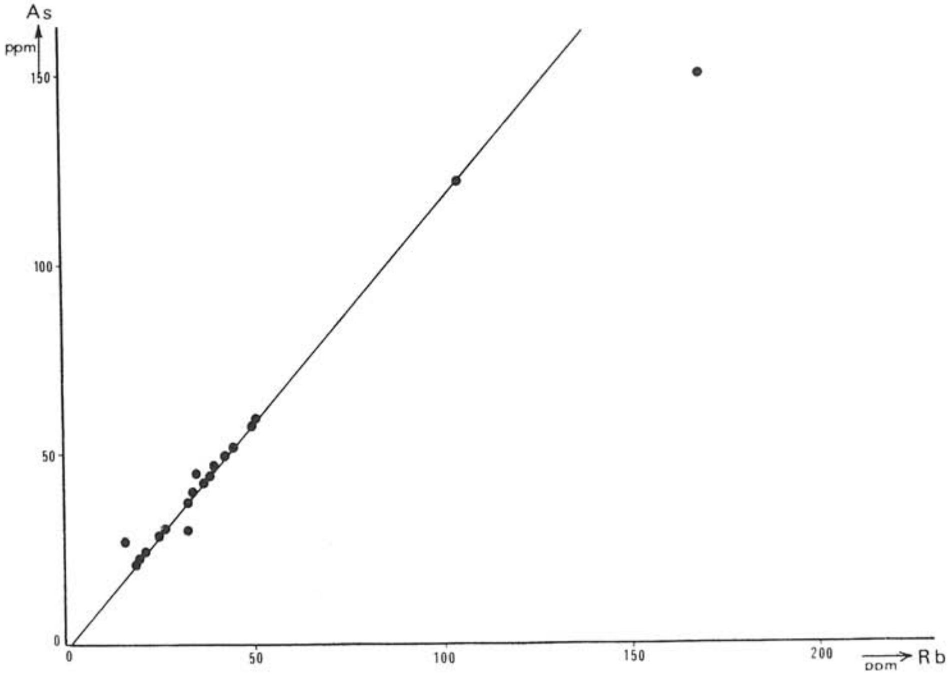

Fig. 2. Relationship between As and Rb in the Hermioni Fe-Mn sediments.

b) C h r o m i u m

Althogh Cr correlates positively with the elements of the above group and negatively with K_2O (Fig. 4) its distribution has been little affected by the changes in the physicochemical environment. There has been no significant correlation between Cr and the Fe/Mn ratios. It has been demonstrated that in hydrothermal processes Cr is partly mobile and it is enriched in hydrothermal sediments without being followed by other "terrigenous" elements (M a r c h i g et al., 1982). This is confirmed here by the positive correlation found between Cr and the elements of group a) and by its negative correlation with K_2O and Zr (see Fig. 4).

c) Z i r c o n

The geochemical behaviour of Zr is completely different from that of the other trace elements. It correlates positively with K_2O showing its "terrigenous" origin and in contrast to the other trace elements it correlates positively with the Fe/Mn ratios (see Fig. 5) suggesting that its incorporation is more favourable close to the vents.

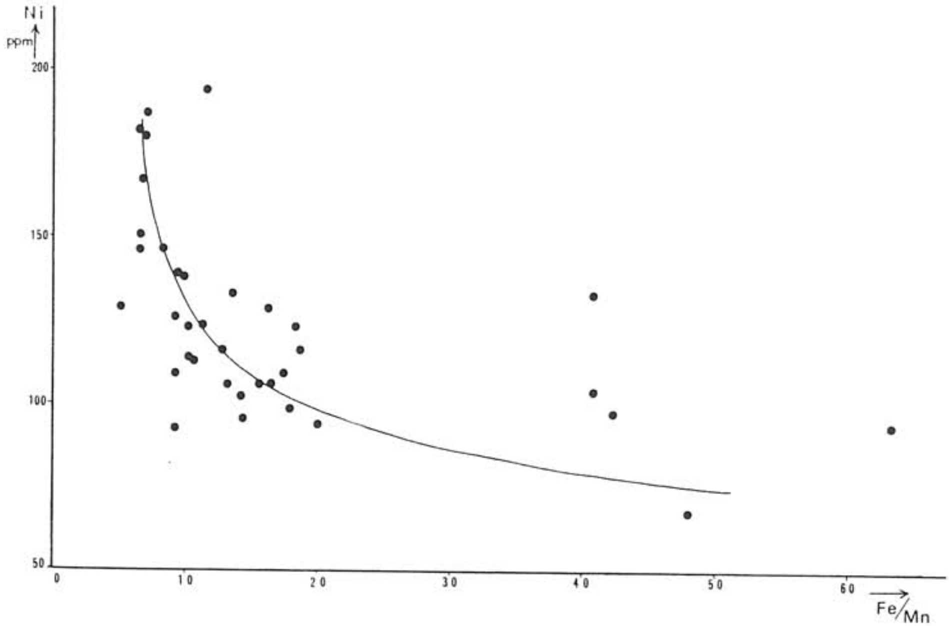

Fig. 3. Relationship between Ni and the Fe/Mn ratios in the Hermioni Fe-Mn sediments.

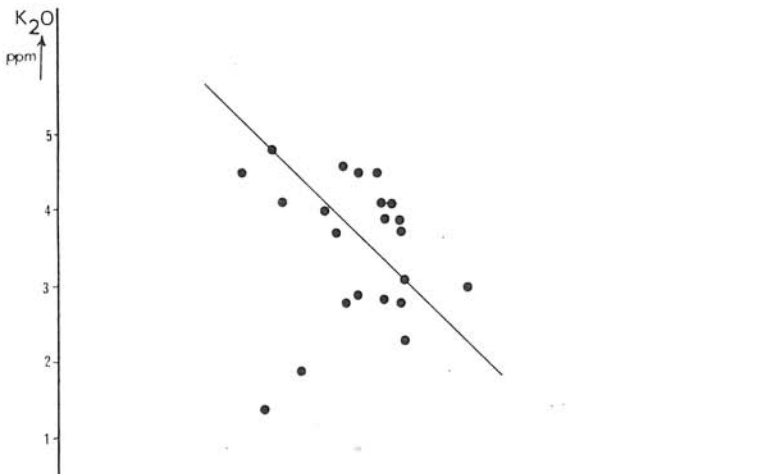

Fig. 4. Relationship between Cr and K_2O in the Hermioni Fe-Mn sediments.

The following geochemical anomalies have been located in the Hermioni Fe-Mn sediments: Arsenic and copper anomalies at Baroutospelia and copper anomalies near the Roros and the Kapsospiti ore bodies.

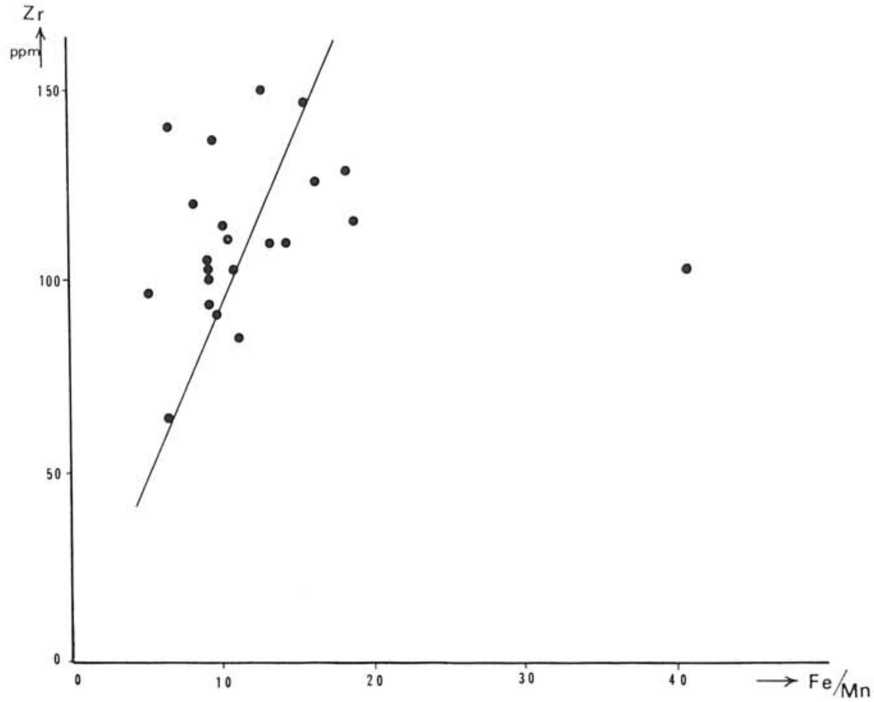

Fig. 5. Relationship between Zr and Fe/Mn ratios in the Hermioni Fe-Mn sediments.

Discussion

The type mineral deposits present in the area investigated, their chemical composition and stratigraphic location suggest that they have been formed on an oceanic spreading center (H u t c h i n s o n, 1973; C r o n a n, 1980). However, it is beyond the scope of the present paper to draw conclusions on the tectonic setting of the deposits. The data presented in this work support discussion on the process of formation of the deposits and the origin of their constituents.

The similar chemical composition of the Hermioni Mn-deposits with that of modern submarine hydrothermal Mn-crusts suggests that they have been formed under similar physicochemical conditions. The high Mn/Fe ratios which characterize the Mn-deposits suggest that a fractionation between Mn and Fe has taken place before their accumulation. This is a result of the different solubility of the two elements (K r a u s k o p f, 1957) and has been described from a number of modern submarine hydrothermal fields such as the Santorini (B o n a t t i et al., 1972; S m i t h — C r o n a n, 1975), the Stromboli (B o n a t t i et al., 1972), the Red Sea (Bignell et al., 1976), the Mid-Atlantic Ridge (Hoffert et al., 1978) and the Galapagos Rift (Varnavas, 1979; Varnavas — Cronan, 1981). However, the presence of significant amounts of Fe (up

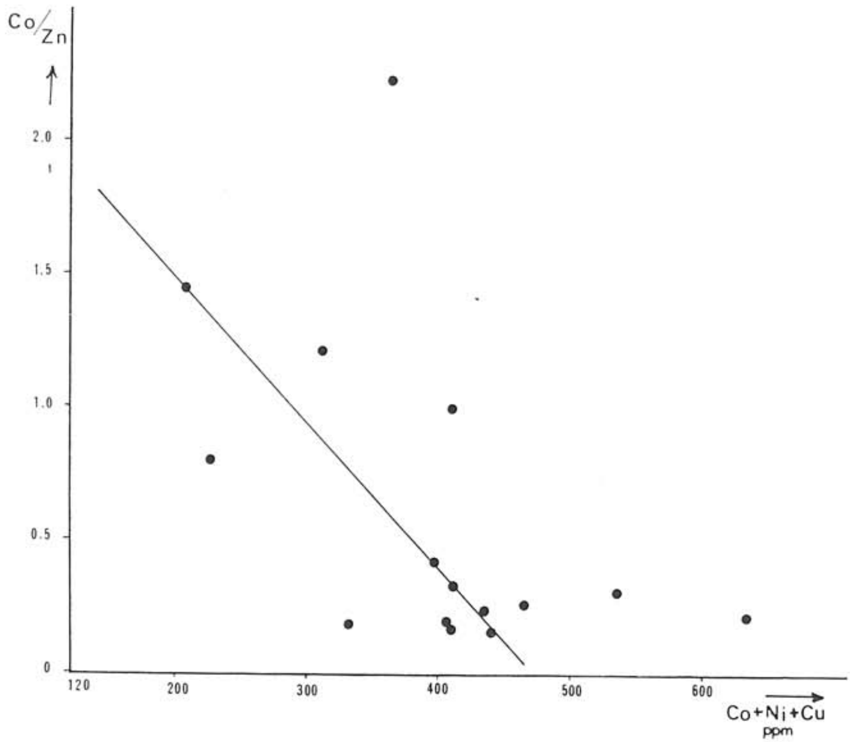

Fig. 6. Relationship between Co/Zn ratios and Co + Ni + Cu in the Hermioni Mn--deposits.

to 6.7 %) in some Mn-deposit samples shows that the fractionation between Mn and Fe is not as complete as in other ancient and modern Mn-deposits. Most of Fe should have precipitated earlier from the hydrothermal solutions forming the pyrite and the Fe-Mn sediments which occur in lower stratigraphic horizons. The low trace metal concentrations in the Mn-deposits is an additional evidence of their hydrothermal origin since it results from their rapid accumulation from hydrothermal solutions which prevents scavenging of metals from seawater (Bonatti et al., 1972a; Toth, 1980) and from the fact that the hydrothermal solutions have higher Mn/trace metal ratios than normal seawater (Toth, 1980). Another alternative is that large quantities of the trace metals are incorporated earlier in the pyrite.

One of the most striking of the Hermioni Mn-deposits is their high concentrations of Al and Zn. Aluminium in marine sediments has generally been considered to be derived from detrital sources. However, laboratory and field observations demonstrated that Al may also be of hydrothermal origin (Seyfried — Bischoff, 1977; Dymond, 1981). Thus, the enrichment of Al in the present Mn-deposits may be due to the fact that a portion of hydrothermal Al is added to the detrital Al. This is supported by the positive correlation found between Al and Fe.

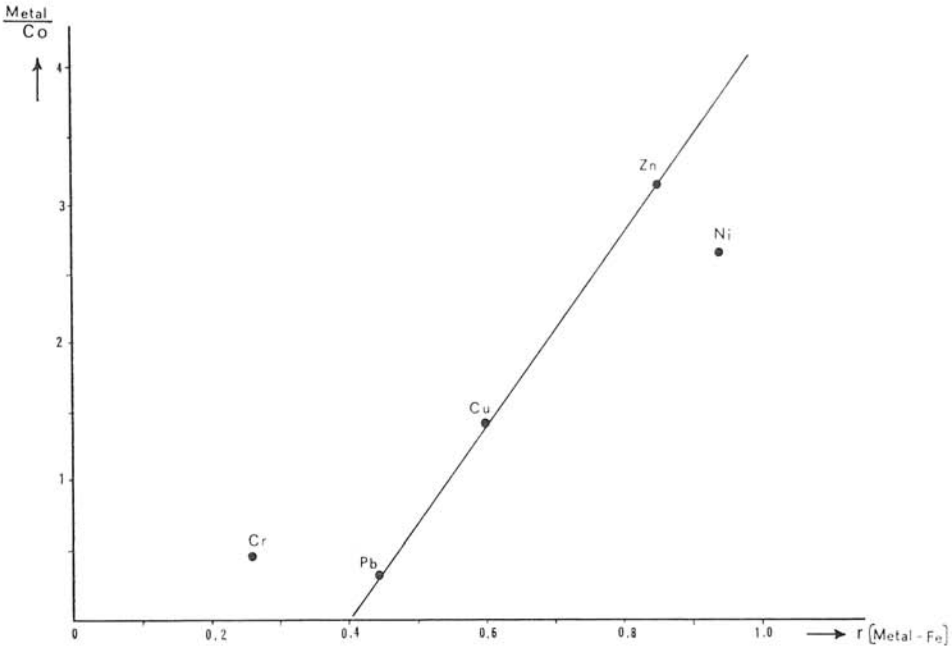

Fig. 7. Relationship between trace metal/Co ratios and the correlation coefficients existing between the metals and Fe in the Hermioni Mn-deposits.

Zinc after Fe and Mn, has been found to be the trace metal taken into solution in highest concentration by basalt-seawater interaction at elevated temperatures and pressures (Seyfried — Bischoff, 1977). On the other hand, Co has been reported not to be enriched in hydrothermal deposits (Scott et al., 1974; Moore — Vogt, 1976; Hoffert et al., 1978). Thus, Toth (1980) used the Co/Zn ratio as an indicator of the degree of hydrothermal supply of metals in submarine Fe-Mn deposits. The same criterion has been used in this study and has been found that there is a negative correlation between the Co/Zn ratios and the Ni + Co + Cu concentrations (Fig. 6) which shows that the samples with the greater hydrothermal supply of metals (low Co/Zn) are characterized by high Ni + Co + Cu contents. These samples are those having high concentrations of Fe. A comparison of the Ni/Co, Zn/Co, Pb/Co, Cu/Co and Cr/Co ratios of the Hermioni Mn-deposits with those of modern Mn-crust and Mn-nodules shows that they are higher, compared with those of Pacific Mn-nodules showing the hydrothermal supply of metals in the formation of the Hermioni deposits. By contrast, they are lower, compared with those of

Mn-crusts recovered from the Galapagos Rift and the Gulf of Aden, suggesting a smaller hydrothermal supply of metals than in latter deposits.

The relative degree of hydrothermal supply of trace metals in the formation of the Hermioni Mn-deposits is as follows:

$$Zn > Ni > Cu > Cr > Pb.$$

Interestingly, the metal/Co ratios correlate positively with the correlation coefficient existing between the trace metals examined and the concentrations of Fe (Fig. 7) suggesting that the latter correlation coefficient may also be used as a measure of the degree of hydrothermal supply of metals.

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