

THE PARTITIONING OF MAJOR AND TRACE ELEMENTS AMONG THE GEOCHEMICAL FRACTIONS OF SEDIMENTS FROM THE IERISSOS GULF AND THE ADJACENT AREA

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ABSTRACT

The partitioning of 20 elements among the various geochemical fractions of 20 sediment samples collected from the Ierissos gulf and the adjacent onshore area was examined, using the sequential extraction analytical procedure of Tessier et al (1979) with a few modifications. The geochemical fractions dealt with are the exchangeable, carbonate hosted, reducible, organic matter-sulphide hosted and the residual. It was found that there is some easily hydrolyzed Mg, Ca and Sr components as well as a minor K-contribution from the residual in the sediments. Calcium and Sr are mainly present as carbonates. A small biogenic contribution of Mn is shown. A carbonate related contribution of Pb and Zn was found. The major part of the non-residual fractions of the metals Fe (72%), Pb (46%), Mn (34%) and Zn (24%) are associated with the reducible fraction that consists of Fe, Mn-oxides which scavenge trace metals. Traces of copper sulphide may occur. The major parts of the elements Ti, Al, Fe, V, K, Cr, Li, Co, La, Ni, Ba, Be, P, Cu, Mg and Zn are hosted in the lattice structure of silicate minerals, clays and other resistant minerals. The contamination of the Ierissos gulf sediments by Pb, Zn and Cu from mining effluents from the Stratoni district is suggested.

ΣΥΝΟΨΗ

Μελετήθηκε η επί μέρους κατανομή 20 στοιχείων στα διάφορα γεωχημικά κλάσματα 20 δειγμάτων ιζημάτων από τον κόλπο της Ιερισσού και την παρακείμενη παραλία. Η αναλυτική μέθοδος που χρησιμοποιήθηκε είναι, με ορισμένες μετατροπές, η τεχνική των Tessier et al (1979). Τα γεωχημικά κλάσματα που εξετάστηκαν είναι: το προσροφημένο στο ίζημα (ανταλλάξιμο), το φιλοξενούμενο στα ανθρακικά, το αναχώνιμο, το ευρισκόμενο σε οργανικά υλικά και θειούχα ορυκτά και η υπολειμματική φάση. Βρέθηκε ότι στο ίζημα υπάρχει μια μικρή ποσότητα εύκολα υδρολυομένων ενώσεων των Mg, Ca και Sr και μία μικρή συμβολή K από το θάλασσο άλας. Το Ca και το Sr βρίσκονται κυρίως με την μορφή ανθρακικών αλάτων. Εντοπίστηκε η ύπαρξη μικρών ποσοτήτων βιογενούς Mn. Το μεγαλύτερο μέρος του μη υπολειμματικού ποσοστού των Fe(72%), Pb(46%), Mn(34%) και Zn(24%) βρίσκεται στο αναχώνιμο κλάσμα που αποτελείται από Fe, Mn-οξειδία που παγιδεύουν ιχνημέταλλα. Πιθανολογείται η ύπαρξη ιχνών χαλκοσυριτη. Το μεγαλύτερο μέρος των στοιχείων Ti, Al, Fe, V, K, Cr, Li, Co, La, Ni, Ba, Be, P, Cu, Mg και Zn βρίσκεται στο δομικό πλέγμα των πυριτικών, αργιλικών και άλλων ανθεκτικών ορυκτών. Διαπιστώθηκε η μόλυνση των ιζημάτων του κόλπου της Ιερισσού από Pb, Zn, και Cu που προέρχονται από τα απόβλητα των μεταλλευτικών εργασιών της περιοχής Στρατωνίου.

* ΣΑΚΕΛΛΑΡΙΑΔΟΥ. Η επί μέρους κατανομή ιχνοστοιχείων και μεγαλοστοιχείων στα γεωχημικά κλάσματα ιζημάτων από τον κόλπο της Ιερισσού και την παρακείμενη παραλία.

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Sequential chemical extraction (partition geochemical analysis) aims to examine the partitioning of the elements among the various geochemical phases of the sediments. This technique, however a time consuming one, has the advantage of furnishing detailed information concerning the source, mode of occurrence, biological and physicochemical availability, mobilization and uptake of trace metals in sediments.

Among the many different procedures for the sediment partition analysis (Chester and Hughes, 1967; Nissenbaum, 1972; Gupta and Chen, 1975; Tessier et al., 1979; Valin and Morse, 1982) the sequential extraction analytical procedure of Tessier et al (1979) with a few modifications was followed in this work. Certain phases of the sediment can be selectively removed for analysis with this method and, thus, studies of various forms and attachments of elements can be considered individually. The five fractions dealt with are the exchangeable, carbonate hosted, reducible, organic matter – sulphide hosted and the residual.

Eighteen samples collected from the Ierissos gulf (and provided by the I.G.M.E.) and two samples from the adjacent onshore area were subjected to partition analysis (Figs 1 and 2).



Fig. 1. Map of Greece: The study area is pointed by an arrow.

Σχ. 1. Χάρτης της Ελλάδας: το βέλος δείχνει την περιοχή που μελετήθηκε.

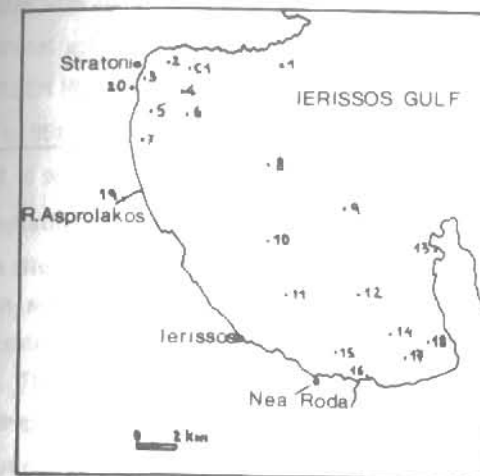


Fig. 2. Ierissos Gulf: map representing the offshore and onshore sample locations.

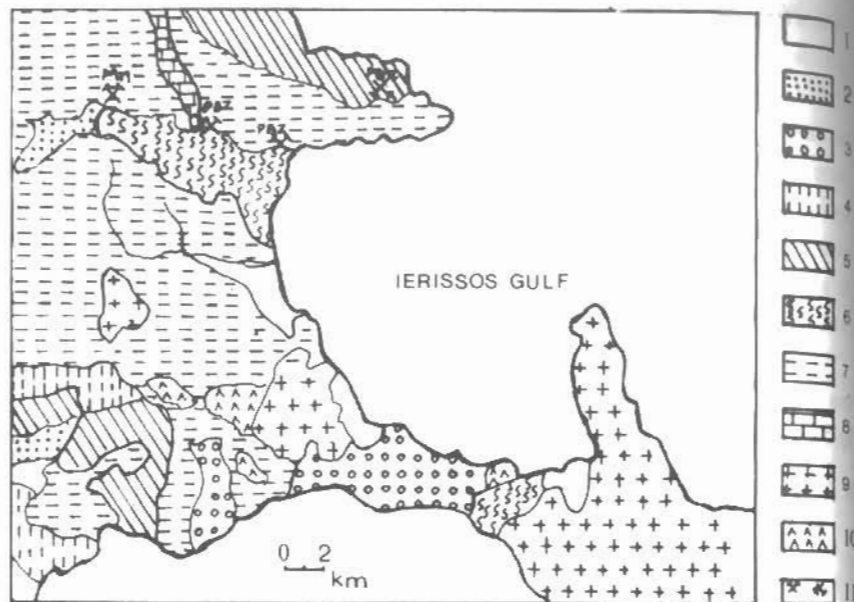
Σχ. 2. Κόλπος Ιερισσού: χάρτης με τις θέσεις δειγματοληψίας των δειγμάτων από τον κόλπο και την παρακείμενη περιοχή.

REGIONAL GEOLOGY OF THE ADJACENT MAINLAND

The study area is a gulf of the Chalkidiki peninsula which geologically belongs to the Serbomacedonian massif (SMM) – a metamorphic belt which lies on the west of the Rhodope massif, on an area extending from the river Strymon westwards. Close to the small town of Stratonis (Fig. 2), extensive masses of amphibolites, significant mixed sulphide ores, manganese oxide deposits and small Cu-bearing porphyry stocks are found (Fig. 3). On the coast near Stratonis, a mineral processing plant operates. Granites and granodiorites are encountered in the region close to the town of Ierissos and the eastern coastal area of Ierissos gulf (Fig. 3). In the southern part of the Ierissos gulf, serpentines, amphibolites, peridotites and dunites with chromite mineralization occur, with a small ultrabasic igneous complex of ophiolitic character outcropping also there (Fig. 3).

ANALYTICAL TECHNIQUES

The samples subjected to partition analysis were treated according to the following sequential steps: (a) Exchangeable fraction: 1g of sample is extracted with 8ml 1M NH_4OAc , at pH 8.2, for 1 hour, at room temperature with continuous agitation; (b) Carbonate hosted fraction: the residue from (a) is leached with 8ml 1M NaOAc , adjusted to pH 5 with HOAc , for 5 hours, at room temperature, with continuous agitation; (c) Reducible fraction: the residue



- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9
- 10
- 11

Fig. 3. Simplified geological map of the mainland (modified from Bornovas and Rondogianni-Tsiambaou, 1983).

Σχ. 3. Απλοποιημένος γεωλογικός χάρτης της παρακείμενης περιοχής (τροποποιημένος από τον χάρτη των Bornovas and Rondogianni-Tsiambaou, 1983).

- Key:
- 1 Alluvial and coastal deposits.
 - 2 Pleistocene - Plio-Pleistocene continental, lacustrine and marine deposits.
 - 3 Pliocene - Upper Miocene marine, terrestrial and lacustrine deposits.
 - 4 Schists, marbles and phyllites.
 - 5 Gneisses.
 - 6 Amphibolites.
 - 7 Gneisses, schists with marble intercalations and amphibolites.
 - 8 Marbles.
 - 9 Granites and granodiorites.
 - 10 Serpentes.
 - 11 ✕ active mine, ✖ idle mine.

from (b) is extracted with 20ml 0.04M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) HOAc at pH 2, for 6 hours, at $96\pm 3^\circ\text{C}$, with occasional agitation; (d) Organic matter-sulphide hosted fraction: to the residue from (c), 3ml of 0.02M HNO_3 and 5ml of 30% H_2O_2 , adjusted to pH 2 with HNO_3 are added; the mixture is heated to $85\pm 2^\circ\text{C}$, for 2 hours, with occasional agitation; a second 3ml aliquot of 30% H_2O_2 , adjusted to pH 2 with HNO_3 , is added. The mixture is heated at $85\pm 2^\circ\text{C}$, for 3 hours, with intermittent agitation. After cooling, 10ml of 3.2M NH_4OAc in 20% (v/v) HNO_3 are added, the mixture is then diluted to a final volume of 40ml and continuously agitated for 30min.

After each successive extraction, separation of the supernatant from the residual solid was done by centrifuging the mixture for 30min., at 2000rev/min. The supernatant liquids are then decanted. The supernatants are subjected to a further treatment involving: (a) addition of a few drops of concentrated HNO_3 ; (b) heating to dryness; and (c) dilution with 1M HCl . The final solutions were analyzed on an ARL-3400 Inductively Coupled Plasma Emission Spectrometry (I.C.P.A.E.S.).

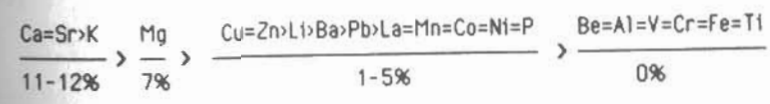
The amounts of elements associated with the residual phase - comprising of the residual solid that remains after the four preceding extractions - are calculated by subtracting the amounts associated with the first four fractions from the total sediment analysis obtained after complete dissolution of the sample by a mixture of HF , HClO_4 and HNO_3 (Thompson and Walsh, 1983).

RESULTS

The results are described separately for each of the five fractions.

(a) Exchangeable fraction

The exchangeable fraction represents the material adsorbed on the sediment. The amounts of metals contained in this fraction are released easier than those in the remaining portion of the non-residual fraction. The following sequence of solubility of the elements in NH_4OAc 1M occurs:



The above sequence makes it clear that among the various elements Ca, Sr, K and Mg are significantly removed with the exchangeable fraction. Therefore, it is indicated that easily hydrolyzed Ca, Sr, and Mg components are likely to be present and that a K-contribution from the seasalt occurs. In addition, a slight dissolution of the carbonate fraction by NH_4OAc 1M at

pH 8.2 may have occurred. Only traces of Al were leached by NH_4OAc , implying that the treatment used does not affect the silicates.

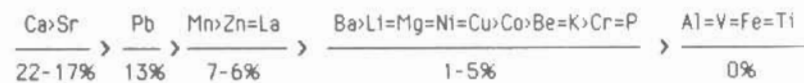
Significant Cu, Zn, and Pb enrichments were found in the offshore samples. They correspond to a Pb-Mn enrichment in the exchangeable fraction of the onshore samples collected from the northwest coast of the Ierissos gulf. These enrichments could be attributed to land sources and man-made pollution, as mixed sulphide and Mn-oxide deposits occur in the mainland surrounding Ierissos gulf, while a mineral processing plant exists in the coastal area of Stratoni.

Among the samples subjected to partition analysis, an exceptionally large metal enrichment in the exchangeable fraction occurs in some of them. From the offshore samples, 2 and 3 show an enrichment in their exchangeable metal content, the former in Cu (9%) and Zn (7%), and the latter in Cu (6%), Pb (6%) and Zn (10%). As both samples were collected off Stratoni district, these enrichments probably reflect the pollution of this area from the nearshore mining activities. The onshore samples (19 and 20) collected from the coastline of Ierissos gulf, exhibit metal enrichments in their exchangeable fraction. Sample 19 has enrichments in exchangeable Zn (5%) and Mn (4%). Sample 20, collected from a beach area close to a fertilizer factory, shows an enrichment in exchangeable Pb (4%).

As the amount of exchangeable metals is a good indicator of the pollution potential of a sediment, the samples mentioned above may be considered to be polluted, in a broad sense, containing portions of metals easily available to the biota.

(b) Carbonate hosted fraction

This fraction represents the elements associated with carbonate minerals in the sediments. Sodium acetate and acetic acid were used as the leaching reagents. The following solubility sequence of elements in this reagent occurs:



The above sequence confirms that biogenic carbonate remains, comprise the phase mainly attacked by NaOAc/HOAc at pH 5.

The aforementioned element solubility sequence shows that:

1. A significant proportion of Pb was leached by NaOAc/HOAc , implying that a part of the total Pb is supplied biogenically – an association of Pb with the acetic acid leachate has been also noted by Varnavas (1979), Varnavas and Cronan (1981) and Shearme et al (1983).
2. Significant proportions of Mn, Zn, Ni, Cu and Co were leached by NaOAc/HOAc , indicating a biogenic contribution for these metals (not as extensive as for Pb). This is consistent with

the work of Varnavas and Cronan (1981) who found that 42% of the total Pb and 10% of the total Cu in the carbonate sediments from DSDP424 in the Galapagos Hydrothermal Mounds Field was associated with the acetic acid soluble fraction. They suggested that this indicates the removal of these elements from biogenic calcium carbonate or from coatings on carbonate materials.

3. Iron was not found in the second leachate, showing that Fe is not likely to be associated with the biogenic matter, and also that Fe-oxides have not been attacked.
4. Aluminium was not leached by NaOAc/HOAc ; obviously, the silicate phase has not been attacked.

It was noticed that in some of the samples subjected to partition analysis low proportions of the total Ca and Sr were leached by NaOAc/HOAc corresponding with high Ca and Sr proportions found in the third leachate (leached by $\text{NH}_2\text{OH}\cdot\text{HCl}$). These samples were collected from areas enriched in carbonates and therefore high proportions of Ca were expected to be found in the NaOAc/HOAc leach. As the NaOAc/HOAc reagent is used to dissolve the carbonates and a high Ca and Sr content is unlikely to occur in the reducible fraction of the sediments, the anomalous Ca and Sr distribution among the second and third leachate of these samples indicates an incomplete dissolution of the sediment carbonates by NaOAc/HOAc .

In 5 samples, the concentrations of Ca occurring as carbonates (carbonate content being measured by gas chromatography (Sakellariadou, 1987)) were compared with the total Ca content of the second and third leachate. This comparison (Table 1) shows that the sum of Ca associated with the second and third leachate represents the total amount of Ca present as carbonates.

Table 1: Calcium content determined by gas chromatography and total Ca content associated with the second and third leachate.

Sample I.D.	Ca ¹ (%)	Ca ² (%)
1	3	3
2	6	3
3	5	5
13	13	12
16	9	7

¹: Ca content determined by gas chromatography; ²: Ca content associated with the second and third leachate.

According to the data obtained, it is evident that the NaOAc/HOAc leach is not completely dissolving the carbonates; change of pH during the NaOAc/HOAc attack could be responsible for the incomplete attack on the carbonates. Comparison of 5 samples, regarding

the anomalous Ca distribution between the second and third leachate (Table 2), shows that the dissolution of carbonates by NaOAc/HOAc is less complete in the samples richest in carbonates.

Table 2: Total calcium carbonate content of selected samples, and proportions of the total Ca content of the same samples associated with the second and the third leachate.

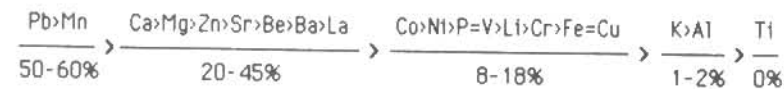
Sample I.D.	CaCO ₃ ¹ (%)	Ca ² (%)	Ca ³ (%)
1	8.2	40	24
2	14.8	21	36
3	11.7	27	44
13	61.6	1	48
16	22.5	21	60

¹: total CaCO₃ content determined by gas chromatography; ²: proportion of the total Ca associated with the second leachate; ³: proportion of the total Ca associated with the third leachate.

(c) Reducible fraction

Hydroxylamine hydrochloride was used for the removal of the reducible fraction. The major phases attacked are reducible ferromanganese oxides, some amorphous iron oxides and other reducible material (Chester and Hughes, 1967; Cronan, 1976; Moorby and Cronan, 1981). It is well established (Jenne, 1968) that iron and manganese oxides occur as nodules, concretions, cement between particles, or simply as coatings on particles. These oxides are excellent scavengers of trace metals. Under anoxic conditions, Fe, Mn-oxides are unstable and they, therefore, tend to dissolve releasing the trace metals bound to them into solution.

The following solubility sequence of the various elements occurs:



The relatively high proportions of total Ca and Sr occurring in the third leachate are attributed to the remaining carbonates, as these elements are not known to form reducible phases in marine sediments. A portion of the Mg leached by NH₂OH·HCl could also be associated with the carbonates left over from the incomplete dissolution by NaOAc/HOAc. It is also possible that, part of the Pb and Zn proportions found in the third leachate is associated with the carbonates. The large proportions of the total Pb, Mn, Zn, Co, Ni, Fe and Cu removed by NH₂OH·HCl indicate the presence of Fe, Mn-oxides in the sediments and demonstrate the

scavenging ability of these oxides for metals. The probability that the trace metals found in the third leachate are associated with the Fe, Mn-oxides rather than with the remaining carbonates is strengthened by the following:

1. The correlation matrices of the data obtained from the bulk geochemical analysis of 750 surface marine sediments collected from the North Aegean Sea (Sakellariadou, 1987), showed that the correlation coefficients of Ca and each of the metals Mn, Fe, Zn, Co, Ni and Cu are very low (-0.08 to -0.63). By contrast, the correlation coefficient of the Ca-Sr pair is high (>0.83).
2. The dendograms, obtained when cluster analysis was applied to the geochemical data produced by the whole sample analysis of 750 surface marine sediments collected from the North Aegean Sea (Sakellariadou, 1987), showed that a mega branch containing only Ca and Sr was formed.
3. The results of experimental work - which concerns acetic acid attack on the carbonates under various conditions (Sakellariadou, 1987) - suggest lack of trace metal association with sediment carbonates. The latter mainly contain Ca and Sr.

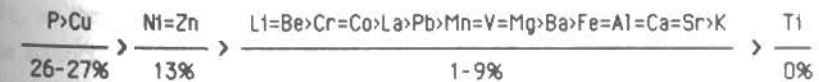
As high as 44% of the total Zn, and 48-62% of the total Pb occurs in the reducible fraction of the samples collected off Stratonis; this could be related to the presence of mixed sulphide mineralization in the mainland. In the Ierissos gulf sediments zinc and lead present average concentrations of 586 and 1,454ppm respectively. In the Strymonikos gulf, Strymonikos plateau and the Kavala gulf sediments the mean Zn and Pb contents were found to be 78 and 49ppm respectively, whereas in the Samothraki plateau sediments the corresponding mean concentrations are 90 and 69ppm (Sakellariadou, 1987).

(d) Organic and Sulphide bound fraction

This fraction represents the elements bound to various forms of organic matter and those present in sulphide minerals.

Hydrogen peroxide was used for the leaching of the organic compounds and sulphide minerals.

The solubility sequence of the various elements in H₂O₂ is presented below:



The above sequence shows that Cu and P have a strong association with the H₂O₂ soluble fraction. Copper in the fourth leachate may be related to sulphides and to organic materials. The former possibility is a more likely situation in the Ierissos gulf sediments, on account of: (a) their contamination by material derived from the mineralization of the

mainland and (b) the event that the Ierissos gulf sediments are poor in organic matter (Sakellariadou, 1987). Phosphorus in the H_2O_2 soluble fraction is attributed to its occurrence largely in organic matter.

The concentrations of Al in the fourth leachate show that relatively little of the total Al (up to 3%) was leached by H_2O_2 ; therefore, there is a minimal attack of the major silicate phase by this reagent.

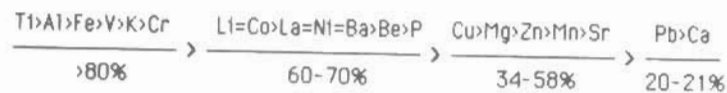
A relatively exceptional enrichment in the metal content of the fourth fraction occurs in some of the sediments subjected to partition analysis. The following enrichments were recorded:

1. Up to 36 and 32% of the total Cu of samples 13 (with 0.5 % organic carbon) and 3 (with 0.1% organic carbon) respectively, and 13% of the total Co and 18% of the total Ni of sample 2 (with 0.14% organic carbon) occur in the H_2O_2 soluble fraction. It is suggested that these enrichments in the fourth leachate are associated with sulphides, as the organic carbon content of these samples is very low. This suggestion is supported by the presence of Cu-bearing porphyry stocks and mixed sulphide ores in the mainland adjacent to the gulf.
2. Up to 46% of the total Zn occurs in the fourth fraction of sample 19. This enrichment can be attributed to traces of sulphides, as mixed sulphide mineralization occurs in the drainage basin of the river from which this sample was collected.

(e) Residual fraction

This fraction contains most of the elements hosted in the lattice structure of silicate minerals, clays and other resistant minerals. These elements are not expected to be released rapidly in the secondary environment under the conditions normally encountered in nature.

The various elements occur in the residual fraction in the following sequence:



The above sequence shows that the major part of all the elements studied, apart from Mn, Sr, Pb and Ca, in the sediments remains in their residual fraction.

CONCLUSIONS

The part of the sediment most easily released is the exchangeable fraction, leached by NH_4OAc . The presence of easily hydrolyzed Mg, Ca and Sr components and a minor K-contribution from the seasalt has been demonstrated. Ammonium acetate has slightly attacked the carbonate fraction. Some exchangeable Mn (1% of the total) was found; this probably

represents small amounts of a reduced form of Mn that could be adsorbed on clay minerals.

Sodium acetate and acetic acid were used as the second leaching reagent, designed to remove the carbonate material. However, this reagent was not successful in dissolving all of it. In complete dissolution of carbonates was recorded mainly in the carbonates enriched samples. The carbonate hosted fraction of the sediments within the study area, contains mainly Ca and Sr, the former representing $CaCO_3$ and the latter substituting for Ca in the carbonates. Partition analysis has indicated a biogenic contribution of Pb, Mn and Zn. Such contribution has also been noted by Varnavas and Cronan (1981), Shearman et al (1983) and Varnavas et al (1983).

The reducible fraction contains Fe, Mn-oxides and shows their scavenging ability for trace metals. Comparison of the amounts of trace metals associated with each of the non-residual fractions shows that the majority of them occurs in the reducible fraction; such elements are Pb, Mn and Zn. Up to 38% of the total Zn was found to be bound to the reducible fraction, as, according to Ballistieri and Murray (1986), Zn can be scavenged from seawater by Mn oxides. Also, up to 52% of the total Mn occurs in the reducible phase indicating that reducible ferromanganese oxides are large Mn reservoirs in the sediments studied. Finally, about 12% of the total P content was found to be associated with the reducible fraction demonstrating the ability of phosphate anions to coprecipitate onto the surface of Fe and Mn oxides (Bortleson and Lee, 1974); according to Fröelich et al (1982) ferric hydroxides can adsorb P from the water column. A significant portion of the non-residual Cu is hosted in the reducible phase, indicating a Cu presence in reducible ferromanganese oxides.

The H_2O_2 attack has leached both the organic matter and the sulphide minerals. The non-residual Cu is primarily associated with the organic/sulphide hosted fraction, about 26% of the total Cu occurring in this fraction. This implies a possible occurrence of traces of copper sulphide, as the Ierissos gulf sediments are poor in organic matter. The H_2O_2 attack has leached the 27% of the total P, indicating the affinity of P for organic matter. Small proportions of Mn (5% of the total) and Fe (3% of the total) were found to be hosted in the organic/sulphide fraction. A minimal attack of the major silicate phase by H_2O_2 was recorded.

The major parts of the elements Ti, Al, Fe, V, K, Cr, Li, Co, Ni, La, Ba, Be, P, Cu, Mg and Zn are hosted in the lattice structure of silicate minerals, clays and other resistant minerals, as they mainly remain in the residual fraction. Thus, the following are suggested with the support of the results of the statistical treatment of the geochemical data of 750 surface marine sediments from the North Aegean Sea (Sakellariadou, 1987). The bulk of Ti is present in terrigenous detrital material; the bulk of Al, K and Ba and the major part of Be are hosted in resistant aluminosilicate minerals and their alteration products (such as clays); Iron is mainly present in resistant Fe-bearing minerals, such as heavy minerals, silicates and clays. The principal route of supply of V, Cr and Ni to the sediments studied is detrital

material of mafic/ultramafic rocks. Cobalt is likely to be mainly present in the lattice of clay minerals; according to Chester and Hughes (1967, 1969), Co in the monovalent state, as CoCl^+ or Co(OH)^+ , may substitute for hydrogen in the (OH) groups of the clay mineral lattices. The comparatively small portion of Ca in the residual fraction implies that a small proportion of the total Ca occurs in the lattice of resistant Ca-bearing minerals.

In general, it was found that the elements determined in the marine sediments subjected to partition analysis occur mainly in the residual and reducible fractions. This is in agreement with the suggestions of Li (1982), and Calvert and Piper (1984); they observed that in marine sediments and ferromanganese nodules, metals tend to primarily associate with silicates and Mn,Fe-oxides. Also, the contamination of the Ierissos gulf sediments by mining effluents was indicated. Concerning the area off Stratoni, the contamination of the sediments (Fe, Mn, Zn and Cu contents higher than 8.0%, 4000ppm, 700ppm and 75ppm respectively) by the mainland mining operation was further supported by the decrease of the non-residual Mn, Fe, Ni and Cu proportions with increasing depth in the uppermost 16cm of the core C1 (Sakellariadou, 1987).

The results of the partition geochemical analysis are fully compatible with those provided by the statistical treatment (cluster and factor analysis) of the geochemical data of 85 samples from the Ierissos gulf (Sakellariadou, 1987).

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