GEOCHEMICAL INVESTIGATIONS OF RECENT SEDIMENTS FROM THE AEGEAN SEA

by

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ABSTRACT

Continental margin sediments from the central Aegean Sea (off Sounion,Andros,Kithnos,Naxos,and Serifos) are mixtures of relict,reworked,and recent bioclastic and terrigenous components. Shelf and shelf edge deposits are mainly bioclastic sands,whereas calcareous muds accumulate seawards of the shelf edge.

The main controls on the chemical composition of the continental margin deposits include admixture of terrigenous components of variable composition with biogenic components depleted in minor and trace elements;hydrogenous manganese oxide accumulation and the associated scavenging of trace elements;and authigenic iron mineral formation in the relict component.

Off Sounion,the concentrations of Pb and Zn are anomolously high because mine waste from local mining operations reaches much of the continental shelf.This dispersal of mine waste into the adjacent marine environment is a potential pollution hazard because the Pb,in particular,appears to be in a form available for uptake by marine biota.

Sediments from in and around the Santorini caldera are also admixtures of biogenic and terrigenous components but the latter mainly comprise the solid products of volcanic activity.Additional controls on the geochemistry of sediments within the caldera include the accumulation of particulate iron and manganese oxides; scavenging of trace elements from seawater by the particulate oxides;and the remobilisation of Mn to form enriched layers at the tops of reducing horizons.

Iron-rich sediments are forming at the centre of the caldera close to submarine hydrothermal activity.Lateral trends in a wide range of elements,partition studies,and the analysis of water samples,are used to investigate the geochemistry of the deposits, with particular reference to the dispersion of Fe,Mn,and heavy metals. The formation of the iron-rich surface layer;the associated zonation of Fe,Mn,and trace elements;and the significance of these studies to geochemical exploration for both modern and ancient volcanogenic stratiform massive sulphide,iron,and manganese deposits is discussed in detail.

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CHAPTER 1 INTRODUCTION

1.1 GENERAL INTRODUCTION

As a contribution to the Applied Geochemistry Research Group investigations of both the application of geochemical techniques to offshore studies and the geochemistry of eastern Mediterranean sediments in general, this thesis presents the results of geochemical and sedimentological studies of continental margin sediments from the Aegean Sea. In the context of marine mineral exploration and environmental assessment, the central Aegean is interesting for several reasons: a variety of mineral deposits occur onshore and their geology suggests that similar deposits could be found on the adjacent continental shelf; a long history of onshore mining will have influenced the chemical composition of the sediments in some areas; and volcanogenic-exhalative deposits are forming at the present time close to submarine fumarolic activity.

Research began in the autumn of 1972 with a reconnaissance survey of six locations in the central Aegean Sea (figure 1.1):

Sounion - the site of lead and zinc mining since ancient times. The geological structure of the deposits is such that they may extend offshore.

Kithnos and Serifos - showings of base metals, iron and manganese occur onshore and similar deposits may occur on the continental shelf.

Andros - ultrabasic rocks with showings of chromite exist within the catchment area feeding the shoreline and the ultrabasic provenance may be detectable in the chemical composition of the sediments.

Naxos - there is little evidence of mineralisation on the southern half of the island adjacent to the survey area and so this was chosen as a control area.

Santorini - a volcanically active caldera with shallow, submarine fumarolic activity at its centre and the associated formation of iron deposits containing manganese and small amounts of heavy metals.

The overall objectives of the reconnaissance survey were to describe the broad nature and distribution of the sedimentary facies in each area, to establish their geochemical characteristics,

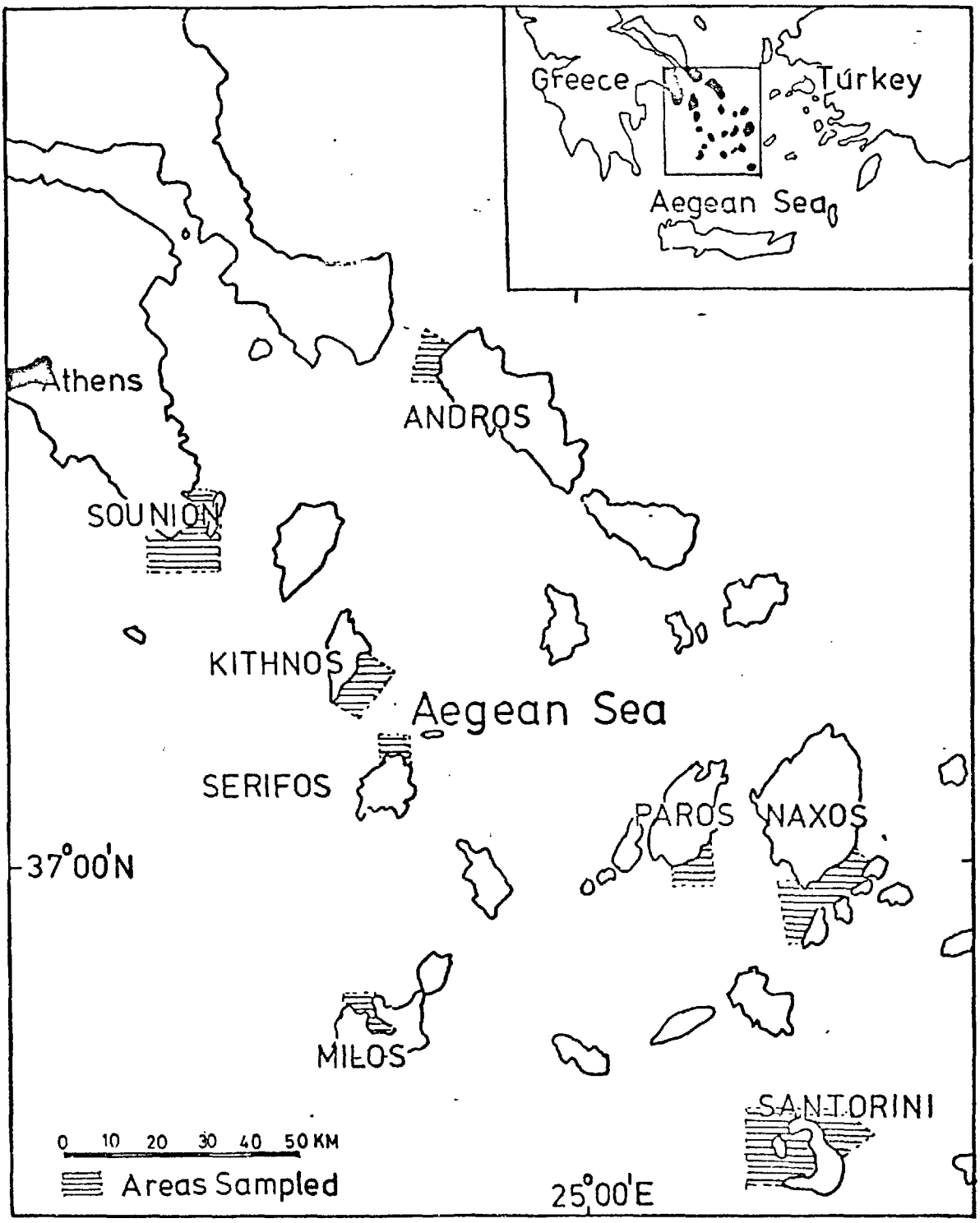


Figure 1.1 Location of the study areas.

to identify the major controls on the chemical composition of the sediments, and to delimit areas for further investigation.

To assess the influence of onshore mining activity on the adjacent marine sediments in greater detail, more beach and offshore samples were collected from Sounion during a joint expedition to the Aegean Sea by the Greek Institute of Oceanographic and Fishing Research and Imperial College in 1973, mainly aboard the Hellenic Ship PLIAS. On the same expedition, sediment and water samples were taken in the shallow zones close to the fumarolic activity at Santorini to examine the geochemical nature of the iron deposits and to assess the dispersion pathways of heavy metals from their hydrothermal source to the open sea.

Finally, in 1974 an opportunity arose to revisit Santorini aboard the R.R.S. SHACKLETON during a University of Cambridge expedition to the eastern Mediterranean. More cores were collected to complete the coverage of the caldera and surrounding continental shelf.

1.2 PHYSIOGRAPHY AND GENERAL GEOLOGICAL SETTING

The major physiographic provinces of the Aegean and eastern Mediterranean have been described by Goncharov and Mikhailov (1963), Emery et al. (1966), Ryan (1969), Maley and Johnson (1970), and Carter et al. (1972). The dominant feature is the Hellenic Arc (Goncharov and Mikhailov, op.cit.) extending from the mountains of Greece, through the islands of Kithera, Crete and Rhodes, and on towards western Turkey. Components of this arc include an outer Mediterranean Ridge (Emery et al., op.cit.) separated from the Cretan Arc (Maley and Johnson, 1970) by the deep, parallel Pliny and Strabo trenches of the Hellenic Trough (Emery et al., op.cit.). Between the emergent Cretan Arc and the inner volcanic arc to the north, are several deep basins which collectively form the Cretan Trough. The inner volcanic arc is variously known as the southern Aegean volcanic arc (Paraskevopoulos, 1956), the Cyclades arc (Maley and Johnson, 1970), or the Hellenic volcanic arc (Ninkovich and Hays, 1972). It is marked by volcanoes such as Santorini, and fumarolic activity on several islands (Georgalas, 1962). To the north of the volcanic arc is an aseismic (Ryan, 1969) Central Aegean Plateau (Maley and Johnson, 1970) which includes the islands of the Cyclades.

The overall morphology of the Aegean and eastern Mediterranean is typical of an island arc complex (Emery et al., 1966; Ryan, 1969; Maley and Johnson, 1970) and geophysical evidence (e.g. Ryan, 1969; Vogt and Higgs, 1969; Papazachos and Delibasis, 1969; Caputo et al., 1970; Makris, 1973; and others), recently reviewed by Lort (1977), supports this hypothesis. McKenzie (1970, 1972) concludes that in addition to the major Eurasian and African plates two smaller plates operate in the area. The first, the Aegean plate, includes part of mainland Greece, the Aegean Sea, and part of western Turkey, and is actively overthrusting the African plate causing a downwarping and the formation of a subduction zone to the south of Crete. Most of Turkey and Cyprus move as the Turkish plate, the second small plate in the system. The closing rate between the Aegean and African plates is of the order of 3.5cm/yr and the Benioff Zone dips at about 30° to the north-east (Caputo et al., 1970; Karnik, 1972; Comninakis and Papazachos, 1972).

Petrographic evidence also supports the hypothesis of an island arc tectonic setting for the Aegean Sea. Nicholls (1971b), Ninkovich and Hays (1972), and Pichler and Kussmaul (1972), broadly agree that the lavas of the southern Aegean volcanic arc are compatible with partial melting within, or along, the margin of a descending plate.

A further manifestation of the overall tectonic environment and Alpine orogenesis is the continuing subsidence of the Aegean. Hsu (1977) reviews the tectonic evolution of the eastern Mediterranean region and states that the Aegean is a marginal sea behind an island arc. The southern Aegean forms a back-arc basin following crustal extension and normal faulting. In the early Miocene the Aegean Sea was emergent but has been subsiding since the middle or late Miocene. Palaeontological evidence also supports a late Tertiary collapse (Pfannenstiel, 1960).

Melentis (1977) reviews the geology of Greece and the Aegean region. The southern half of the Attica peninsula and the islands of the Cyclades form part of the Attic-Cyclades massif (Rentz et al., 1954) which is, in turn, part of the Pelagonian Zone (Aubouin et al., 1963). The Attic-Cyclades basement rocks mainly comprise Palaeozoic metamorphic rocks such as crystalline schists and marbles. Tertiary acidic intrusives are found on Serifos (Zachos and Maratos, 1965), Naxos (Papastamatiou, 1951), and at Sounion (Marinos and Petrascheck, 1956). Extrusive volcanic rocks

also occur throughout the area and are related to the active subduction zone underlying the area. Nicholls (1971a) describes four groups of lavas on Santorini, all broadly classified as calc-alkaline.

Zachos and Maratos (1965) have compiled a metallogenetic map of Greece and it is evident from this that the Cyclades Islands contain a wide range of mineral deposits: base metals (particularly Pb and Zn), iron and manganese deposits associated with the acid intrusives and the Pliocene/Miocene lavas (Marinos, 1948; Frangato, 1951; Marinos and Petrascheck, 1956; Anastopoulos, 1963; Marakis, 1968); chromite is found in ultrabasic rocks; and the emery of Naxos probably derives from the metamorphism of bauxite (Papastamatiou, 1951).

1.3 PREVIOUS MARINE GEOLOGICAL AND GEOCHEMICAL INVESTIGATIONS

Very little data on either the nature of the continental margin sediments from the central Aegean Sea or their geochemistry has been published to date. Most research has concentrated on the nature of sediments from the deeper basins (e.g. Olausson, 1960; Emery et al., 1966; Wong and Zarudski, 1969; Ryan, 1969; Opdyke et al., 1972; Venkatarathnam and Ryan, 1972), their relevance to the study of ancient flysh deposits (e.g. Stanley, 1973, 1974), and seismic reflection studies of unconsolidated sediment thicknesses (Watson and Johnson, 1969; Jongsma, 1975; Stanley and Perissoratis, 1977). These hemipelagic sediments (Stanley, 1977) consist largely of calcareous lutites (Opdyke et al., 1972) with intercalated volcanic ash, sapropelic mud layers, and the occasional turbidite sequence. Opdyke et al. report accumulation rates as high as 75cm/1000 years but generally they range between 4 and 20 cm/1000 years (Wong and Zarudski, 1969; Pastouret, 1970).

Stanley (1977) reviews post-Miocene deposition in the Aegean but only makes passing reference to continental shelf deposits. Similarly, Blanc (1968, 1972) and Emel'yanov (1965, 1972) include the shallower parts of the central Aegean in their surveys of bottom sediments from the Mediterranean but their descriptions are brief. Nekritz (1963) compiled a map of sediment types around the Aegean Islands from information found on nautical charts. Müller (1972) describes sediments between the islands

of Naxos and Paros in some detail, and Schwartz and Tziavos (1974, 1975) describe the sedimentary provinces found in the adjacent Saronic Gulf. However, none of these studies are sufficiently detailed to be of great help to the present investigation.

Geochemical data is even scarcer. Apart from the previously published, preliminary results of the present investigation (Smith and Cronan, 1975a; Smith, 1977), the only other geochemical data concerns pollution studies close to the Athens sewage outfall (Hopkins et al., 1972; Papakostidis et al., 1975). Of course, the deposits from in and around the Santorini caldera are a different matter - they have been the subject of a wide range of investigations and the published information is reviewed where appropriate in chapter 7.

1.4 THESIS STRUCTURE

The first part of the thesis deals with the continental margin sediments from Kithnos, Serifos, Andros and Naxos (chapter 2 to 5). It was necessary first of all to create a sedimentological framework for the geochemical discussion, and this was achieved by combining the results of textural analyses of the sediment and bathymetric charts compiled from precision depth recorder profiles taken during the sampling programme. Geochemical studies are mainly based on bulk chemical analyses, but these are supplemented by selective leaching and a limited amount of mineralogical data. In chapter 6, the discussion of the Sounion deposits follows a similar scheme but also considers the impact of coastal mining on the composition of the adjacent marine sediments, including an assessment of its environmental significance.

Chapter 7 covers the geochemistry of waters and sediments from in and around the caldera of Santorini, with particular reference to submarine hydrothermal activity. The chapter includes a review of the sedimentological characteristics, and geochemical studies are based on a combination of bulk chemical analyses, partition studies, and lateral trends in elemental abundance from the fumaroles to the deeper waters of the caldera.

Mineral exploration is the theme of chapter 8: the results from each area are re-examined in the context of the exploration for bedrock mineralisation on the continental shelf, and both modern and

ancient volcanogenic - exhalative deposits.

Finally, chapter 9 presents a review of the main results and conclusions.

CHAPTER 2 KITHNOS

2.1 INTRODUCTION

Kithnos is one of the Cyclades group of islands and is situated in the southern Aegean Sea, approximately 90km south-east of Athens (figure 1.1). Geologically the island is part of the Attic-Cyclades massif which mainly comprises complex metamorphic rocks dominated by mica-and chlorite-schists (Rentz et al., 1954). Showings of base metals, iron and manganese occur on the south-east side of the island (Zachos and Maratos, 1965). Accordingly, 47 samples of the upper 5 to 15cm of sediment were obtained off the south-east coast of Kithnos (figure 2.1), covering an area of about 50km^2 between depths of 100m and 200m.

2.2 SHELF TOPOGRAPHY

The topography of the study area, based on Precision Depth Recorder profiles taken during the sampling programme, is shown in figure 2.1. Broadly, there are three distinct zones:-

(a) a narrow, gently sloping 'shelf' shorewards of the 120m isobath;

(b) the 'shelf edge' between depths of 120m and 160m and characterised by a complex, relict morphology of alternating headlands and embayments similar to the present shoreline;

and (c) a fairly flat 'offshore' zone, seawards of the 160m isobath.

2.3 NATURE AND DISTRIBUTION OF SEDIMENTS

2.3.1 Sediment Distribution

The proportions of mud, sand, and gravel are used to classify the sediment samples from Kithnos according to the scheme of Folk (1954) to provide a preliminary assessment of the distribution of major sediment types (figure 2.2). Sediment distribution appears to be strongly related to topography. Seaward of the 170m isobath (approximately the foot of the scarp) muds are most abundant, whereas landward, to the limit of the survey area (95m isobath), sands cover most of the shelf.

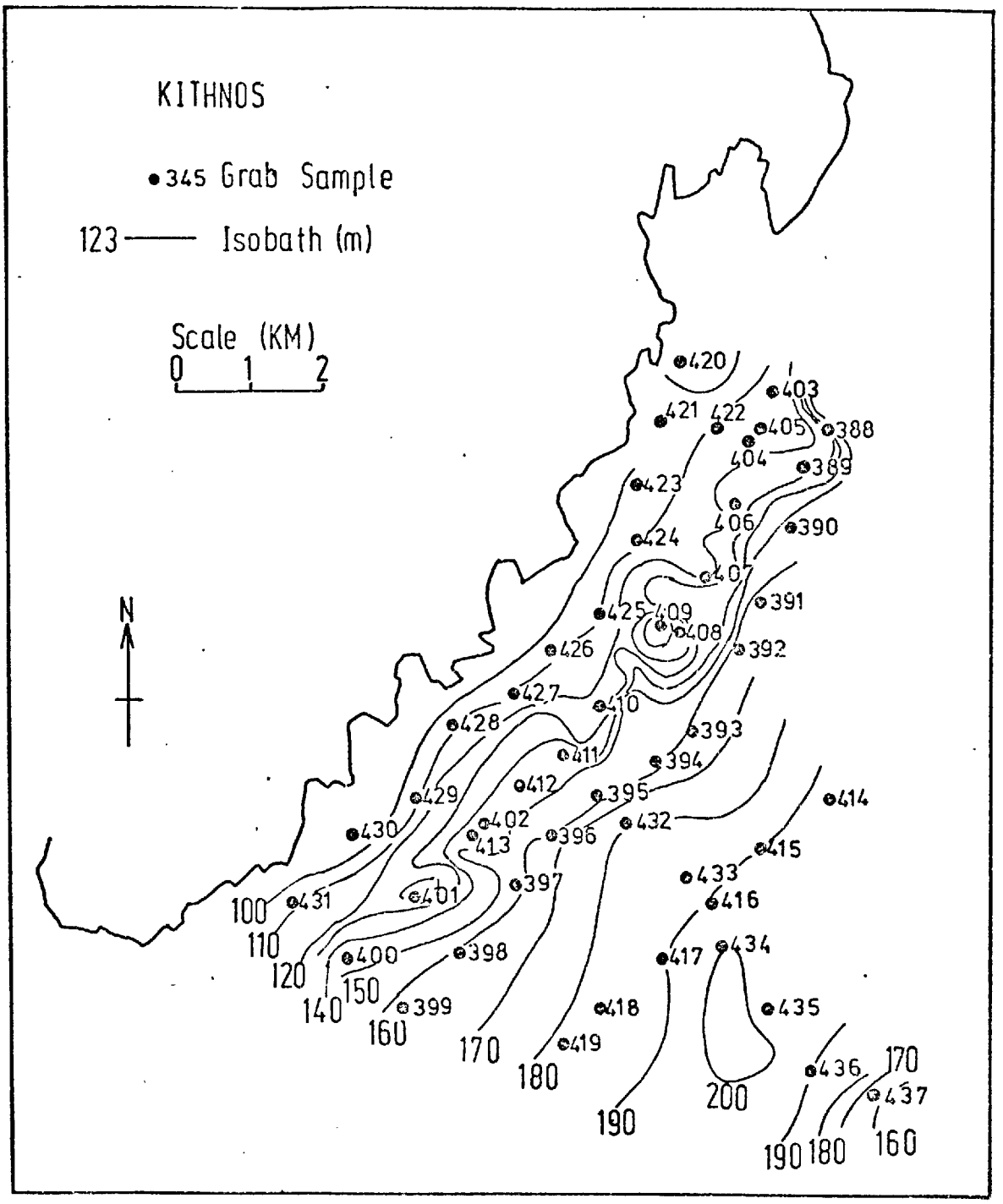


Figure 2.1 Location of samples and bathymetry off Kithnos

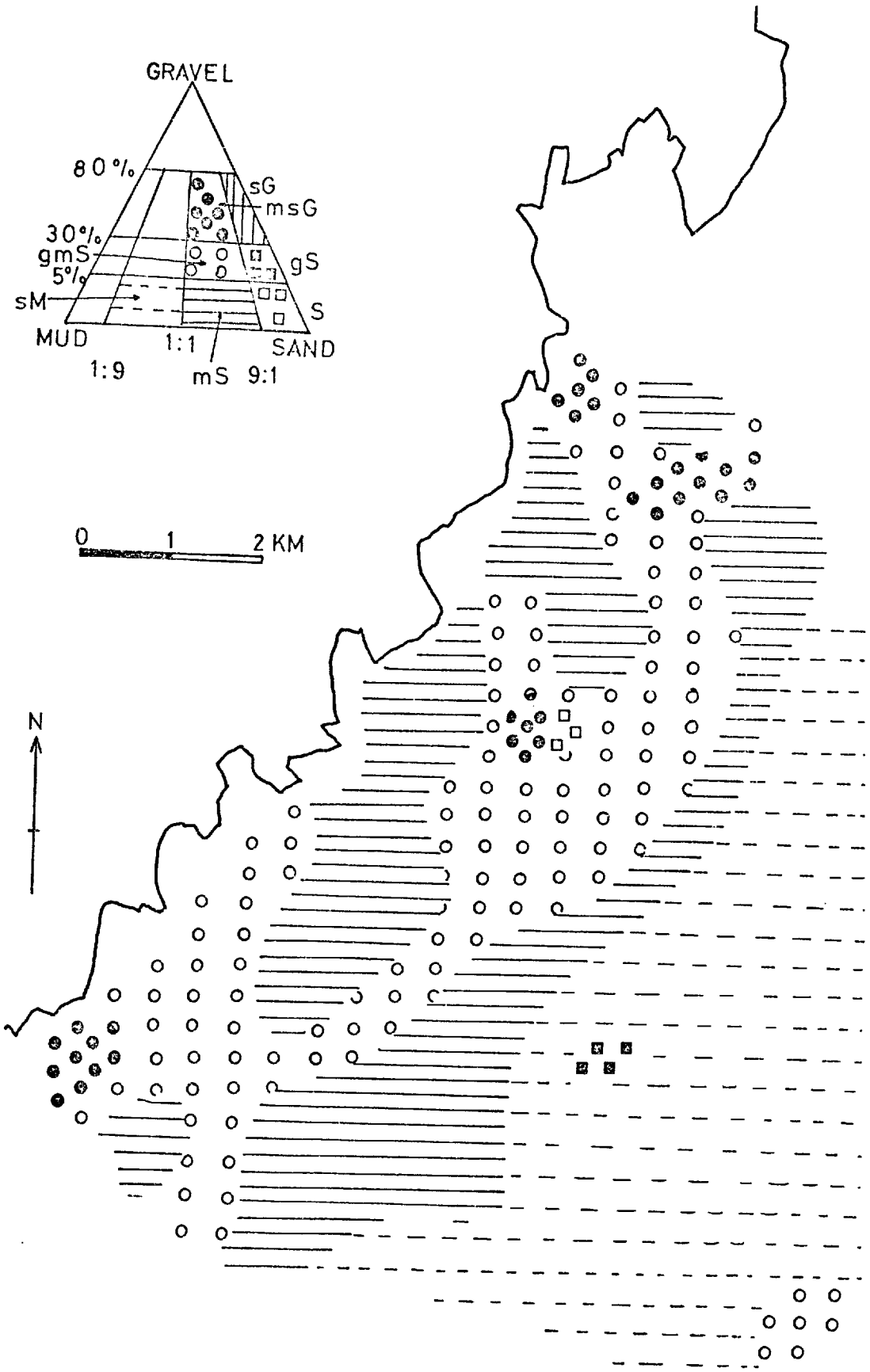


Figure 2.2 Kithnos - distribution of sediment types.(Samples classified according to the scheme of Folk, 1974)

Muddy sands form two lobes extending in a southerly direction from the 90m to the 150m isobaths, following the prominent valleys in the shelf topography. A further belt of muddy sand straddles the 170m isobath at the foot of the scarp.

Gravelly muddy sands cover the shelf edge and much of the south-western part of the shelf.

Gravels occur as isolated patches on topographic highs above 120m depth, either on the shelf edge between 110 and 120m or at shallower depths on shoals related to the extension of onshore headlands. Most of the gravel size material is coralline algae.

Sandy muds are most abundant seaward of the 170m isobath. In the deeper parts of this zone mud content is as high as 60%.

2.3.2 Sediment Components and Their Distribution

Coralline algae are the most abundant calcareous component of the Kithnos sediments. They are the dominant constituents in the gravelly muddy sands that cover most of the shelf above the 170m isobath. Where the branching form of calcareous algae is most abundant the sediments resemble the gravelly sands called "maerl", which have been found in many parts of the Mediterranean and elsewhere (Pérès and Picard, 1958; Blanc, 1968; Caulet, 1972; Milliman, 1974).

Bryozoan fragments are common on many shelves of the world including the Mediterranean (Wass et al., 1970; Caulet, 1972; Bee, 1974; Milliman, 1974) and are most conspicuous in samples from depths between 120 and 170m, on the steeper terrace of the north-eastern half of the shelf edge. Both the algal and bryozoan sands in the Aegean are grouped under the collective title "Lithothamnion and bryozoan bottoms" by Kiseleva (1961) as they often occur together. A general reworked appearance is also characteristic of the algal and bryozoan sands - the fragments, including subordinate molluscan debris, are often broken, abraided and bored - characteristics typical of relict sediment (Emery, 1965; Leclaire, 1972; Bee, 1974).

The source of the algal and bryozoan sands is the "biocoenosis coralligènes" of Pérès and Picard (1964) (Caulet, 1972; Blanc, 1972) consisting of encrusting and branching coralline algae with subordinate bryozoa. The "biocoenosis coralligènes" requires a

hard substrate and low detrital sedimentation for development. According to Milliman (1974), such encrusting algal communities are common along many outer shelves. At Kithnos this is also the case as the 'gravels' on topographic highs of the shelf edge include abundant encrusting algae.

Algal balls or nodules ("Praline" facies - Dangeard, 1929; Gautier and Picard, 1957) are also a prominent component of the gravels and are associated with submarine plateaux swept by currents (Blanc, 1972) or other areas of bottom instability (Milliman, op.cit.). According to Pérès (1967), they are formed by algal layers growing on the surface of the ball as it is rolled on the bottom by either currents or animals. Milliman et al. (1972) found that the algal nodules are able to accrete in depths exceeding 100 metres - this appears to be the case at Kithnos.

Bivalves, gastropods, and Foraminifera are also abundant in the sand fraction of most samples, particularly those from the lobes of muddy sand. Many of the bivalves and gastropods are fresh in appearance, thin shelled, and complete and so probably represent a modern assemblage. In contrast, the same sample might also include thick shelled verieties which are often broken, abraided, bored and covered in worm tubes.

Benthonic Foraminifera are the most abundant varieties,but the planktonic species increase with increasing depth. Most appear to be fresh in appearance but, once again, they are occasionally broken or infilled with inorganic material.

Minor biogenous components include ostracods, echinoid spines and fragments, sponge spicules, worm tubes and the rare piece of coral.

Detrital components are most abundant in the inshore belt of muddy sands and are mainly angular to sub-rounded schist and platey mica or chlorite fragments. Samples from the outer part of the muddy sand lobes also contain rounded grains of iron-stained quartz.

Qualitative x-ray diffraction analyses of the residue from an acetic acid leach on two samples, one from the sand lobe (427) and one from the offshore mud (435), indicate mineral assemblages dominated by quartz, feldspar, chlorite and micas. (No attempt was made to distinguish between chlorite and montmorillonite, nor micas and illite - for the purposes of the following discussion, these minerals are collectively referred to as the 'chlorite-mica'

group). This is consistent with the visual observations of the sand fraction of sediments, and Davis (1966) reports that schists from the nearby island of Siphnos are rich in quartz, feldspars, chlorite and muscovite.

2.3.3 Calcium Carbonate

Although $CaCO_3$ has not been measured in any samples, selected samples were leached with a 25% v/v solution of acetic acid and the amount of Ca in the residues determined. The loss in Ca due to leaching is attributed to carbonate calcium. The results are shown in Table 1. Basing $CaCO_3$ on total Ca only overestimates leached calcium carbonate by 1% to 1.5% and so total Ca is used to estimate the distribution of $CaCO_3$ in the sand and mud fraction on the Kithnos continental shelf. Obviously lithogenous calcium is a minor component in these carbonate-rich sediments.

Isolines of total Ca (Ca_{tot}) are based on the histogram shown on figure 2.3. Ca_{tot} ranges between 15.1% inshore and 33.9% in a relict sand offshore - an approximate calcium carbonate range of 35% to 85%. The general distribution of Ca (or calcium carbonate) reflects the general pattern of sediments shown in figure 2.2. The highest abundances of Ca_{tot} (>27% or > approximately 67% $CaCO_3$) occur in the belt of sands which straddle the shelf edge along its strike, and in isolated patches of relict sand which form windows within the offshore mud zone. Between this high Ca_{tot} zone and the inshore detrital-rich muddy sands is a belt of transitional sands with $CaCO_3$ ranging between approximately 50% and 65%.

Offshore, because $CaCO_3$ is also less than in the coarser sands of the shelf, detrital silts and clays by-pass the shelf to settle offshore and mix with the offshore carbonate components. To assess the relative proportions of detrital and calcareous material in the mud fraction of the offshore zone, that fraction of the sediment finer than 4 phi (mud) of the two samples (416 - relict coarse sand; 435 - sandy mud) was analysed for Ca_{tot}. Sample 416 (minus 4 phi fraction) contained a Ca_{tot} equivalent $CaCO_3$ of 58.5% (Ca_{tot} = 22.8%). Most of this fine calcareous component is probably a mixture of carbonate "flour" derived from the breakdown of coarser skeletal debris during erosion

TABLE 1 Acetic acid soluble Ca (Ca_{HAc}), total Ca (Ca_{tot}), and $CaCO_3$ based upon both acetic acid soluble and total Ca ($Ca_{HAc}CO_3$ and $Ca_{tot}CO_3$ respectively), for selected samples from the Aegean Sea. All values in percent.

Location	Sample Number	Ca_{HAc}	Ca_{tot}	$Ca_{HAc}CO_3$	$Ca_{tot}CO_3$
SOUNION	327	26.9	27.3	67.1	68.3
	328	27.8	28.1	69.4	70.2
	329	29.1	29.3	72.7	73.2
	341	24.0	24.5	60.0	61.3
	344	27.5	27.8	68.7	69.5
	347	28.8	29.0	71.8	72.5
	349	31.7	32.0	79.3	80.0
	350	27.3	27.5	68.3	68.7
	351	27.6	27.9	69.0	69.7
ANDROS	357	9.8	10.6	24.4	26.5
	365	20.8	21.3	52.0	53.3
	367	28.8	29.0	71.8	72.5
	373	25.2	25.5	63.0	63.8
KITHNOS	411	23.4	24.0	58.6	60.0
	416	33.7	33.9	84.3	84.7
	427	15.6	16.0	39.0	40.0
	432	26.4	26.8	66.0	67.0
	435	29.5	28.0	68.7	70.0
SERIFOS	445	25.9	26.5	64.6	66.3
	448	27.2	28.0	68.2	70.0
	453	28.4	28.8	71.1	72.0
	464	30.7	31.0	76.7	77.5
NAXOS	471	26.1	27.2	65.3	68.0
	472	25.9	26.6	64.6	66.5
	473	27.6	28.4	69.2	71.0
	474	23.0	23.9	57.5	59.8
	475	23.2	24.2	58.0	60.5
	476	24.1	25.0	60.1	62.5
	478	25.3	26.0	63.3	65.0
	516	32.4	33.0	80.9	82.5
	517	22.1	23.0	55.3	57.5
	518	24.1	25.0	60.2	62.5

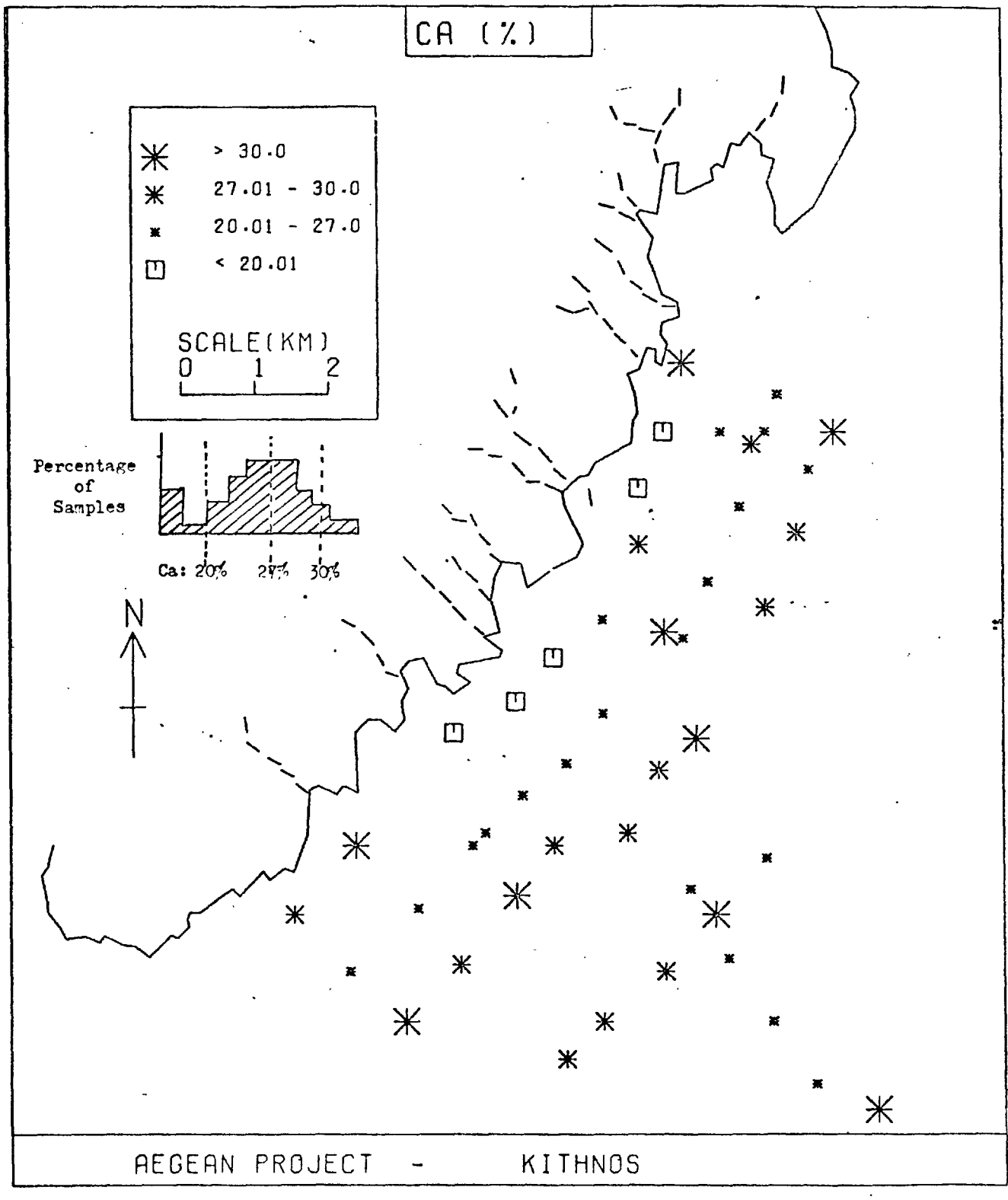


Figure 2.3 Kithnos - distribution of total calcium (gravel fraction removed)

(Molnia and Pilkey, 1972; Folk and Robles, 1964), and fine foraminiferal assemblages.

As total calcium carbonate for 435 is approximately 72% and only about 32% is provided by the mud fraction (mud $CaCO_3$ converted to total sample) the sand fraction must be almost entirely calcareous. Close to the scarp the calcareous components are are mainly relict sands but further offshore they also include a modern molluscan and foraminiferal assemblage.

2.3.4 Reclassification of the sediments

Because most of the material of gravel size is simply calcareous algae or large shells, it has been removed prior to analysis. Consequently, the geochemical and textural analyses of the sediments are based on that fraction of the sediments finer than 2mm and so the Folk classification scheme is no longer appropriate. Instead, a classification scheme based on the abundance of calcium carbonate and the amount of mud (that fraction less than 63 microns) is used and which conveniently divides the sediment samples into three main types - the detrital sands with less than 50% Ca_{tot} CO_3 (or 20% Ca_{tot}) and less than 30% mud; the bioclastic sands with more than 50% Ca_{tot} CO_3 and less than 30% mud; and the calcareous muds with greater than 50% Ca_{tot} CO_3 and greater than 30% mud (figure 2.4). The bioclastic sands are a large group and so they are further subdivided into bioclastic sands (I) (less than 67.5% Ca_{tot} CO_3 i.e. 27% Ca_{tot}) and bioclastic sands (II) (greater than 67.5% $Ca_{tot}CO_3$).

Such a classification scheme is useful for both textural and geochemical comparison between sediment types from each area. Both $CaCO_3$ and mud are important in controlling the chemical composition of the sediments because $CaCO_3$ acts as a diluent of detrital and authigenic phases, whereas heavy metals tend to be enriched in finer grained sediments. Furthermore, in later sections it is shown that the sand to mud ratio is the most important factor controlling the texture of the sediments. Calcium carbonate abundance is also related to texture in that coarse sand modes tend to be rich in bioclastic material and, hence, calcium carbonate.

Figure 2.4 charts the distribution of the major sediment types. Detrital sands are confined to the nearshore zone of the valleys in the shelf topography. Bioclastic sands (1) form a belt between the

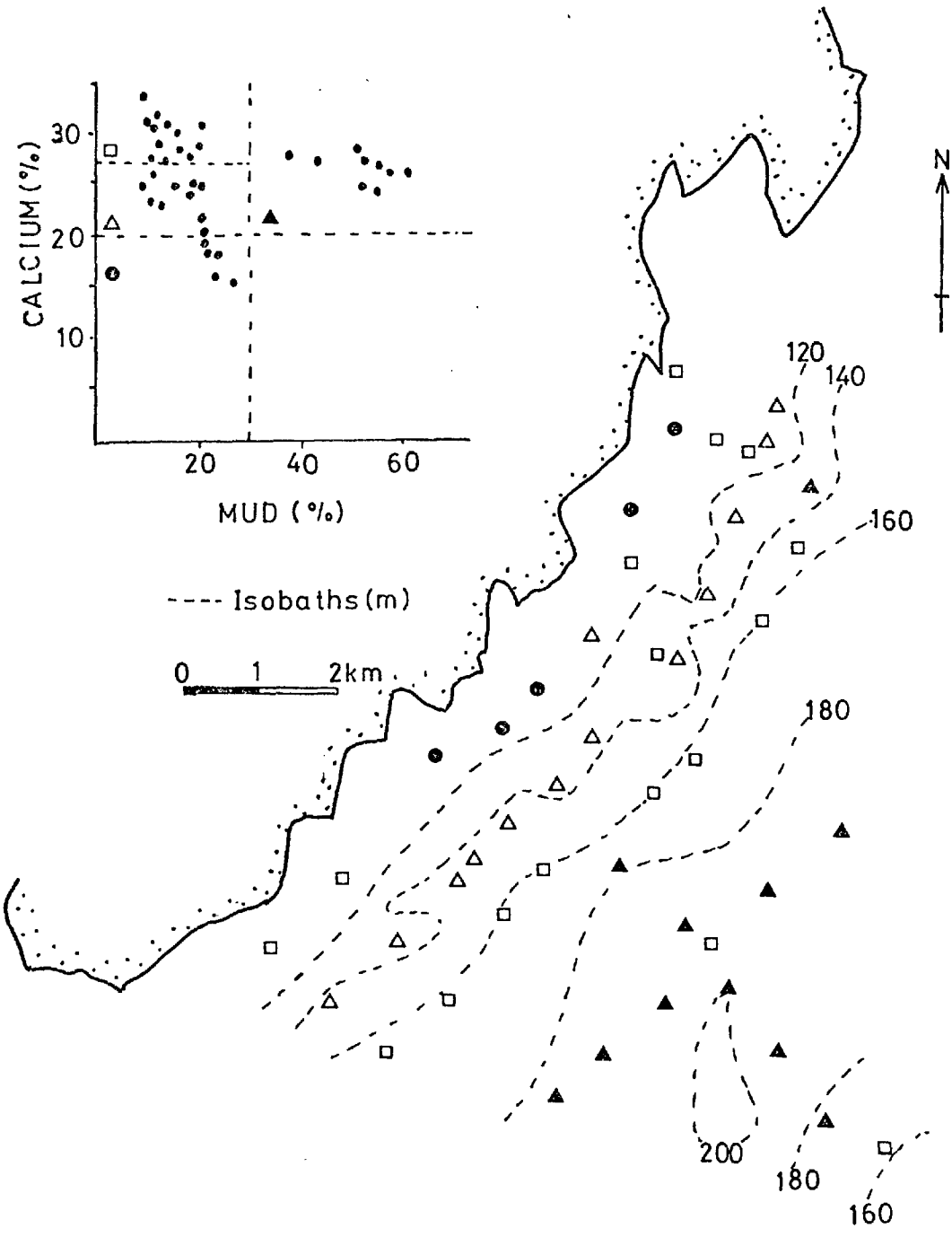


Figure 2.4 Distribution of sediment types based on the proportions of total calcium and mud. (● detrital sands, △ bioclastic sands I, □ bioclastic sandsII, ▲ calcareous muds)

120m and 150m isobaths along the shelf edge. Bioclastic sands (II) straddle the 160m isobath along the base of the shelf edge and on elevated areas of the shelf and shelf edge, in association with coralline algal reefs that may be developing at the present time. Windows of probably relict bioclastic sands (II) also exist within the offshore calcareous mud blanket (e.g. 416). Deposits accumulating in the deeper waters offshore are mainly calcareous muds.

2.3.5 Discussion and Conclusions

Milliman (1974) points out that most shelf carbonate assemblages reflect a mixture of both modern and relict components. Which of these is dominant on the Kithnos shelf is difficult to assess but analogies with other areas of the Mediterranean provide some clues. For example, Caulet (1972) describes sediments from the Algerian shelf, between depths of 90 and 150m, which have similar carbonate assemblages to sediments from the same depths at Kithnos. The Algerian 'deep' maerls and bryozoan sands are considered to be relict and deposited in shallower waters during the last regression when the shoreline coincided with the present Algerian outer shelf. In contrast, modern maerls are forming between 10 and 60m, and bryozoan sands on the middle shelf between 50 and 80m.

Similarly, C^{14} dating of algal and bryozoan sands from shallow banks of the Alboran Sea (Milliman et.al, 1972) reveal that samples from below 80m are usually relict (early Holocene) except for two nodules of contemporary age. It would seem that, on the basis of analogy with other areas of the Mediterranean, the algal and bryozoan sands below 90m on the Kithnos shelf are dominantly relict.

However, differences in environmental parameters are also significant (Pérès and Picard, 1958; Blanc, 1968; Caulet, 1972; Milliman, et.al., 1972). In particular, the clarity of the water in the Aegean allows certain organisms to live in waters deeper than would otherwise be expected. For example, Pérès and Picard (1958) report that the "biocoenosis coralligènes" can occur as deep as 120m in the eastern Mediterranean because of the perfect clarity of the water and low terrigenous sedimentation. Elsewhere the "biocoenosis coralligènes" occurs at less than 100m (50-80m on the Algerian shelf - Caulet, 1972). Similarly, maerls normally develop between 20 and 40m in the western Mediterranean but in the Aegean the depth range may be extended to 100m (Blanc, 1972).

Despite the probable extensions of the depth range of assemblages in the Aegean, the occurrence of algal and bryozoan sands at depths in excess of 120m is anomalous. Therefore, they are probably relict carbonate assemblages. This conclusion is supported by:-

(1) the presence of rounded, iron-stained quartz and sub-rounded, coarse schist fragments in sediments on the inner margins of the algal sands, perhaps coinciding with an old shoreline;

(2) the generally reworked appearance of algal, bryozoan, and subordinate molluscan debris;

and (3) the association of these sediments with a relict morphology.

In contrast, coralline algal communities (gravels) may represent a modern assemblage, particularly the algal nodules and encrusting algae found on shoals at depths of approximately 100m. Such algal communities may be a significant source of biodetritus (Blanc, 1972) contributing modern algal and bryozoan debris to otherwise relict sediment.

Apart from the age relationships of carbonate assemblages on the shelf, certain dynamic characteristics are also apparent from the general distribution of sediment types. As carbonate predominates, detrital influx is either small or currents prevent accumulation (Milliman, 1974). The formation of algal nodules on topographic highs suggests a certain amount of current activity as they require current swept platforms for growth (see section 2.3.2). Other coralline algal communities on the shelf edge also require low detrital accumulation to survive. Either a mechanism of "sediment by-pass" (Curray, 1965) is preventing accumulation or the very small catchment area and limited, seasonal runoff restricts the detrital input (or both).

2.3.6 Summary

(1) Carbonate assemblages on the Kithnos shelf are a mixture of both modern and relict components.

(2) Based on the preliminary investigation the sediments may be divided into five zones:-

(a) an inner detrital-rich sand belt with a mainly modern carbonate assemblage;

(b) an outer algal/bryozoan sand belt with a significant relict component;

(c) a transitional sand belt between (a) and (b);
(d) isolated shoals of coralline algae, possibly developing at present;
and (e) an offshore mud zone rich in fine grained carbonates and detrital sediment by-passed from the shelf.

2.4 TEXTURAL ANALYSIS OF SHELF SEDIMENTS AND SHELF SEDIMENTATION

2.4.1 Introduction

The major aim of the textural analysis of shelf sediments is to provide a sedimentological framework for subsequent geochemical investigations. In polymodal sediments the textural characteristics are a function of the mixing of several distinct sub-populations (Folk and Ward, 1957; Doeglas, 1946). For example, Spencer (1963) suggested clastic sediments to be mixtures of three fundamental sub-populations of log-normal grain size - gravel (-3.5phi to -2phi), sand (1.5phi to 4phi), and clay (7phi to 9phi). The present study precludes a gravel population as only that fraction finer than -2phi has been analysed for reasons stated previously (section 2.3.4). Furthermore, calcareous skeletal debris, and their breakdown products of distinctive grain size, contribute additional sub-populations (Folk and Robles, 1964; Upchurch, 1972; Bee, 1974). Nevertheless, although the fundamental sub-populations differ from those of Spencer, the textural characteristics still reflect the admixture of those that are present. Consequently, to interpret the sedimentological features of the Kithnos shelf, it is important to have a clearer understanding of the sub-populations present and their distribution. This also has obvious attractions to geochemical interpretation if the constituent sub-populations can be related to mineralogical or geochemical phases.

2.4.2 Analysis of Phi-cumulative Probability Curves

2.4.2.a Introduction

In comparing the standard techniques of facies interpretation, including textural parameter inter-relationships, factor analysis, and cumulative phi-probability curves, Glaister and Nelson (1974) found the latter most useful. Perhaps this is not surprising as

cumulative curves are the closest description of the grain size distribution within a sample. Statistical parameters, for example, are solely an attempt to numerically describe the cumulative curve. As cumulative curves are considered to contain the most information they are used in this study to identify the major sub-populations. Initially, all straight-lined portions of the phi-cumulative probability plot are considered to be separate log-normal sub-populations (see Moss, 1962, 1963; Visher, 1969). To aid the examination of mud sub-populations, selected samples (covering the main sediment groups) have been analysed by pipette techniques to extend the cumulative frequencies into the finer size range. Frequency distributions of grain size are used to clarify aspects of the cumulative phi-probability plots. For the subsequent discussion the samples are grouped according to the classification scheme based on the abundance of $CaCO_3$ and mud (section 2.3.4).

2.4.2.b Detrital sands (421, 423, 426, 427, 428)

Detrital sands are polymodal sediments with two major sand sub-populations (figure 2.5a). Sub-population 2 has an approximate mode of 3phi and is separated by a truncation point at 2.5phi from sub-population 3 with an approximate mode of 2phi. As an example, the frequency distribution for sample 427 shows modes at 2.3phi and 3phi (figure 2.6). A general mud sub-population (sub-population 1) is also present with a mode in the coarse silt range.

As sub-population 3 (2phi mode) becomes more abundant the truncation point at 2.5phi becomes more pronounced. For example, in sample 423 (figure 2.5a) sub-populations 2 and 3 are in approximately equal proportions and overlap to such an extent that a truncation point is not present. However, a truncation point is well developed in sample 428 in which sub-population 3 is more abundant (c.45%).

Sample 426 differs from the remainder in that sub-population 3 is replaced by a sub-population with a mode of approximately 1.5phi (possibly sub-population 4 - see later).

2.4.2c Bioclastic sands

As there is wide variation, the bioclastic sands are sub-divided into groups according to the similarity of their cumulative

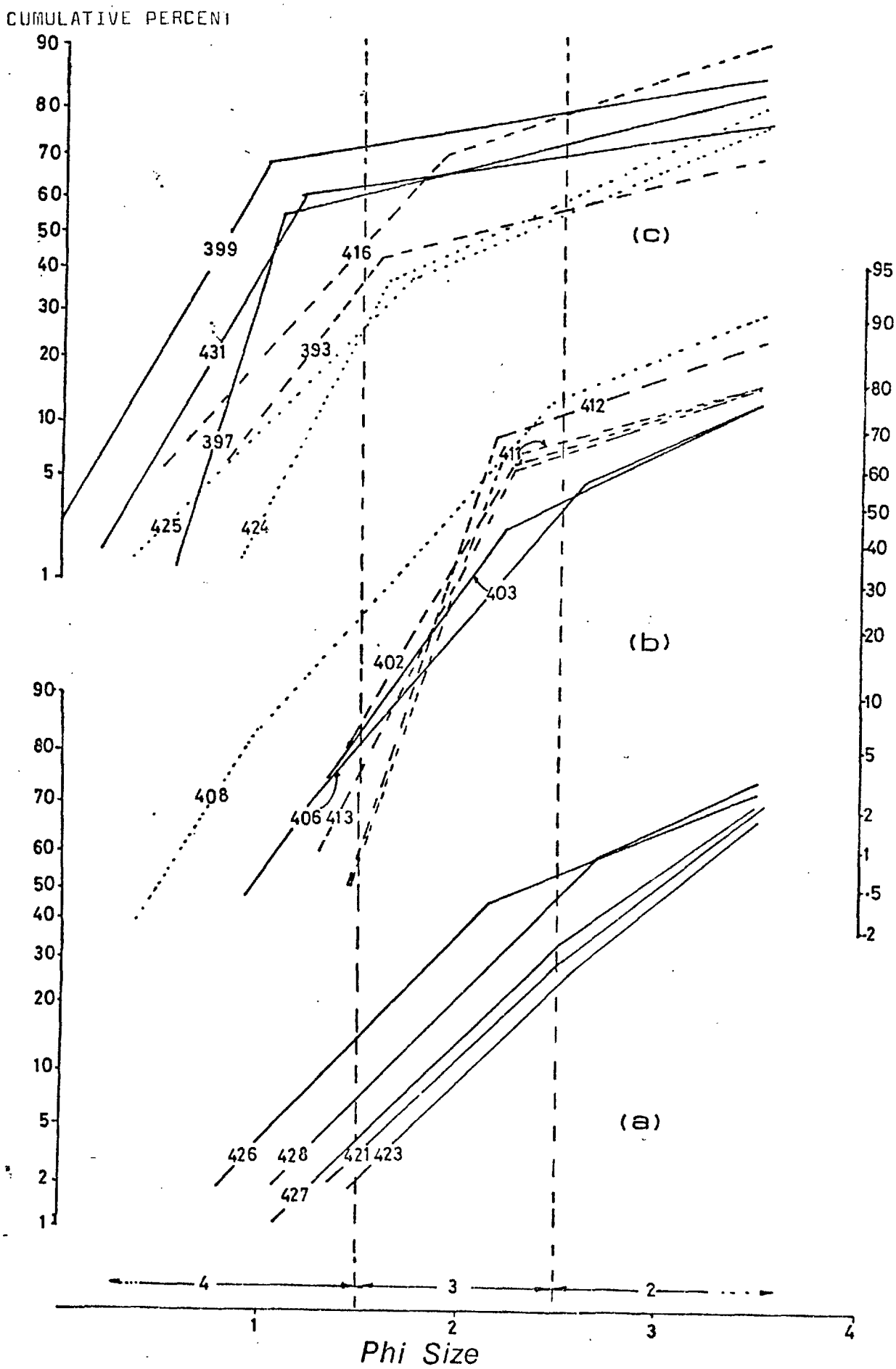


Figure 2.5 Phi - cumulative probability grain size curves.
(a) detrital sands;(b) bioclastic fine sands;
(c) bioclastic medium/coarse sands.

phi-probability curves (figure 2.5b).

Group A (406 and 403), although not richer in detrital material, have similar cumulative curves to the detrital sands. Sub-populations 1, 2 and 3 are present.

Group B (402, 411, 412, 413) have distinctive, almost uni-modal curves in which sub-populations 1, 2 and 3 are present but in which sub-population 3 contributes between 60% and 70% of the total sample. A mode of 2phi is indicated by the frequency distribution of sample 411 (figure 2.6), with a sub-population 1 mode in the coarse silt range.

Group C (408), like group B, also has a very well sorted coarse component (figure 2.5b) but this apparently single sub-population has a coarser mode (about 1.5phi) and could be a combination of sub-populations 4 (see later) and 3.

Group D (397, 398, 399, 400, 401, 409, 431, 437) have two distinct sand sub-populations separated by a truncation point in range 1.0 to 1.5phi (figure 2.5c). The coarsest sub-population has a mode of approximately 1phi or coarser (sub-population 4) and represents between 60% and 80% of each sample. The second sub-population has a mode of approximately 2phi and appears to correspond to sub-population 3. The median diameter of samples in Group D exceeds 1.5phi.

Group E (390, 393, 404, 410, 416, 420, 430) samples contain the same sub-populations as group D (figure 2.5c) but the mode of sub-population 4, which is most abundant, appears to be finer (between 1.0 and 1.5phi). The median diameter of Group E samples are between 1.5phi and 2.0phi.

Group F (391, 394, 405, 407, 424, 425) cumulative curves appear to comprise the same sub-populations but sub-population 4 is finer and less abundant (figure 2.5c). The median diameters of this group are between 2phi and 2.5phi.

2.4.2.d Calcareous muds (389, 414, 415, 417, 418, 419, 432, 433, 434, 435, 436)

All the offshore calcareous muds samples have a distinct truncation point between 1.5phi and 2phi (figure 2.7) separating sub-population 4 (mode coarser than 1.5phi) from a poorly sorted sub-population ranging between 2phi and 8phi.

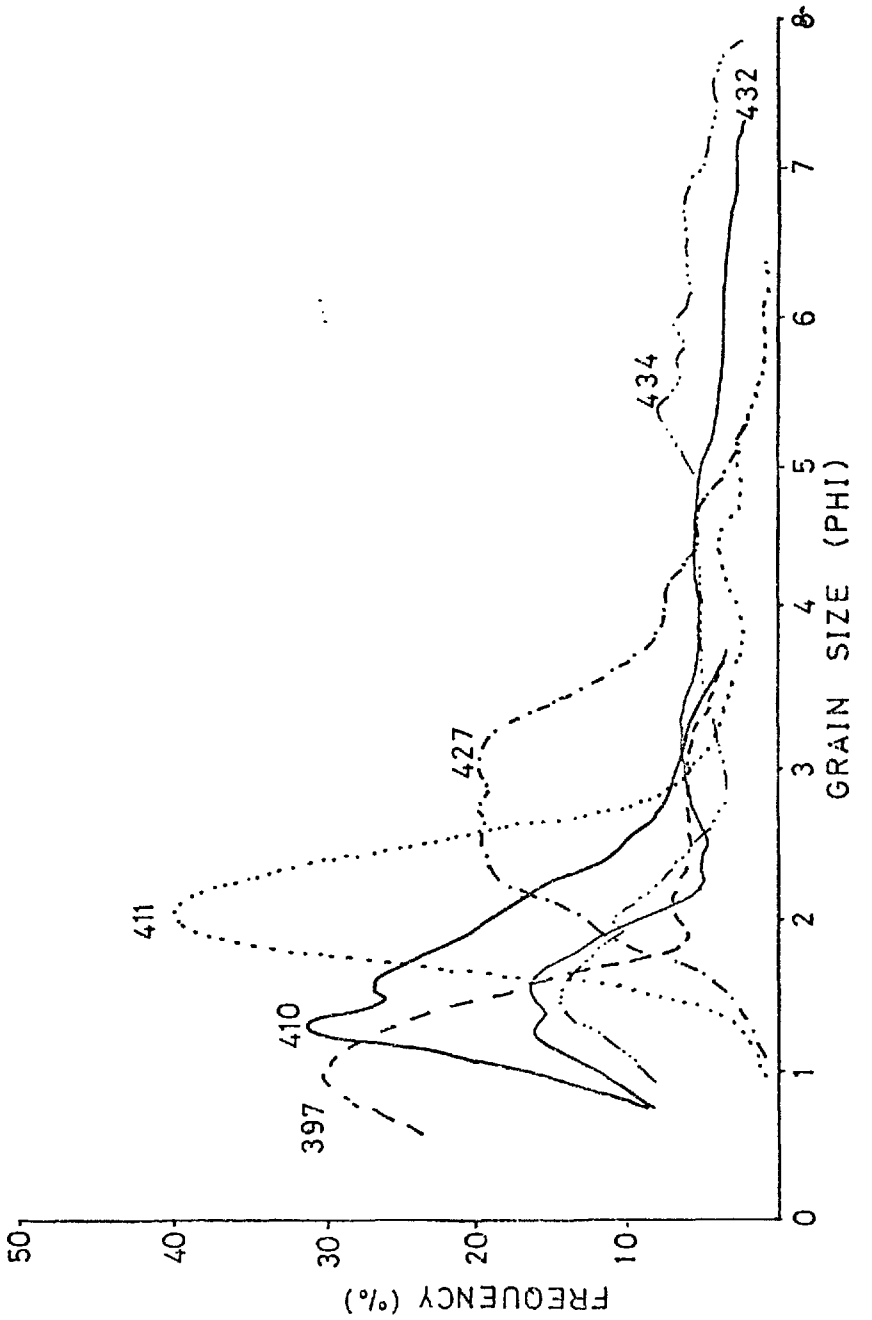


Figure 2.6 Grain size frequency distributions of selected samples from Kithnos.

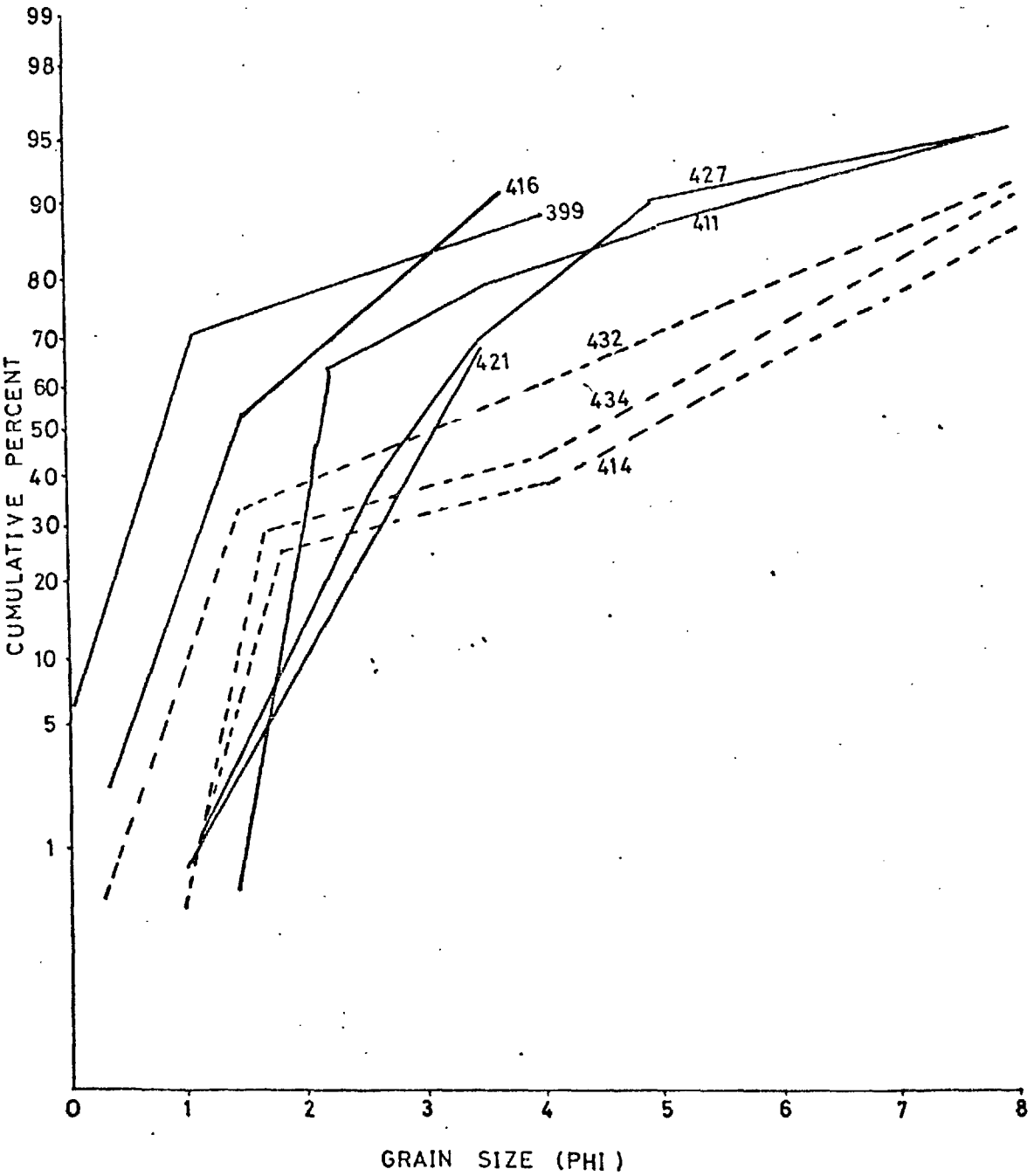


Figure 2.7 Phi cumulative-probability plots for calcareous muds and other selected samples from Kithnos.

From the frequency distribution of sample 432 (figure 2.6) it is difficult to distinguish a particular mode although sample 434 does show a mode in the fine silt (5phi - 8phi) range. This mud component is called sub-population 1 although it is appreciated that this may represent a different fundamental sub-population than the sub-population 1 in the detrital sands.

There is a distinctive trend, however, in the mode of sub-population 1 from inshore to offshore. Inshore (e.g. sample 427) the phi cumulative-probability curve of sub-population 1 is strongly positively skewed (parabolic shape) because of coarse silt dominance (figure 2.7); on mid-shelf (sample 411) slightly positively skewed (figure 2.7); on the outer shelf (sample 432) phi-normal (figure 2.7) as coarse and fine silt are approximately equal in abundance; and in the deeper water (sample 434) slightly negatively-skewed (hyperbolic shape) (figure 2.7) because of fine silt dominance. A progressive change from coarse to fine silt with increasing distance offshore could reflect progressive sorting across the shelf, but the greater abundance of calcareous components in the offshore samples complicates this simple interpretation.

2.4.3 Nature, Origin and Distribution of the Major Sub-populations

From the preceding sections it seems that sediment samples from the Kithnos continental shelf are admixtures of four major sub-populations:-

(1) mud, with a mode ranging between coarse and fine silt;

(2) very fine sand with an approximate mode of 3phi;

(3) fine sand with an approximate mode of 2phi;

and (4) coarse/medium sand with modes generally coarser than 1.5phi.

The approximate proportions of the three sand sub-populations in each sample are shown in figure 2.8.

In general, the distribution of sub-population 1 (mud) can be divided into two zones (figure 2.9) - inshore lobes of detrital (section 2.3.4) coarse silt (section 2.4.2b), and an offshore mud blanket of dominantly fine silt (section 2.4.2d) in which calcareous and detrital components are equally abundant (section 2.3.4).

Mud accumulation in both zones is thought to be late Holocene. The accumulation of coarse silt in the nearshore samples probably post-dates the passage of the transgressing shoreline because wave

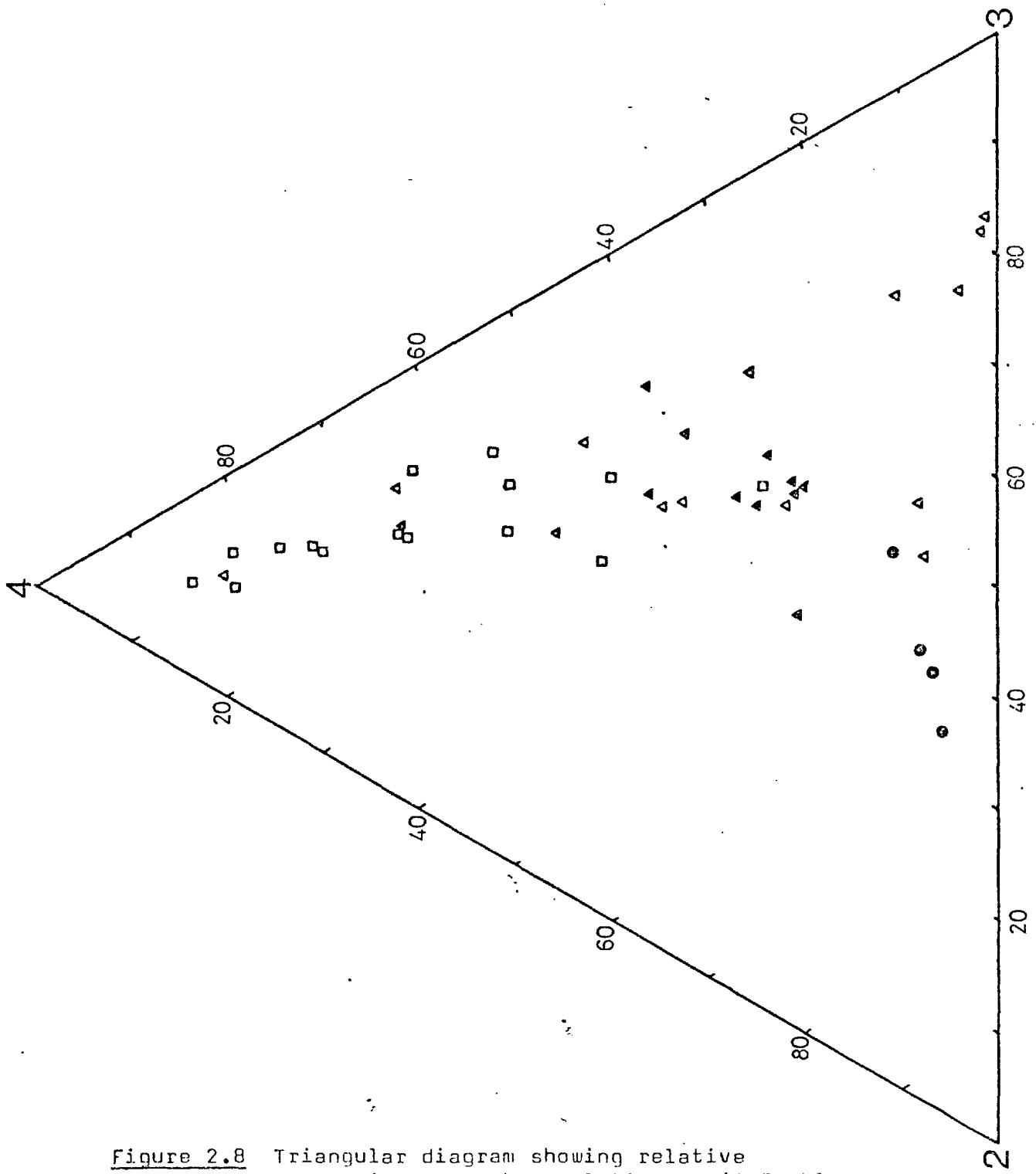


Figure 2.8 Triangular diagram showing relative proportions of sub-populations 2 (2.5 phi to 3.5 phi),3 (1.5 phi to 2.5 phi),and 4 (coarser than 1.5 phi).(● detrital sands, △bioclastic sandsI, □ bioclastic sandsII, ▲calcareous muds.)

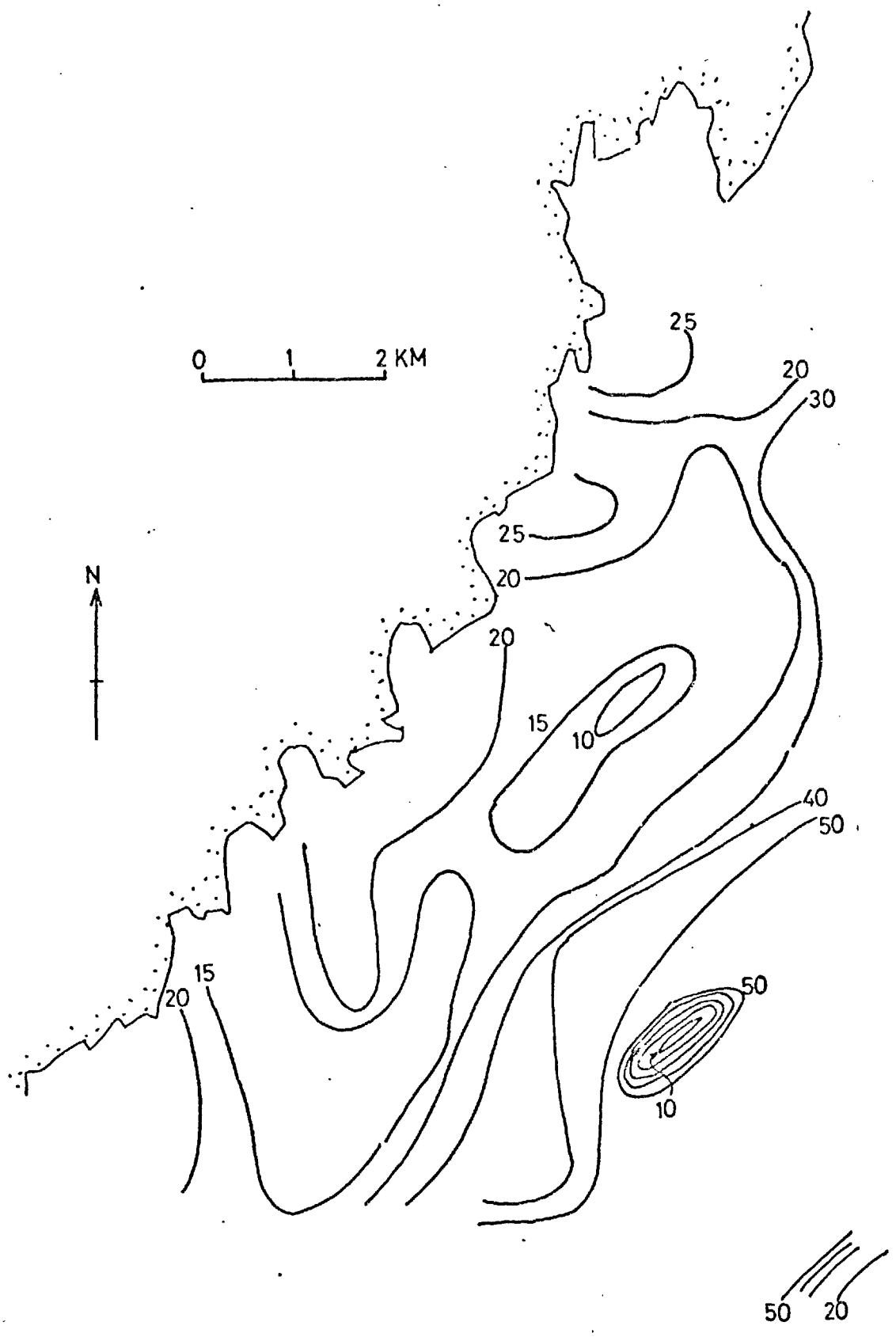


Figure 2.9 Kithnos - distribution of mud.(Contours are in percent mud of the combined sand/ mud fraction.)

action would probably have removed the coarse silt out of the nearshore system into deeper water (Friedman, 1967). Similarly, the transgressing surf zone would tend to redistribute the sediments (Swift, 1976) thereby removing evidence of previous transport paths. Consequently, the survival of the lobate distribution of silts following the valleys of the shelf topography also may suggest deposition subsequent to the passage of the transgressing shoreline.

Cores from the deeper areas of the offshore mud zone show several tens of centimeters of mud overlying relict coarse sands. This suggests that the muds are dominantly 'modern' sediments. Further evidence includes the way in which the muddy sediments blanket the relict topography of the shelf-edge, and the presence of windows of relict sands in the pervasive offshore mud blanket.

McCave (1972) suggested that mud is moved across the shelf advectively in streams due to net horizontal water movements, and diffusively either continuously in suspension or through a process of bed/water exchange. Both mechanisms may be important in the study area. Coarse silt concentrated in the inshore samples may have been transported advectively in some form of turdid layer density flow (Drake, 1976) (see later discussion on sub-population 2). Diffusive transport is more likely to account for the detrital mud accumulating offshore.

Mud accumulation at the shelf edge is prevented by wave induced currents (Kuenen, 1950; Shepard, 1963). Algal nodule formation on shoals of the shelf edge also indicate current activity. Alternatively, mud may not reach topographic highs if mud transport is in diffuse near-bottom layers (see Drake, 1976). Shoal areas are isolated by their relative elevation as the near-bottom layers hug the floors of the valleys (see e.g. ; Kulm et al., 1975). Instead mud by-passes the outer shelf to accumulate in the more quiescent conditions in deeper waters offshore.

From figure 2.10 it can be seen that sub-population 2 (that fraction between 2.5phi and 3.5phi) is most abundant in the nearshore detrital sands and gradually decreases in abundance seawards, until the offshore zone where the abundance increases slightly. This distribution is considered to reflect two factors. Primarily, the presence of very fine sand sized detrital fragments in the nearshore samples. Secondly, modern assemblages of Foraminifera and ostracods in both the nearshore and offshore samples.

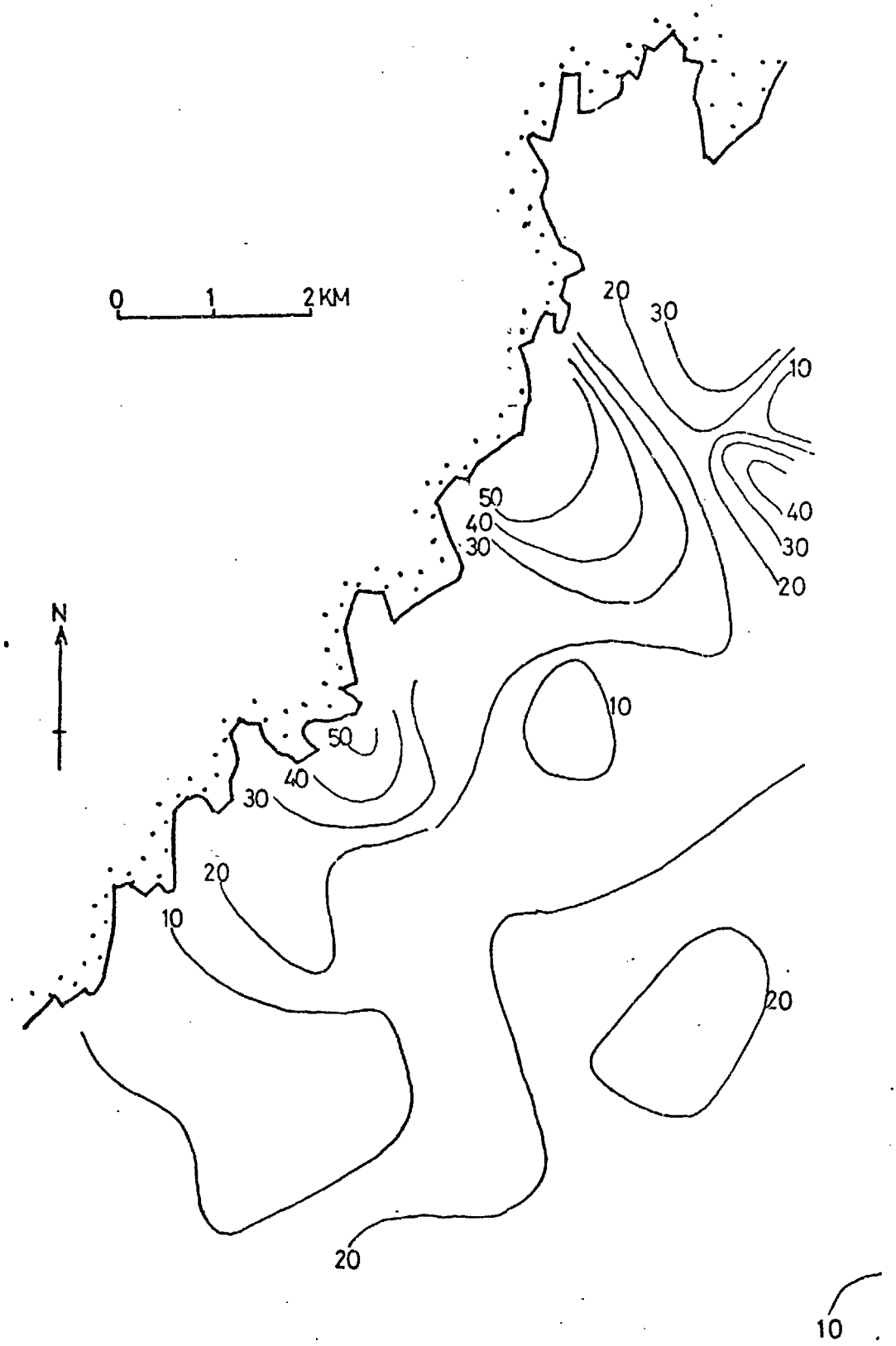


Figure 2.10 Kithnos - distribution of sub-population 2(2.5phi to 3.5 phi) as a percentage of the sand fraction.

In the nearshore samples, detrital fragments are thought to be the dominant component of sub-population 2 and so the gradual decrease in abundance seawards reflects a gradual decrease in the detrital component which, inturn, suggests transport seawards of detrital material. Nevertheless, it is difficult to estimate exactly when during the Holocene transgression deposition took place, but it is possible for it to be occurring at the present time because:-

(1) very fine sand can escape the nearshore zone as suspended load (Kulm et al., 1975);

(2) the shelf inshore of 90m is very narrow and slopes are steep (locally up to 10°) which is conducive to gravity driven downslope movement of a turbid flow;

(3) it is possible that channels extend from the nearshore zone and these could serve to localise such flows;

and (4) the contribution of detrital sediment to the shelf area is low but run-off is seasonal and sediment may accumulate, therefore, in stream channels during summer months of limited rainfall, allowing the first heavy rains to provide a fairly dense sediment load. Very fine sand and silt escaping from the nearshore zone is then channelled across the very narrow and steep inner shelf as some form of advective turbid current, depositing very fine sands and coarse silts in deeper waters. Finer sediment may continue to move seawards, either diffusively through resuspension or as a continuation of the turbid current. Such a near-bottom low density current has been observed by Kulm et al. (1975) carrying very fine sand and silt across the Oregon shelf.

Alternatively, aeolian transport may carry very fine sand and silt past the nearshore zone and into deeper waters, particularly during the dry, summer months. On reaching the seafloor, wind-blown material may then move diffusively across the shelf but would be concentrated along the major dispersion path ways (hence the lobate distribution).

At this point it is apparent that the lack of knowledge of the nature of the Kithnos shelf shallower than 90 metres, particularly the sediment distribution, topography and dynamic regime, severely limits an assessment of the phenomena acting as dispersal agents.

To assess the distribution of the sub-population 3 (mode approximately 2phi), the abundance of the 1.5phi - 2.5phi fraction of the sand from each sample is charted in figure 2.11. There appears to be a marked relationship between topography and the abundance of sub-population 3. The largest concentrations (greater than 50% and up to 80%) are confined to embayments in the relict topography of the shelf, particularly in the large embayment of the south-western sector, at an approximate depth of 150 metres. Sub-population 3 is also abundant (greater than 40%) in the troughs shorewards of the 140 metre isobath and in sediments from the offshore zone.

For shelf samples, calcareous and detrital components are in approximately equal proportion in sub-population 3. Sub-angular to rounded yellow-stained quartz, feldspar and schist fragments are the most abundant detrital materials. The stained appearance and the coarse size suggest the detrital components are not 'modern' deposits.

Foraminifera are the most abundant calcareous component. Many may be relict in that they are occasionally infilled, worn, and broken, or have an origin in shallow water. Planktonic forams appear to be 'modern'. In the offshore sediments, the sub-population 3 consists almost entirely of Foraminifera (especially planktonic), ostracods, and sponge spicules.

From the preceding discussion it seems that sub-population 3 is mainly a relict or reworked fine sand. This conclusion is based on the following points:-

(1) similar fine sands exist in the region of shores and bay bottoms on the present-day Mediterranean between depths of 10m and 50m (Blanc, 1972);

(2) the sub-population is most abundant in the embayments of the relict topography and at depths consistent with a shoreline between 110m and 120m below the present sea-level, i.e. at the lowest level of the last regression;

and (3) some of the components of the sediment have a typically relict character (see section 2.3.2) e.g. stained quartz grains and broken and worn shallow water Foraminifera.

Although most abundant in the embayments, sub-population 3 forms a sand sheet across the broad troughs in the shelf topography. This could mean that sub-population 3 also represents a transgressive sand sheet - a well known feature on many shelves of the world (Curray, 1965).

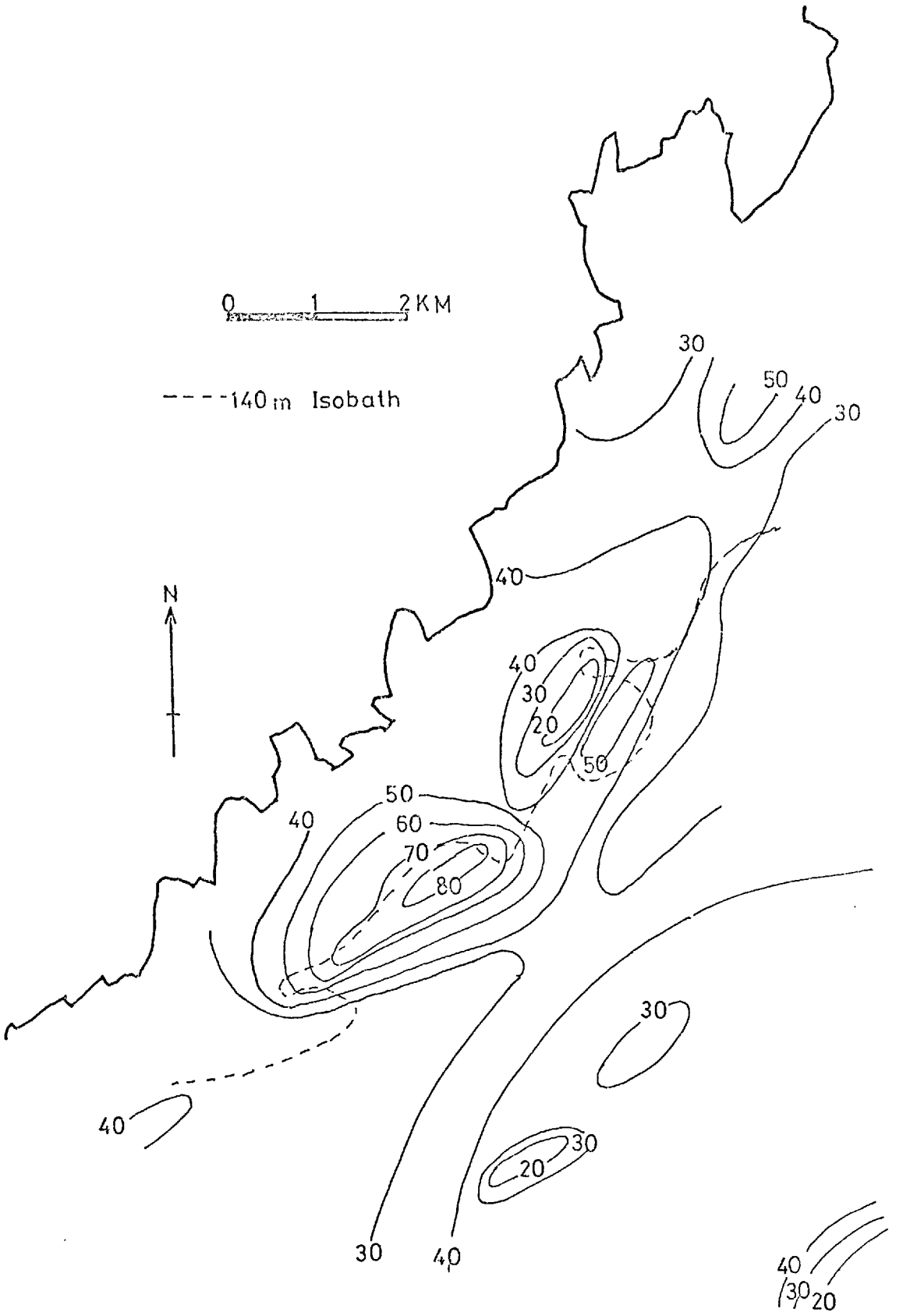


Figure 2.11 Distribution of sub-population 3 (1.5 phi to 2.5 phi)(percent of the sand fraction).

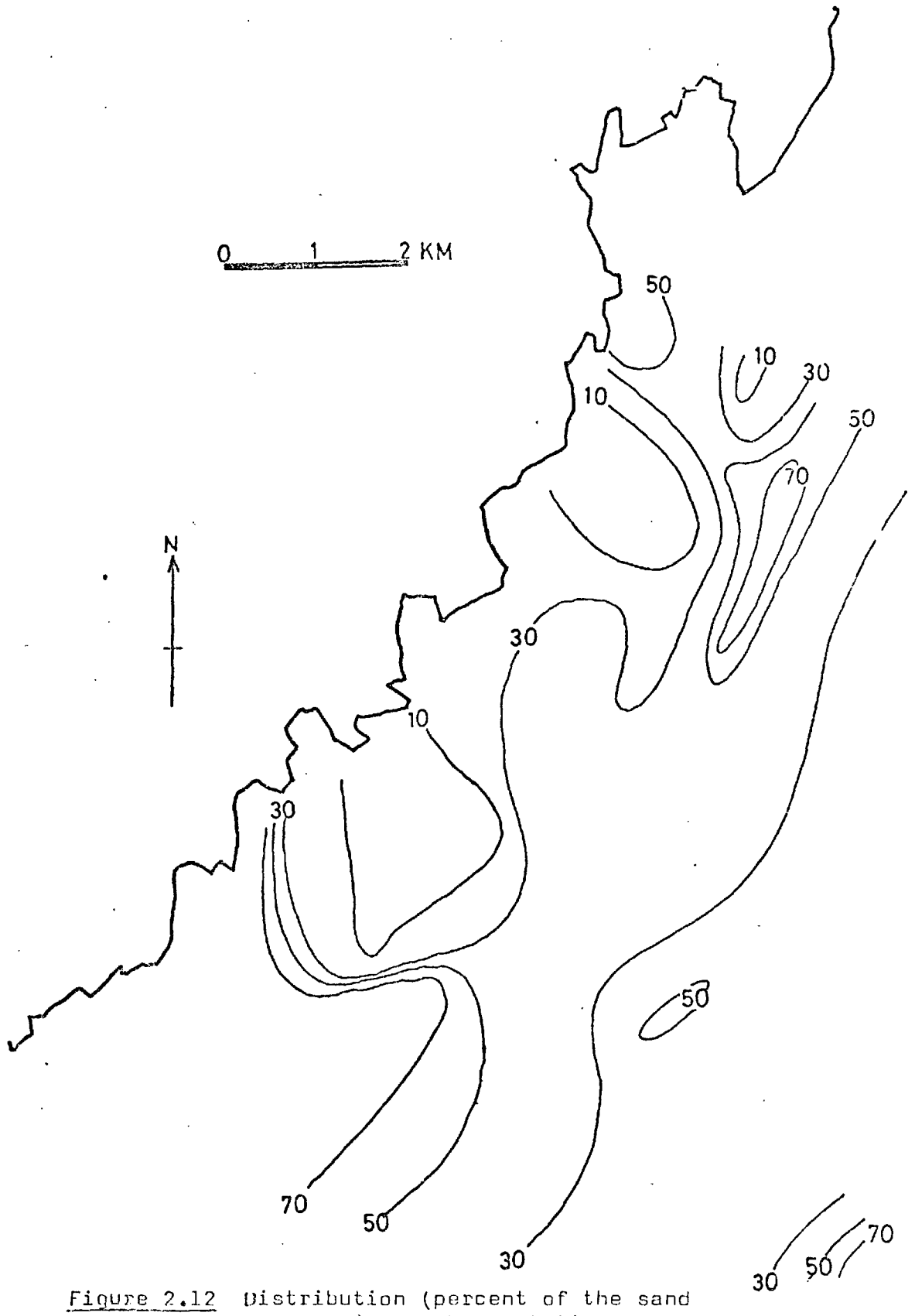


Figure 2.12 Distribution (percent of the sand fraction) of sub-population 4.

Sub-population 4 is mainly coarse calcareous material. In some samples (e.g. 401, 426) coarse schist fragments (sometimes covered in worm tubes) are present. The nature of the calcareous components (mainly algal and bryozoan debris) is discussed in sections 2.3.2 and 2.3.5. As might be expected from the discussion in section 2.3.2, sub-population 4 is most abundant on the topographic highs and ridges, and in windows of relict sediment in the offshore zone (figure 2.12).

2.4.4 Sediment Texture

It is common practice to describe continental shelf sediments in terms of textural parameters (e.g. median, mean, sorting, skewness, kurtosis). As these parameters are an attempt to numerically describe the cumulative curve of the grain size distribution, it is unlikely that much is to be gained from a detailed study because the cumulative curves have already been considered in detail. However, so that sediments from elsewhere may be broadly compared with those from Kithnos, the average and range of median size, mean size and sorting of the main sediment types (section 2.3.4) are given in Table 2. The relationship between mean size and sorting is shown in figure 2.13.

In general, the sorting becomes poorer as the mean size becomes finer, reflecting the gradual decrease in the sand-to-mud ratio. The samples with the lowest sorting coefficient (well sorted) are those with least mud, and those with the most mud have the highest sorting values (i.e. most poorly sorted). Within any group of sediments with a similar sand to mud ratio, however, sorting improves (value decreases) with a decrease in mean size - a mixture of fine sand (sub-population 3) with mud will be better sorted than a mixture of coarse sand (sub-population 4) and mud.

The calcareous muds have the finest average mean size (4.11phi) but several samples (418, 389, 432), occuring closer to the relict coarse sand belt (figure 2.1), have median and mean sizes in the sand range. Marginal muds would be a more appropriate description as they are mixtures of the relict sand and the modern mud blanket.

Although the bioclastic sands (II) have the coarsest average median and mean size (table 2), there is a considerable

TABLE 2 Average and range of textural parameters (Ø units) for the major sediment types found in each area. The number of samples is given in parentheses, 1 - average, 2 - range.

Sediment Type	Location		Median	Mean	Sorting
DETRITAL SANDS	Kithnos	1	2.84	3.48	1.82
	(5)	2	2.40 - 3.10	3.20 - 3.77	1.68 - 2.04
	Serifos	1	2.71	3.38	2.18
	(3)	2	2.52 - 3.01	3.19 - 3.68	1.98 - 2.49
	Andros	1	1.95	2.30	1.16
	(4)	2	1.31 - 2.66	1.50 - 2.66	0.59 - 2.59
	Naxos	1	-	-	-
	(0)	2	-	-	-
	Sounion	1	-	-	-
	(0)	2	-	-	-
BIOCLASTIC SANDS I	Kithnos	1	2.15	2.58	1.42
	(13)	2	1.09 - 2.67	1.51 - 3.15	0.72 - 2.01
	Serifos	1	0.93	1.75	1.81
	(2)	2	0.67 - 1.18	1.56 - 1.94	1.16 - 2.47
	Andros	1	1.14	1.57	1.18
	(3)	2	0.76 - 1.62	1.10 - 1.91	0.47 - 2.16
	Naxos	1	2.58	3.20	1.94
	(19)	2	1.92 - 3.10	2.17 - 3.75	0.81 - 2.42
	Sounion	1	2.79	3.04	1.38
	(2)	2	2.72 - 2.85	2.83 - 3.25	1.25 - 1.51
BIOCLASTIC SANDS II	Kithnos	1	1.51	2.03	1.47
	(15)	2	0.83 - 2.17	1.34 - 2.71	0.94 - 2.24
	Serifos	1	1.41	2.27	1.94
	(3)	2	1.11 - 1.68	1.73 - 2.55	1.44 - 2.26
	Andros	1	0.96	1.49	1.25
	(6)	2	0.66 - 1.21	0.85 - 1.95	0.50 - 1.88
	Naxos	1	1.62	2.06	1.38
	(21)	2	1.21 - 2.43	1.31 - 3.19	0.70 - 2.46
	Sounion	1	2.01	2.12	0.99
	(20)	2	1.39 - 2.83	1.46 - 2.71	0.51 - 2.20
CALCAREOUS MUDS	Kithnos	1	3.96	4.11	2.70
	(11)	2	2.31 - 4.81	3.67 - 4.65	2.34 - 2.87
	Serifos	1	3.77	4.07	2.74
	(6)	2	2.87 - 4.53	3.57 - 4.43	2.58 - 2.81
	Andros	1	2.68	3.43	3.01
	(1)	2	-	-	-
	Naxos	1	3.36	3.95	2.34
	(12)	2	2.35 - 4.65	3.30 - 4.77	2.24 - 2.57
	Sounion	1	2.52	3.39	2.81
	(1)	2	-	-	-

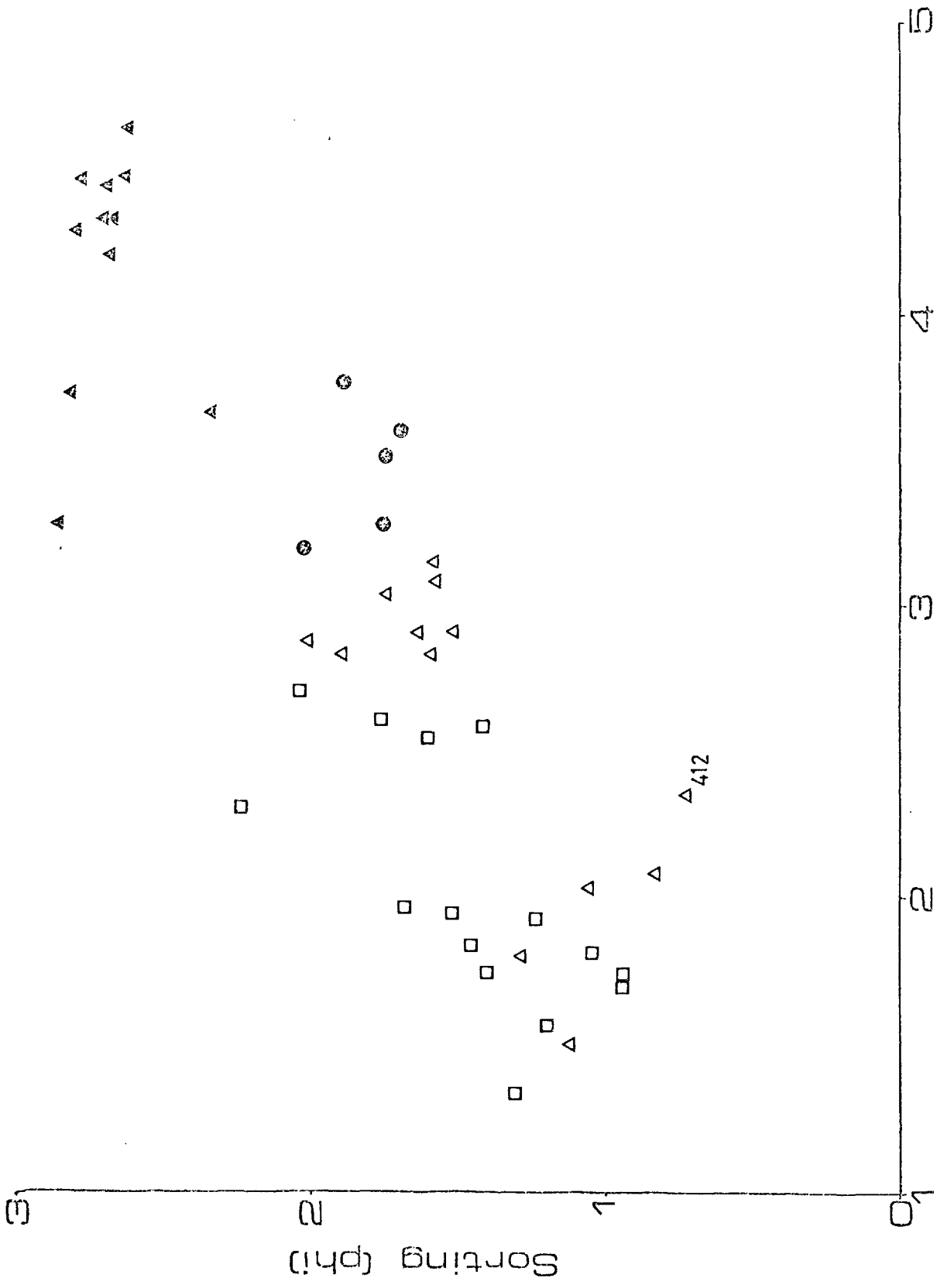


Figure 2.13 Kithnos - Mean size against sorting.
(for key see figure 2.4).

overlap in the range of these parameters with the bioclastic sands (I) (table 2, figure 2.13). As sub-population 4 (calcareous coarse/medium sand) is dominant, the bioclastic sands (II) are generally coarser and higher in calcium carbonate. The variation in the mud fraction, however, causes a wide range in mean size. For example, samples 391, 393 and 394 are close to the zone of accumulation of the modern mud blanket (figure 2.4) and so have a higher mud fraction than the bioclastic sands (II) on topographic highs. The bioclastic sands (II) broadly correspond to a relict sand belt (see figure 2.4).

Similarly, admixture of sub-population I (mud) and sub-population 3 (fine sand) results in a wide range of mean and median size for the bioclastic sands (I). This group also includes samples 400 and 401 in which sub-population 4 (coarse/medium sand) is dominant but has a greater detrital component than usual. Bioclastic sands (I) broadly correspond to a transgressive and sheet (see figure 2.4).

The detrital sands are a distinctive group with a fairly narrow range of median and mean size and moderate sorting (see table 2).

2.4.5 Shelf Sedimentation

On the basis of the preceding discussion, a simplified description of shelf sedimentation is proposed in this section. Figure 2.14 charts the distribution of the major elements and the resultant facies.

As on many other continental shelves of the world, the sediments from Kithnos are composed of relict, reworked, or modern sediment, or mixtures of these three components. In approximately 20,000 B.P., the sea level would have stood about 120m below the present level (Curray, 1965). At this time well sorted fine sands would have been deposited in the nearshore zone of the embayments. Coarse, algae-rich sands would have accumulated offshore to form the relict belt of coarse algal sands mantling the present-day shelf edge.

During the rapid transgression that followed, sediments would have been redistributed to form a transgressive sand sheet across the shelf. Shorewards of the embayments in the relict morphology, the transgressive sand sheet is composed of fine sands.

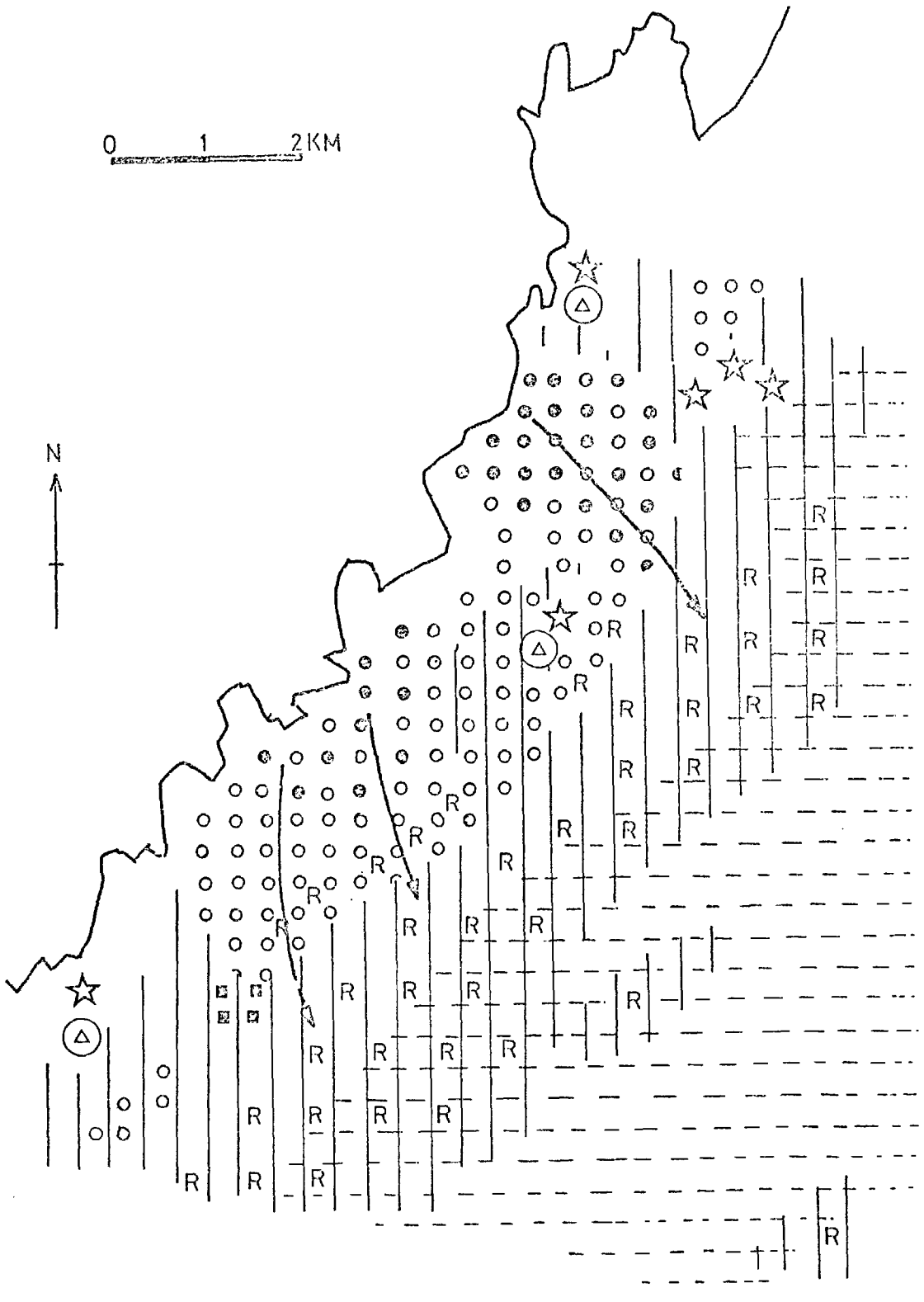


Figure 2.14 Distribution of sedimentary facies at Kithnos.(for key see overleaf).



Bioclastic medium/coarse sands and/or 'maerls'



Bioclastic sands with a large relict component



Bioclastic sands with rock fragments



Coarse detrital sand



Bioclastic fine sands (mainly transgressive or relict below a depth of 90m)



Mixed medium/coarse and fine bioclastic sands



Terrigenous very fine sands and coarse silts



Terrigenous coarse silts



Calcareous muds



Mixed terrigenous sand/silt and fine bioclastic sand



Mixed terrigenous sands/silts,bioclastic fine sands,and bioclastic coarse/medium sands



Mixed bioclastic sands and muds



Encrusting and/or branching coralline algae



Nodular coralline algae



Possible dispersion pathways for modern, terrigenous material

Key to figure 2.14 (and to figures 3.7,4.8,5.12,and 6.10).

This represents a period of autochthonous sedimentation in which sediments are mainly of a local origin (Swift, 1976).

Following the decrease in the rate of sea level rise, apparently between 5,000 and 9,000 B.P. (Curray, 1965), the Kithnos shelf appears to have entered an allochthonous phase (Swift, 1976) in which 'modern' sediment, derived from alluvial or aeolian input, began to accumulate on the shelf. Unlike most allochthonous shelves, however, the island of Kithnos does not have major rivers to contribute a large sediment load. Instead, sediment may accumulate in stream beds during the dry season and then, with the onset of the first rain, this is flushed into the nearshore zone. Because of the very narrow width of the inner shelf, the sediment plumes are able to contribute very fine sands and silts to the deeper water of the shelf. Here they are mixed with the transgressive sand sheet, possibly through bioturbation or current action.

Fine silts probably move diffusively seawards and deposit in the quieter zone offshore to form the offshore mud blanket.

Calcareous algae may still be growing on isolated shoals at the shelf edge and, consequently, may act as a source of 'modern' algal and other bioclastic debris for the adjacent sediments.

2.4.6 Summary

(1) The minus 2mm fraction of the sediments from Kithnos consist of four major sub-populations:-

- (a) mud, in which:-
  - (i) the mode ranges between coarse silt on the inner shelf to fine silt offshore,
  - (ii) the detrital and calcareous constituents are in approximately equal proportions offshore, but detrital constituents are dominant on the inner shelf,
  - (iii) most constituents are 'modern';
- (b) a very fine sand, in which:-
  - (i) detrital constituents are dominant,
  - (ii) most constituents are 'modern';
- (c) a fine sand, in which:-
  - (i) the detrital and calcareous constituents are in approximately equal proportion,
  - (ii) most constituents are either relict or have been reworked to form a transgressive sand sheet;

(d) a medium to coarse sand, in which:-

(i) most constituents are calcareous,

(ii) most constituents are relict, although some may be 'modern', especially close to topographic highs along the middle and outer shelf.

(2) The range of facies across the study area reflects admixture of the main sub-populations. Broadly, four zones are apparent:-

(a) inshore lobes of muddy sand in which detrital rich very fine sands and silts are mixed with the transgressive fine bioclastic sand sheet;

(b) a transgressive fine bioclastic sand sheet;

(c) a belt of coarse and medium relict to modern bioclastic sands mantling the outer shelf and platforms on the middle-shelf;

(d) an offshore calcareous mud blanket.

(3) Modern transport of sediment is tentatively suggested to be:-

(a) advective for detrital very fine sands and coarse silts on the inner shelf (turbid current);

(b) diffusive, in either continous suspension or intermittently through bed/water interface exchange, for muds of the offshore zone.

Aeolian transport may be significant but this is difficult to assess in the present study.

2.5 GEOCHEMISTRY OF SEDIMENTS

2.5.1 Introduction

The aims of investigating the geochemistry of the sediments from Kithnos are:-

(1) to establish the general levels of abundance of the elements Ca, Fe, Al, Ti, Mg, Mn, Cu, Zn, Ni, Cr and Pb;

(2) to pinpoint the major controls on the abundance of these elements;

and (3) to chart the dispersion pathways of the heavy metals.

The discussion is based upon a combination of selective leaching of the samples, R-mode factor analysis, and other features of the bulk composition of the samples. (Details of the analytical techniques, precision and accuracy are given in the appendices.)

2.5.2 Bulk Composition

The average partial composition, and the range of element concentrations, of the four main sediment types are given in table 3. For comparison, analyses of carbonate-rich continental margin sediments from other parts of the world are also included in table 3. The areal distribution of individual elements are shown in figures 2.3 (Ca), 2.15 (Fe), 2.16 (Al), 2.17 (Mg), 2.18 (Mn), 2.19 (Cu), 2.20 (Zn), 2.21 (Ni),and 2.22 (Cr).

In a preliminary study Smith and Cronan (1975) suggested that the composition of sediments from the Aegean could largely be explained by admixture of detrital and calcareous components. This appears to be broadly correct for sediments from the shelf (i.e. detrital and bioclastic sands) because the abundance of all elements, except Ca and Mg, decrease from the detrital sands to the bioclastic sands (II). Not surprisingly, Ca and Mg show a reverse trend. A detrital/carbonate admixture may also account for the abundance of Fe, Al, Ti, and Cr in the offshore calcareous muds, but additional controls are necessary to explain the apparent enrichment of Mg, Mn, Cu and possibly Zn, Ni and Pb in them.

2.5.3 Composition of the Detrital Fraction

In addition to the bulk analyses, selected samples were leached for 24 hours in 25% v/v acetic acid. Residues from the attack were analysed in a similar way to the bulk samples and analyses then corrected to total sample by multiplying by a 'weight loss on leaching' factor (see appendices). Hirst and Nicholls (1958) first used this technique to distinguish between the detrital and non-detrital fractions of sediment, and Hirst (1962b) subsequently applied it to the study of sediments from the Gulf of Paria. More recently it has been incorporated into a variety of selective leaching schemes (e.g. Chester and Hughes, 1966 and 1967; Cronan and Garrett, 1973) to study the partition of elements in marine sediments (see also 7.6.6c).

TABLE 3 Average and range of the partial chemical composition of the main sediment types from each area - major elements (in percent). Number of samples in parentheses; 1 - average value, 2 - range.

Sediment Type	Area		Ca	Fe	Al	Mg
DETRITAL SANDS	Kithnos	1	17.0	2.40	3.00	1.75
	(5)	2	15.1-20.0	1.90-2.80	2.70-3.50	1.70-1.85
	Serifos	1	18.9	2.46	3.46	2.07
	(3)	2	17.8-20.0	2.04-2.85	2.97-3.74	1.90-2.35
	Andros	1	15.8	1.68	3.07	1.84
	(5)	2	10.6-19.6	1.05-2.30	1.71-4.77	1.63-1.95
	Naxos	1	-	-	-	-
	(0)	2	-	-	-	-
	Sounion	1	-	-	-	-
	(0)	2	-	-	-	-
Gulf of Mexico (Holmes, 1973)			15.1	1.85	-	1.49
BIOCLASTIC SANDS I	Kithnos	1	23.6	1.64	2.20	1.85
	(14)	2	20.9-26.0	1.35-1.89	1.37-2.70	1.50-2.30
	Serifos	1	24.9	1.70	1.75	2.03
	(2)	2	24.1-25.7	1.30-2.10	1.50-2.00	2.00-2.05
	Andros	1	23.4	1.20	1.74	1.97
	(4)	2	21.2-25.5	0.90-1.50	1.30-2.20	1.90-2.10
	Naxos	1	25.6	1.12	1.91	1.65
	(18)	2	22.8-27.0	0.75-1.60	1.40-2.54	1.40-2.25
	Sounion	1	24.0	1.34	1.39	1.43
	(2)	2	23.4-24.5	0.90-1.78	1.33-1.45	1.10-1.75
BIOCLASTIC SANDS II	Kithnos	1	29.7	1.10	1.00	2.04
	(16)	2	27.1-33.9	0.40-1.60	0.50-1.80	1.75-2.30
	Serifos	1	30.0	0.84	1.01	2.14
	(3)	2	28.8-31.0	0.63-1.15	0.85-1.06	2.10-2.18
	Andros	1	29.0	0.86	1.09	2.26
	(7)	2	27.5-32.1	0.43-1.15	0.71-1.80	2.10-2.55
	Naxos	1	30.1	0.65	0.98	1.81
	(22)	2	27.4-33.7	0.30-1.10	0.53-1.91	1.45-2.15
	Sounion	1	29.2	0.96	0.81	1.59
	(23)	2	27.3-32.0	0.37-1.40	0.50-1.11	1.18-1.99
South-west Africa (Calvert, 1976)			31.0	0.79	1.19	0.44
CALCAREOUS MUDS	Kithnos	1	26.1	1.64	2.16	2.13
	(10)	2	23.3-28.3	1.45-1.90	1.69-2.44	1.70-2.35
	Serifos	1	25.2	2.00	2.60	2.12
	(6)	2	22.5-28.0	1.80-2.13	2.46-2.82	1.90-2.23
	Andros	1	21.8	2.03	3.01	2.18
	(4)	2	20.8-23.0	1.90-2.40	2.65-3.76	1.90-2.30
	Naxos	1	25.3	1.14	1.98	1.64
	(13)	2	22.4-30.6	0.57-1.50	1.03-2.57	1.20-1.80
	Sounion	1	29.5	1.13	1.26	2.20
	(1)	2	-	-	-	-

continued .....

TABLE 3 (continued) Minor and trace elements (in ppm except Ti in percent).

Ti	Mn	Cu	Zn	Ni	Cr	Pb
.18	360	15	48	54	84	37
.10-.27	350-380	11-18	39-56	45-70	65-120	30-45
.20	343	18	45	46	102	35
.15-.25	300-380	15-20	40-50	40-55	65-150	30-45
.17	315	13	33	38	92	32
.07-.25	225-560	9-21	21-41	18-65	33-140	15-45
-	-	-	-	-	-	-
-	-	-	-	-	-	-
-	-	-	-	-	-	-
-	-	-	-	-	-	-
.24	519	9	-	21	52	21
.17	330	13	42	27	67	28
.14-.23	270-390	10-17	29-52	5-40	40-85	20-45
.12	280	12	30	29	40	33
.11-.12	250-310	12-13	29-30	25-33	40/40	30-35
.11	250	14	32	26	45	29
.10-.13	210-310	10-17	29-43	15-30	30-68	20-35
.12	199	11	29	12	33	25
.08-.17	130-600	9-19	18-44	5-40	5-50	5-50
.11	272	14	206	35	67	258
.11/.11	188-355	14/14	90-322	30-40	65-68	90-425
.08	290	12	32	17	38	26
.04-.14	120-400	10-15	21-49	5-25	5-75	15-40
.10	237	13	33	18	42	17
.10-.11	200-280	12-14	30-39	5-30	25-60	5-25
.08	289	12	29	15	32	21
.01-.12	180-430	10-16	13-45	5-35	10-65	5-35
.09	124	10	24	12	20	23
.05-.17	75-215	7-16	13-57	5-25	5-45	10-35
.08	235	11	88	18	32	112
.05-.15	132-310	8-16	36-227	5-30	5-66	55-285
.07	-	37	38	62	-	7
.14	512	19	45	38	54	32
.12-.20	225-670	12-23	27-70	25-55	38-65	25-45
.21	456	20	49	48	69	33
.15-.22	370-510	18-22	44-57	40-53	65-81	20-45
.16	695	26	48	81	104	35
.13-.22	500-890	20-34	40-63	55-110	75-140	20-45
.14	174	12	29	15	40	25
.09-.22	110-250	8-15	15-45	5-23	15-65	10-45
.10	600	22	185	45	61	160
-	-	-	-	-	-	-

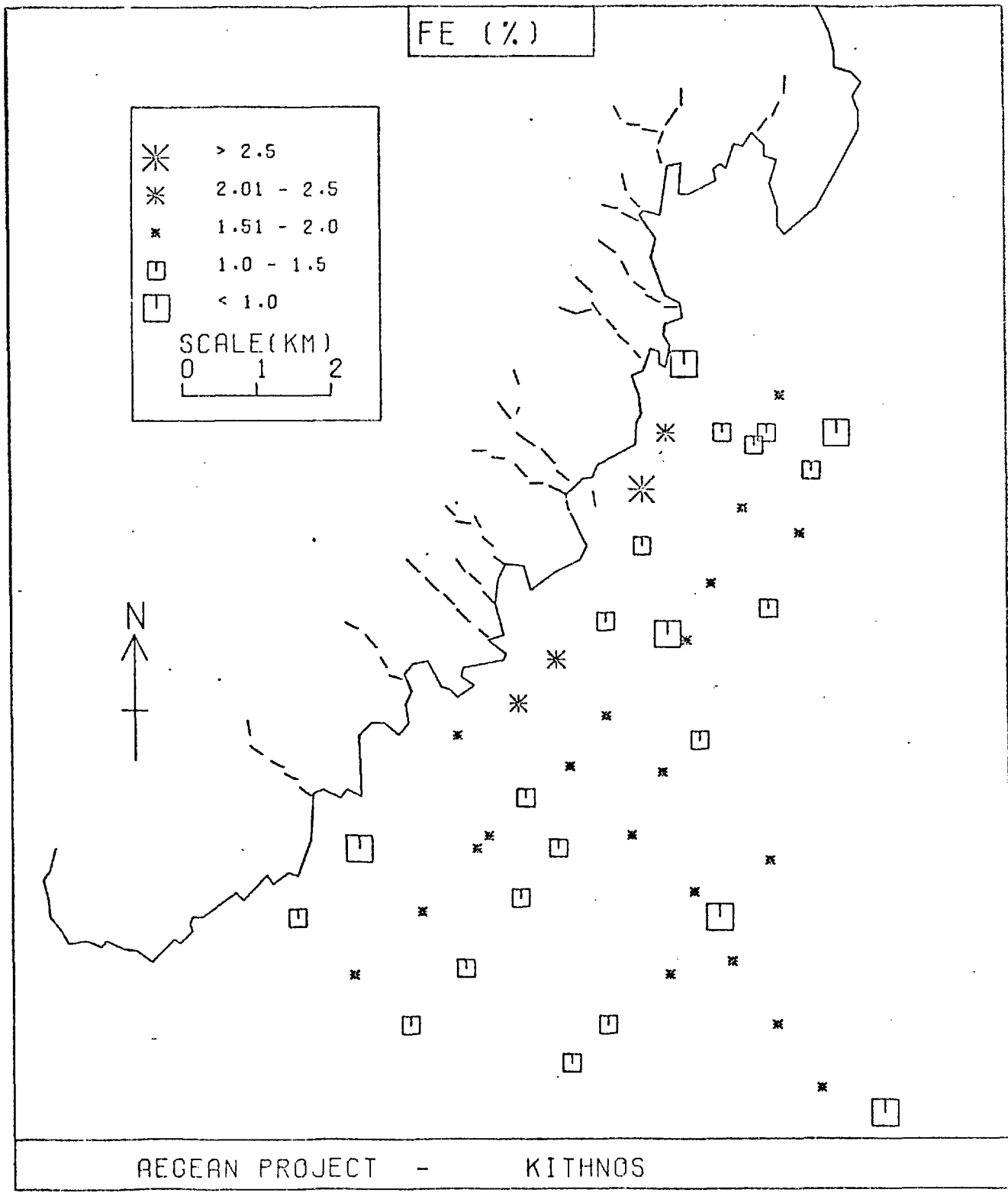


Figure 2.15 Distribution of total iron in samples from Kithnos.

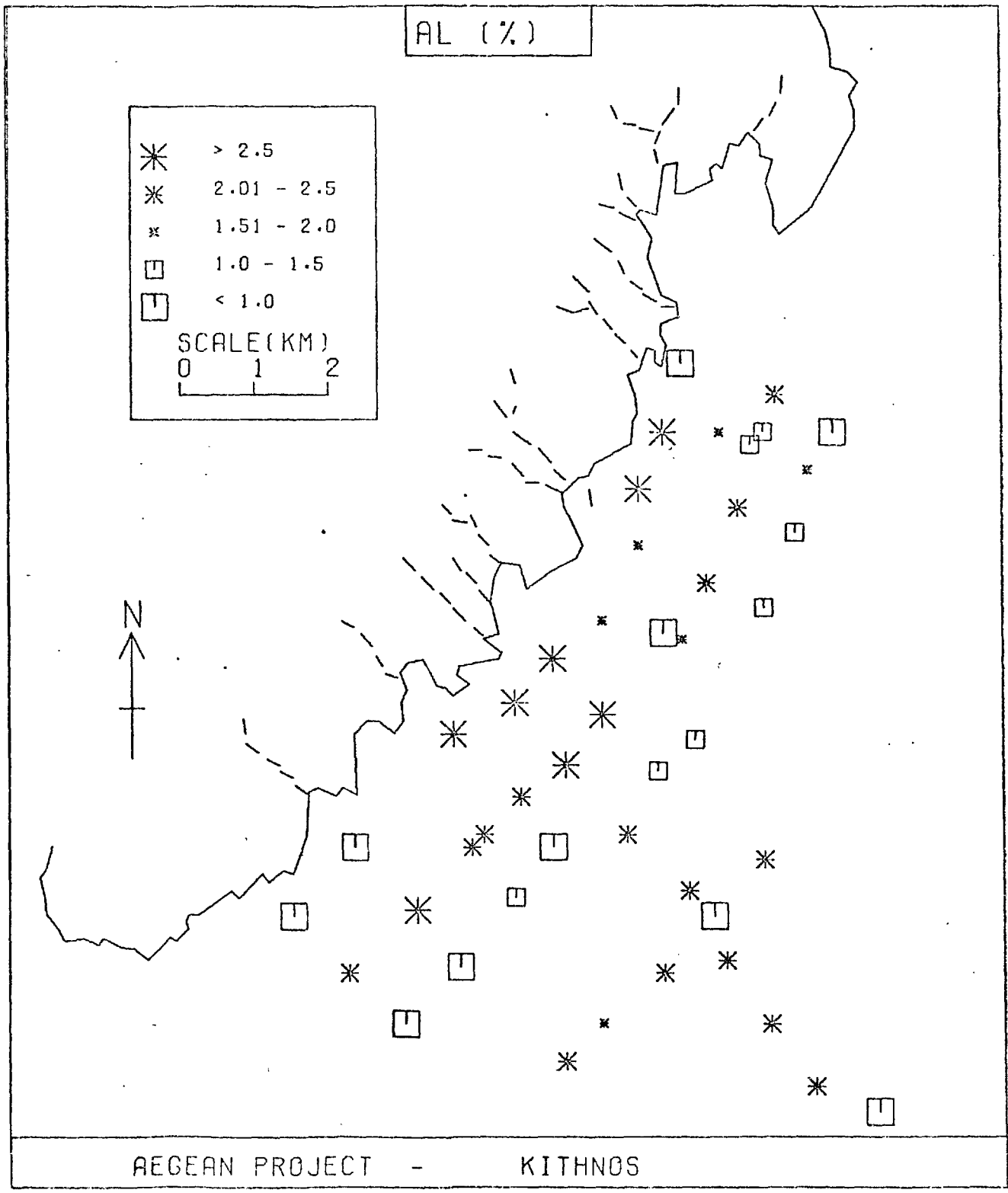


Figure 2.16 Distribution of aluminium.

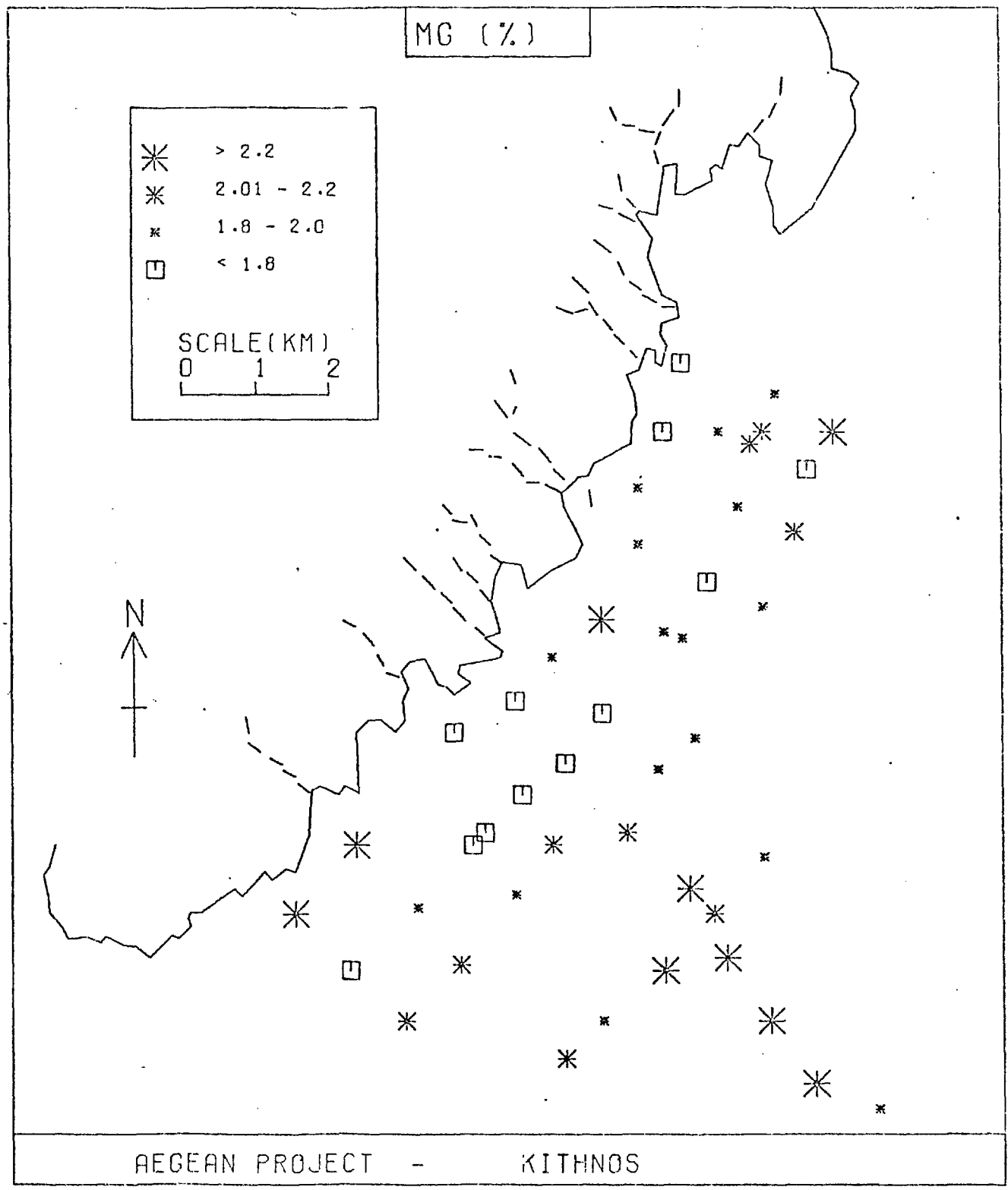


Figure 2.17 Distribution of magnesium.

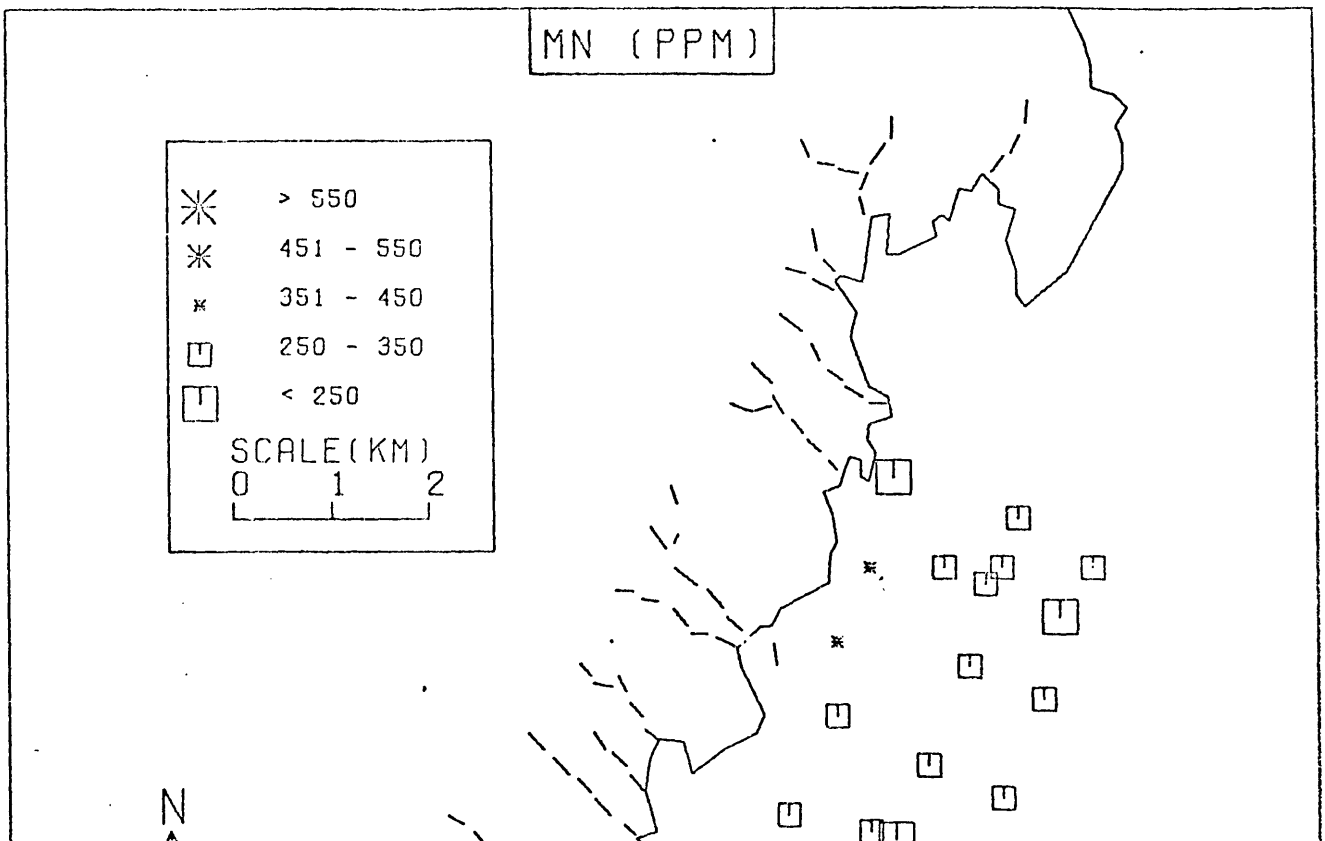


Figure 2.18 Distribution of manganese.

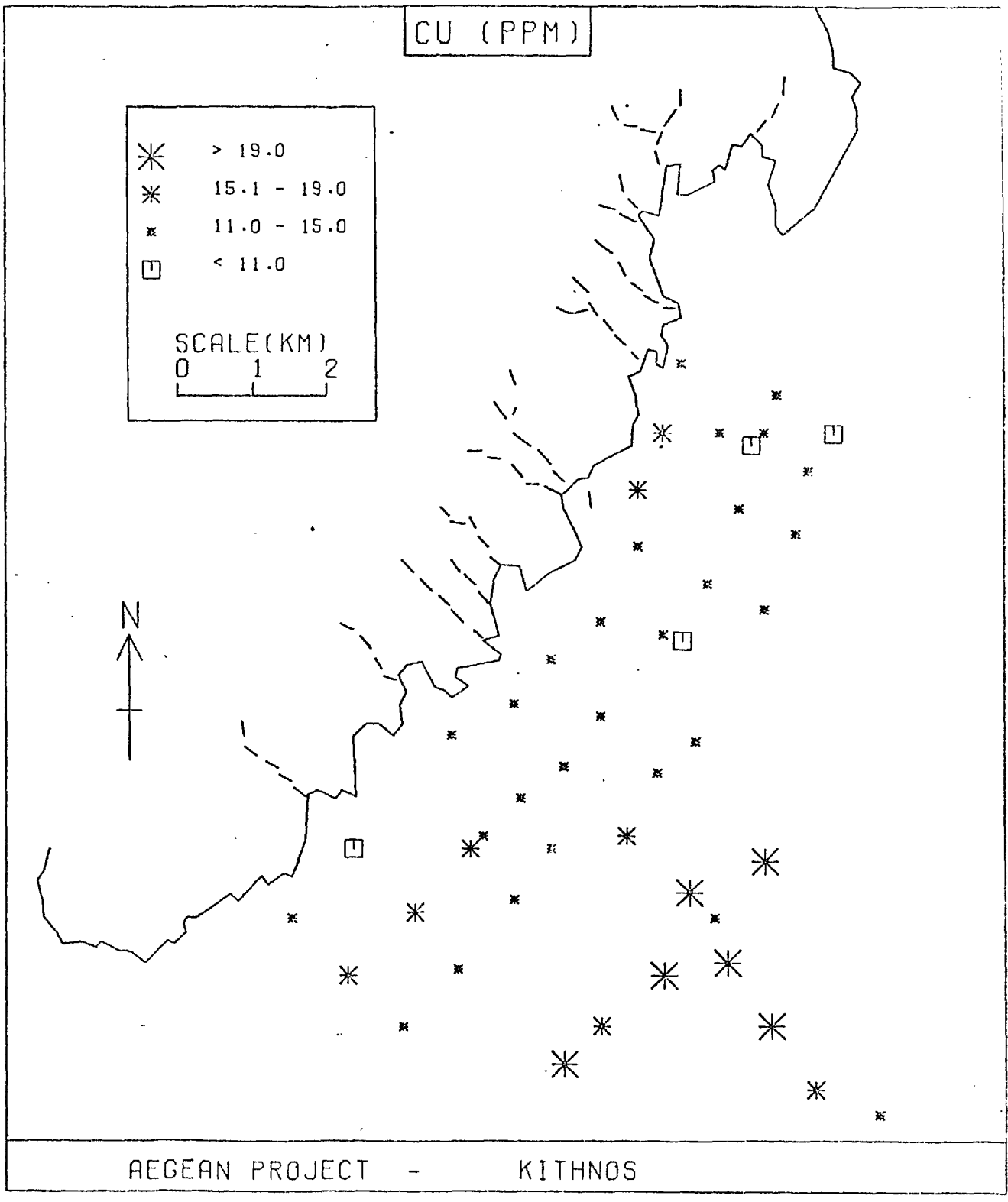


Figure 2.19 Distribution of Copper.

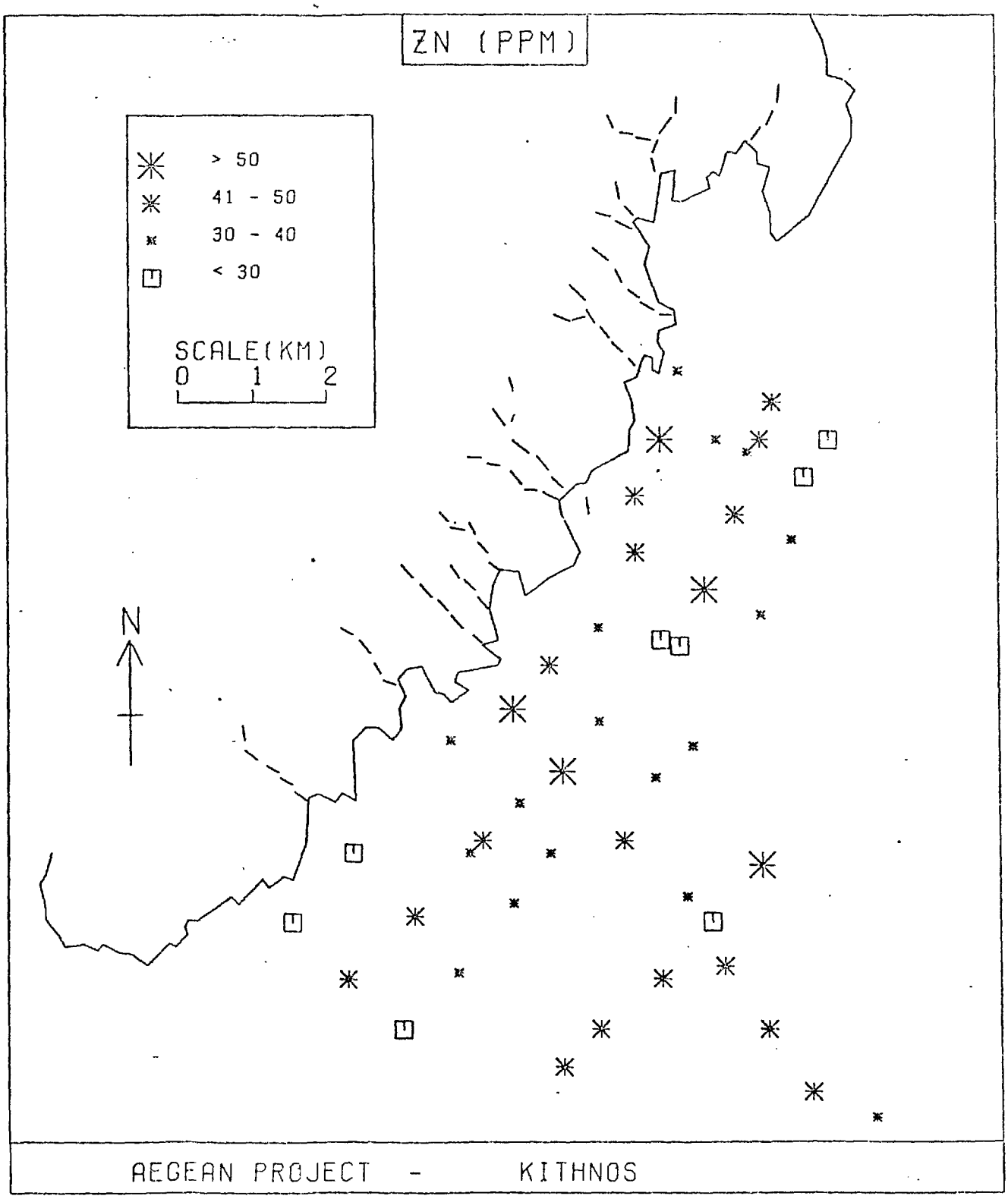


Figure 2.20 Distribution of Zinc.

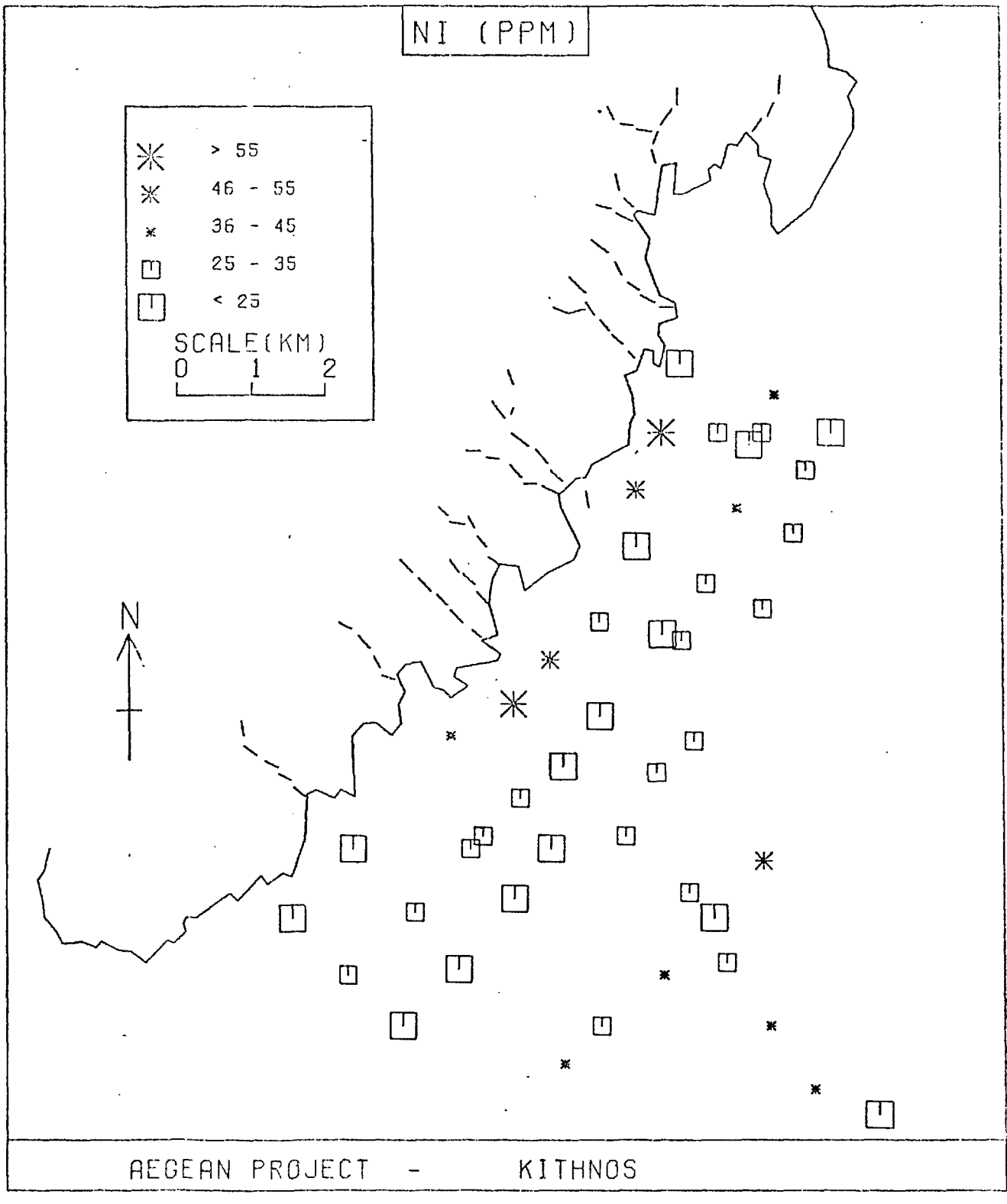


Figure 2.21 Distribution of Nickel.

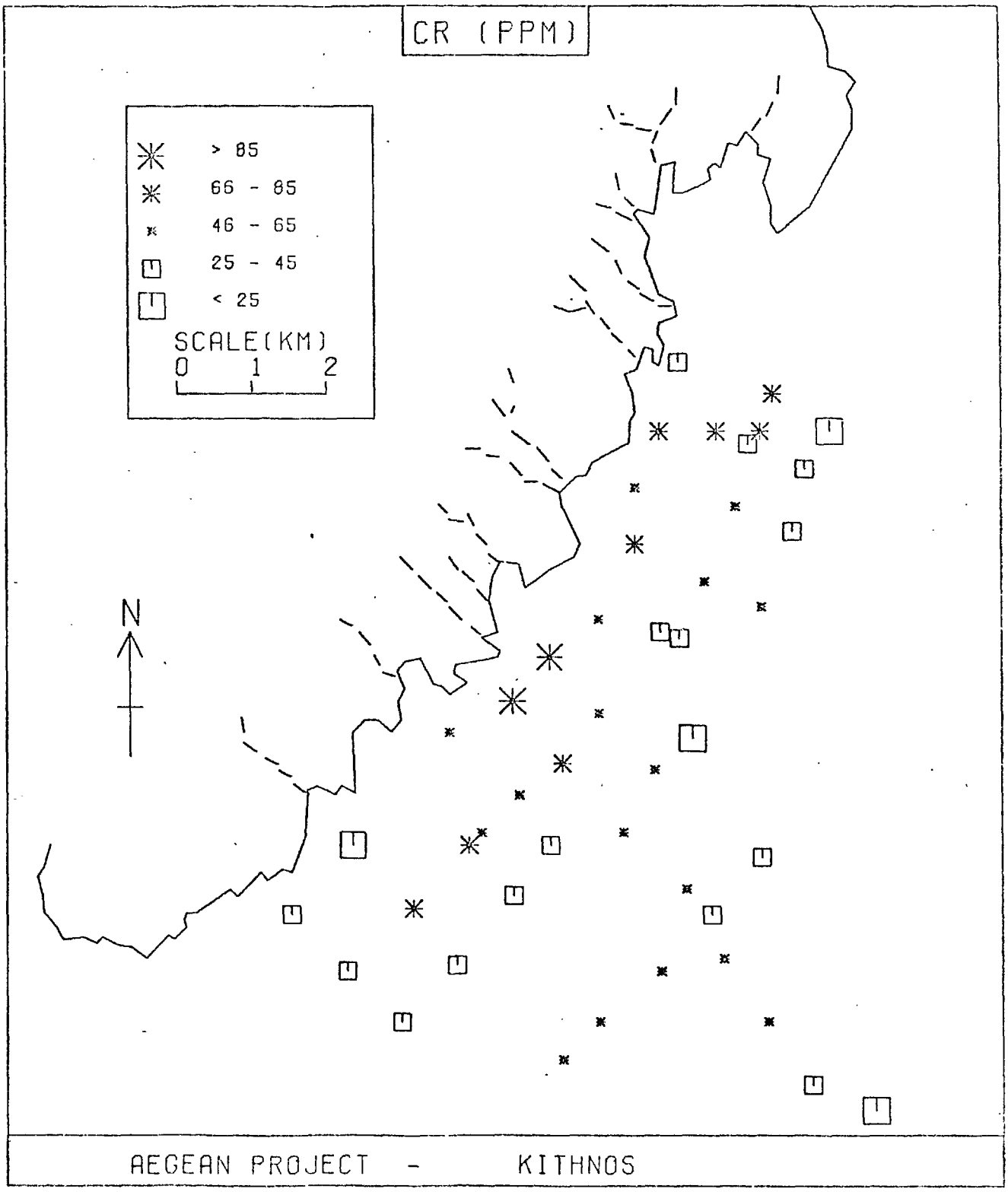


Figure 2.22 Distribution of Chromium.

'Detrital' elements comprise those residing in acid-resistant detrital minerals and insoluble authigenic components. Carbonates, loosely absorbed ions and acid-extractable iron and manganese oxides form the bulk of the 'non-detrital' fraction (Hirst, 1962b).

Samples chosen for selective leaching represent a traverse from nearshore to offshore (427, 411, 416, 432, 435). The partial composition of the detrital fraction (i.e. the residues and the detrital contribution to the total sample elemental abundances are given in table 4. For comparative purposes, analyses of average shale (Turekian and Wedepohl, 1961) and detrital sediments off the coast of Oregon and Washington (White, 1970) are also given.

Quartz, feldspar and the 'chlorite-mica' group (including any clay minerals) dominantly comprise the detrital fraction (section 2.3.2), either as discrete particles or as components of schist and other rock fragments. The relative proportions of these minerals, plus any insoluble authigenic phases, control the geochemistry of the detrital fraction. For example, the major elements are more abundant in the offshore samples (416, 432, 435) and are probably held in the lattices of the fine-grained alumino-silicates (i.e. chlorite, micas and the clay minerals). Elemental abundance in the detrital fraction of 427 and 411 is lower and this may reflect dilution of the chlorite-micas by quartz and/or feldspars which are relatively depleted in many of the elements, especially Fe, Mg and the heavy metals (see section 6.6.4 for further discussion). The influence of the accumulation of authigenic Mn 'oxides' on the composition of the 'detrital' fraction is shown by the greater Mn and Mn/Mg values in the calcareous muds from the offshore zone (table 4). The manganese oxides (or hydroxides) may occur either as coatings on the detrital grains or as dispersed particles within the sediment.

The contribution of the 'detrital' fraction to the total abundance also varies with each element. In general, the 'detrital' contribution decreases in the order Fe, Al, Ti, Ni, Cr>Zn>Cu>Mn, Mg>Pb>Ca. Consequently, in the absence of a diluting carbonate component, the total abundance of the elements Al, Ti, Ni and Cr is mainly controlled by the range in detrital mineralogy. For Fe there is some evidence of a further component in the 'detrital' fraction to contribute to its total abundance. In sample 416, for example, there appears to be an excess of iron probably attributable to an insoluble authigenic iron mineral (section 2.5.5a).

TABLE 4 The partial chemical composition of the detrital fraction of selected samples from the continental margins of the Aegean Sea.

1 - element concentration (Ca,Fe,Al,Ti,Mg,and K are in percent, the remaining elements are in ppm);

2 - the percentage contribution by the detrital fraction to the total element abundance;

A. - average composition of detrital sediments off the coast of Oregon and Washington(White,1970);

B. - average shale (Turekian and Wedepohl,1961).

		Sample Numbers - SOUNION								
		327	328	329	341	344	347	349	350	351
Ca	1	1.06	1.10	1.30	1.60	1.25	1.15	1.70	1.70	1.60
	2	.9	1.2	.8	1.2	1.0	.9	.9	1.6	2.2
Fe	1	4.53	5.00	4.70	4.80	3.96	5.10	3.20	3.75	2.20
	2	87	84	84	86	86	89	76	100	81
Al	1	3.92	3.98	4.46	3.55	3.50	4.34	3.60	3.26	3.02
	2	100	91	97	86	100	100	81	87	75
Ti	1	.26	.26	.29	.22	.26	.28	.26	.31	.26
	2	59	100	100	80	72	92	70	100	78
Mg	1	1.46	1.55	1.60	1.80	1.41	1.75	2.00	2.00	1.50
	2	22	20	19	23	24	24	20	26	28
K	1	1.2	1.6	1.4	1.3	1.2	1.5	1.5	2.0	-
Mn	1	230	230	270	230	235	232	400	320	240
	2	18	16	16	18	23	19	32	32	42
Cu	1	20	20	25	27	20	26	41	39	26
	2	41	40	50	46	43	41	50	67	62
Zn	1	130	129	137	292	176	190	440	547	477
	2	53	53	47	65	59	51	37	64	50
Ni	1	83	95	85	75	63	92	145	105	105
	2	68	100	60	75	47	80	100	93	100
Cr	1	183	190	185	180	168	198	240	260	230
	2	65	100	100	98	100	96	100	100	100
Pb	1	39	63	50	61	47	49	127	128	105
	2	14	23	13	15	14	17	8	12	8
Fe/Al		1.15	1.26	1.05	1.35	1.13	1.17	.89	1.15	.73
Mg/Al		.37	.39	.36	.51	.40	.40	.56	.61	.50

continued .....

TABLE 4(continued)

		ANDROS				KITHNOS				
		357	365	367	373	411	416	427	432	435
Ca	1	1.20	1.40	1.40	1.15	1.40	1.95	0.80	0.50	1.70
	2	8.0	2.5	0.8	1.1	2.4	0.6	2.5	1.4	1.8
Fe	1	2.70	5.50	5.65	3.54	3.65	7.60	3.90	5.20	5.30
	2	81	94	81	90	94	100	93	86	88
Al	1	5.93	7.42	6.25	4.88	5.94	6.52	4.82	6.52	6.95
	2	86	100	78	93	84	95	77	93	79
Ti	1	.41	.48	.46	.27	.50	.42	.50	.46	.48
	2	100	100	81	65	90	67	100	100	85
Mg	1	1.45	2.46	2.30	1.58	1.60	2.53	1.90	2.70	2.60
	2	56	40	18	20	39	13	57	31	32
K	1	1.70	2.20	2.40	1.40	1.50	2.20	1.90	2.05	2.20
Mn	1	260	1480	420	255	300	355	270	580	880
	2	60	67	16	28	32	14	40	32	37
Cu	1	17	53	49	19	21	41	20	42	40
	2	98	80	50	45	64	38	71	56	54
Zn	1	58	109	117	60	78	120	103	120	116
	2	98	98	61	52	61	50	94	67	50
Ni	1	65	220	165	53	95	142	105	145	145
	2	100	90	77	87	100	100	100	100	93
Cr	1	180	290	270	160	180	220	200	250	240
	2	89	78	100	100	92	60	100	100	100
Pb	1	7	34	35	10	16	24	14	17	18
	2	14	37	20	7	24	15	17	13	17
Fe/Al		.45	.74	.90	.72	.61	1.17	.81	.80	.76
Mg/Al		.24	.33	.37	.32	.27	.39	.39	.41	.37

continued.....

TABLE 4 (continued)

		SERIFOS				NAXOS			
		445	448	453	464	471	472	473	474
Ca	1	2.05	2.35	2.10	2.30	3.35	2.60	3.80	2.95
	2	2.4	2.7	1.2	1.1	3.9	2.8	2.7	3.7
Fe	1	5.40	5.80	6.95	4.80	3.30	3.60	4.00	3.55
	2	97	93	100	96	88	89	80	82
Al	1	7.10	7.00	6.56	6.73	5.61	5.93	6.25	5.40
	2	82	91	100	89	100	96	98	95
Ti	1	.50	.50	.41	.47	.32	.30	.34	.27
	2	89	73	64	60	81	78	92	100
Mg	1	2.80	2.76	2.74	2.95	2.15	2.10	2.30	2.03
	2	41	40	21	20	43	39	25	38
K	1	2.80	2.50	2.20	2.20	2.00	2.40	2.10	1.30
Mn	1	840	585	375	400	300	300	380	305
	2	56	41	28	29	48	50	54	54
Cu	1	43	41	43	46	17	17	21	16
	2	64	68	54	58	49	53	47	52
Zn	1	115	114	120	117	58	63	75	59
	2	65	82	70	44	49	58	37	58
Ni	1	145	143	127	135	53	55	85	28
	2	89	100	74	100	85	100	100	100
Cr	1	260	250	255	300	120	120	130	168
	2	100	100	100	73	100	100	100	100
Pb	1	33	23	68	13	26	32	21	27
	2	44	35	48	40	55	30	14	16
Fe/Al		.76	.83	1.06	.71	.59	.61	.64	.66
Mg/Al		.39	.39	.42	.44	.38	.35	.37	.38

continued .....

TABLE 4 (continued)

		NAXOS(continued) 475	476	478	516	517	518	A.	B.
Ca	1	3.20	2.80	2.70	4.10	2.35	2.60	2.36	1.47
	2	4.2	3.8	2.8	1.9	4.0	3.7		
Fe	1	3.60	2.90	2.70	2.60	3.00	2.60	3.00	4.72
	2	81	85	82	82	100	89		
Al	1	5.51	5.56	5.51	5.30	4.40	5.93	6.90	8.00
	2	97	100	98	98	66	98		
Ti	1	.35	.30	.35	.37	.36	.37	.54	.46
	2	100	90	83	83	92	92		
Mg	1	2.05	2.05	2.00	2.68	1.55	1.80	1.81	1.50
	2	39	42	33	22	39	42		
K	1	1.80	1.70	1.50	1.30	1.80	-	-	2.66
Mn	1	400	280	320	275	240	260	620	850
	2	63	53	55	57	63	61		
Cu	1	15	16	17	30	17	21	28	45
	2	39	49	45	43	51	51		
Zn	1	62	58	58	68	55	65	95	107
	2	65	40	56	37	60	51		
Ni	1	45	45	55	68	35	45	100	68
	2	100	75	100	100	70	100		
Cr	1	120	140	135	150	110	135	191	90
	2	100	100	100	100	100	100		
Pb	1	23	20	15	12	11	13	10	20
	2	24	33	27	7	17	48		
Fe/Al		.65	.52	.49	.49	.68	.44	.44	.59
Mg/Al		.37	.37	.36	.51	.35	.30	.26	.19

The remaining elements (Zn, Cu, Mn, Mg, Pb and Ca) have a substantial 'non-detrital' component in their total abundance. Biogenic carbonate minerals contain most of the 'non-detrital' Ca and Mg and may also account for some of the 'non-detrital' Cu and Zn, particularly as the non-detrital levels of these elements are low (5-9ppm, 3-20ppm respectively). Further amounts of Cu and Zn could also be adsorbed onto fine-grained detrital particles or organic matter, or associated with 'non-detrital' manganese oxides, but which of these factors is most important is difficult to assess.

'Non-detrital' Mn is much greater (200-400ppm) and so it is unlikely to be held within the carbonate minerals. Instead, it probably occurs as coatings on the bioclastic fragments. Unlike manganese 'oxide' coatings on detrital grains, or as discrete particles in the sediment, coatings on calcareous fragments are more likely to be removed by the acetic-acid following dissolution of the host.

2.5.4 R-mode Factor Analysis

2.5.4a Introduction

The concentration of an element in any one component and the relative proportions of the various components, govern the concentration of an element in a sediment sample (see Calvert, 1976). Furthermore, the number of geochemically significant components is generally less than the number of elements analysed. The major aims of the geochemical investigation in each area are to identify geochemically significant components and to estimate their relative significance in controlling the abundance of a particular element. To solve this problem one approach is to use R-mode factor analysis to identify underlying factors which account for much of the data variance and which may be geochemically meaningful. It is an approach which has been widely used to investigate the geochemistry of continental margin sediments (see e.g. Spencer et al., 1968; White, 1970; Summerhayes, 1972; Calvert, 1976).

Factor analysis uses the matrix of correlations amongst the original variables (in this case chemical element abundance) to define new, hypothetical variables called factors. Very often, a few statistically dominant factors account for a large proportion

of the data variance. If such factors have geochemically meaningful element associations then they may help to clarify the nature of the sediment components governing element abundance.

The principal factor matrix, however, has as many factors as original variables and the choice of a smaller number of significant factors is based on the subjective assessment of 'making sense' geochemically (see e.g. Summerhayes, 1972). For consistency, only those factors with eigenvalues greater than one (Kaiser's criteria, cited by Child, 1970, as being indicative of non-significance of a factor - Howarth, personal communication) and with high loadings on more than one element (high loadings on one element are considered to reflect analytical variance) are generally chosen.

In addition to the problem of selecting an appropriate factor model, there are further limilations:

(1) The total sum of the variables totalling 100% is a constraint which may induce false correlations. For example, in this investigation the diluting effect of the abundant calcium carbonate may induce positive correlation between unrelated variables because they are all negatively correlated with a major constituent (Chave and McKenzie, 1961). Consequently, subtler controls on element abundance may be obscured in a factor model based on bulk analyses.

For this reason, the data are recalculated on an approximate carbonate-free basis and R-mode factor analysis is used once again to interpret the data variance. There are numerous problems in this approach because:-

(a) elements may partly occur in the carbonates and so the recalculated value is artificially high;

(b) analytical errors are exagerated by recalculation;

and (c) errors in carbonate determination, especially where carbonate values are high, can give misleading results.

Because of these limitations, carbonate-free data are only used in conjunction with R-mode factor analysis to extract the most significant factors explaining the carbonate-free data variance.

(2) A similar areal distribution may also induce correlations between unrelated variables.

(3) For stable estimation of the correlation matrix, Ball (1965) recommends that the number of samples should be at least ten times the number of variables (Howarth, personal communication).

Small sample sets may also affect the assessment of the significance of a factor loading (Glasby et al., 1974). A level of 0.3 has been used (e.g. Summerhayes, 1972; Glasby, et al., 1974; Calvert, 1976) but a higher value might be more appropriate for smaller sample sets, analogous with the significance level of the correlation coefficient (Glasby, et al., 1974). For consistency, a factor loading of 0.3 is also used in this investigation.

Although the list of limitations is substantial, the constraints on the choice of factor model ensure that only the most significant factors are extracted. Elemental associations that might be due to the problems listed are duly noted. Consequently, factor analysis is used because it has the following advantages:-

(1) it provides a rapid assessment of the structure of the data matrix and can be used as a basis for subsequent discussion on subtler aspects of sediment geochemistry;

(2) plotting the factor scores in a map form display:-

(a) the areal distribution of a factor, and

(b) the influence of a particular factor on a given sample, in contrast to single element data which reflect a composite response.

Factors were computed using a program from the University of California BIOMED package (BMD03M)(Dixon, 1968). The data were not transformed but the principal factor matrix was rotated to produce a varimax orthogonal solution. Each factor solution provides:-

(1) the factor loading, which is a measure of the correlation between the element and the underlying factor;

(2) the communality of an element, which is a measure of the amount of variance of each element explained by the factor model chosen;

(3) the eigen value (expressed as a percentage), which is a measure of the amount of the original variance explained by a particular factor; and

(4) factor scores which are an indication of the weighting of each rotated factor on individual samples (N.B. they are given in units of standard deviation and are distributed about a zero mean).

2.5.4b Bulk data

R-mode factor analysis of 10 variables (excluding Ca) in Kithnos samples produces a 2 factor model accounting for 71.1% of the original data variance (table 5).

The communality for most elements is reasonable and consistent with the level of analytical variance. The communality for Pb is particularly poor but so also is the analytical precision at the low levels of this element.

Factor 1 is statistically the most dominant and accounts for almost 53% of the original data variance. A strong association of the elements Al, Fe, Ti, Cr, Zn and Ni, and an inverse loading on Mg characterise this factor. When Ca is included in the correlation matrix it has a very strong inverse loading on factor 1. A high loading on the detrital elements Fe, Al, Ti, Ni, and Cr (section 2.5.3) and an inverse loading on the biogenous elements Ca and Mg suggest that factor 1 reflects the important diluting influence of calcium carbonate. Factor scores for this 'detrital' factor are highest in the detrital sand lobes nearshore and lowest in the bioclastic sands (II) rich in calcium carbonate (c.f. figures 2.3 and 2.23).

Factor 2 accounts for approximately 18% of the original data variance and comprises a strong association between Mn and Cu, with lesser loading on Mg, Zn, Ni, Fe and Al. Factor scores are highest in the offshore muds and lowest on the shelf and so the areal distribution of this factor broadly parallels the mud distribution (c.f. figures 2.2 and 2.24). Selective leaching of samples (section 2.5.3) indicates that manganese oxides (or hydroxides) and the chlorite-mica group of minerals are most abundant in the offshore calcareous muds. An enrichment in Mn and Mg is the result and this accounts for the loading of both elements on factor 2. Consequently, because of the coincident areal distribution of the manganese 'oxides' and the chlorite-mica group of minerals, factor 2 is a dual 'oxide/chlorite-mica' factor, dominantly controlled by the distribution of Mn but significantly affected by the distribution of the chlorite-mica group of minerals.

The heavy loading of Cu on this factor may suggest scavenging by the Mn 'oxides' although other forms of hydrogenous or biogenous

TABLE 5 Varimax rotated factor matrix for bulk chemical analyses of sediment samples from Kithnos.

Variable	Factor 1.	Factor 2.	Communality
Fe	0.86	0.35	0.864
Al	0.90	0.35	0.936
Ti	0.84	-	0.751
Mg	-0.66	0.56	0.746
Mn	-	0.90	0.854
Cu	-	0.86	0.796
Zn	0.64	0.50	0.659
Ni	0.64	0.40	0.570
Cr	0.80	-	0.651
Pb	-	0.49	0.279
Cumulative percentage of original data variance accounted for :-	52.7	71.1	

N.B. Factor loadings between $\pm$ 0.30 are omitted.

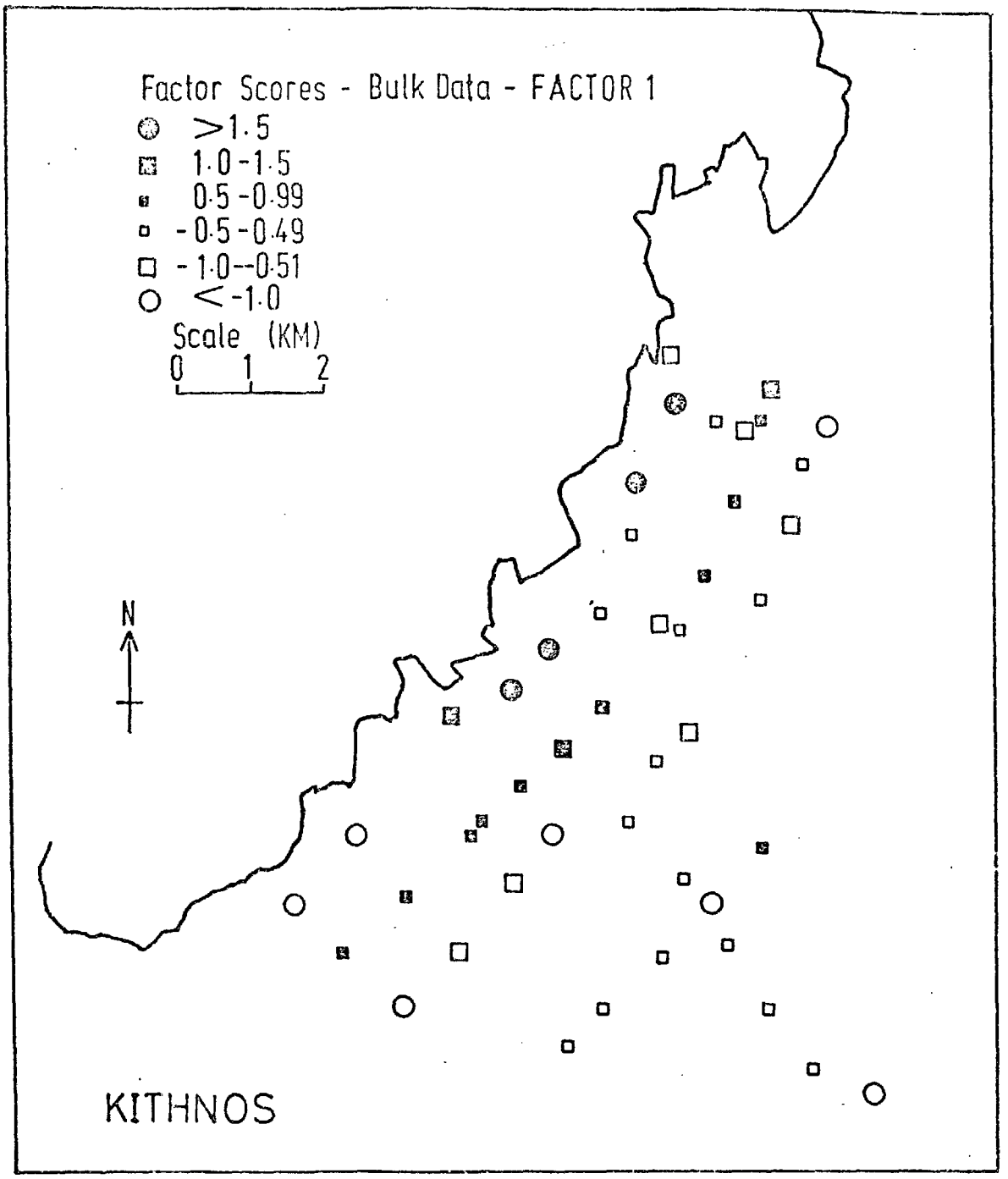


Figure 2.23 Distribution of factor scores - Factor 1.

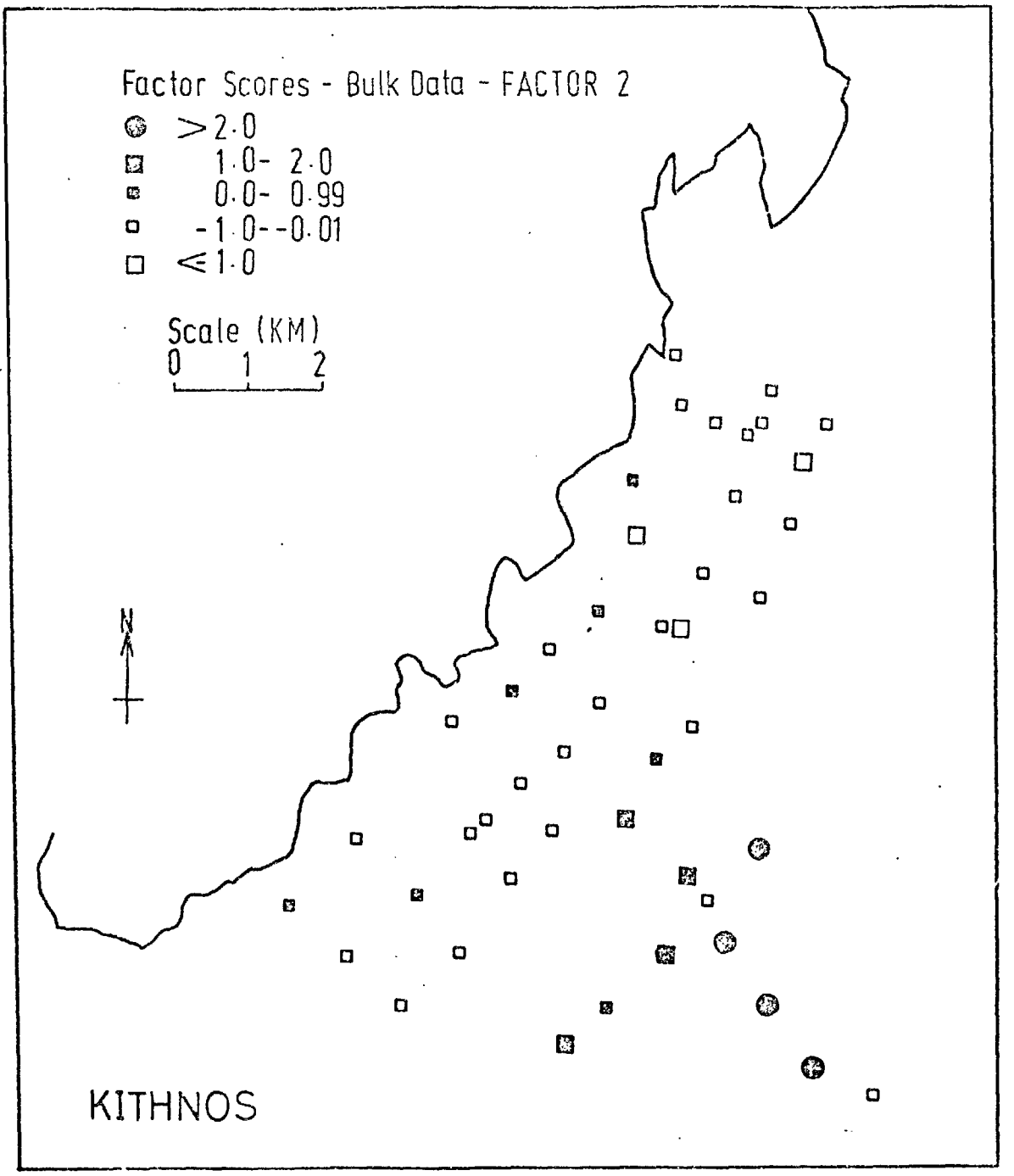


Figure 2.24 Distribution of factor scores - Factor 2.

Cu (see section 2.5.3) may have a similar distribution to the 'oxides' (i.e. highest in the fine-grained sediments), inducing a strong correlation with the 'oxide' factor. Furthermore, Zn, Ni, Pb and Cu are also enriched in the chlorite-mica minerals and this feature could also contribute to moderate loadings of these elements on factor 2.

In conclusion, factor analysis of the bulk data supports both the preliminary observations on the average composition and conclusions based on selective leaching of a limited number of samples. The most important influence on the composition of the sediments is the diluting affect of the calcium carbonate. Superimposed on the inverse detrital-carbonate relationship is a combined 'oxide/chlorite-mica' factor reflecting the similar areal distribution of manganese 'oxides' and the detrital chlorite-mica group of minerals. Heavy metal associations vary according to the significance of the non-detrital fraction and their concentration in the chlorite-mica group.

2.5.4c Carbonate-free data

In an attempt to partially remove the influence of the calcium carbonate, the data have been recalculated on an approximate carbonate-free basis (N.B. carbonate value is based on Ca_{tot} - see 2.3.3) and re-examined by factor analysis. For obvious reasons, Ca and Mg have been excluded from the analyses. Lead is also excluded becuase of it's poor precision which could produce misleading results on a carbonate-free basis.

Factor 1 accounts for 39% of the data variance and is characterised by a strong association of Cu, Mn and Zn and a minor loading of Fe (table 6). It appears to represent a 'manganese oxide' factor with the highest factor scores occurring in the zones of lowest sediment accumulation rate. By examining the data on a carbonate-free basis the influence of calcium carbonate is removed and the 'oxide' and 'chlorite-mica' groups separated (show as a combined factor when using the bulk data). Consequently, a much clearer picture of the distribution of the manganese 'oxide' factor is achieved (figure 2.25). Interestingly, it reveals that a significant 'oxide' factor is not restricted to the offshore muds but is also important in the belt of mainly relict

TABLE 6 Varimax rotated factor matrix for chemical analyses of sediment samples from Kithnos corrected to a carbonate-free basis.

Variable	Factor 1.	Factor 2.	Communality
Fe	0.57	0.57	0.657
Al	-	0.87	0.810
Ti	-	0.88	0.778
Mn	0.91	-	0.877
Cu	0.95	-	0.911
Zn	0.85	-	0.744
Ni	-	0.42	0.264
Cr	-	0.70	0.492
Cumulative percentage of original data variance accounted for:-	39.4	69.2	

N.B. Loadings between $\pm$ 0.30 are omitted.

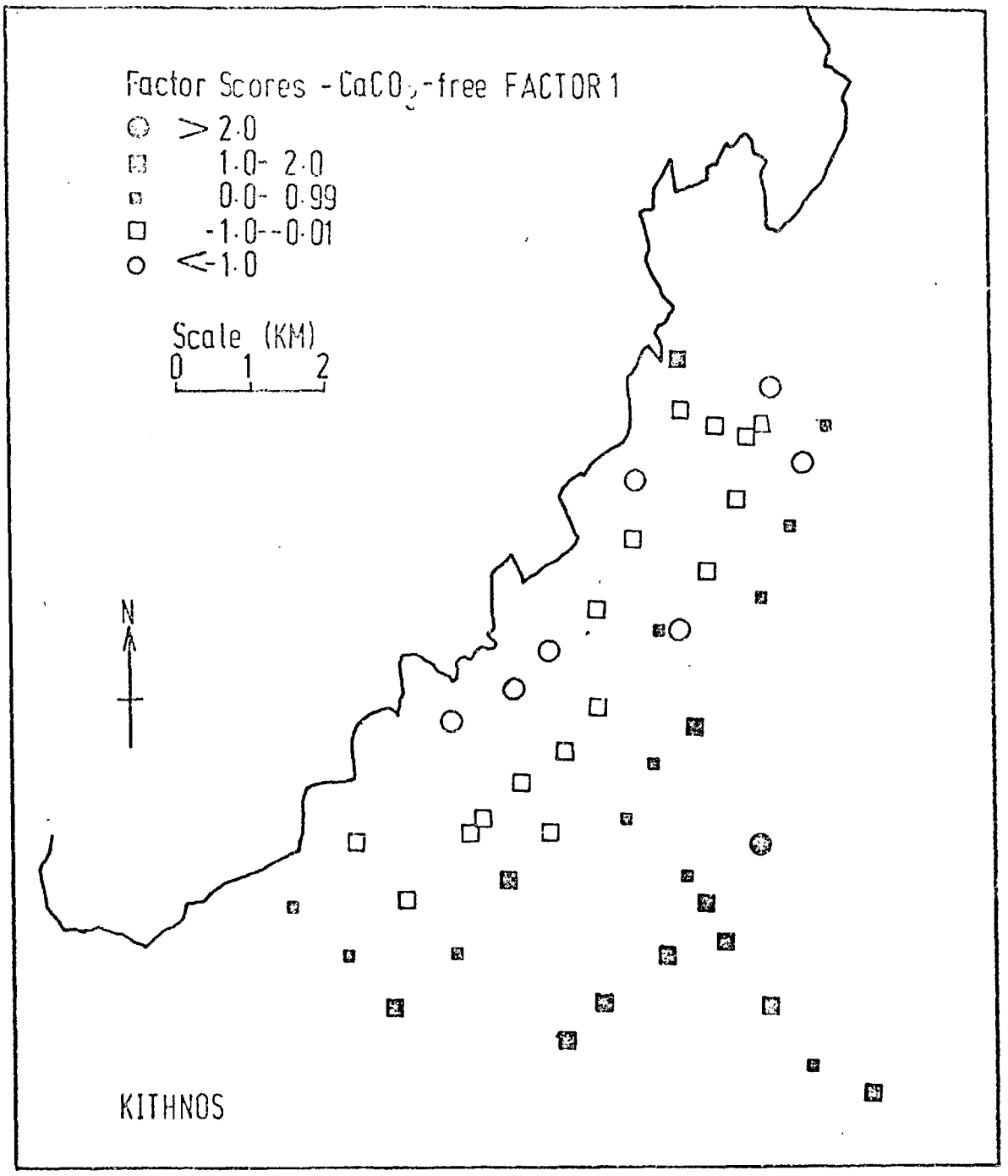


Figure 2.25 Distribution of factor scores - $CaCO_3$ free Factor 1.

bioclastic sands (II). Both zones are characterised by lower sediment accumulation rates.

Once again, Cu and Zn, two elements with a significant non-detrital component (section 2.5.3), are strongly associated with the oxide factor. This feature might reflect scavenging by manganese oxides but other non-detrital controls (e.g. adsorption on fine-grained detrital material) would have a similar areal distribution and this could induce a significant correlation between Mn and these elements.

Factor 2 comprises an association between the detrital elements Ti, Al, Cr, Fe and Ni (table 6). Highest scores on this factor (figure 2.26) are not limited to the offshore samples rich in fine-grained aluminosilicates but also occur in sandy sediments with a smaller fine-grained aluminosilicate component (e.g. 401), probably because Al, which is heavily loaded on this factor, occurs in feldspars as well as the fine-grained aluminosilicates (i.e. the chlorite-mica group). Here it is considered that factor 2 reflects the relative enrichment in Al through the enrichment of feldspars and/or fine-grained aluminosilicates. Perhaps a more appropriate term to describe factor 2 would be a 'aluminosilicate' factor. On applying R-mode factor analysis to the data of Hirst (1962, a and b) Spencer et al., (1968) proposed a similar factor (termed a 'quartz-dilution' factor) to account for the variability of Ti, Al, Cr and Ni in sediments from the Gulf of Paria. An 'aluminosilicate' factor found by Calvert (1976) on re-examining the Buzzards Bay data of Moore (1963) is also similar to the 'aluminosilicate' factor found at Kithnos.

An apparent weakness of both factor solutions is that neither isolates the chlorite-mica group as a single factor. The poor communality of Ni, particularly in the carbonate-free solution, may reflect this feature because factor 2 only partly accounts for its variability.

2.5.5 Discussion

2.5.5a Authigenic Components and their Influence on Sediment Composition

Certain aspects of the iron abundance suggest that the

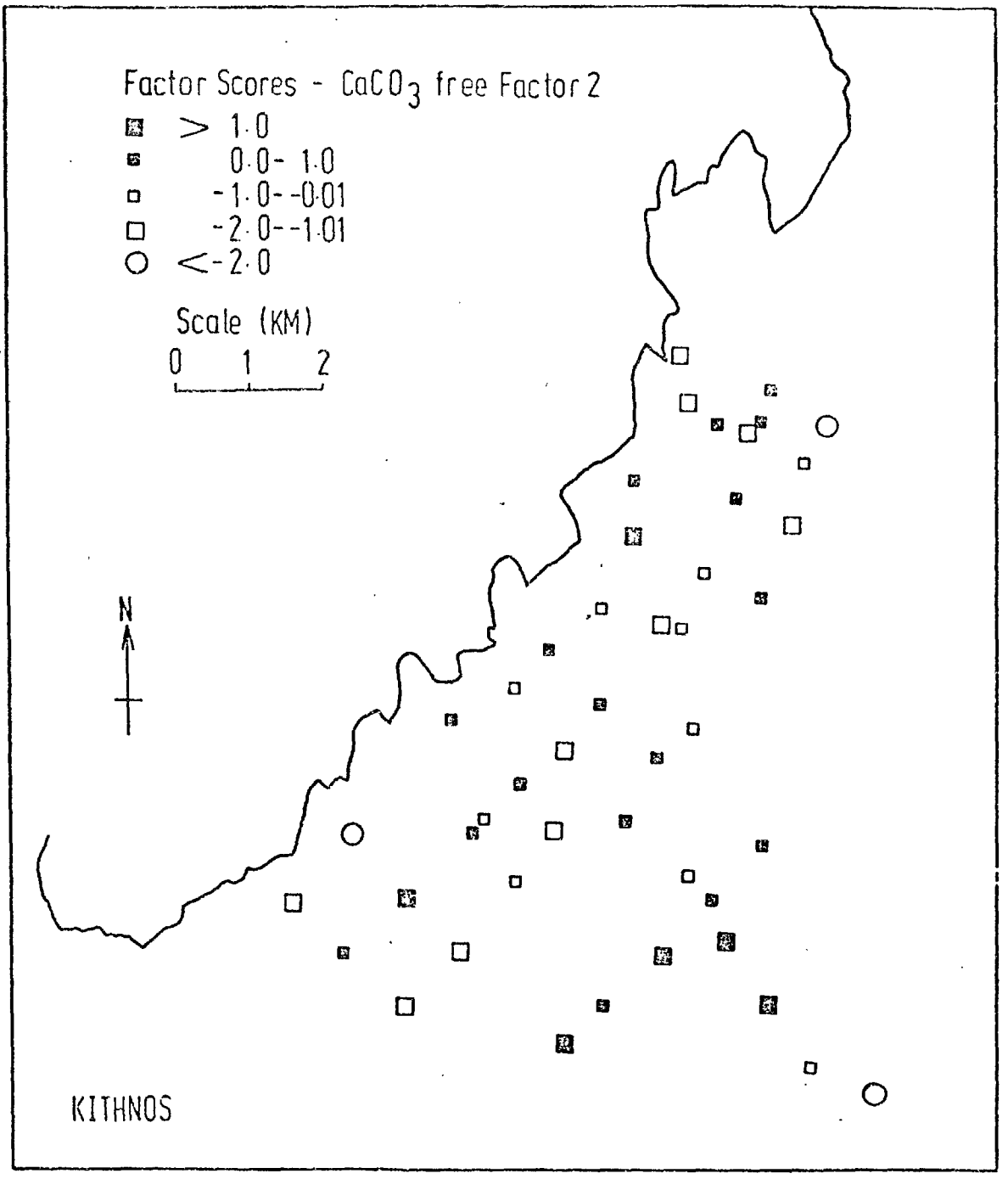


Figure 2.26 Distribution of factor scores - $CaCO_3$ free Factor 2.

detrital components are not the sole contributor of this element to the sediment composition. Unlike other elements mainly held in the detrital fraction of the sediments (e.g. Al, Ti), Fe has only a moderate loading on carbonate-free factor 2 (table 6). Instead, it is moderately loaded on the 'oxide' factor (i.e. $CaCO_3$- free factor 1). From examination of the scatter plots of Mn and Fe against Al (figures 2.27 and 2.28) it is evident that the bioclastic sands (II) are enriched in both elements relative to Al. In contrast, there is a considerable enrichment of Mn in the calcareous muds but no apparent enrichment in iron. Thus Fe is only partly associated with the 'oxide' factor.

There are several possibilities that might account for the apparent enrichment of Fe in the bioclastic sands (II). First of all, it may occur as an iron 'oxide' in a similar fashion to Fe on other shelves of the world (see e.g. Hirst, 1962a; Summerhayes, 1972; Calvert, 1976). At Kithnos, the absence of Fe enrichment in the calcareous muds suggests that if the iron is in the 'oxide' form it is not associated with modern accumulations of manganese 'oxides'. Instead, it may have formed in a relict environment. This is certainly a possibility as iron oxide staining on grains are a common feature of relict sediments, including those from other parts of the Mediterranean (Caulet, 1972; Leclaire, 1972). A critical point, however, is whether the iron 'oxide' would be at least partly soluble in the acetic acid as suggested by Chester and Hughes% (1966) and as found in sediments studied elsewhere (see e.g. Hirst, 1962b; and Summerhayes, 1972). In the sample from the bioclastic sands (II) leached by acetic acid (sample 416) there is a substantial excess of Fe (reflected in an Fe/Al ratio of 1.17 compared to an approximate average of 0.80 - table 4) but none appears to be soluble in acetic acid (table 4), indicating perhaps that an alternative explanation for the behaviour of Fe should be sought.

A second possibility is that mineralogical variation in the detrital components might account for the apparent enrichment in iron. This may be true for some samples but for 416 the detrital Mg/Al ratio is not anomalous, unlike the Fe/Al ratio. Because Mg and Fe probably covary in the detrital components, mineralogical

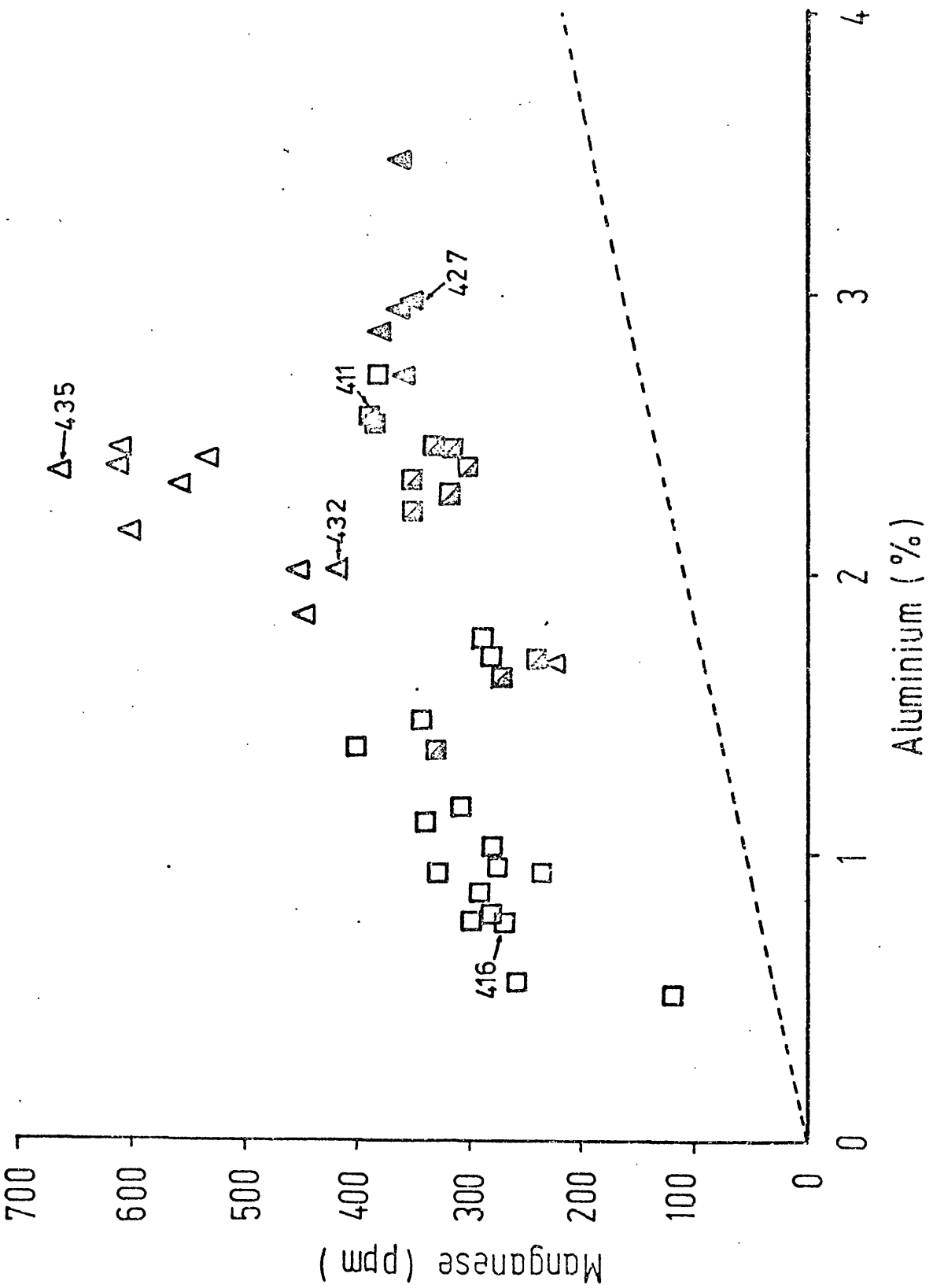


Figure 2.27 Manganese against Aluminium for Kithnos samples.(▲ detrital sands, □ bioclastic sands II, bioclastic sandsI ▨ , △ calcareous muds.) The broken line represents an approximate detrital Mn to Al regression line.

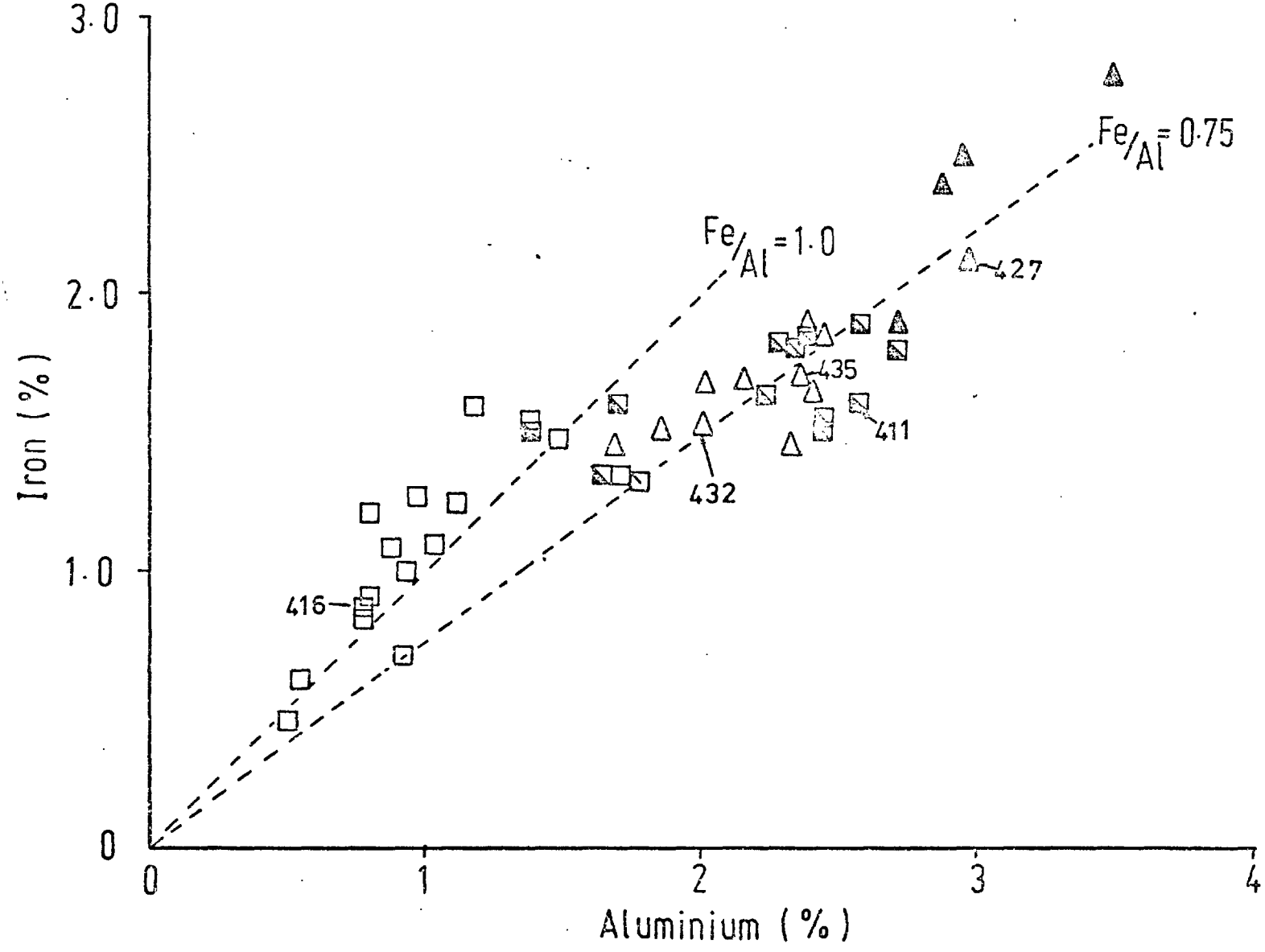


Figure 2.28 Iron against Aluminium for Kithnos samples.
(For key see figure 2.27.)

variation would also result in an anomolous Mg/Al ratio. This is not the case and so the excess of Fe in sample 416 is probably attributable to an insoluble authigenic component.

The likeliest insoluble authigenic component to account for the behaviour of Fe is the mineral observed to be infilling some foraminiferal tests in the dominantly relict bioclastic sands. Although found infilling foraminiferal tests on the Alboran Banks (Western Mediterranean - Milliman et al., 1972), glauconite is not likely to be significant here because potassium levels are too low (Hirst, 1962a) in sample 416 (table 4), but a precursor of glauconite (e.g. iron-rich chlorite or montmorillonite - see Calvert, 1976) might well be present. Authigenic iron minerals (whether 'oxide', e.g. staining on quartz feldspar grains, 'aluminosilicate' or 'silicate') may also occur in the bioclastic sands (I) but iron enrichment may be masked by the more abundant iron - and aluminium - bearing detrital components.

Furthermore, there is no apparent enrichment in minor or trace elements in sample 416 and so any association between heavy metals and the authigenic iron component is likely to be masked by more significant controls on heavy metal abundance.

In conclusion, the most important authigenic component is the manganese 'oxide' presently accumulating in the sediments and which may be scavenging Cu and Zn from solution. An authigenic iron mineral also occurs in association with the dominantly relict bioclastic sands. These iron-rich relict bioclastic sands are probably equivalent to the 'ferruginous calcarenites' occurring elsewhere in the Mediterranean between depths of 70m and the edge of the shelf (Blanc, 1968).

2.5.5b Controls on Elemental Abundance

As described, a variety of components control the abundance of the elements in Kithnos sediments. Most significant is the anti-pathetic relationship between their biogenic (calcium carbonate) and detrital components. Superimposed on the carbonate dilution control is a contribution from an authigenic manganese 'oxide' which is most important in zones of lowest sediment accumulation. A minor authigenic iron mineral is also present in the relict sands. Variation in the composition of the detrital components reflects the relative proportions of quartz, feldspar,

schist fragments and chlorite-mica group minerals.

The importance of each of these components in controlling the abundance of a particular element are summarised below.

Calcium

Over 95% of the Ca in the sediments occurs in the biogenic components. The remainder occurs mainly in the feldspars although minor amounts may be present in the chlorite-mica group. Consequently, the distribution of Ca (figure 2.3) almost entirely reflects the distribution of calcium carbonate.

Iron

Because Fe is concentrated in the detrital components, its distribution (figure 2.15) mainly reflects the relative proportions of the detrital and biogenous components. Within the detrital components it is mainly controlled by the abundance of the chlorite-mica group but an additional authigenic iron mineral is present in the relict sands. This is thought to be in the form of iron-rich aluminosilicate infillings of Foraminifera tests but may include iron 'oxides'.

Aluminium

Aluminium occurs in both the feldspars and the chlorite-mica group and thus the main control on its abundance in the bulk sediment is dilution by the biogenous components. Within the detrital components abundance is controlled by the relative proportions of quartz and the Al-bearing feldspars and/or chlorite-mica group.

Titanium

Titanium follows Al very closely and is probably controlled by similar components. There is no evidence for discrete Ti-bearing heavy minerals.

Magnesium

The distribution of Mg reflects a dual control (figure 2.17). It is a major constituent of both the carbonate and the chlorite-mica group components.

Manganese

Although a significant amount of Mn is held in the detrital fraction of the sediment, most Mn occurs as an 'oxide' (or hydroxide), either as dispersed particles or as coatings on grains of carbonate or detrital material. Most samples appear to include some 'oxide' Mn but it is most abundant in the zones

of lowest sediment accumulation (i.e. the bioclastic sands II and the offshore calcareous muds).

Copper

Studies on the detrital fraction of the sediments suggest that Cu is fairly evenly divided between the detrital and non-detrital fractions. Detrital Cu appears to follow the relative abundance of the chlorite-mica group.

A strong 'oxide' association for the non-detrital Cu may be caused by the scavenging ability of the manganese 'oxides' but adsorption on detrital particles is also a possibility. Furthermore, the non-detrital copper may not be solely hydrogenous (see Chester and Hughes, 1966) because, at these low levels, it is possible that a significant proportion of the non-detrital Cu may reside in the carbonate minerals.

Zinc

Controls on the abundance of Zn are very similar to those on Cu except that the detrital contribution is greater. Once again, the hydrogenous Zn appears to be associated with the oxide component but could equally be adsorbed onto the finer particles accumulating in the offshore zone.

Nickel

Nickel is almost entirely contained within the detrital components, and in the chlorite-mica group in particular.

Chromium

Control on the chromium abundance is very similar to Ni. Cr is concentrated mainly in the chlorite-mica component of the sediments.

Lead

Like the other heavy metals, detrital Pb is concentrated in the chlorite-mica group of minerals. However, it appears that Pb has an important non-detrital component. Unfortunately, analytical precision for Pb in the bulk analyses is poor at the low concentrations present. Consequently, much of the apparent non-detrital fraction could be a result of the limitations of the analytical method used.

2.5.5c The Dispersion Pathways of the Heavy Metals

One of the aims of this investigation is to establish the

dispersion pathways of heavy metals into the sediments. In this section the discussion is limited to the dispersion pathways found off Kithnos and an examination of the wider implications of dispersion pathways to applied geochemical investigations on the continental shelf is left to a later chapter(8.2).

The dispersion of heavy metals at Kithnos appears to be mainly a function of the dispersal of solid particles of the chlorite-mica group of minerals - either as discrete particles or as constituent minerals within schist fragments. 'Modern' dispersal from the adjacent land-mass is mainly restricted to discrete particles because coarser schist fragments would tend to be trapped within the nearshore zone. It can be in two forms:-

(1) Very fine sand and coarse silts derived from the erosion of the adjacent land mass are flushed or wind-blown into the marine environment to accumulate as lobes of detrital muddy sand offshore of their landward source. Further dispersal is limited.

(2) Fine silt and clay sized particles bypass the shelf and accumulate in the offshore zone. Minerals in these deposits are likely to have been derived from a much wider source area and reflect regional provenance rather than local.

A certain amount of <u>in-situ</u> weathering of rocks cropping-out on the seafloor may be a further source of 'modern' material. Although it is thought to be a minor component at most, the actual significance of this potential source is not known.

Dispersion pathways of material derived during previous sedimentary environments are much more complex. Sources could include, for example:-

(1) alluvial material derived from a relict drainage system;

(2) sub-serial erosion at a lower stand of the sea-level;

and (3) shoreline erosion at a lower stand of the sea-level.

The situation may be complicated by present-day <u>in situ</u> weathering. More importantly, matters are made much worse by the redistribution by, or since, the last transgression of the shoreline. Sources and, therefore, dispersion pathways of material not derived from 'modern' processes are extremely difficult to pinpoint.

To summarise, the dispersion pathways of the heavy metals are controlled by the dispersion of detrital chlorite-mica minerals which, in turn, is a function of both the modern and ancient sedimentological history of the Kithnos continental margin.

2.5.6 Summary of major conclusions

(1) A combination of selective leaching and the treatment of the analytical data by R-mode factor analysis reveals that the following points govern the sediment composition at Kithnos:-

(a) dilution of detrital minerals by bioclastic calcium carbonate;

(b) an authigenic manganese oxide which is important in zones of low sediment accumulation rate;

(c) mineralogical variability within the detrital fraction (i.e. the relative abundance of quartz, feldspar, and the chlorite-mica group);

(d) a minor authigenic iron mineral in relict sediments;

and (e) an undetermined non-detrital phase, strongly associated with the manganese oxide component.

(2) Dispersion pathways of the heavy metals are controlled by the dispersion of chlorite-mica minerals which, in turn, reflect the sedimentological history of the area.

CHAPTER 3 SERIFOS

3.1 INTRODUCTION

The island of Serifos lies in the southern Aegean Sea, 110km to the south east of Athens (figure 1.1), and is a member of the Cyclades Group, with Kithnos directly opposite to the north-west. Ktenas (1917) first described the geology of Serifos. The northern half of the island, adjacent to the survey area, consists of micaceous schists with the occasional outcrop of marble.

Base metals and silver occur in rocks to the north of the island (Zachos and Maratos, 1965, based on Marinos 1951). Accordingly, samples were taken offshore from streams draining the mineralised area. Only sixteen samples were obtained, solely to assess the general levels of element abundance in the sediments. Sample locations are shown in figure 3.1. The survey area covers about 12km^2 between depths of 80m and 200m.

3.2 SHELF TOPOGRAPHY

The survey area can be divided into two distinct topographic zones. At depths shallower than 160m the shelf is characterised by a series of ridges and valleys trending approximately NNW and which appear to be extensions of the onshore topography (figure 3.1). The sides of the ridges are steep and irregular but the valley floor to the west of the central ridge is flat-lying. In contrast, the seafloor to the east of the central ridge is highly irregular, perhaps due to coralline algal reef development.

Seawards of the 160m isobath and to the north (i.e. towards Kithnos) the sea floor is flat lying and is probably continuous with a similar zone off Kithnos.

To the east and west, however, shelf breaks are prominent at 175m and 162m respectively.

3.3 NATURE AND DISTRIBUTION OF SEDIMENT

3.3.1 Sediment Distribution

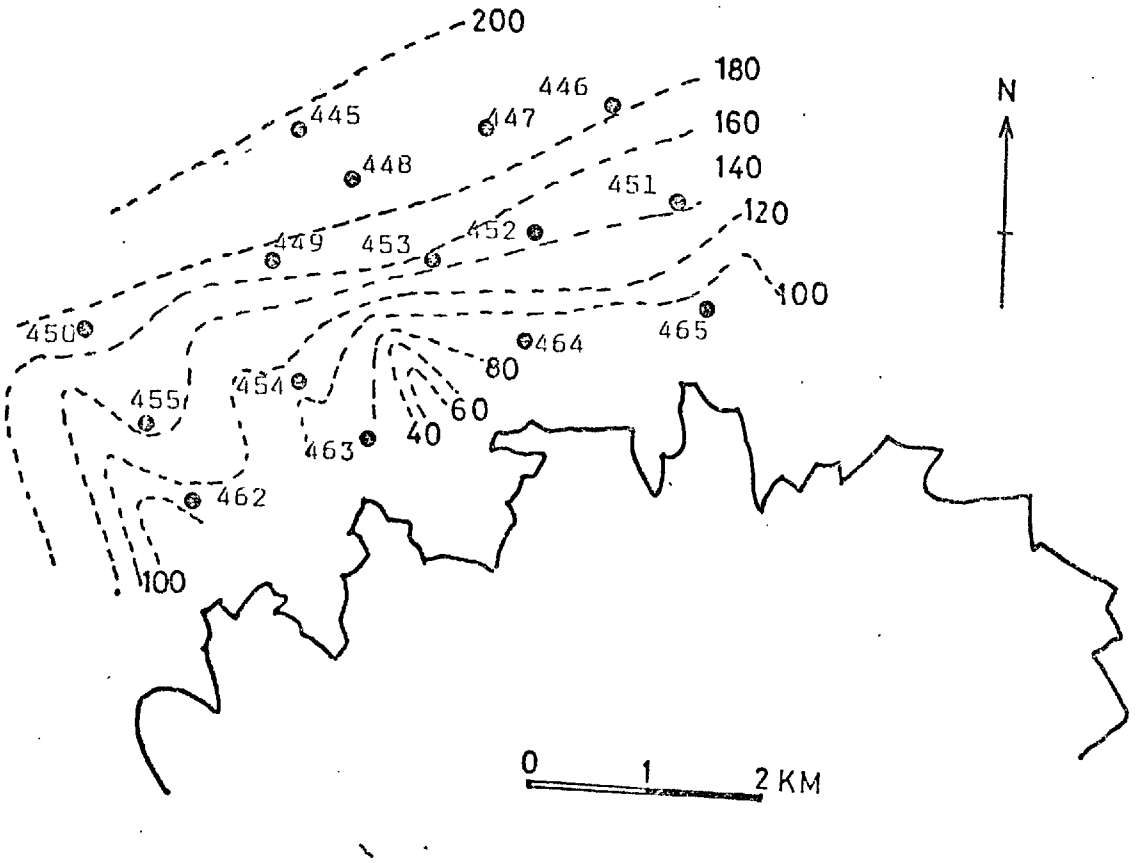


Figure 3.1 SERIFOS - Sample locations and bathymetry.

Sediment samples are initially classified according to the scheme of Folk (1954), based on the relative proportions of gravel, sand, and mud. Figure 3.2 shows the distribution of the major groups.

In the western half of the survey area the 160m isobath effectively separates the sandy muds offshore from dominantly sandy sediments nearshore. A threefold zonation exists in the eastern half where the 180m isobath separates muds offshore from the sands, whereas the 120m isobath marks the boundary between the sands and the gravels nearer to shore.

The sandy muds are light tan to brown oozes, very similar in appearance to the offshore muds found at Kithnos. These deposits form a broadly continuous belt between the two islands at depths greater than 170m.

Sample 455 is distinctly sandy and occurs on the flank of a ridge in the western half of the survey area (figure 3.1). Abundant angular detrital fragments occur in the coarse sand fraction and Foraminifera in the finer fractions.

The muddy sands are highly variable. Samples 462, 463 and 454 contain small amounts of gravel (mainly coralline algal debris) and abundant fine angular detritus. Recent organic debris is found in sample 463, closest to the shore (figure 3.1) Samples 446, 449, and 452 are from further offshore and include a larger mud fraction. The coarse components in these samples consist of a variety of biodetritus including algal and bryozoan fragments. Worm tubes often cover these fragments, suggesting considerable residence time on the seafloor. Foraminifera are abundant in the finer sand fractions. Finally, sample 453 has a larger gravel component than the other sands. Algal and bryozoan fragments are the most conspicious components.

The gravels found in the eastern half of the survey area consist of pieces of branching and encrusting coralline algae. The irregular seafloor in the vicinity is consistent with algal reef development.

3.3.2 Calcium Carbonate

In section 2.3.3 the relationship between total Ca and $CaCO_3$ is examined and it is concluded that a $CaCO_3$ value based

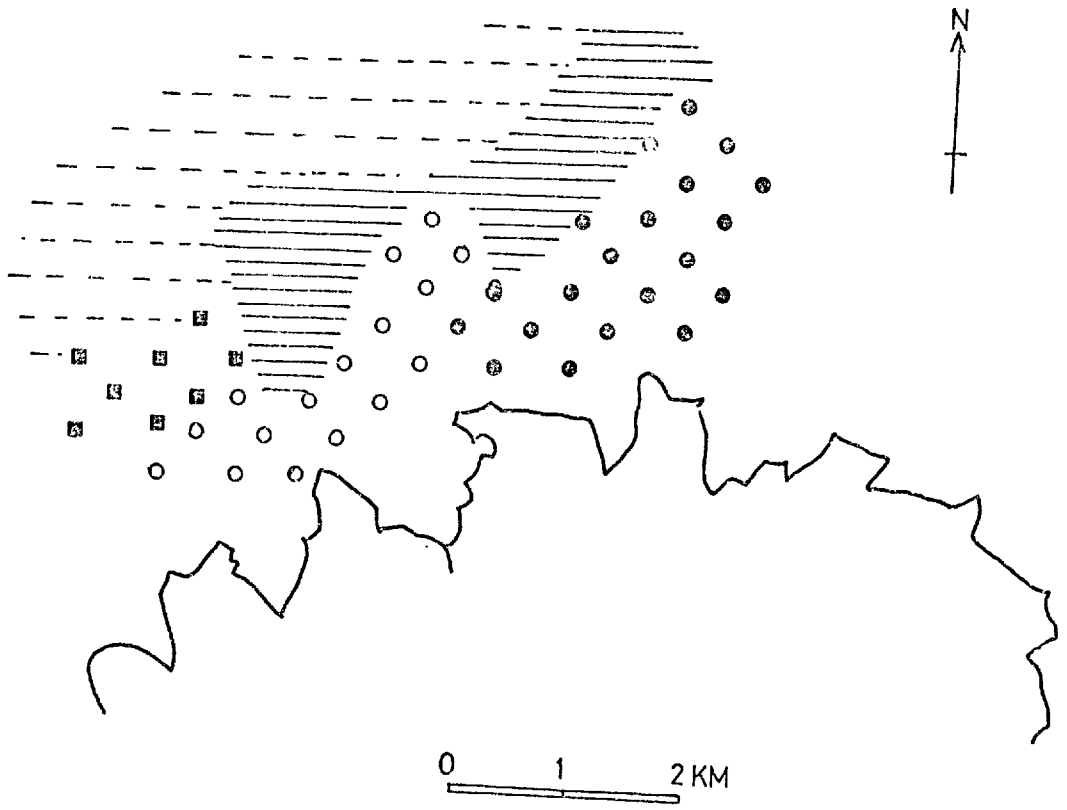


Figure 3.2 Distribution of sediment types (Folk,1954). (See figure 2.7 for key)

on the total Ca (i.e. Ca_{tot} CO_3) is a reasonable estimate of the biodetrital calcium carbonate (in the minus 2mm fraction) in areas where detrital calcium carbonate is a minor component. Such is the case at Serifos where, like Kithnos, metamorphic schists are the major rock type to crop out.

Total Ca ranges between 17.8% and 31.0%, representing an equivalent Ca_{tot} CO_3 range between 44.4 and 77.5% (N.B. Ca_{tot} CO_3 overestimates bioclastic $CaCO_3$ by about 1% to 2%). Figure 3.3 charts the distribution of Ca_{tot} and, not surprisingly, Ca_{tot} is highest in the skeletal rich sands. Lowest Ca_{tot} abundances are found in samples with a conspicuous angular detrital component (e.g. 454, 462, 463). Sandy muds found offshore have moderate Ca_{tot} levels.

3.3.3 Reclassification of the Sediments

Most of the geochemical and textural analyses of the sediments are based on that fraction of the samples finer than 2mm. Consequently, the Folk classification is not appropriate and so samples from Serifos are reclassified according to the relative proportions of Ca_{tot} (representing $CaCO_3$) and mud (figure 3.4). It is considered that this simple classification scheme provides a convenient means of comparing the sedimentological and geochemical characteristics of sediments from all areas (see section 2.3.4).

Detrital sands are confined to the valley floor in the nearshore zone of the western half of the survey area (figure 3.4). The nearshore sediments rich in algal and skeletal debris in the eastern half of the survey area are classified as bioclastic sands (II). Both of the bioclastic sands (I) lie on the 140m isobath at the eastern and western extremities of the survey area. Finally, the most abundant sediment type, the calcareous muds, are found seawards of the 160m isobath.

3.3.4 Mineralogy of the Detrital Fraction

Only the acetic-acid residues from two samples (445 and 448) were analysed by X-ray diffraction techniques. Based on these limited data, the major mineral assemblage is similar to that found at Kithnos, namely quartz, feldspar, chlorite and micaceous minerals, which is consistent with a local geology dominated by

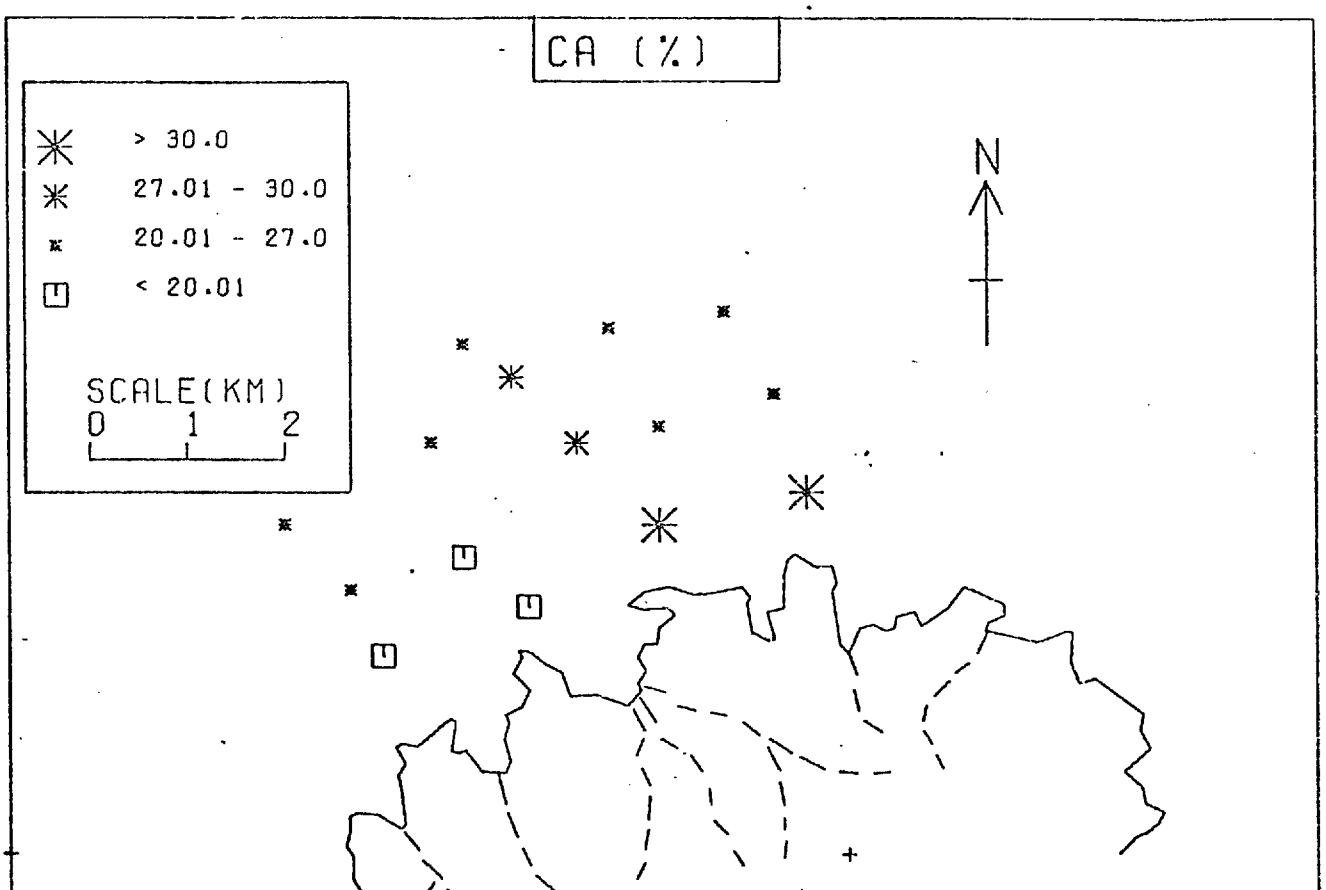


Figure 3.3 Distribution of total calcium.

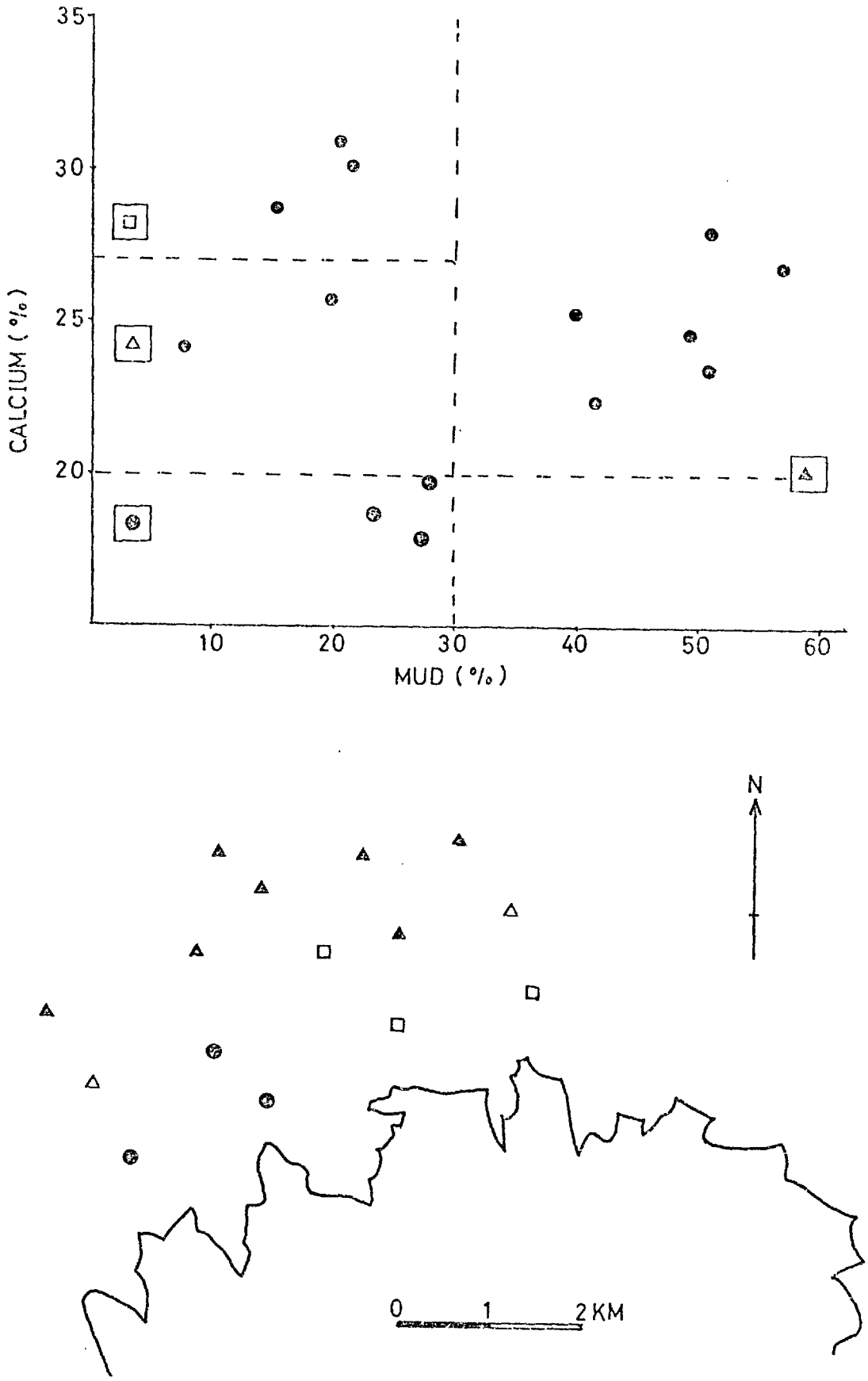


Figure 3.4 Distribution of sediment types reclassified on the basis of the relative proportions of total calcium (representing $CaCO_3$) and mud.(● detrital sands, △ bioclastic sandsI, ▲ bioclastic sandsII, ▲ calcareous muds.)

micaceous schists (Ktenas, 1917).

3.4 TEXTURAL ANALYSIS AND SHELF SEDIMENTATION

3.4.1 Sediment Texture

The textural characteristics of sediments from Serifos and Kithnos are compared in this section. Table 2 gives the average and range of the median size, mean size and sorting of the main sediment types found at Serifos and figure 3.5 shows the relationship between mean size and sorting. The detrital sands, the calcareous muds, and the bioclastic sands (II) are texturally similar to the same groups found at Kithnos (table 2). Only the two samples classified at bioclastic sands (I) are dissimilar, being coarser and more poorly sorted.

Like the Kithnos samples (section 2.4.4), the textural parameters of the Serifos samples are mainly governed by the relative proportions of sand and mud. For a given major sand mode, a decrease in the amount of mud is matched by an increase in the mean size and an improved sorting coefficient. A direct relationship between mean size and sorting coefficient results (see figure 2.13 and 3.5). Because the proportions of mud decreases in the order calcareous muds > detrital sands > bioclastic sands (I) > bioclastic sands (II), mean size increases and sorting improves in the same order.

Superimposed on this trend, however, is variation in the mean size and sorting caused by variation in the size of the major sand modes. For a given amount of mud, as the major sand mode increases in size the mean size will increase but the sorting coefficient will also increase (i.e. worsen). In the sand samples, the coarsest sand modes generally consist of bioclastic material and occur in the bioclastic sands (II); whereas, the finest sand modes tend to consist of detrital material. Therefore, for a given amount of mud, the mean size tends to decrease and the sorting improves in the order:-

bioclastic sand (II) > bioclastic sands (I) > detrital sands (see section 2.4.4).

Bioclastic sands (I) at Serifos are an exception to the general trends because the coarse component is detrital rather

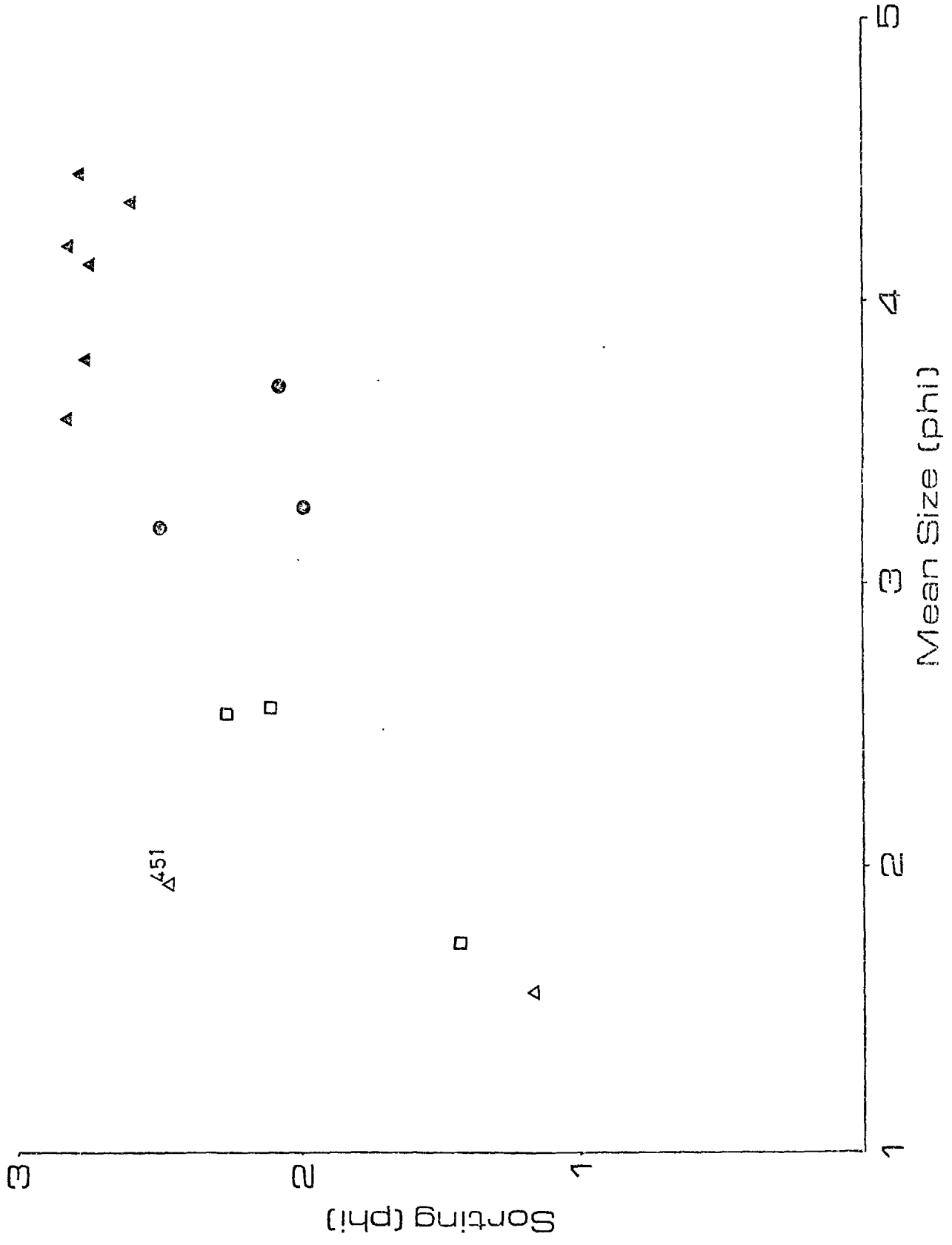


Figure 3.5 SERIFOS - Mean size against sorting.(For key see figure 3.4.)

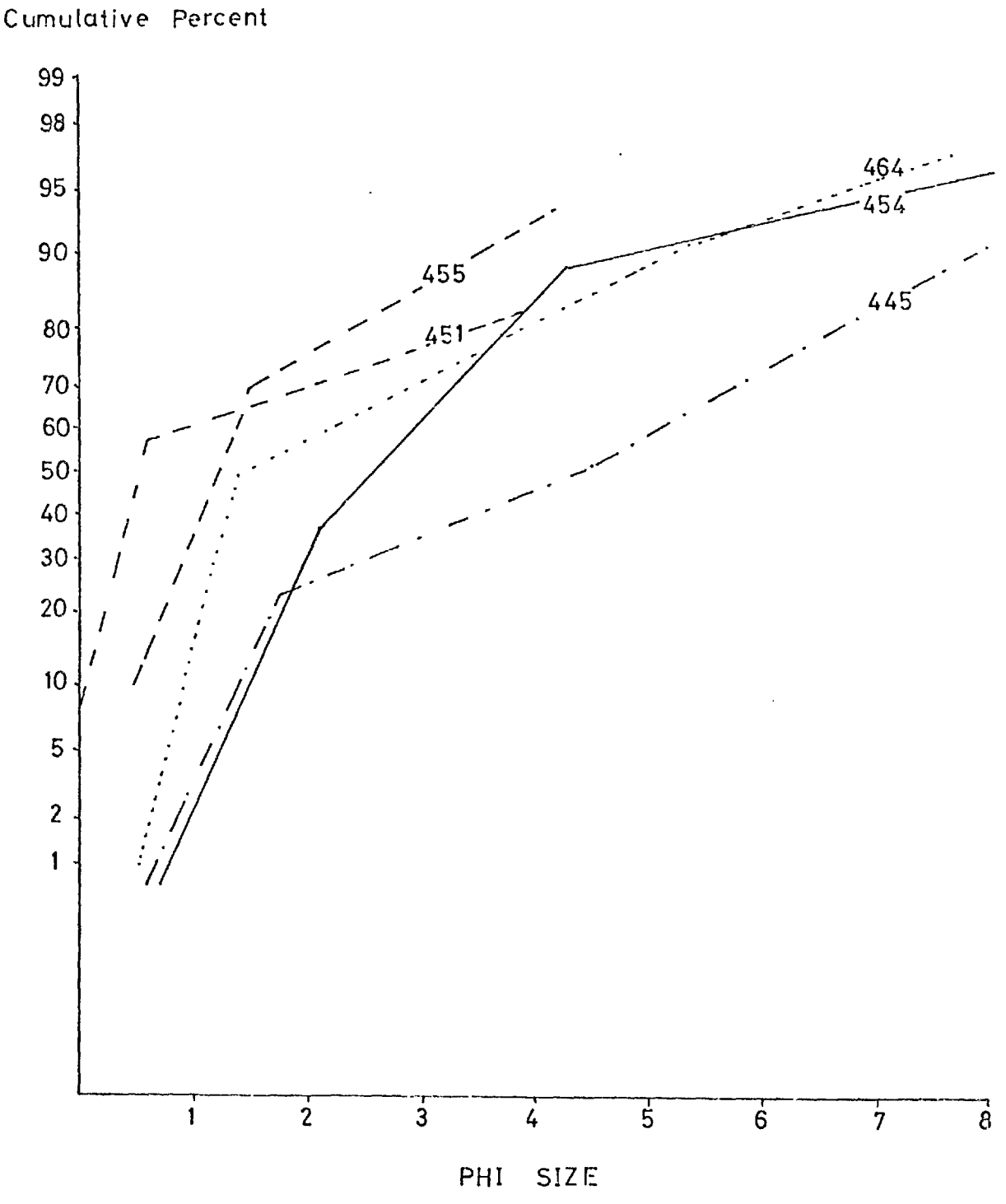


Figure 3.6 Cumulative probability grain size curves for selected samples from Serifos.

than calcareous. Where the coarse sand component is rich in detrital material (e.g. samples 400 and 401 at Kithnos - section 2.4.4) the relative proportions of calcium carbonate and mud cause the sample to be classified as a bioclastic sand (I) even though it has textural characteristics closer to the bioclastic sands (II). This accounts for the anomalous sorting and mean size for the two samples (451 and 455) classified as bioclastic sand (I) at Serifos.

Comparison of cumulative curves of samples from Kithnos and Serifos (c.f. figure 2.7 and 3.6) confirm the impression that the sediments found in both areas are similar.

To conclude, in general the textural characteristics of sediments off Serifos are similar to those off Kithnos.

3.4.2 Shelf Sedimentation

Broad similarities between the nature and distribution of sediments found off the islands of Kithnos and Serifos are noted in the preceding discussion.

To summarize:-

(1) the biodetrital components are similar in that the coarse fragments are dominantly coralline algae and bryozoan, whereas the fine fragments are mainly Foraminifera;

(2) coarse, angular detrital fragments occur in relict sands and very fine, angular detrital material in the near-shore detrital sands;

(3) although only based on limited evidence, it seems that the mineral assemblages within the detrital fraction from each area (i.e. Kithnos and Serifos) are similar, but the relative proportions of individual minerals change from sample to sample;

(4) the distribution of facies is similar in both areas - a belt of calcareous muds lie offshore of bioclastic and detrital sands;

and (5) the textural characteristics of the main facies are similar.

It follows that the processes that govern the distribution of the sediment facies in both areas are similar. These processes are considered in detail in section 2.4.5 and are only summarised below. The main elements and the resultant facies

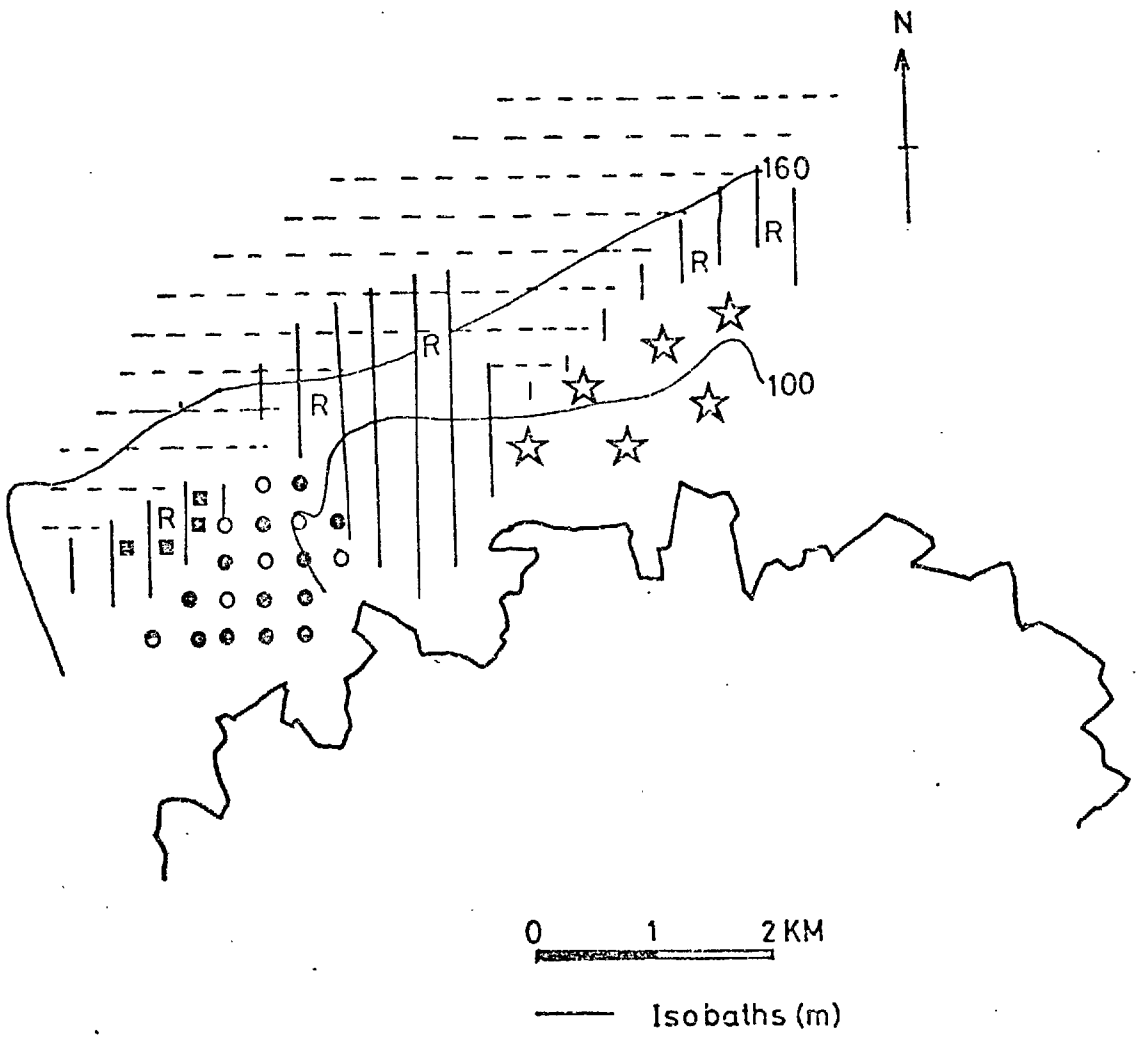


Figure 3.7 Distribution of sedimentary facies off Serifos.(For key see figure 2.14)

are shown in figure 3.7.

(1) Approximately 20,000B.P. the sea-level stood at about 120m below the present level. Coarse sediments (i.e. bioclastic sands) found seaward of the 120m isobath are considered to consist of dominantly relict material;

(2) subsequently, as the sea-level rapidly transgressed, sediments were redistributed to form a transgressive sand sheet;

(3) as the rate of transgression decreased, the shelf entered an allochthonous phase of sedimentation and modern muds began to accumulate in the more quiescent zones offshore and detrital very fine sands and silts in the nearshore zone. The latter mixed with the transgressive sand sheet, probably through bioturbation or current action;

(4) calcareous algal reef communities may have acted as sources of biodetritus throughout the Holocene transgression.

3.5 GEOCHEMISTRY OF SEDIMENTS

3.5.1 Introduction

The main reasons for determining the chemical composition of the samples from Serifos are to assess the general levels of selected elements and to reveal any unusual influence on the composition of the sediments.

Because the geochemistry of the sediments off Kithnos have been studied in some detail (see section 2.5), the discussion in this section is limited, mainly, to a comparison between the geochemistry of the major sediment types from Serifos and Kithnos.

3.5.2 Bulk Composition

The average and range of concentration for each element and sediment type is given in table 3. It is evident that the overall composition of the major sediment types are similar in both areas.

At Kithnos, elemental abundance patterns appear to follow particular trends. Elements concentrated in the detrital fraction (e.g. Fe, Al, Cr) tend to decrease in average abundance in the order:-

detrital sands > calcareous muds > bioclastic sands (I) >

bioclastic sands (II) because of an increasing dilution by $CaCO_3$. At Serifos a similar pattern is evident for Fe, Al and Cr which suggests that these elements are similarly concentrated in the detrital fraction. As an example of the distribution of one of these elements, figure 3.8 charts the distribution of Cr. Highest values (85ppm) occur in the near-shore lobe of detrital sands and moderate values (66ppm-85ppm) in the calcareous muds.

Other elements may be concentrated dominantly in the detrital fraction but tend to be slightly more abundant in the calcareous muds, either because the elements are preferentially concentrated in the silt and clay sized particles, or because the elements have a limited hydrogenous component associated with the slow accumulation rates of the calcareous muds. The order of abundance is generally:- calcareous muds $\overset{\text{slight}}{>}$ detrital sands> bioclastic sands (I)> bioclastic sands (II). At Serifos, Ti, Cu, Zn and Ni follow this pattern. As an example, the distribution of one of these elements, Ni, is shown in figure 3.9.

Elements with a major hydrogenous component in samples from areas of low accumulation rate have an abundance sequence similar to the previous group, but the enrichment in the calcareous muds is much more pronounced. Manganese is the major element in this category (see figure 3.10).

Other groups of elements include those held dominantly in the carbonate fraction (e.g. Ca - figure 3.3) and the order of average abundance is the reverse of that found for the first group (the detrital alements); elements which occur in both the carbonate and detrital fraction (e.g. Mg) and for which average abundances are similar throughout the major sediment types; and Pb which is generally low with little apparent trend except to say that it is lowest in the bioclastic sands (II).

3.5.3 Composition of the Detrital Fraction

Four samples (445, 449, 455, 464), selected to represent a traverse offshore (see figure 3.1), were leached with acetic acid and the residues analysed. The partial composition of the detrital fraction of each sample is given in table 4, together with the percentage contribution that the detrital fraction

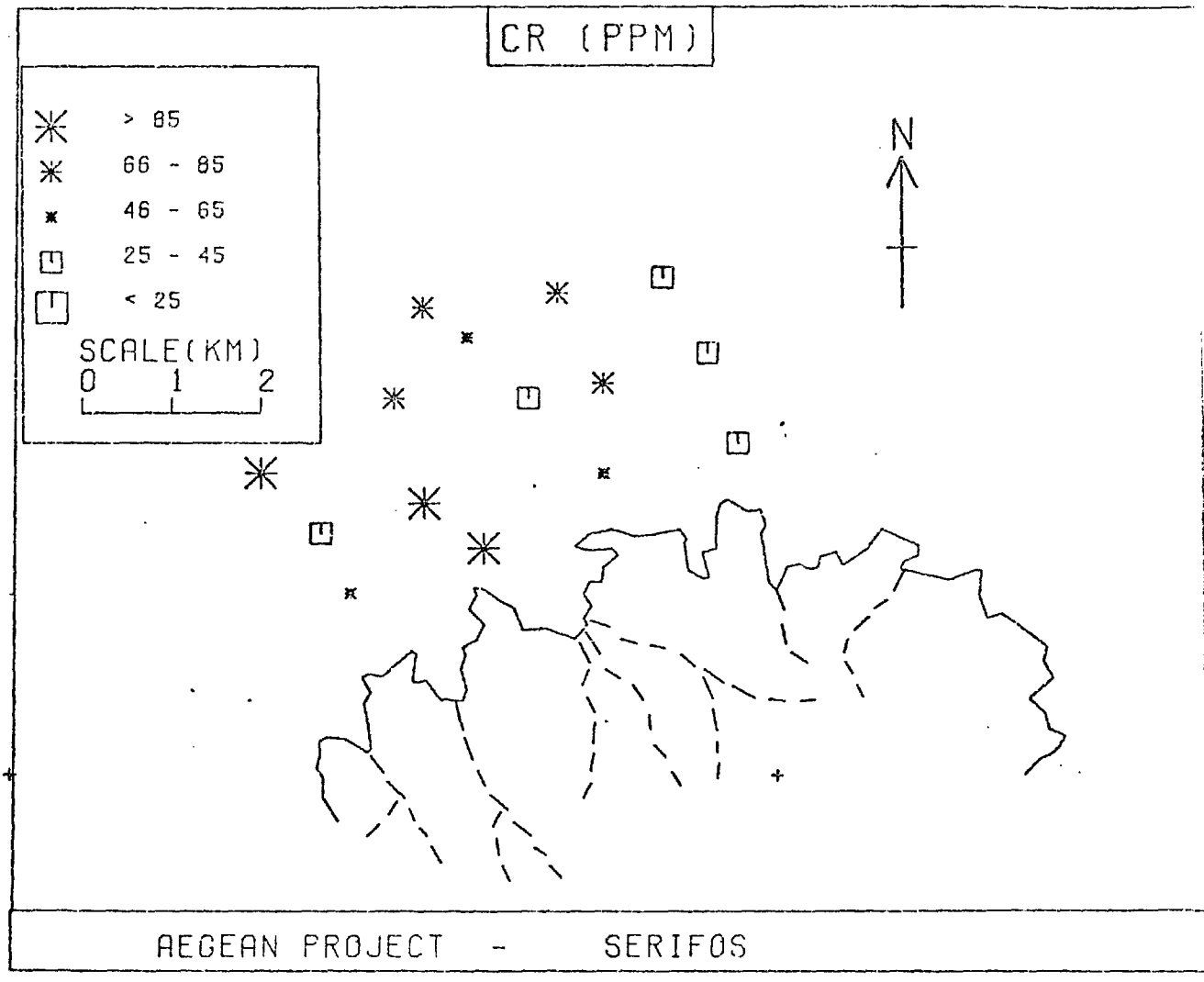


Figure 3.8 Distribution of Chromium.

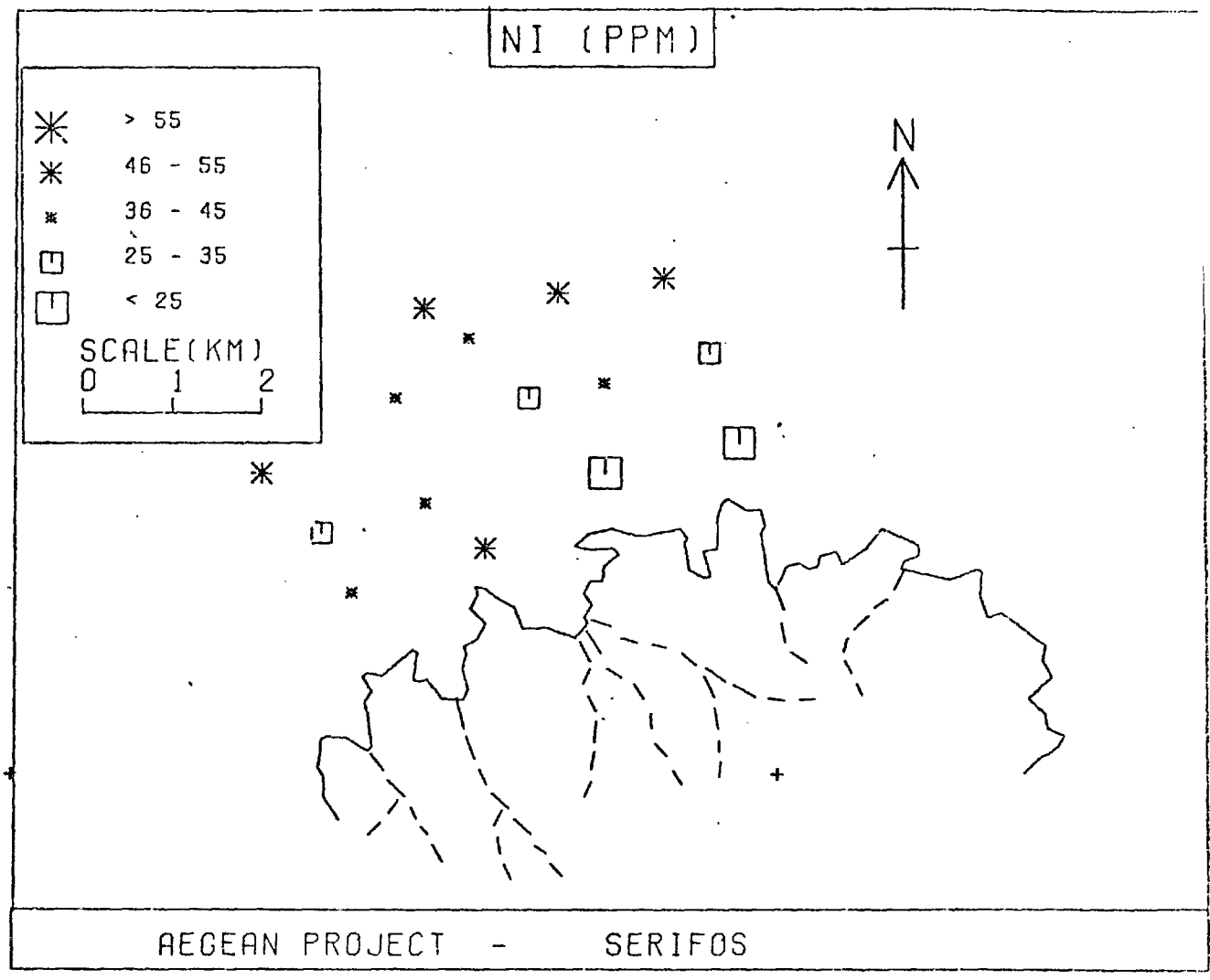


Figure 3.9 Distribution of Nickel.

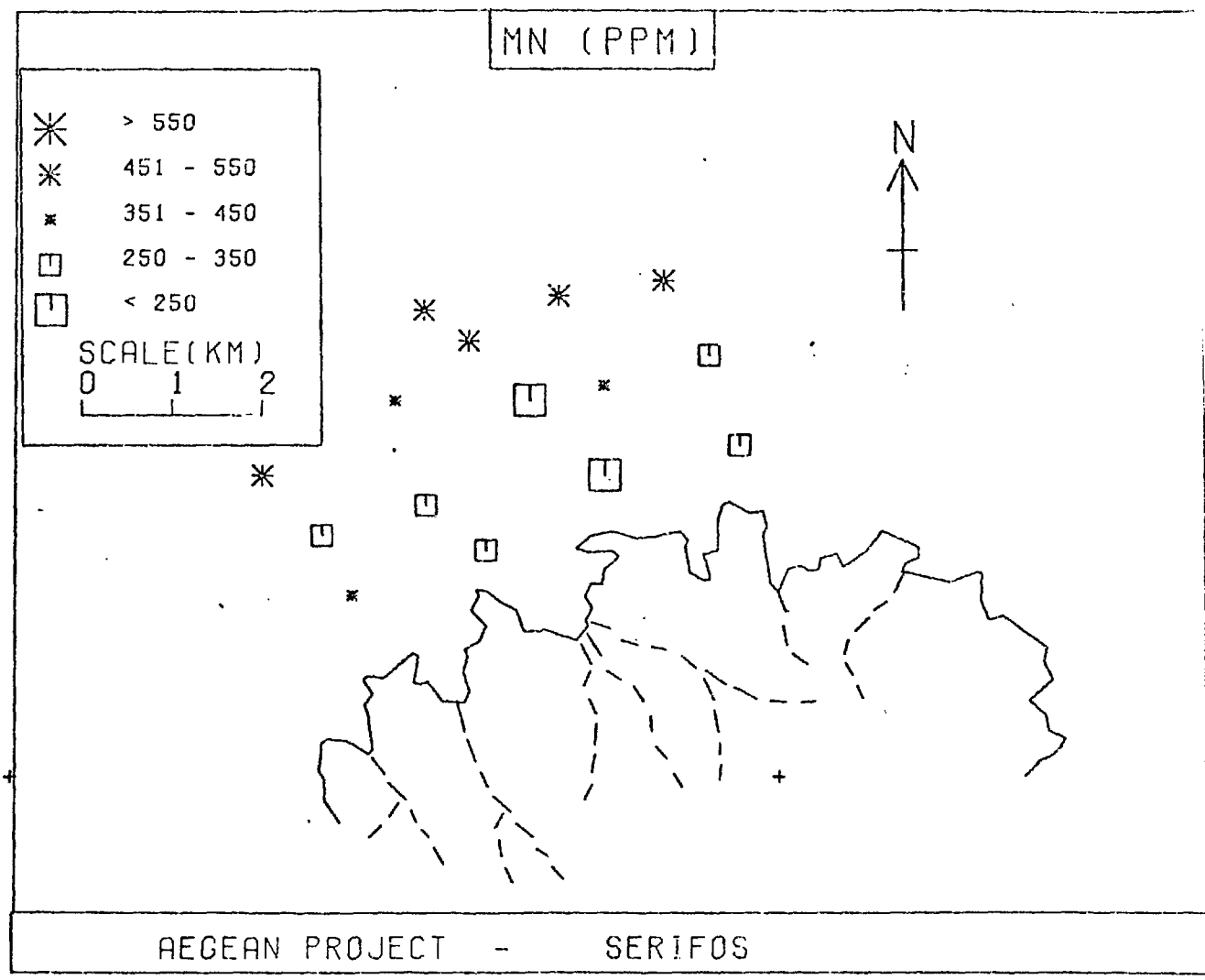


Figure 3.10 Distribution of Manganese.

makes to the total abundance of each element.

In most cases element abundances for the four samples are similar to each other and to samples 432 and 435 from Kithnos (table 4). Once again, Cr and Ni are enriched compared to detrital sediments from other parts of the world (table 4).

The contribution made by the detrital fractions to the total abundances (see table 4) also follows a similar pattern to that found at Kithnos. The detrital contribution decreases in the order:-

Fe, Al, Ni, Cr (About 80%-100%)>Ti (about 70%)>Zn, Cu (about 60%-70%)>Pb, Mn (between 30%-50%)>Mg (between 20%-40%) > Ca (about 1%-2%).

3.5.4 General Discussion and Conclusions

From the preceding discussion it is apparent that both the composition of sediments from Kithnos and Serifos and the main factors controlling element abundance are similar. The main factors are the degree of dilution of the detrital fraction by the carbonate fraction; the accumulation of hydrogenous manganese oxides in areas of low sediment accumulation rate offshore; and the enrichment of certain elements in the finer sediments, either through association with the hydrogenous fraction or enrichment in the fine-grained detritus.

At Kithnos, however, two further factors have some influence, namely mineralogical variation in the detrital fraction, especially quartz and feldspar dilution and authigenic iron enrichment in relict sediments. The variability in the composition of the detrital fraction of the samples from Kithnos is attributed mainly to variation in the relative proportions of quartz, feldspar and the chlorite-mica group of minerals. At Serifos, this variability is not as apparent (table 4) but this could reflect limited sampling rather than the absence of mineralogical variability.

In contrast, iron enrichment in certain relict sediments may exist in samples off Serifos. In section 2.5.5a an Fe/Al ratio in excess of 1.00 is considered to be an indicator of Fe enrichment, providing the Mg/Al remains about the same as in other samples. This is the case for the detrital fraction of 453 (table 4). Both the Fe/Al value and the concentration of detrital Fe (about 7%) is close to that of sample 416 (from Kithnos), in which the excess

iron is thought to be due to the formation of authigenic iron minerals within the biodetrital component of relict sediments.

The distribution of samples with a bulk Fe/Al ratio in excess of 1.00 are shown on figure 3.11. All are bioclastic sands and occur seawards of the 120m isobath. All are likely, therefore, to have an important relict biodetrital component.

To summarize, the geochemical controls on the abundance of elements at Serifos are similar to those described in detail at Kithnos.

3.6 GENERAL SUMMARY

(1) The nature and distribution of sediments at Serifos are similar to those described in detail at Kithnos, except that the well sorted bioclastic sands (I) have not been found.

(2) The general levels of element abundance are similar to those found at Kithnos, as are the factors controlling the composition of the sediments.

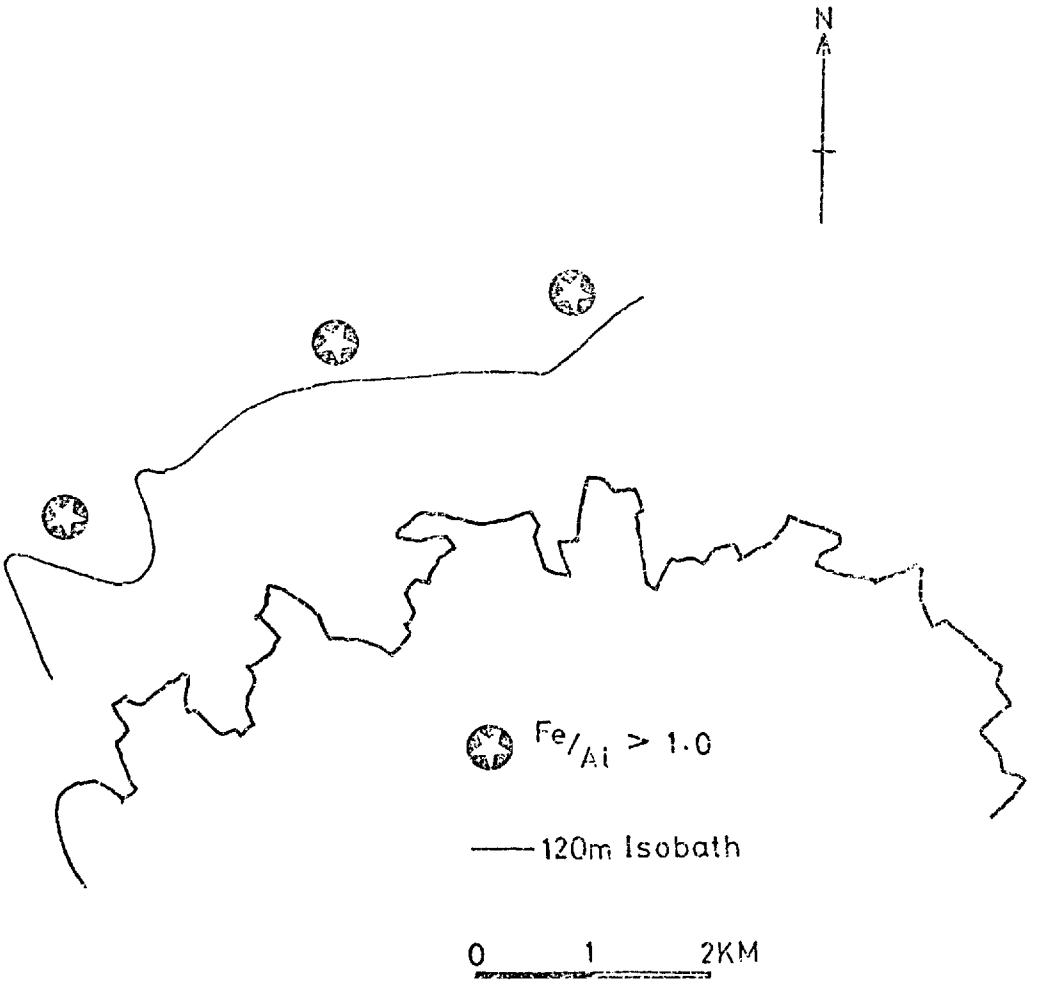


Figure 3.11 Distribution of samples with an Fe/Al ratio greater than 1.00.

CHAPTER 4 ANDROS

4.1 INTRODUCTION

Andros is the most northerly of the Cyclades islands and lies almost 100km due east of Athens (figure 1.1). Marinos (1954) describes Andros as belonging to the Attica-Cyclades metamorphic massif. The north-western part of the island, adjacent to the survey area, consists of micaceous schists with the occasional outcrop of marble and, on high ground, peridotite. Marbles are the major rock type to crop out on the peninsula forming the landward extension of the southern boundary of the survey area.

According to the metallogenetic map of Greece (Zachos and Maratos, 1965), chromite is associated with the peridotite outcrops. The deposits are limited in extent and so it is not anticipated that major chromite deposits occur offshore. Enhanced levels of Ni and Cr, reflecting an ultrabasic provenance, may be present in the sediments, however, and this would distinguish Andros from the other areas surveyed.

The 20 sample locations are shown in figure 4.1 covering an area of about 12km^2 off the north-west coast of Andros.

4.2 SHELF TOPOGRAPHY

A prominent shelf break between depths of 130m and 140m, approximately 2km from the shoreline, divides the survey area into two distinct zones (figure 4.1). Seawards of the shelf break the depths plunge rapidly to depths in excess of 350m. Off Kithnos and Serifos, in contrast, the depths rarely exceed 200m. A submarine canyon intersects the continental slope in the centre of the survey area.

Depths shoal more gradually shorewards of the shelf break but the isobaths are irregular due to the series of small ridges trending perpendicular to the shoreline. Flanks of these ridges can be steep and irregular, particularly the ridge to the west of sample 362 (figure 4.1).

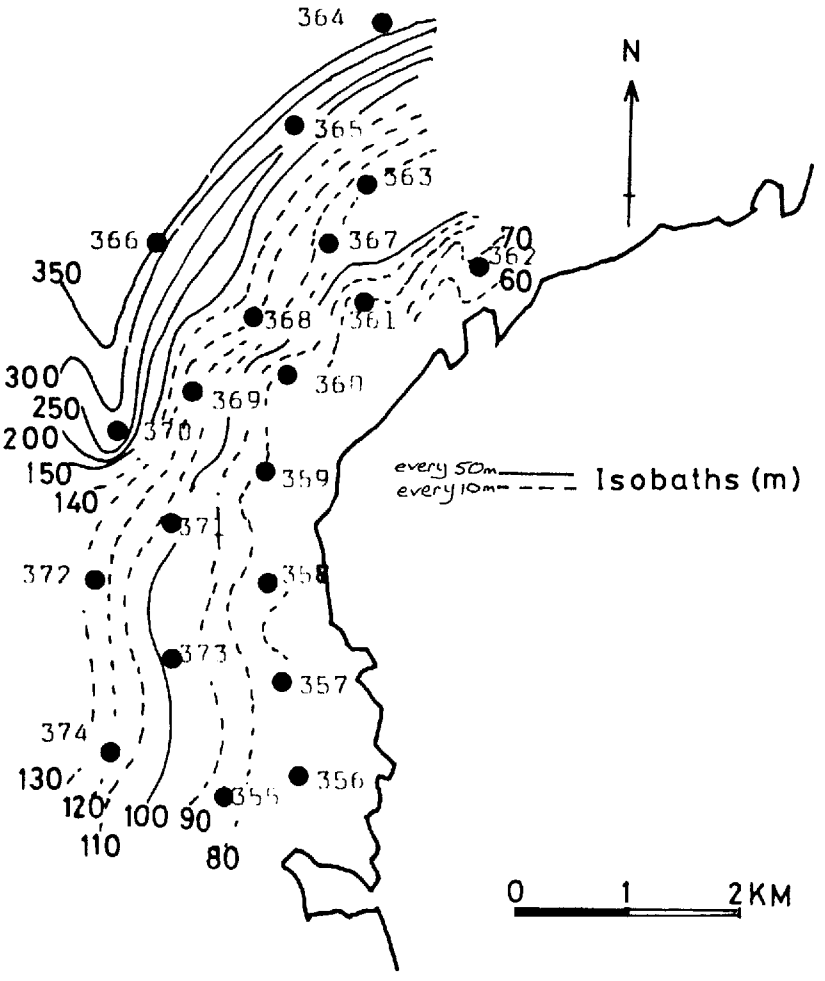


Figure 4.1 ANDROS - sample locations and bathymetry.

4.3. NATURE AND DISTRIBUTION OF THE SEDIMENTS

4.3.1 Sediment Distribution

A scheme based on the relative proportions of mud, sand, and gravel (Folk, 1954) is used initially to classify the sediment samples. Figure 4.2 charts the distribution of the major groups.

Sandy gravels cover most of the shelf and consist mainly of algal nodules set in a "maerl" matrix. The nodules are characteristic of current swept platforms (Blanc, 1972; and see section 2.3.2) and are more abundant than the branching andencrusting forms of coralline algae found at Kithnos and Serifos. Detrital fragments are also evident in the course sand fraction of several samples (particularly 368 and 355). The mud component of the gravels gradually increases seawards with the 100m isobath effectively seperating the muddy sandy gravels from the sandy gravels.

Sands form a north-westwards trending strip of sediment between the gravel plateaux (figure 4.2). Bioclastic components range between "maerl" and mixed assemblages, with molluscan (including gastropods), bryozoan and algal fragments making up the latter. Detrital components, including fragments of schist, quartz, and feldspar, are particularly abundant in the sands nearest the shore. Like the gravels, the mud component of the sands increases markedly seawards of the 100m isobath. Muds are found only in the deepest waters offshore.

An interesting feature of the mud distribution (see figure 4.3) is the gradual increase in the mud component seawards. Unlike Serifos and Kithnos, there is little evidence for the accumulation of muddy sand lobes between the depths of 90m and 120m, but this could simply reflect limitations of the sample spacing in relation to shelf and deposit morphology. Off Andros, the shelf width between the 90m and 120m isobaths is narrower than off either Kithnos or Serifos. Consequently, the size of the deposits may also be smaller and less likely, therefore, to be sampled, especially as the sample spacing used is similar in all areas.

Deposits from depths less than 90m have not been sampled off Kithnos or Serifos because sampling aboard the R.R.S SHACKLETON was restricted to further than ½km from the shoreline. Off Andros, such deposits generally contain less than 10% mud. Either very little fine-grained material is supplied to the shelf from erosion on land,

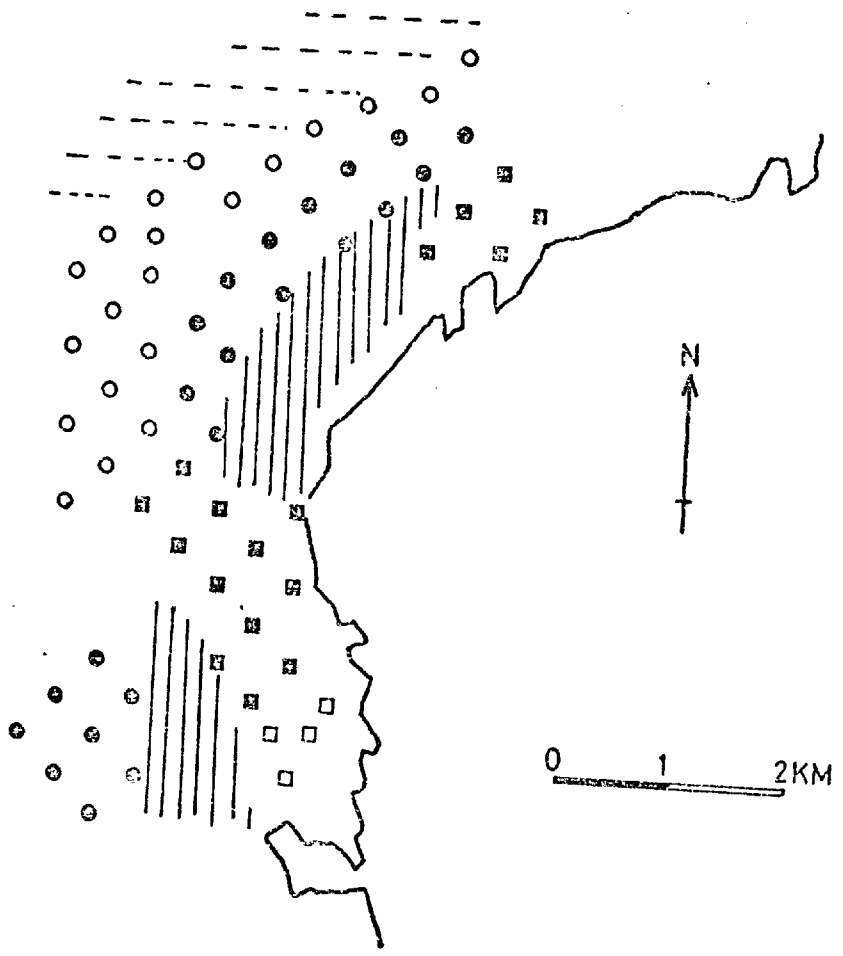


Figure 4.2 ANDROS - Distribution of main sediment types (Folk,1954).(For key see figure 2.2.)

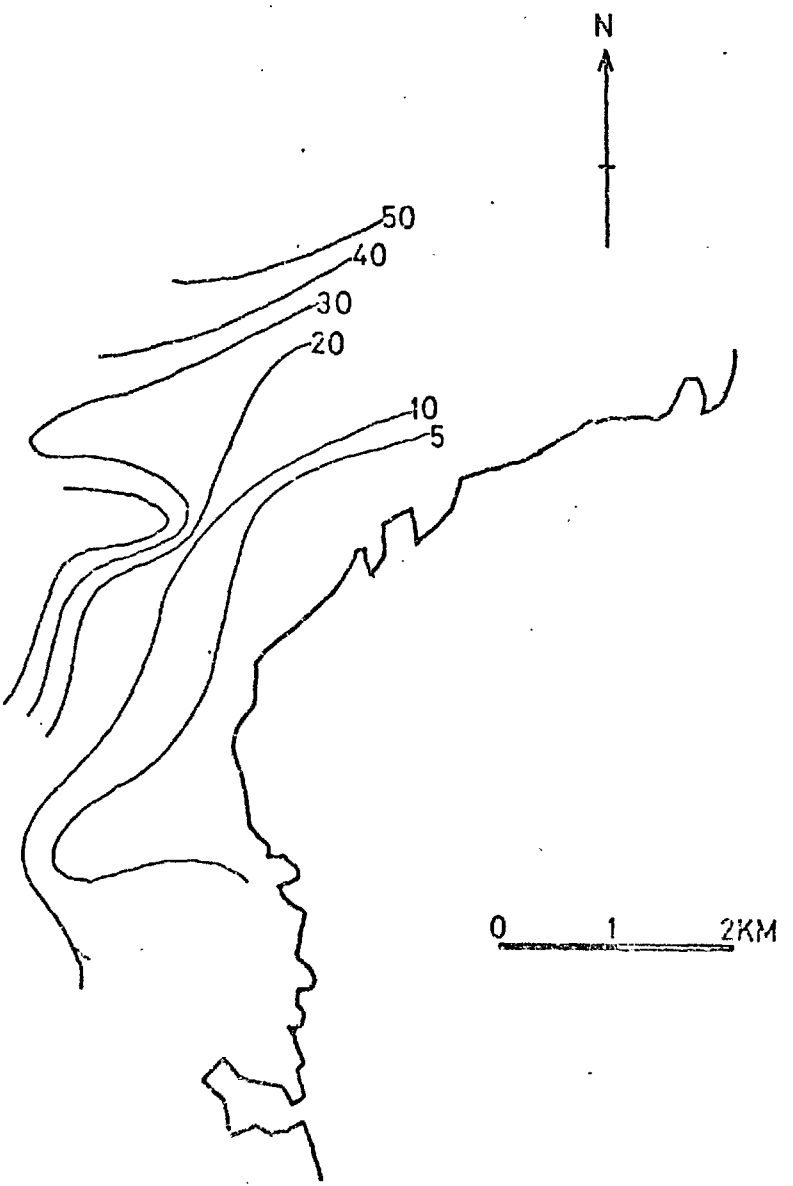


Figure 4.3 ANDROS - distribution of mud (% of the fraction finer than 2mm.)

or the energy regime on the shelf is sufficiently high to prevent accumulation of fine-grained sediments. The dominance of algal nodules over other forms of coralline algae is certainly testimony to a certain amount of current activity which could be related to the flow of surface water from the Black Sea to the Mediterranean passing through the straits separating the north-easterly islands of the Cyclades (see Lacombe and Tchernia, 1972). According to the Mediterranean Pilot for the area (vol IV), current velocities of upto 7knots (setting to the south) have been experienced in the straits separating Andros from the island of Euboea. Furthermore, the Andros survey area may well be more exposed to the prevailing winds than either Serifos or Kithnos (which provide mutual shelter for each other). Storm waves, therefore, may be more effective in preventing fine-grained sediment accumulation on the shelf.

4.3.2 Calcium Carbonate

As before, total Ca is used as an estimate of the biodetrital $CaCO_3$ in the minus 2mm fraction of sediments (see section 2.3.3). According to table 1, Ca_{tot} CO_3 overestimates acetic-acid soluble $CaCO_3$ by only 2% at the worst.

Dolomitic marbles crop out adjacent to the survey area and the erosion of these outcrops may supply a certain amount of detrital $CaCO_3$ to the sediments. The significance of the detrital $CaCO_3$ is difficult to estimate but preliminary evidence indicates that it is, at most, a minor component. Dolomitic marbles are only partially leached by acetic acid, therefore there should be evidence of carbonate minerals in the acetic-acid residues. Neither Ca enrichment (section 4.4.2) nor the presence of carbonate minerals (section 4.3.3) is indicated by the analysis of the limited number of acetic-acid residues.

Total Ca ranges between 10.6% and 32.1% representing an approximate $CaCO_3$ range between 24% and 77%. Figure 4.4 shows the distribution of Ca_{tot}. As might be expected, the greatest amounts of $CaCO_3$ are found in the bioclastic matrix of the coralline algal gravel deposits (c.f. figures 4.4 and 4.2). In contrast, the minus 2mm fraction of the sands between the two areas of coralline algae generally contain less than 50% $CaCO_3$. Sample 366 (figure 4.1) is also a detrital sand but from a depth exceeding 350m.

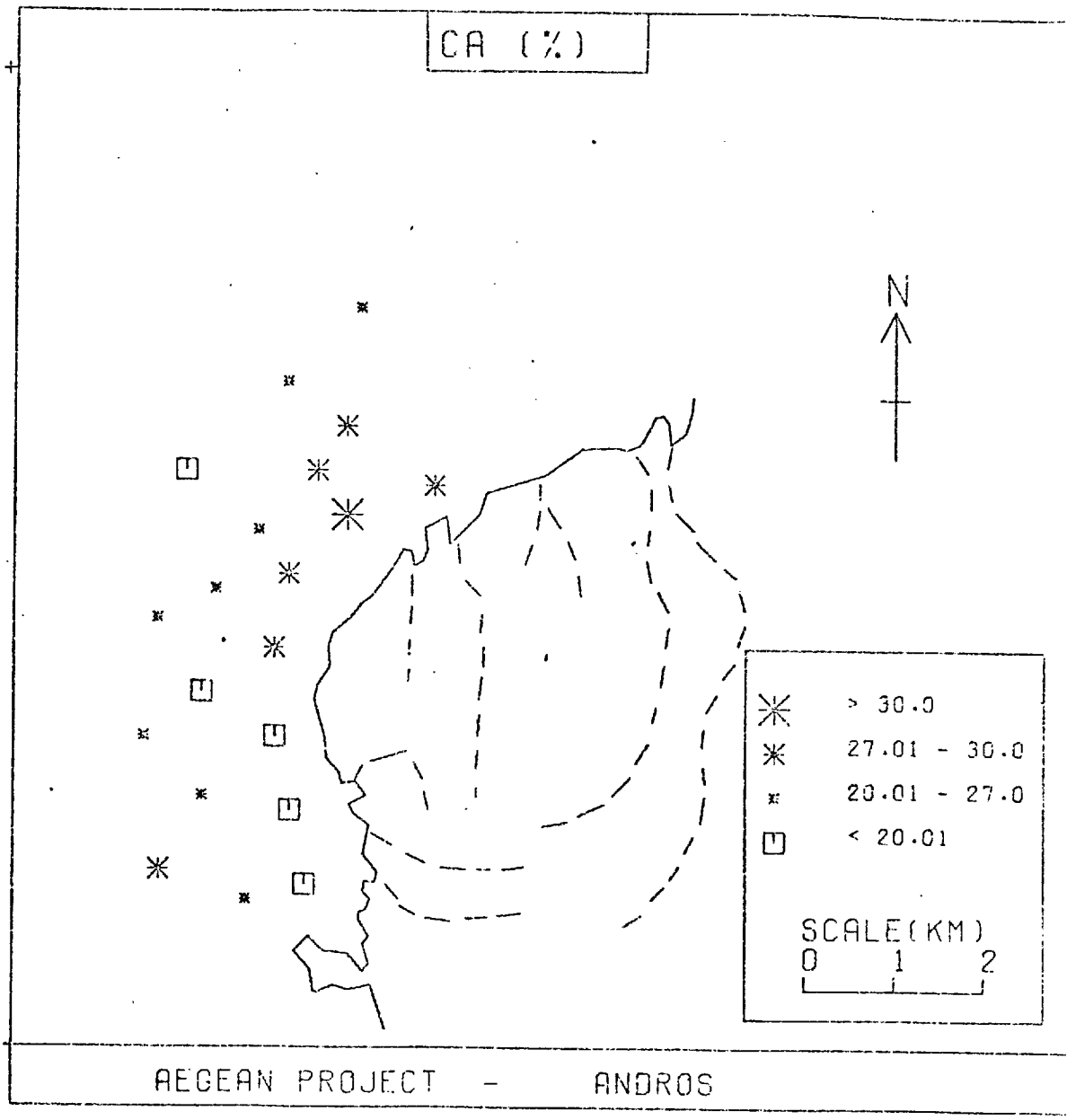


Figure 4.4 Distribution of total calcium.

4.3.3 Mineralogy of the Detrital Fraction

On the limited basis of X.R.D. analyses of the acetic-acid residues of samples 357 (from the nearshore sands) and 365 (an offshore mud) the mineral assemblages appear to be similar to those found off Kithnos and Serifos, namely quartz, feldspar, and the chlorite-mica group. A noteable difference, however, is found in the detrital sand, sample 357. Feldspar is much more abundant than in detrital sands elsewhere and this is consistent with the sandy texture of this sample compared to the muddier detrital sands from Serifos or Kithnos.

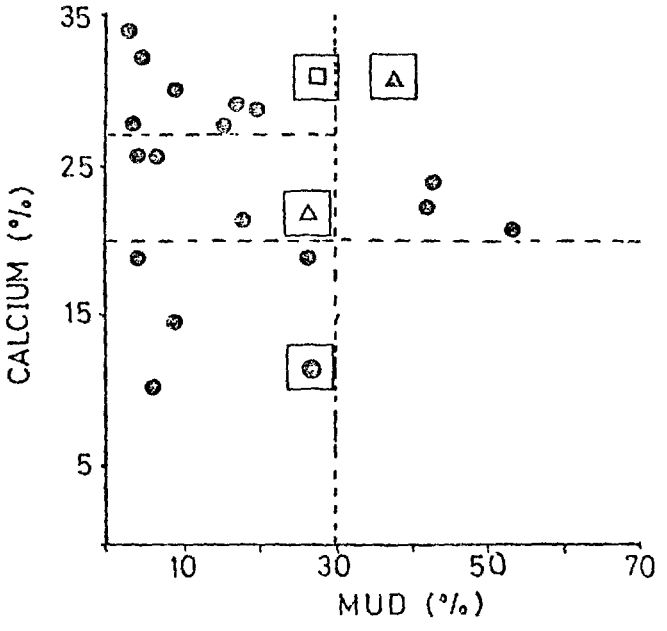
4.3.4 Re-Classification of Sediments

The Folk scheme of classification is not appropriate for much of the following discussion because the gravel fraction of the sediment samples is excluded from the textural and geochemical analyses. Instead, a simple scheme based on the relative proportion of calcium (as an estimate of $CaCO_3$) and mud is used. The details of this classification scheme are given in section 2.3.4.

Figure 4.5 charts the distribution of the major sediment types. Between the two zones of bioclastic sands (II) (the matrix of the algal nodule deposits) lies a strip of detrital sand. The bioclastic sands (I) tend to be transitional deposits between the bioclastic sands (II) and the detrital sands. Calcareous muds are restricted to water depths greater than about 135m.

4.3.5 Sediment Texture

The average and range of the median size, mean size, and sorting are given in table 2 and the relationship between mean size and sorting is shown in figure 4.6. An effect of the limited mud accumulation on the Andros continental shelf is apparent when comparing the textural characteristics of the sandy sediment types from Kithnos and Andros. For each sediment type (excluding the calcareous muds) the average median and mean size is coarser and the sorting better (lower value) at Andros than at Kithnos because the textural parameters are governed mainly by the relative proportions of sand and mud (see section 2.4.4 and 3.4). For a given major sand mode, a decrease in the amount of mud is matched



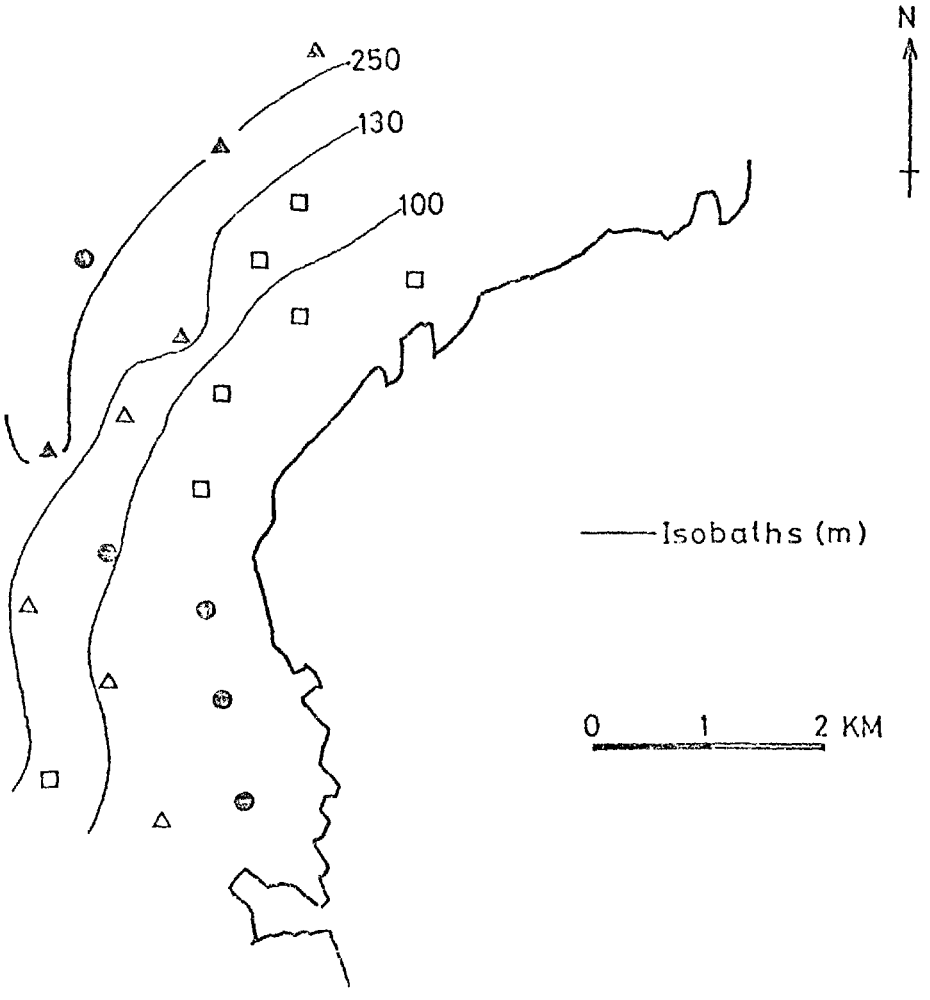


Figure 3.5 ARDROS - distribution of reclassified sediment types. (The key is the same as in figure 3.4.)

Figure 4.6 ANDROS - mean size against sorting. See figure 3.4 for key.

by an increase in the median and mean size and an improvement in the sorting coefficient. Consequently, the detrital sands (except 366) are texturally closer to the well-sorted bioclastic sands (I) (e.g. 412) (compare figures 4.6 and 2.13) from Kithnos. Nevertheless, the sand fractions of samples 356 and 357 from close to the shoreline (see figure 4.1), have similar cumulative curves to the detrital sands from Kithnos (figure 4.7) and contain a large proportion of very fine sand (equivalent to sub-population 2) of possibly modern origin. On the other hand, sample 358 is mainly a medium detrital sand (figure 4.7) and is more likely, therefore, to be part of a transgressive sand sheet. Finally, because it has a larger mud component, the deep-water detrital sand, sample 366, is texturally similar to the detrital sands from Kithnos and Serifos. Its position at the base of the slope and close to the submarine canyon (figure 4.1) suggests that the sand component might be derived from some form of downslope movement, but exactly when it is difficult to say. A large 'excess Mn' component in this sample (section 4.4.4) indicates, however, that accummulation rates are low at the present time and so the sample may represent a relict turbidite sand subsequently admixed with a modern mud component and associated manganese oxides.

Bioclastic sands (I) from Andros are texturally similar to those bioclastic sands (I) from Kithnos with a low mud component (compare figure 4.6 and 2.13). One bioclastic sand (I) (369), like sample 451 from Serifos (figure 3.5), is texturally similar to the coarser bioclastic sands (II) with a moderate mud component because detrital fragments constitute a larger proportion of the coarse sand (see section 3.3.6).

Only one calcareous mud from Andros (368) was analysed texturally and this sample is similar to the marginal calcareous muds found at Kithnos (e.g. 418) (compare figure 4.6 and 2.13).

4.3.6 Shelf Sedimentation

Sediment samples from the continental shelf off the north-western coast of Andros are distinguished from their counterparts from Kithnos and Serifos by generally containing less mud, particularly the detrital sands from close to the shoreline. Because of a higher energy regime, it seems that mud does not accumulate on the shelf but by-passes it to accumulate

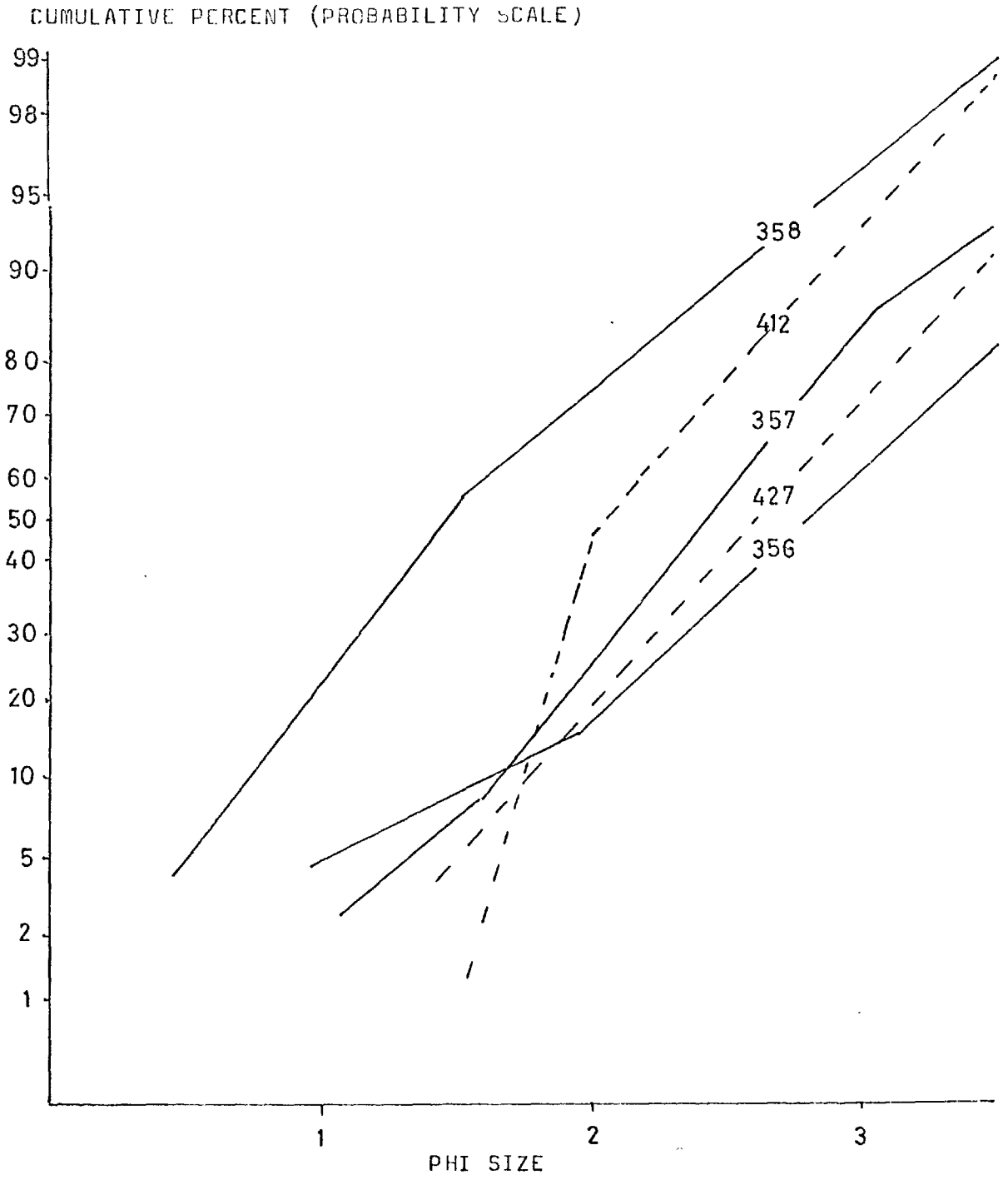


Figure 4.7 Grain size curves for selected samples from Andros and Kithnos.

in deeper water. Consequently, the modern, allochthonous component of the shelf deposits mainly comprises very fine sand. Otherwise, factors controlling the broad pattern of sediment distribution are similar to those described in previous chapters. To summarise (see figure 4.8), a transgressive sand sheet was formed by the redistribution of sediments during the rapid rise in sea-level of the Holocene transgression. Erosion of rock outcrops contributed coarse schist and other detrital fragments to the sediments. As the rate of sea-level decreased fine-grained sediments began to escape from the nearshore zone. Because of storm wave or current activity, however, only very fine sand can survive on the shelf and mud-sized material by-passes the shelf to settle in the deeper waters offshore. Throughout the Holocene, coralline algal communities contributed bioclastic material to the adjacent sediments.

4.4 GEOCHEMISTRY OF THE SEDIMENTS

4.4.1 Introduction

Geochemical investigation of sediments from Andros aims to assess the general levels of abundance and clarify the controls on the abundance of the selected elements, particularly in the context of a possible ultrabasic provenance. Much of the following discussion is based on a comparison between the geochemistry of sediments from Andros, Kithnos, and Serifos.

4.4.2 Bulk Composition

The average and range of abundance for each element and each sediment type is given in table 3.

Several features of the average partial composition of the main sediment types from Andros distinguish them from those found at Kithnos and Serifos.

(1) In the calcareous muds there is a relative enrichment of Ni (81ppm c.f. less than 50ppm) and Cr (104ppm c.f. less than 50ppm) and, to a lesser extent, Mn and Cu.

(2) In contrast, the detrital sands from Andros are depleted in Fe, Mn, Cu, Zn and Ni despite containing, on average, less diluting calcium carbonate than elsewhere.

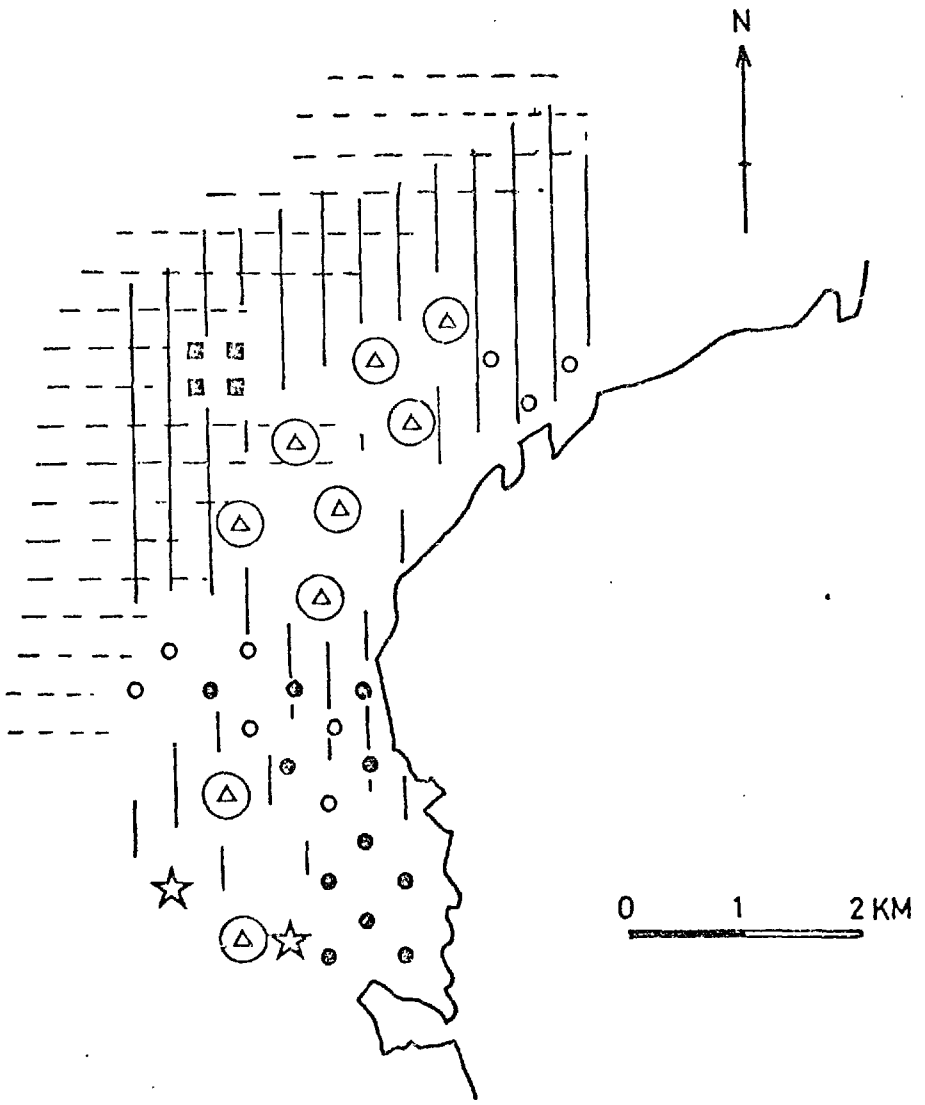


Figure 4.8 Distribution of sedimentary facies at Andros (see figure 2.14 for key).

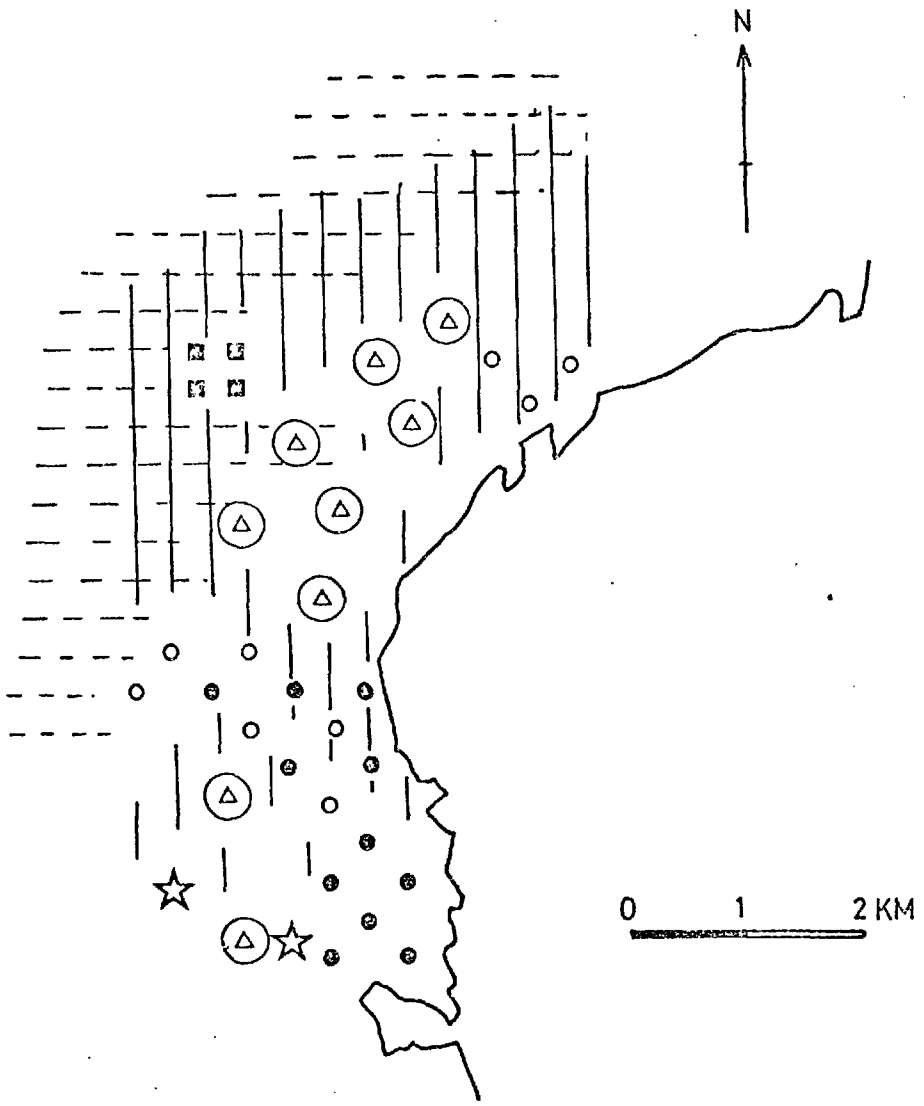


Figure 4.8 Distribution of sedimentary facies at Andros (see figure 2.14 for key).

(3) Although the average Al abundance in the detrital sands is similar at Andros the range is much larger (1.71%-4.77%).

Two major factors could account for these differences. First of all, at Andros the paucity of a fine-grained (mud) sub-population in samples from the continental shelf could partly account for the apparent depletion of Fe, Mn, Cu, Zn and Ni in the detrital sands. In the detrital fraction these elements tend to be concentrated in the "chlorite-mica" group of minerals which, in turn, tend to occur in the fine-grained sub-population. The greater range for Al in the detrital sands also suggests a wide range in the detrital mineralogy.

Secondly, the enrichment of Mn andother elements in the muds from Andros may be related to deeper depositional environments. Andros muds include samples from water depths greater than those found off either Kithnos or Serifos. Deeper environments may equate with lower sediment accumulation rates and, therefore, a larger hydrogenous Mn 'oxide' component and a greater proportion of a fine-grained detrital material. These factors could certainly account for the enrichment of Mn and Cu. Whether or not they could account for the higher levels of Ni and Cr is discussed in section 4.4.4.

Mineralogical differences in the detrital fraction of the sediments, and the significance of the hydrogenous Mn oxide component in the calcareous muds, are greater than at Kithnos or Serifos and so the trends in element abundance within survey areas observed elsewhere (e.g. section 3.5.2) no longer hold. For example, elements concentrated in the detrital fraction at Serifos (Fe, Al, Cr) decrease in average abundance in the order detrital sands > calcareous muds > bioclastic sands, reflecting simple carbonate dilution of a fairly consistent detrital mineralogy. At Andros, none of the elements follow this trend even though they are concentrated in the detrital fraction (e.g. Al).

Instead, Al, Ti, Cr and Pb follow the following trend:- detrital sands $\overset{approx}{=}$ calcareous muds > bioclastic sands. Obviously, carbonate dilution is still a major control on element abundance but the paucity of the 'chlorite-mica' group causes a relative depletion of these elements (Al, Ti, Cr, Pb) in the detrital sands. As examples, the distribution of Al and Cr are shown in figures 4.9 and 4.10 respectively.

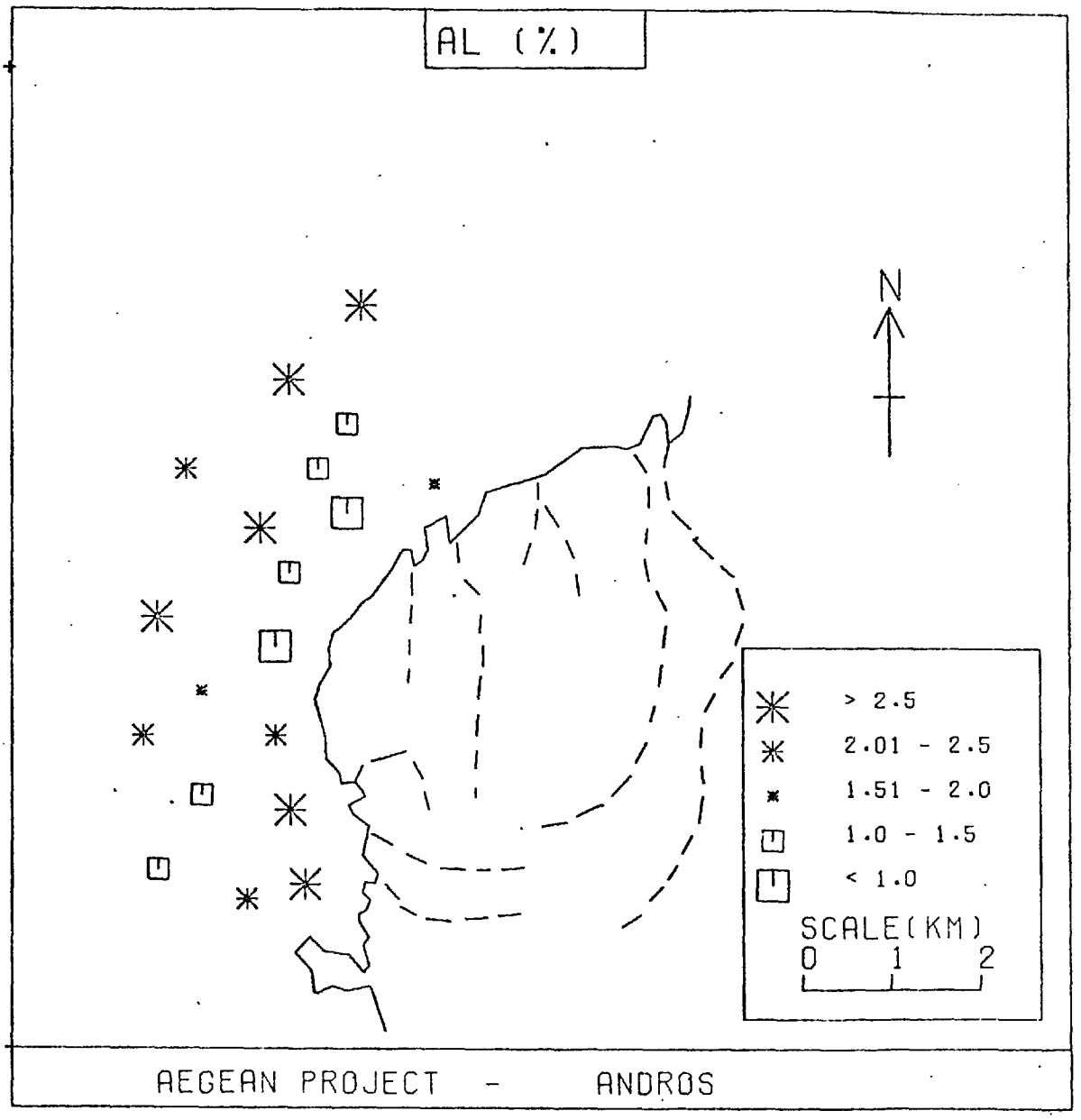


Figure 4.9 Distribution of Aluminium.

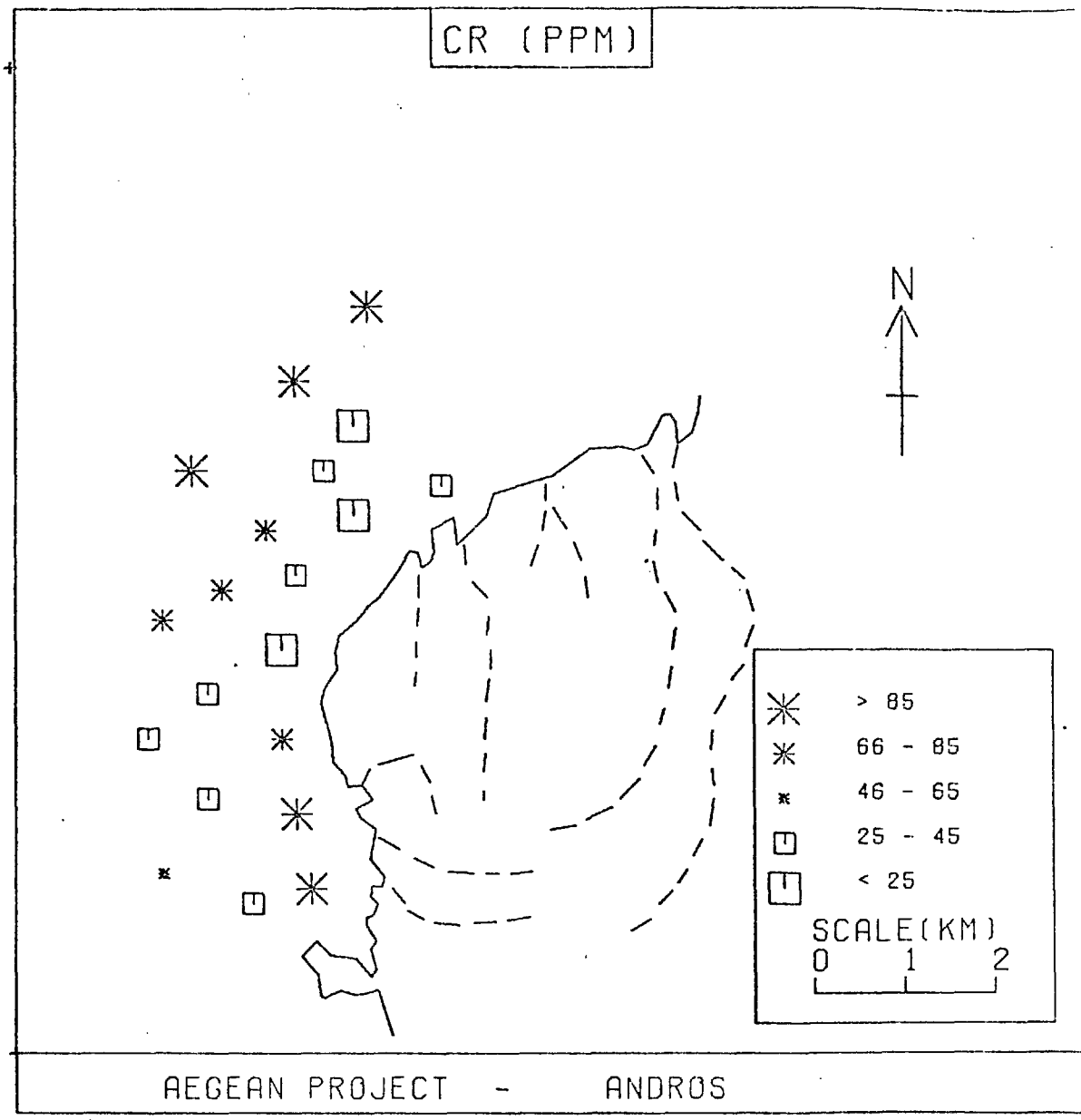


Figure 4.10 Distribution of Chromium.

For Fe, Mn, Cu, Zn and Ni there is a marked enrichment in the calcareous muds reflecting both mineralogical factors (Fe) and the increased importance of the hydrogenous Mn 'oxide' component. As examples of this group, the distribution of Mn, Ni and Cu are charted in figures 4.11, 4.12 and 4.13 respectively.

4.4.3 Partial Composition of the Detrital Fraction

Four samples selected to cover the range of sediment types, were leached with acetic-acid and the residues analysed. The partial composition of the detrital fraction, and the percentage contribution made by the detrital fraction to the total element abundance (except for K) are given in table 4.

Although there is a wide range in the composition of the detrital fraction there are broad similarities with samples from Kithnos and Serifos. The composition of the detrital fraction depends on the relative proportions of four main components: quartz (depleted in all the elements considered); feldspar (depleted in all elements except Al); the 'chlorite-mica' group (containing Fe, Mg, Al, Cu, Zn, Ni and Cr), either as discrete particles in the fine fraction, or as coarse schist fragments; and a component consisting of either hydrogenous manganese 'oxides' (containing Mn and possibly Cu, Ni and Zn) or authigenic iron minerals (containing Fe). The influence of these components on the concentration of Fe and Al in the detrital fraction of sediments from Andros, Serifos, and Kithnos is illustrated in figure 4.14.

Calcareous muds, e.g. sample 365, tend to be richest in the 'chlorite-mica' group and so the detrital fraction of this sample, like its' counterparts at Kithnos (e.g. 432, 435) and Serifos (e.g. 445, 448), generally has the highest abundances offe, Mg and Al. Detrital manganese 'oxides' are also most abundant in these samples particularly in sample 365 (1480ppm Mn c.f. less than 880ppm Mn elsewhere).

An increase in the relative proportion of feldspar reduces the concentration of Fe and other trace elements but not Al. Consequently, the Fe/Al ratios are lower in samples where the relative proportion of feldspar is greater. An example from Andros is the detrital sand, sample 357, which is known to be rich in feldspar (4.3.3). Sample 411, from Kithnos, has the closest detrital composition to 357 and this sample is also thought to be relatively

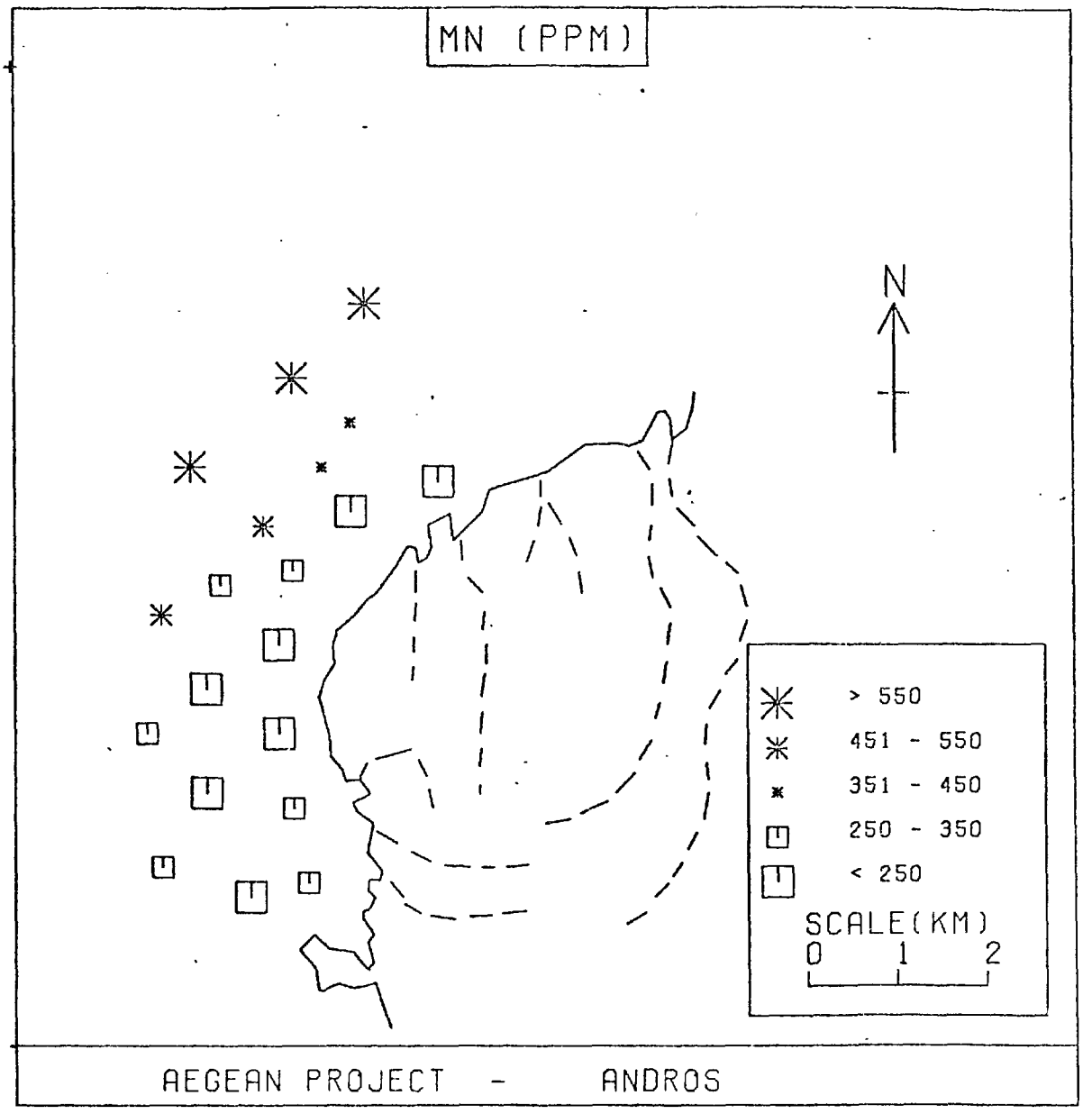


Figure 4.11 Distribution of Manganese.

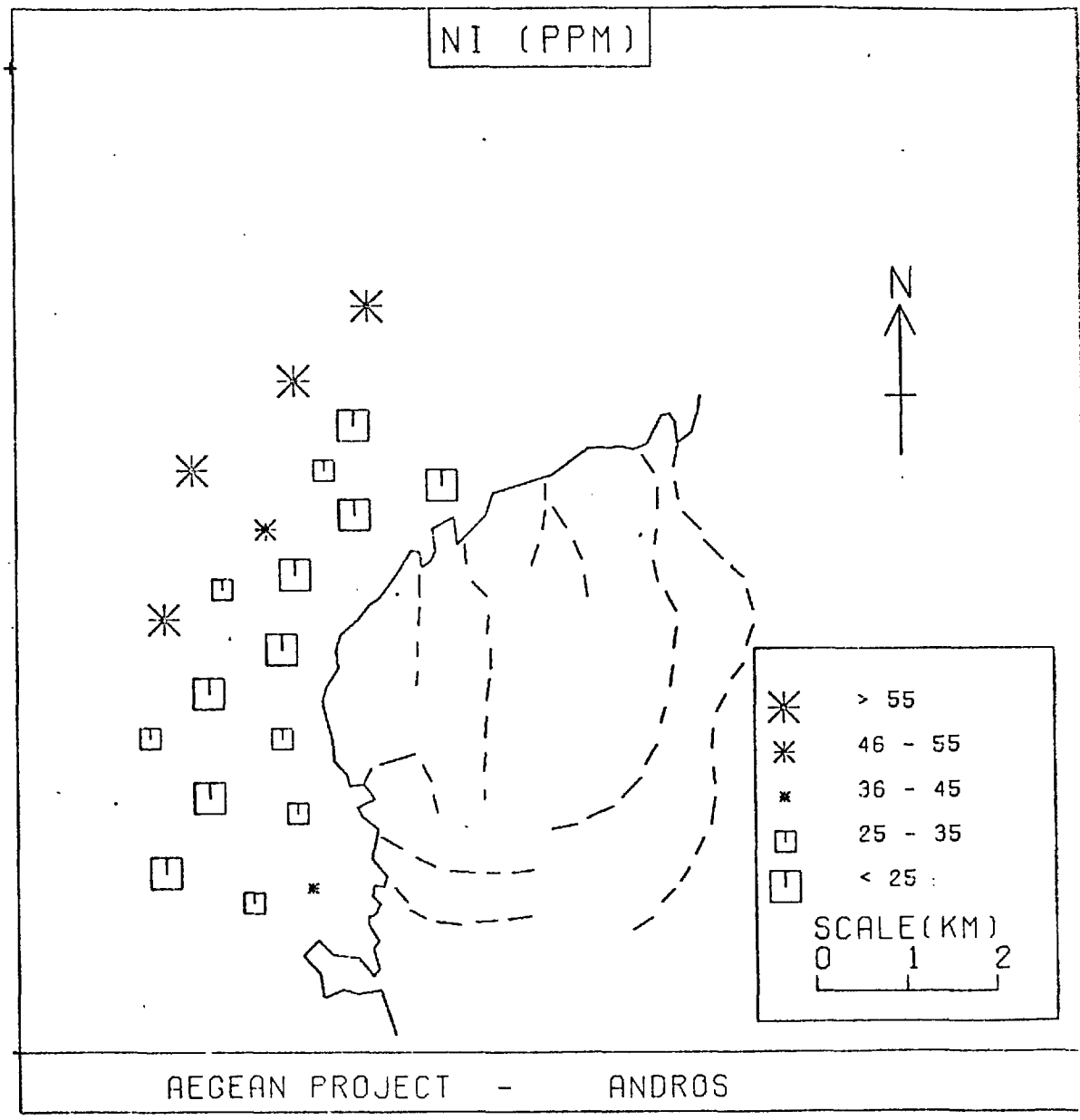


Figure 4.12 Distribution of Nickel.

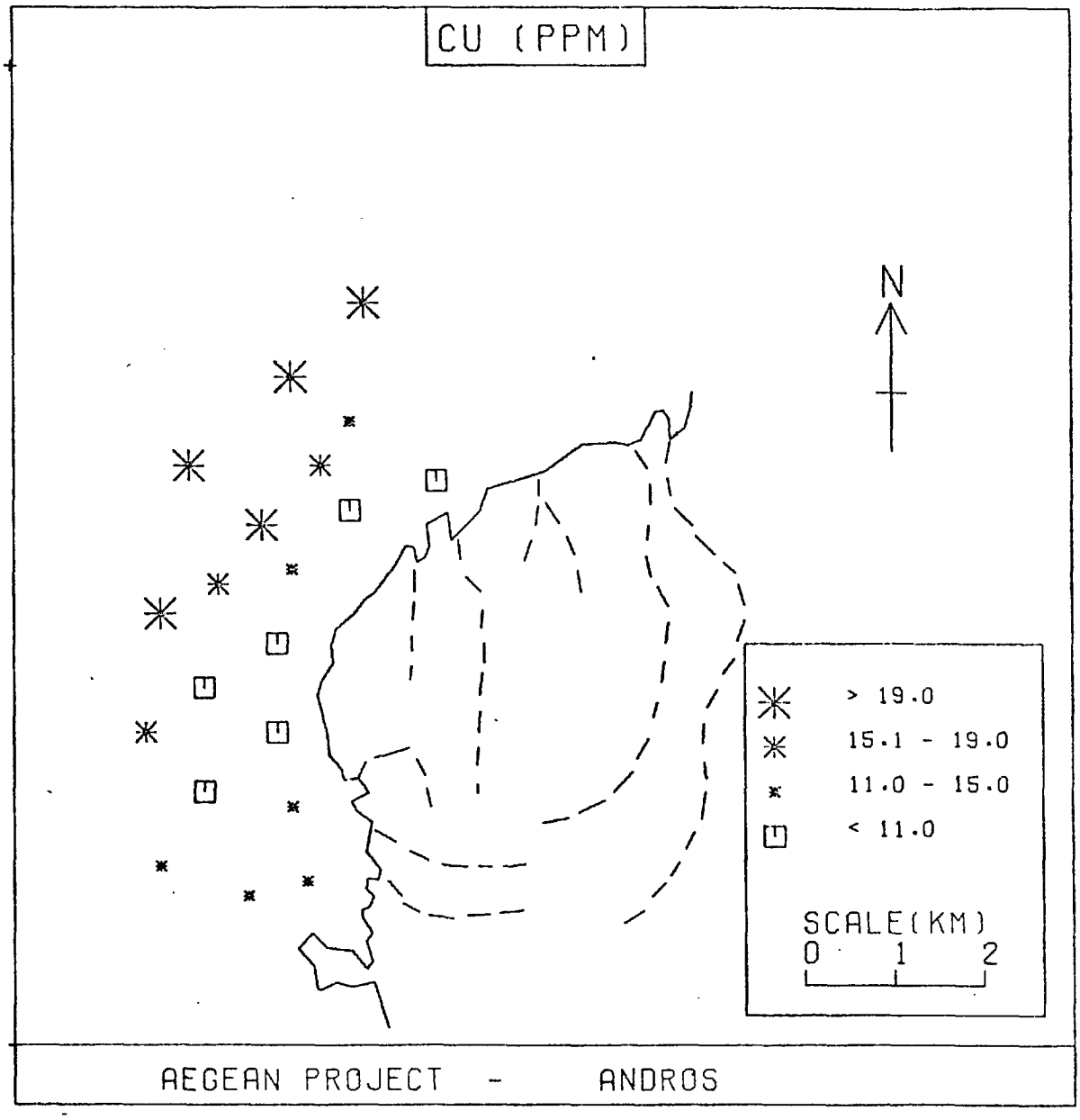


Figure 4.13 Distribution ofCopper.

rich in feldspars but not to the same extent as 357 (see figure 4.14).

Increase the relative proportions of quartz, however, and the concentration of all elements are reduced but the Fe/Al ratio remains constant (figure 4.14). Consequently, the relative proportion of quartz is thought to be greater in sample 373 to account for the depletion in most elements, but it has a normal Fe/Al ratio. From Kithnos the detrital fraction of sample 427 has a similar composition.

The composition of the detrital fraction of sample 367 is similar to the detrital fraction of the calcareous mud (sample 365). The small detrital fraction of this bioclastic sand (11) is probably derived from the small mud component in the sample. (For further discussion on the influence of detrital mineralogy on chemical composition-see section 6.6.4.)

The contribution by the detrital fraction to the total element abundances decreases in the order:- Fe, Al, Ti, Cr, Ni, (about 80% or more)> Cu, Zn, (variable between 48% and 98%)> Mn, Mg (variable between 16% and 67%)> Pb (less than 40%)> Ca. Elsewhere the trends are broadly similar but for those elements with a wide range of contribution (i.e. Cu, Zn, Mn, Mg), the detrital component is much more significant in the calcareous mud (i.e. sample 365).

4.4.4 Major Factors Governing the Chemical Composition of the Sediments from Andros

From the preceding discussion it is apparent that the most important factors governing the chemical composition of the sediments from Andros are broadly similar to those found at Kithnos and Serifos, namely:-

(a) carbonate dilution of detrital elements;
(b) range in mineral composition of the detrital fraction;
(c) accumulation of hydrogenous Mn 'oxides' in the offshore zone;
and (d) calcareous components contributing Ca, Mg and possibly non-detrital trace elements.

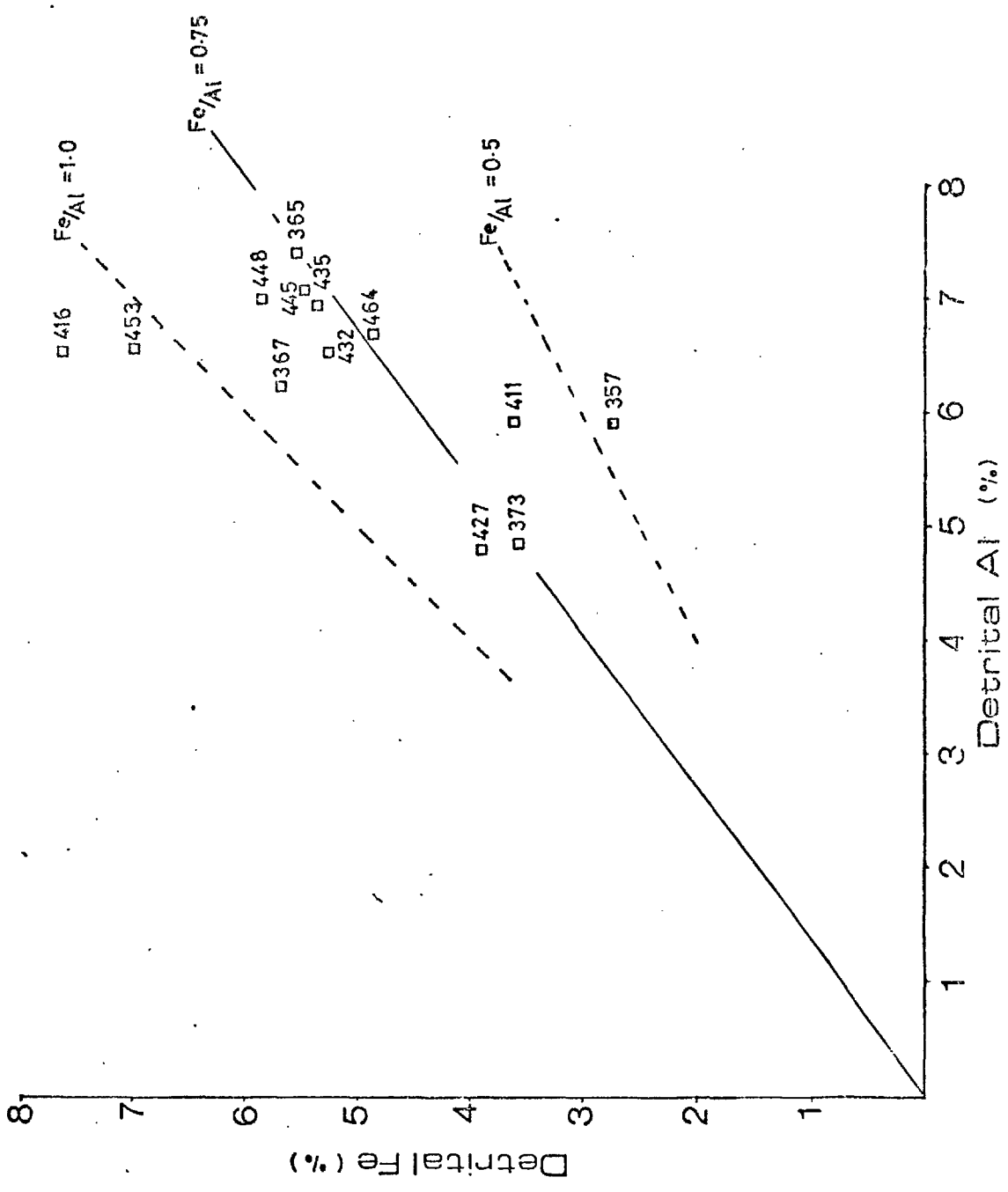


Figure 4.14 Iron against aluminium for the detrital fraction of selected samples from Kithnos, Serifos, and Andros.

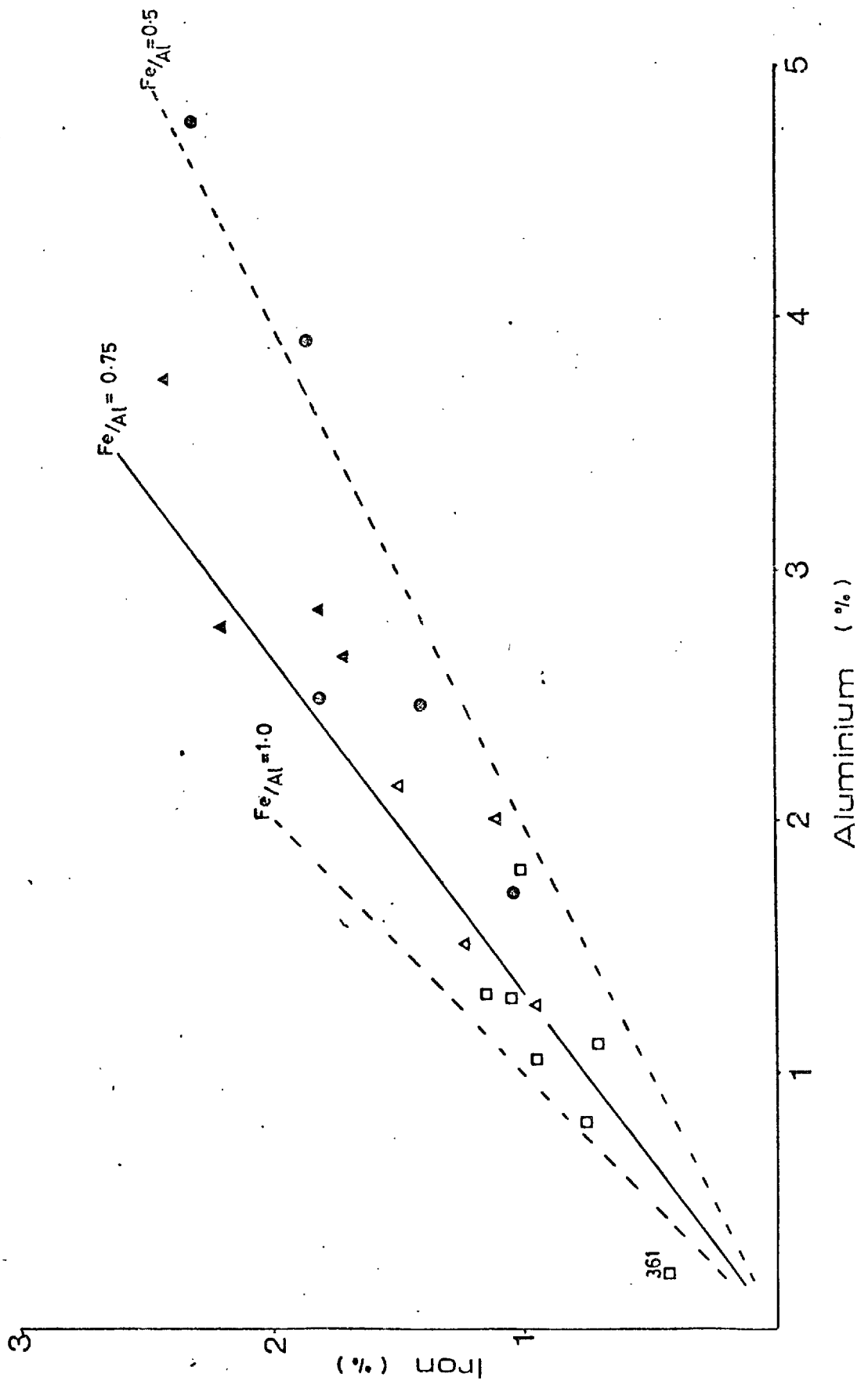


Figure 4.15 Iron against aluminium for bulk samples from Andros (see figure 3.4 for key).

Undoubtedly carbonate dilution remains the major factor governing the chemical composition of the sediments, but the influence on composition of the range in mineralogy of the detrital fraction is more apparent at Andros than elsewhere. This is particularly so in the detrital sands in which some appear to be rich in quartz and others feldspar (4.4.3) and overall tend to be depleted in the 'chlorite-mica' group of minerals and the elements concentrated therein (e.g. Fe, Ni, Cr, Cu, etc.). These differences in the mineralogy (and also texture) and, hence, chemical composition of the detrital sands, seem to partly be a function of the different oceanographic regimes at Andros compared to Kithnos or Serifos. Currents sweeping across the continental shelf off Andros limit the accumulation of silt-sized 'chlorite-mica' minerals.

Manganese 'oxide' accumulation is also more pronounced off Andros. If, as might be expected, sediment accumulation rates decrease with increasing depth, then a corresponding increase in the relative proportion of the manganese 'oxide' component will follow. This would explain the greater abundance of Mn in the calcareous muds from Andros.

A further factor, the formation of authigenic iron minerals in bioclastic sands with a large relict component, is not as common as elsewhere. Recognition of this factor at Kithnos and Serifos is based on Fe/Al ratios exceeding 1.00. From figure 4.15 it is evident that only one sample (361) fulfils this criterion. In this case, sub-aerial exposure at a lower stand of the sea level resulting in Fe-staining may be an alternative explanation for the high Fe/Al ratio because it was recovered from a depth of less than 80m, and many of the fragments are iron-stained. Although a variety of factors could account for the apparent scarcity of authigenic iron mineral formation, the probable reason is that the equivalent deposits simply were not sampled. At Kithnos and Serifos, Fe/Al ratios exceeding 1.00 are generally confined to samples recovered from depths greater than 120m. Either similar deposits have not accumulated at these depths because of the greater slopes involved off Andros (figure 4.1), or the limited sample density meant that the deposits, being less extensive, were not sampled.

One of the principal objectives of investigating samples from Andros was to examine the influence of a possible ultrabasic provenance on the concentrations of Cr and Ni in particular.

Average Cr and Ni concentrations are greater in the calcareous muds than the average concentrations found in equivalent deposits from Kithnos and Serifos but does this reflect provenance or some other influence? To assess this problem, the covariance of trace elements with Fe is examined in the following discussion.

An ultrabasic provenance is not necessary to account for the greater average Cr abundance in the calcareous muds from Andros. Cr and Fe strongly covary (figure 4.16) which suggests that both are held within the same component - the 'chlorite-mica' group of minerals. Consequently, the amount of both elements (Cr and Fe) depends upon the proportions of the 'chlorite-mica' group relative to other components depleted in these elements (e.g. quartz, feldspar, and calcium carbonate). Furthermore, the 'detrital' Cr/Fe ratios at Andros (45×10^{-4} to 67×10^{-4}) are similar to those found at Kithnos and Serifos (43×10^{-4} to 63×10^{-4}) and so relative enrichment of Cr in the calcareous muds from Andros can be explained solely by:-

(i) on average, less calcium carbonate (table 3)

and (ii) a greater proportion of the 'chlorite-mica' group in the detrital component of the calcareous muds compared to those from Kithnos or Serifos.

Nickel, like chromium, is enriched in the calcareous muds from Andros, but further factors, in addition to those described above, are needed to account for the observed relationship between Fe and Ni (figure 4.17). Sandy deposits have a fairly consistent Ni/Fe ratio similar to that found in other areas (e.g. the detrital sands from Serifos, also shown in figure 4.17). Unlike the relationship between Fe and Cr, however, the Ni/Fe ratio for the calcareous muds is greater than that found in other deposits. Nevertheless, like Cr, it is not necessary to invoke 'provenance' to account for the enrichment of Ni in the calcareous muds. Instead, it is much more likely to be related to scavenging by Mn 'oxides'. Comparing figures 4.17 and 4.18, it is evident that both Ni and Mn are related to Fe in similar ways. The greater Mn/Fe ratios for the calcareous muds from Andros and Serifos (both shown in figure 4.18) are attributed to the accumulation of authigenic manganese 'oxides' and the additional amounts of Ni seem to be correlated with the additional Mn.

Figure 4.16 Chromium against iron for bulk samples from Andros(key as for figure 3.4)

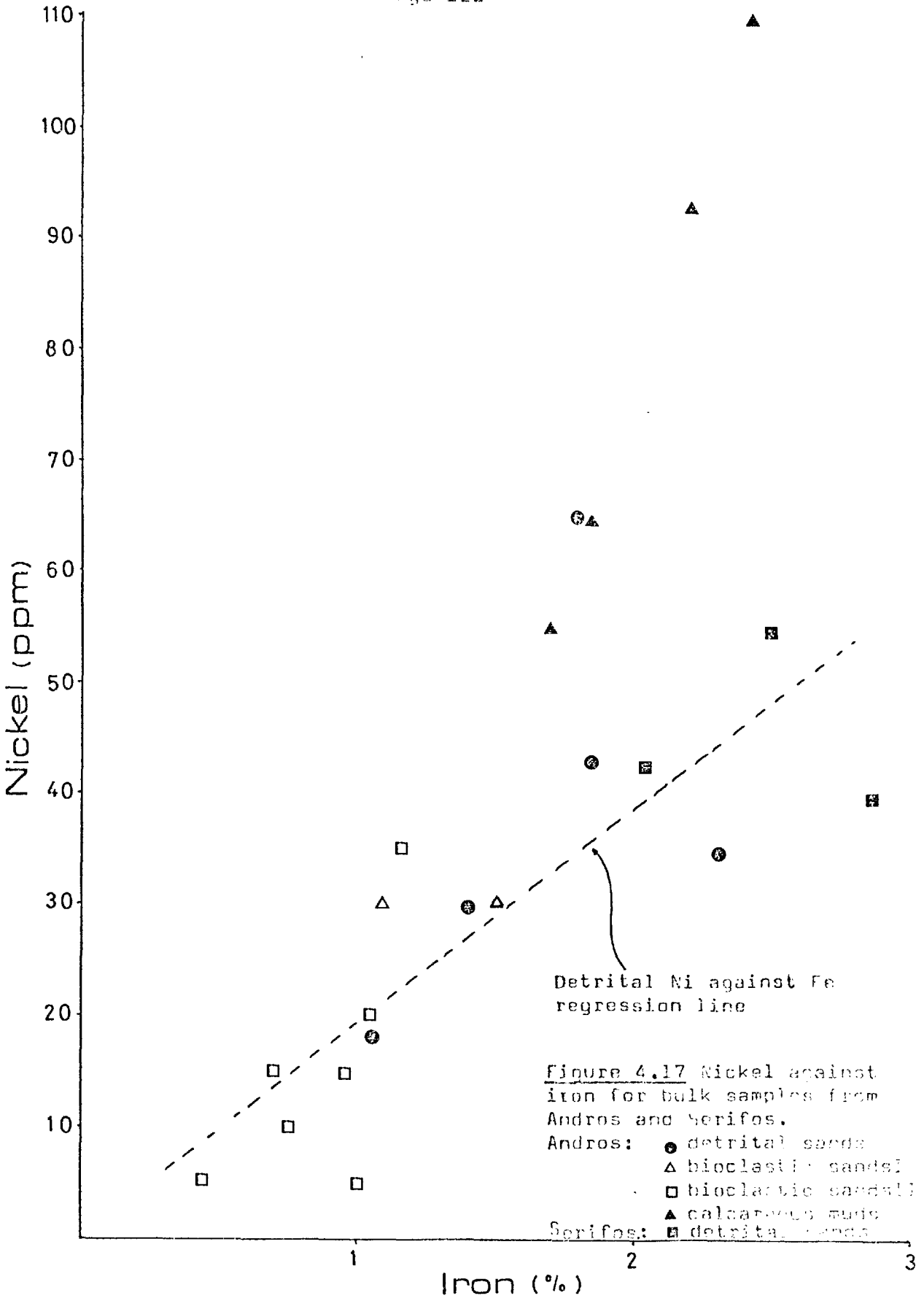


Figure 4.17 Nickel against iron for bulk samples from Andros and Serifos.
Andros: ● detrital sands
△ bioclastic sands
□ bioclastic sands
▲ calcareous muds
Serifos: ■ detrital sands

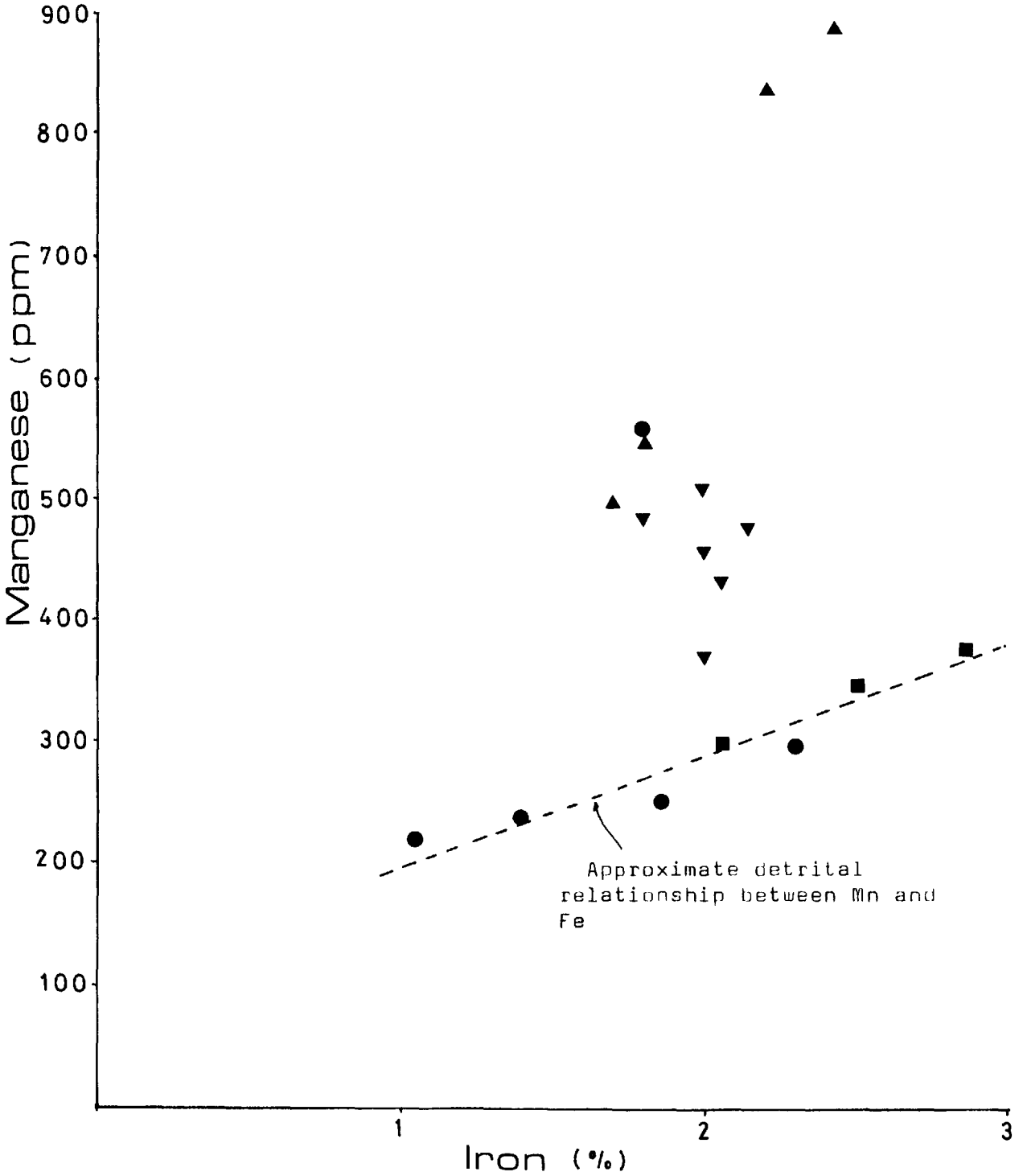


Figure 4.18 Manganese against iron for bulk samples from Andros and Serifos. Andros: ● detrital sands; ▲ calcareous muds. Serifos: ■ detrital sands; ▼ calcareous muds.

Estimates of 'excess' Ni and 'excess' Mn seem to confirm this correlation between Mn 'oxides'and the additional Ni for the calcareous muds. 'Detrital' Ni and Mn (i.e. that held mainly within the 'chlorite-mica' group) can be estimated from the approximate regression lines shown in figures 4.17 and 4.18. An estimate of the 'excess' Ni and Mn is determined by subtracting the 'detrital' Ni and Mn from the observed values. Table 7 gives these estimates and figure 4.19 shows the strong, positive covariance between 'excess' Ni and 'excess' Mn, and it is difficult to imagine that anything other than a direct relationship between Mn 'oxide' scavenging and excess Ni could account for this relationship.

A small amount of future research could check the relationship between manganese 'oxide' scavenging and trace metal accumulation. Leaching the calcareous muds with a combined acid-reducing agent should partition the elements between a soluble manganese 'oxide' phase and an insoluble, truly detrital phase (see e.g. section 7.6.6c).

The high correlation between Cu and Ni (r=0.9) and the similarity of the Cu/Fe and Ni/Fe scatter plots (c.f. figures 4.17 and4.20) indicates that Cu, like Ni, is enriched in the calcareous muds due to the scavenging ability of the manganese 'oxides'. Zinc may also be scavenged by the manganese 'oxides' but this form is subordinate to 'detrital' Zn (figure 4.21).

To conclude, the influence of an ultrabasic provenance on the chemical composition of sediments is not discernible in the limited number of samples taken from off the north-west coastline of Andros. It is more likely that the enrichment of Fe, Mn, Ni, Cr, and Cu in the calcareous muds, compared to similar deposits elsewhere, is due to:-

(1) on average, less calcium carbonate;

(2) greater proportion of the 'chlorite-mica' minerals (these two factors alone account for the enrichment of Fe and Cr); and (3) the accumulation of, and scavenging by, manganese 'oxides'.

4.5 SUMMARY OF MAJOR CONCLUSION

The major factors governing the texture, mineralogy, and composition of the sediment samples from Andros are similar to

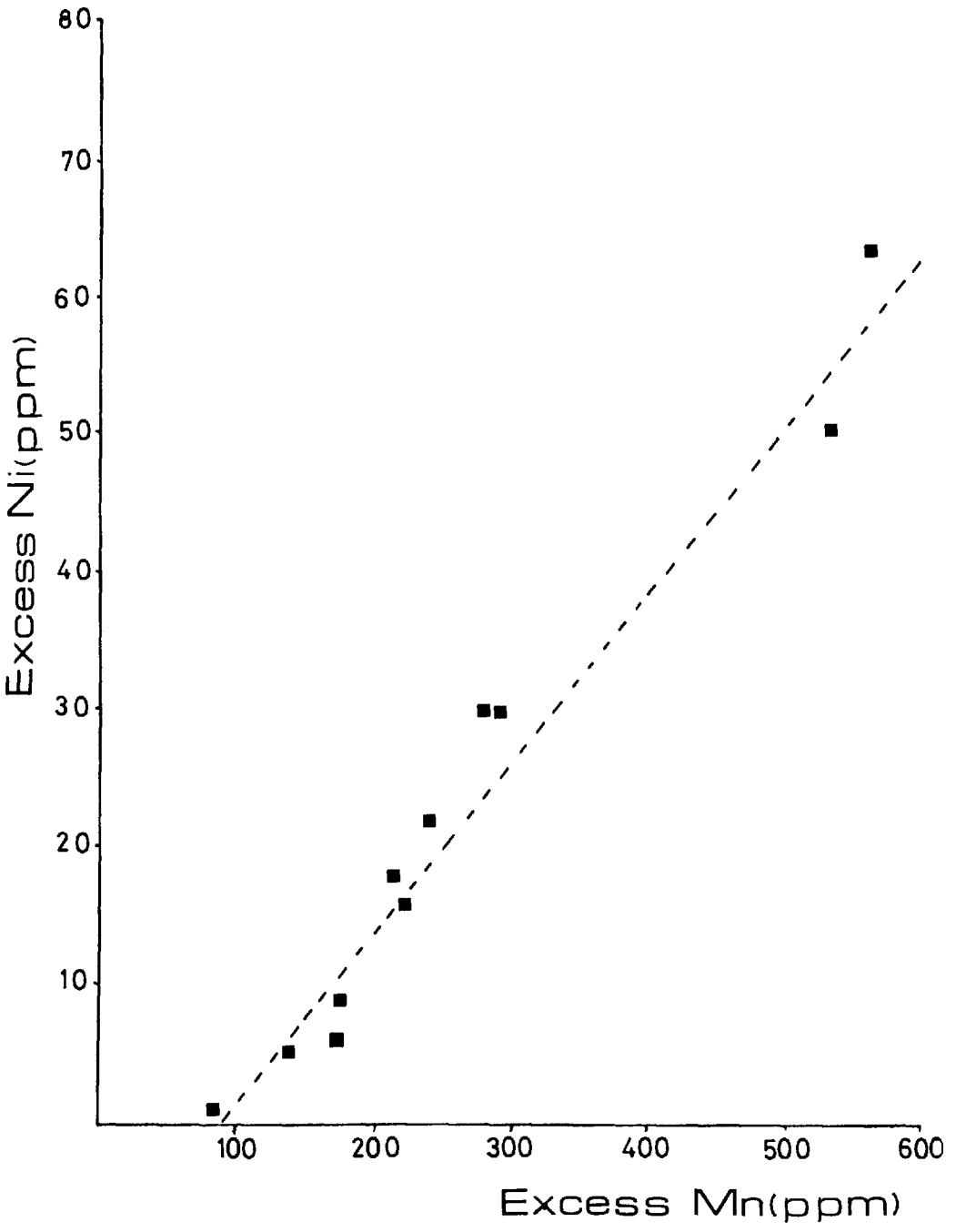


Figure 4.19 Excess nickel against excess manganese for calcareous muds from Andros and Serifos (plus one deep-water detrital sand from Andros). (See table 7.)

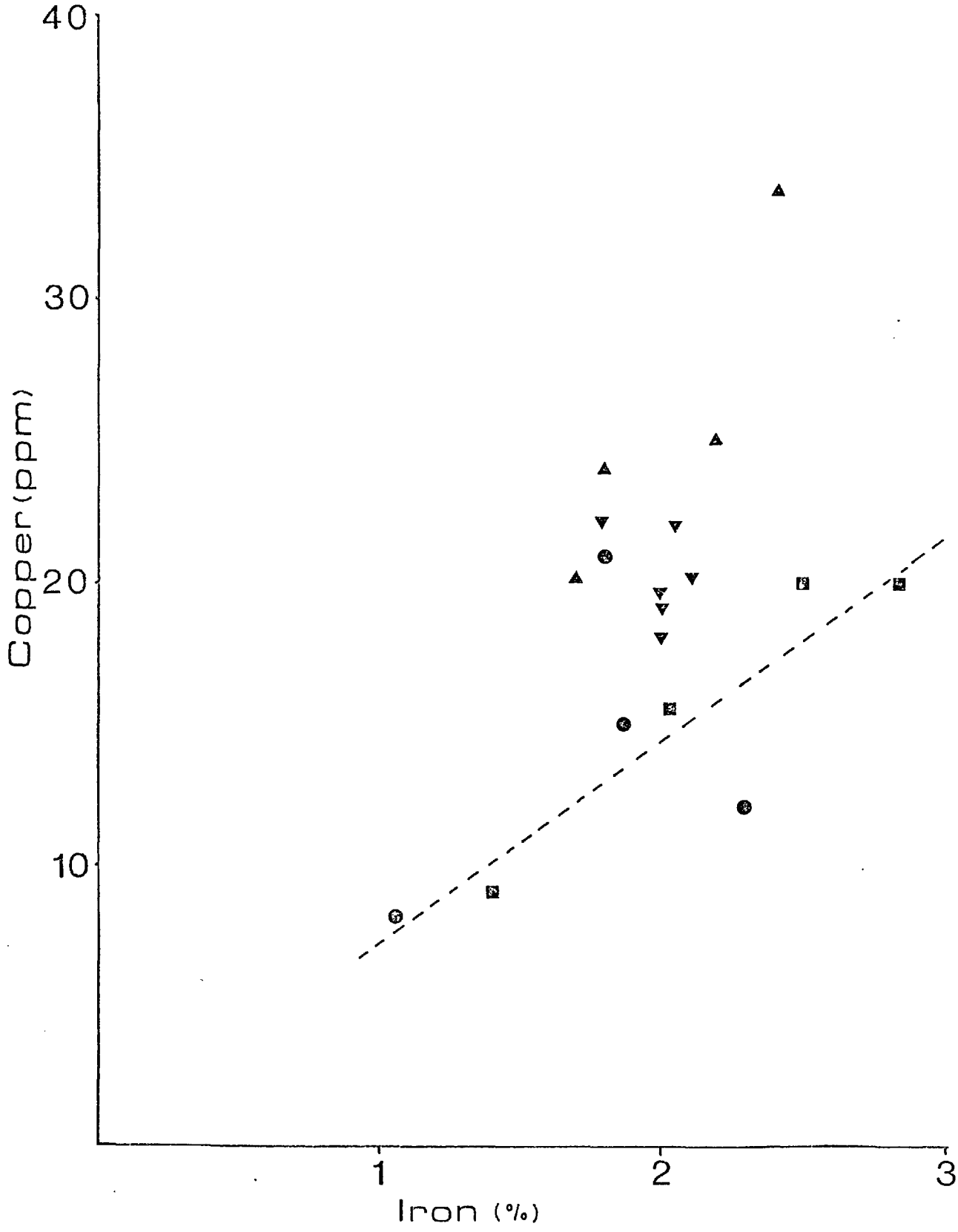


Figure 4.20 Copper against iron for bulk samples from Andros and Serifos (see figure 4.18 for key).

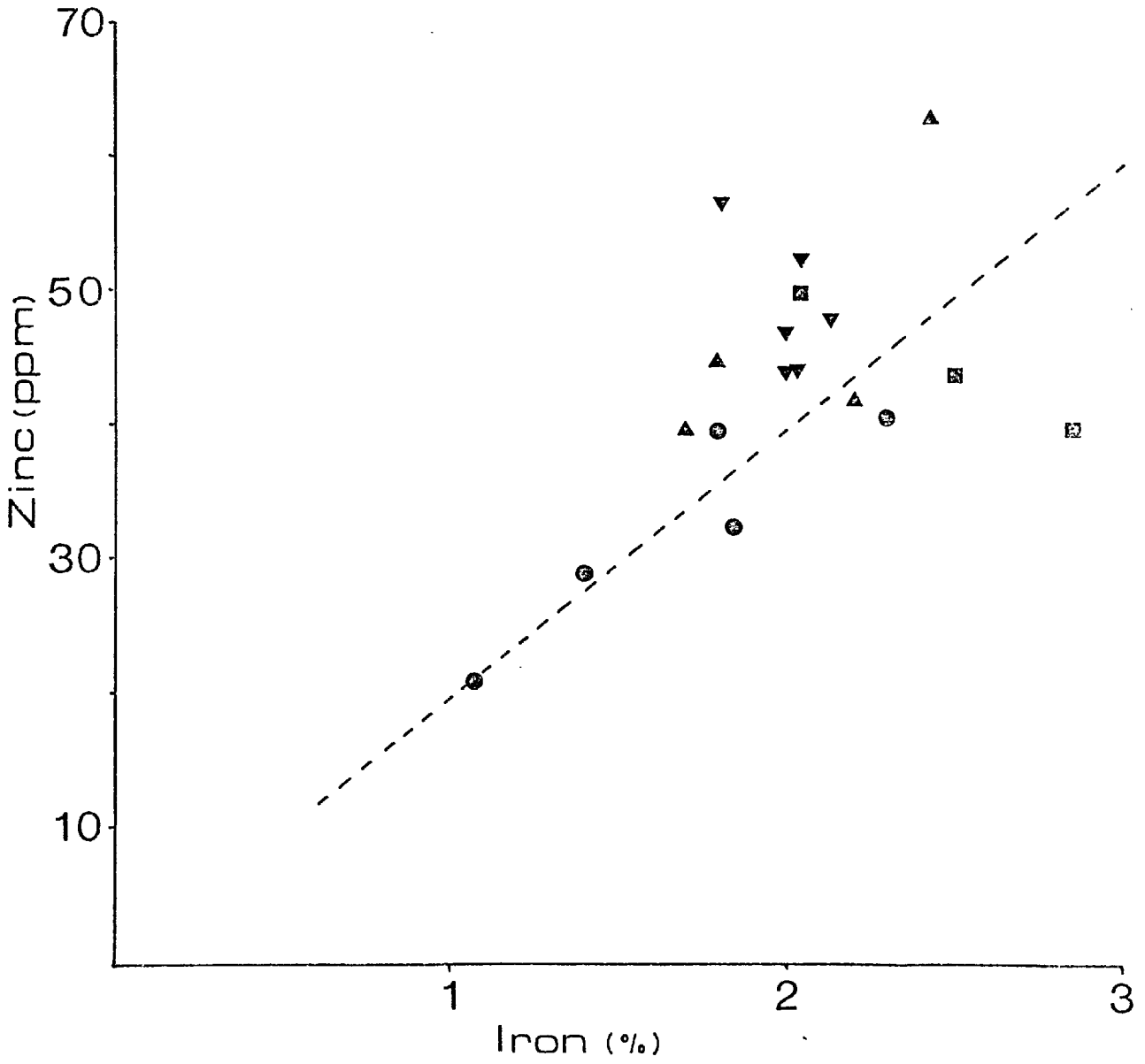


Figure 4.21 Zinc against iron for bulk samples from Andros and Serifos (see figure 4.18 for key).

TABLE 7 Excess manganese and excess nickel for calcareous muds from Andros and Serifos. Values in ppm.

Area	Sample Number	Excess Mn	Ni
ANDROS	364	562	63.5
	365	532	50.5
	366	290	30
	368	240	22
	370	280	30
SERIFOS	445	215	18
	447	220	16
	448	170	6
	449	140	5.5
	450	175	9
	452	80	1

N.B. Sample 366 is a detrital sand but from deeper water and with a large 'excess' Mn.

those found at Kithnos and Serifos. However:-

(1) a certain amount of current activity on the shelf appears to limit the accumulation of 'modern', allochthonous silt-sized particles. This, in turn, means that:-

(a) shelf sediments from Andros tend to be coarser and better sorted;

(b) detrital sands lack a significant fine-grained fraction and are consequently generally depleted in the 'chlorite-mica' group and enriched in quartz and feldspar;

and (c) as the 'chlorite-mica' group contain most of the Fe and trace elements, the detrital sands from Andros are depleted in these elements compared to similarly named deposits from Kithnos and Serifos;

(2) deeper waters of the offshore zone equate with lower sediment accumulation rates and, hence, a greater proportion of hydrogenous manganese 'oxides' in the calcareous muds, compared to similar deposits from Kithnos or Serifos. Accordingly elements associated with the manganese 'oxides' through scavenging (i.e. Ni and Cu) are also more abundant;

(3) the greater proportion of the 'chlorite-mica' group minerals in the detrital fraction of the calcareous muds accounts for the enrichment of Fe and Cr, compared to similar deposits from Kithnos and Serifos;

and (4) enhanced levels of trace elements attributable to an ultrabasic provenance have not been found.

CHAPTER 5 NAXOS

5.1 INTRODUCTION

Naxos is the largest of the Cyclades Islands and lies about 200km to the south-east of Athens (figure 1.1). According to Papastamatiou (1951), the rock types found on the southern half of the island, adjacent to the survey area, consist of rocks characteristic of the Attic-Cyclades massif, that is schists and marbles. But, in contrast to the areas described previously, marbles rather than schists are the dominant rock type. As far as is known, there is no base metal mineralisation on the southern half of the island (see Zachos and Maratos, 1965). Naxos was originally chosen, therefore, as a control area, to assess the geochemistry of the sediments in the absence of onshore base metal mineralisation. In retrospect, as a control it is less important because none of the samples from the areas (except Sounion) seem to show any detectable influence of mineralisation in their chemical composition. Nevertheless, Naxos remains a useful area of study because:-

(1) marbles, instead of schists, are the dominant rock type and this differing 'provenance' of the terrigenous component may affect the chemical composition of the sediments;

(2) the sea floor in the survey area is much shallower than in other survey areas and so the nature and distribution of the sediments may differ.

Samples were taken to cover the survey area (about 100km^2) at a sample density similar to that used elsewhere (about 1 sample per km^2) and the locations are shown in figure 5.1. Of these, 101 were used for chemical, and 52 for textural, analysis.

5.2 SHELF TOPOGRAPHY

The survey area lies between the south-east coast of Naxos and the group of small islands to the south-east. In contrast to the other areas studied so far, in which depths generally exceed 90m, the maximum depth in the survey area is outlined by the 90m isobath (figure 5.2). Apart from the ridge marked by the 75m isobath and extending in a southerly direction from the south-

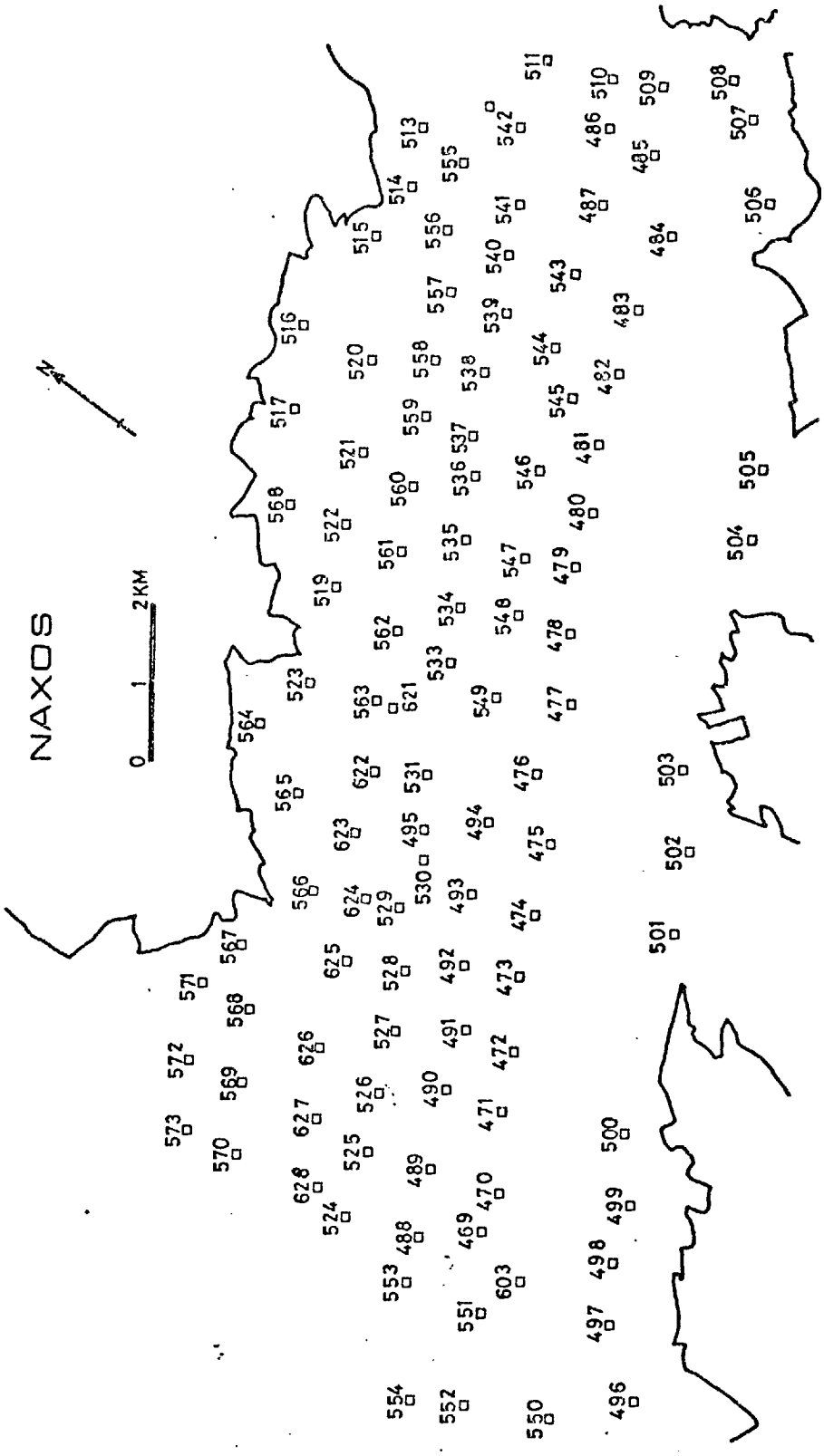


Figure 5.1 NAXOS - sample locations.

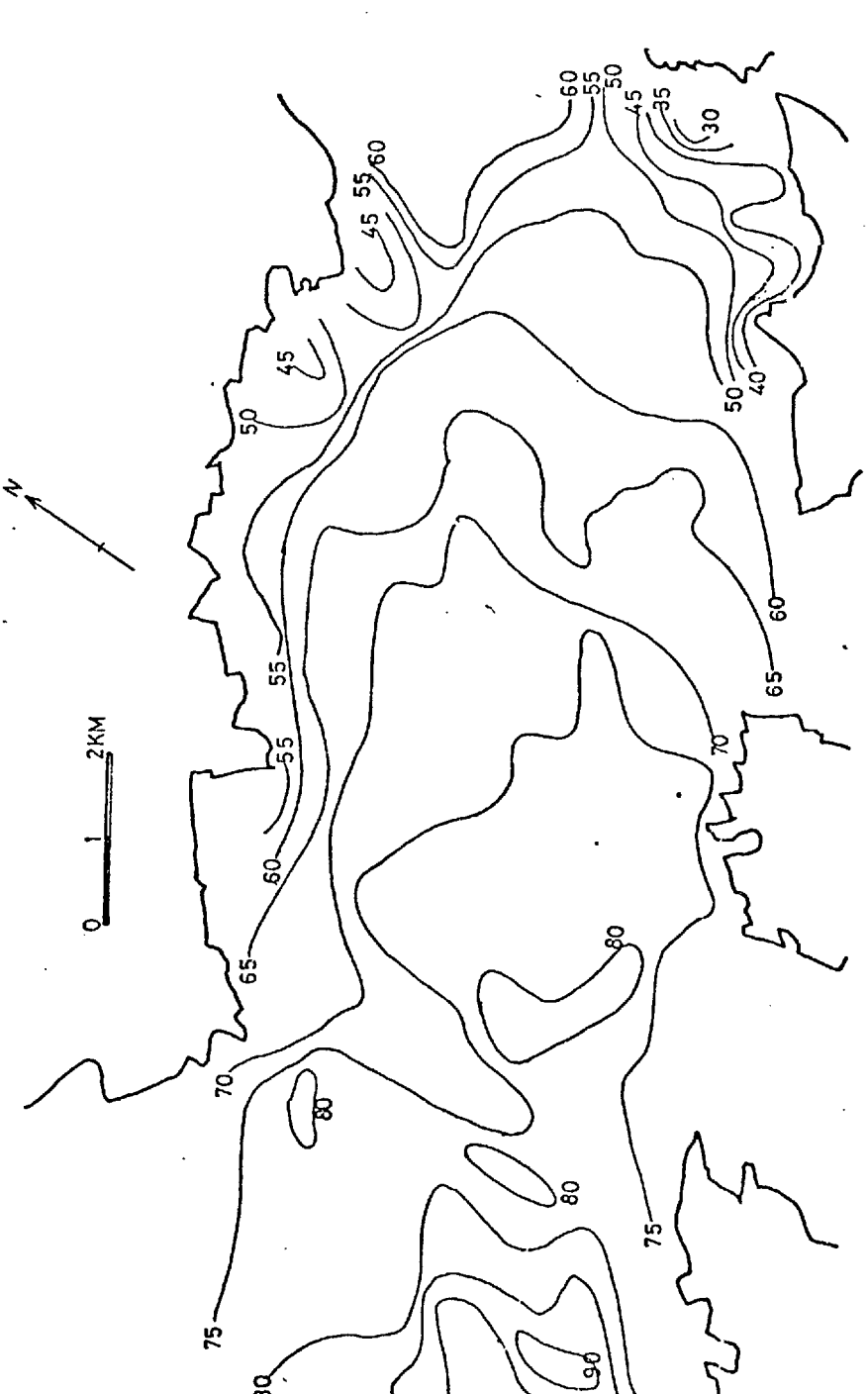


Figure 5.2 NAXOS - Bathymetry (contours in meters).

western corner of Naxos, the depths gradually shoal from the 90m basin, along the axis of the survey area, to depths of less than 30m in the north-eastern corner.

5.3 NATURE AND DISTRIBUTION OF THE SEDIMENTS

5.3.1 Sediment Distribution

Sediment samples are classified according to the scheme of Folk (1954), using the relative proportions of mud, sand and gravel. Because of the large number (100), only every other sample is used (making 52 in all) for the sedimentological studies. Figure 5.3 charts the distribution of the major groups of sediment.

Muddy sands cover most of the sea floor. They are shelly deposits with the proportion of gravel increasing the closer the samples are found to the gravelly sands found on ridges (e.g. 530) and on the shallower sea-floor in the north-eastern sector (e.g. 541). Although coralline algae debris is still a significant component in the gravelly sands, molluscan debris is much more abundant. Gravels, consisting elsewhere of large pieces of nodular, branching or encrusting coralline algae, are not found. Sandy muds accumulate in two areas - in the basin marked by the 90m isobath and in the nearshore zones (e.g. 518).

5.3.2 Calcium Carbonate

Although bioclastic $CaCO_3$ may be the dominant source of Ca, terrigenous Ca (i.e. that derived from the erosion of the marbles) may also contribute significantly to the total Ca abundance. Like the Ca in samples from other areas, most of it is soluble in acetic acid (table 1) but if terrigenous carbonate consists mainly of calcite it too will be soluble in acetic acid. Total Ca, therefore, may not be a reasonable estimator of bioclastic $CaCO_3$. Nevertheless, the broad pattern of total Ca distribution (figure 5.4) seems to agree with observations on the general nature of the sediments. It is highest in the coarser skeletal sands and lowest in the muddier zones.

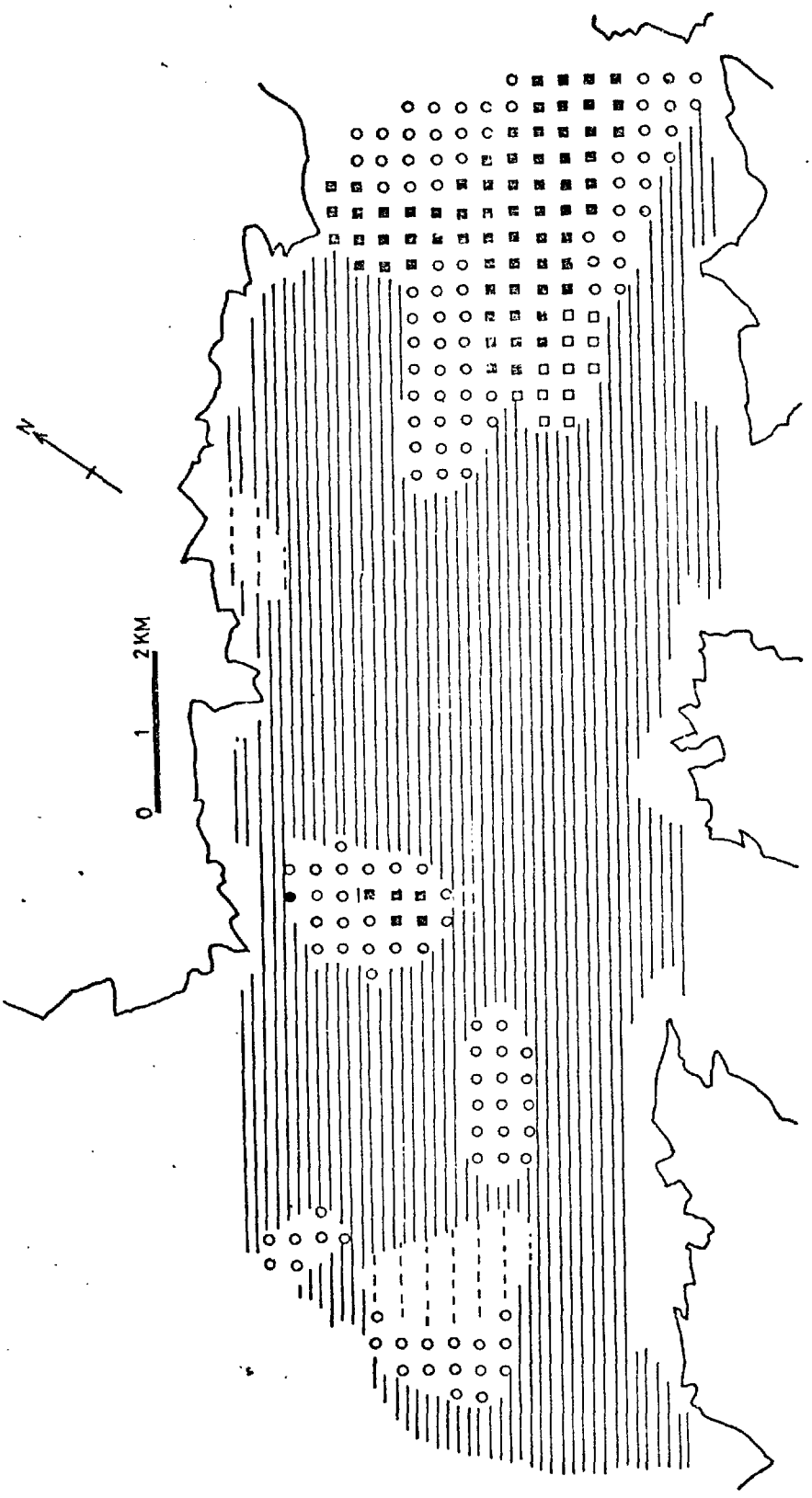


Figure 5.3 Distribution of sediments at Naxos, classified according to the scheme of Folk (1954)(see figure 2.2 for key).

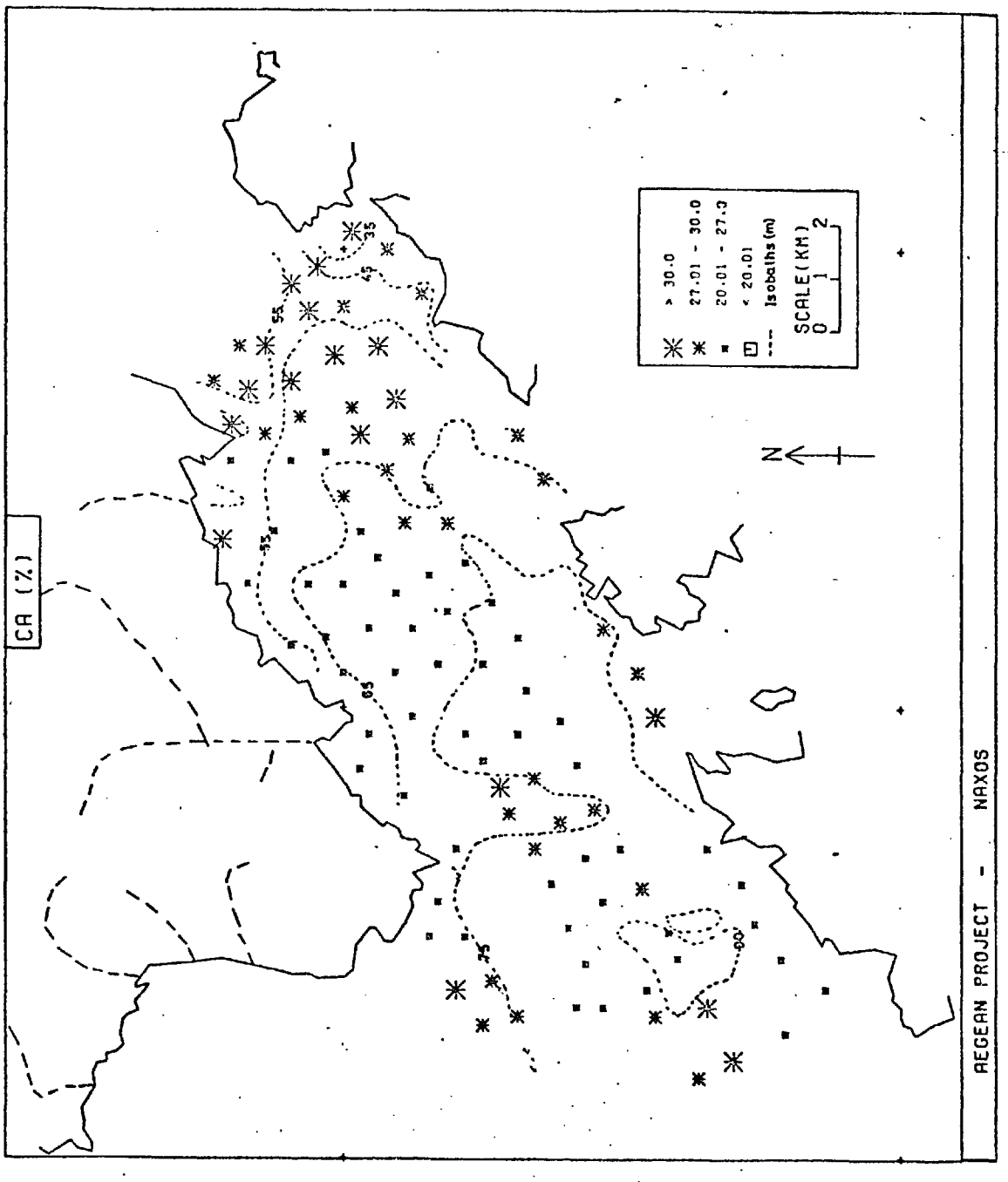


Figure 5.4 Distribution of total calcium in samples fromNaxos.

5.3.3 Reclassification of the Sediments

Because the gravel fraction is removed for the textural and chemical analyses, the Folk classification scheme is not appropriate for comparison of the characteristics of the major sediment types. Elsewhere a simple scheme based on the relative proportions of mud and total Ca (as an estimater of $CaCO_3$) is used instead. Despite the problem of total Ca possibly being a poor estimater of bioclastic $CaCO_3$, the scheme is retained. Because total Ca remains a good estimater of total $CaCO_3$, and because both terrigenous and bioclastic $CaCO_3$ dilute the metal-bearing detrital minerals, the classification scheme is still appropriate for geochemical comparisons.

Textural comparisons are more of a problem using this classification scheme because the very fine sands and course silts (dominantly detrital elsewhere) may be carbonate-rich. A sample classified as a bioclastic sand may, therefore, be texturally equivalent to the detrital sands off Kithnos or Serifos (see section 5.4.)

Obviously the broad distribution of the sediments types (figure 5.5) reflects the major areas of accumulation of total Ca and mud (see figure 5.4 and 5.8). Nearshore sediments with greater than 30% mud are classified as calcareous muds, as are the samples found in the basins of the deeper parts of the survey area. Bioclastic sands (11) occur on ridges and topographic highs and are particularly extensive in the north-eastern sector. Bioclastic sands (1) cover the remaining area and detrital sands are not found, perhaps for reasons stated previously.

5.3.4 Mineralogy of the Detrital Fraction

Although the mineralogy of the 'detrital' fraction of only three samples (473, 475, 478) is known, a local geology dominated by marbles, rather than schists, is reflected in the mineral assemblages found. The most significant feature is the paucity of the 'chlorite-mica' group. Quartz and feldspar are the major minerals and dolomite is an additional mineral not found in samples from Kithnos, Serifos or Andros. The limited range in the chemical composition of the 'detrital' fraction, based on a larger number of samples (see section 5.5.3), suggests that a detrital mineral

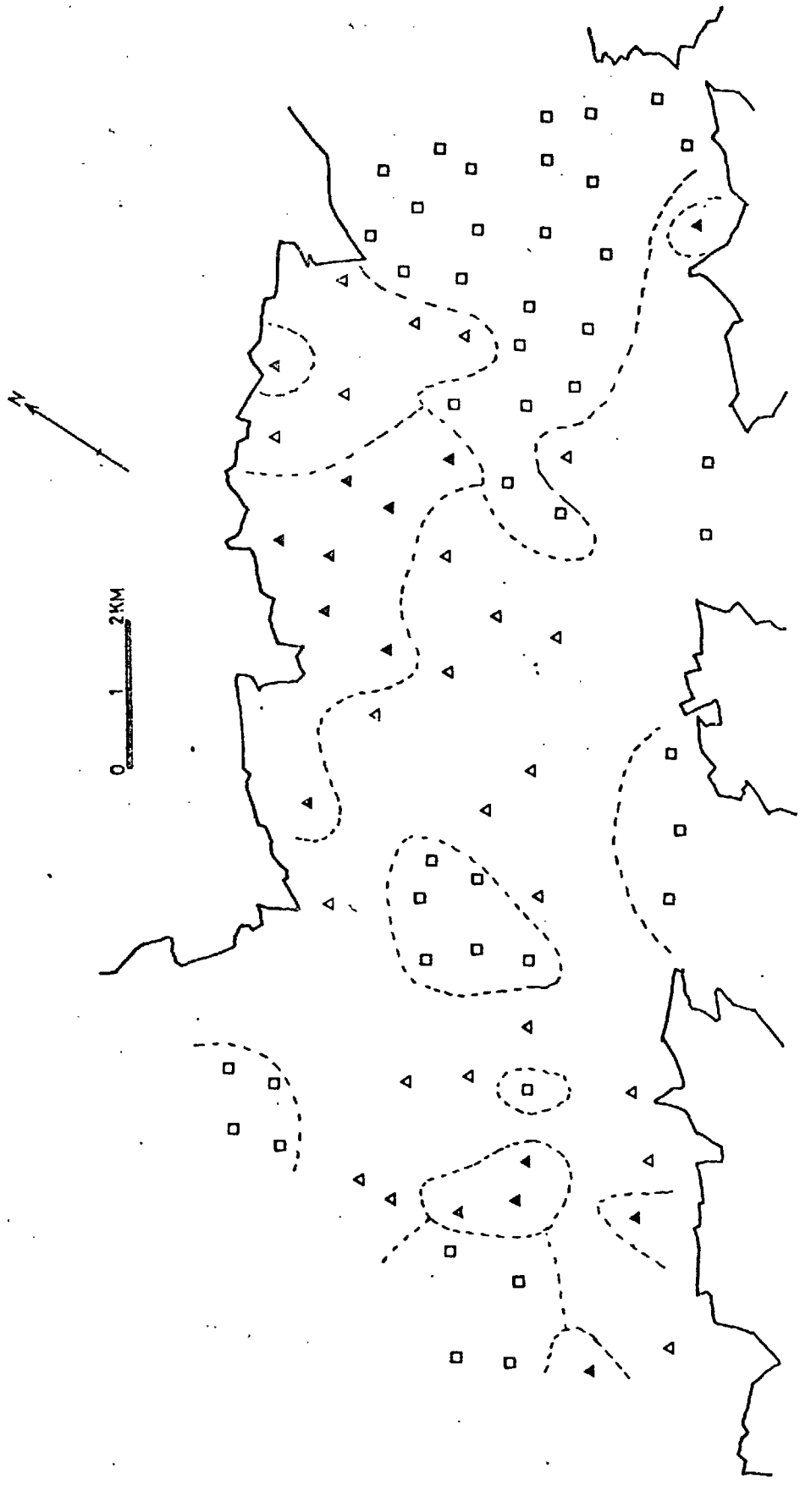


Figure 5.5 Distribution of sediments, reclassified according to the proportions of mud and total Ca (see figure 3.4 for key).

assemblage dominated by quartz, feldspar, and dolomite is typical off Naxos.

5.4 TEXTURAL ANALYSIS OF THE SEDIMENTS AND SHELF SEDIMENTATION

From table 2 it is apparent that the bioclastic sands (II) and the calcareous muds have average textural parameters similar to equivalent deposits off Kithnos. The Naxos bioclastic sands (I), however, have a finer average median and mean size, plus a poorer sorting. These differences are mainly caused by the greater amounts of mud in the bioclastic sands (I) from Naxos.

The scatter plot of mean size against sorting (figure 5.6) illustrates the general textural characteristics of the sediment samples. Once again, the relative proportion of mud and sand is the major factor governing the texture. Samples 526 and 474 illustrates this feature well because both have very similar sand sub-populations (figure 5.7) but widely different proportions of mud (5% and 22% respectively). For a given sand mode, an increase in the proportion of mud is matched by a decrease in the mean size and an increase in the sorting coefficient (see section 2.4.3). Hence, sample 474 is finer and more poorly sorted than sample 526 (see figure 5.6).

Superimposed on this trend is the influence of the range in size of the major sand modes. Samples 474 and 556, for example, have similar proportions of mud but different sand modes (i.e. finer than $2\frac{1}{2}$phi for 474, and coarser than 1phi for 556 - figure 5.7). For a given amount of mud, an increase in the size of the major sand mode is matched by an increase in the sorting coefficient (section 2.4.3). Accordingly, sample 556 is coarser but more poorly sorted than sample 474 (see figure 5.6).

To illustrate the nature of the sediments in more detail figure 5.7 shows the size distribution for the sand fraction of typical examples of the main sediment types. The major sand sub-populations appear to be similar to those found at Kithnos (section 2.4.2d), namely:-

(2) very fine sand with a mode about 3phi;

(3) fine sand with a mode about 2phi;

and (4) coarse/medium sand with a mode coarser than 1.5phi.

(Sub-population (1) is the mud component and at Naxos it has a mode in the coarse silt range). The sand fractions of all the

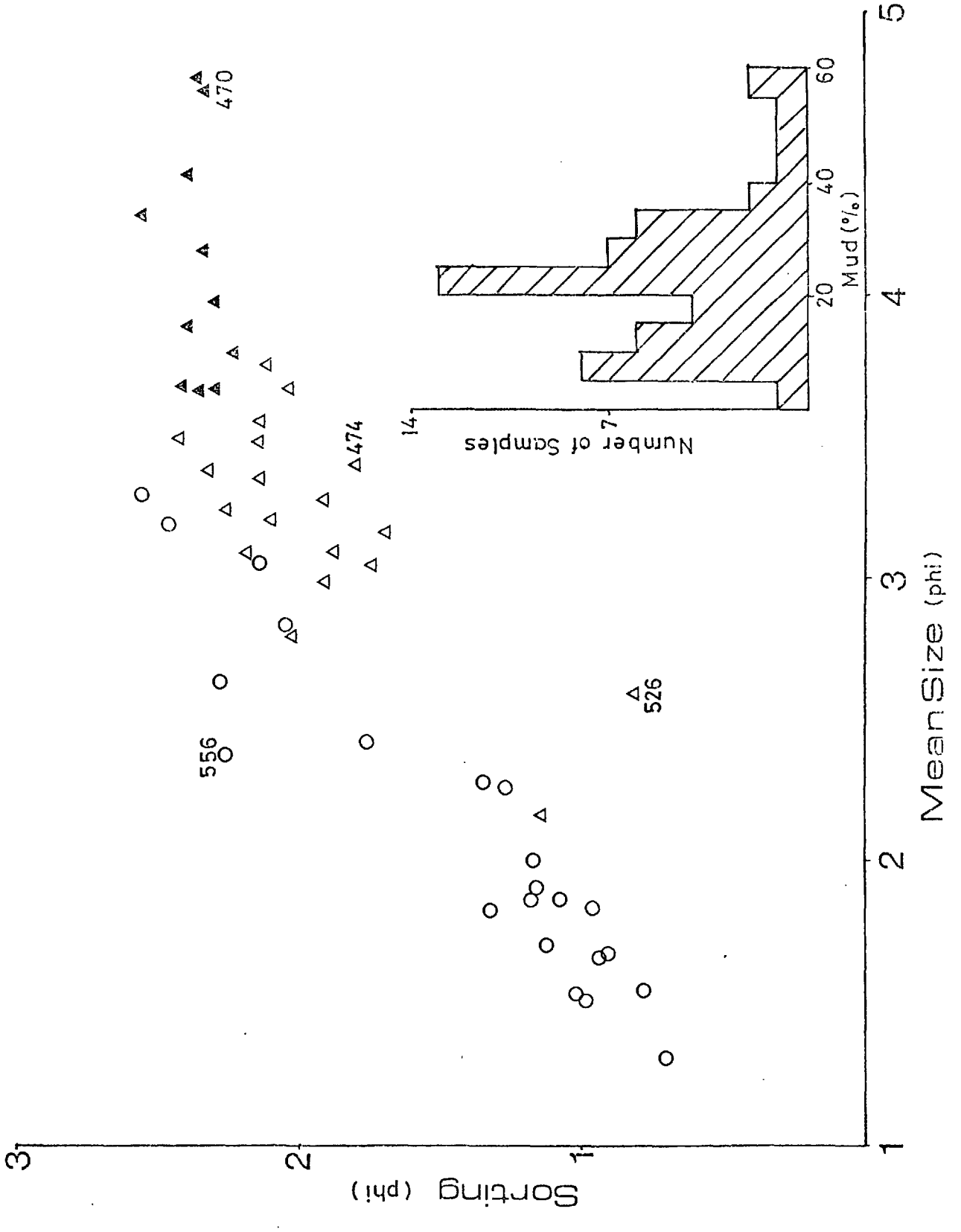


Figure 5.6 NAXOS - mean size against sorting : Δbioclastic sands I, Obioclastic sands II, ▲calcareous muds.

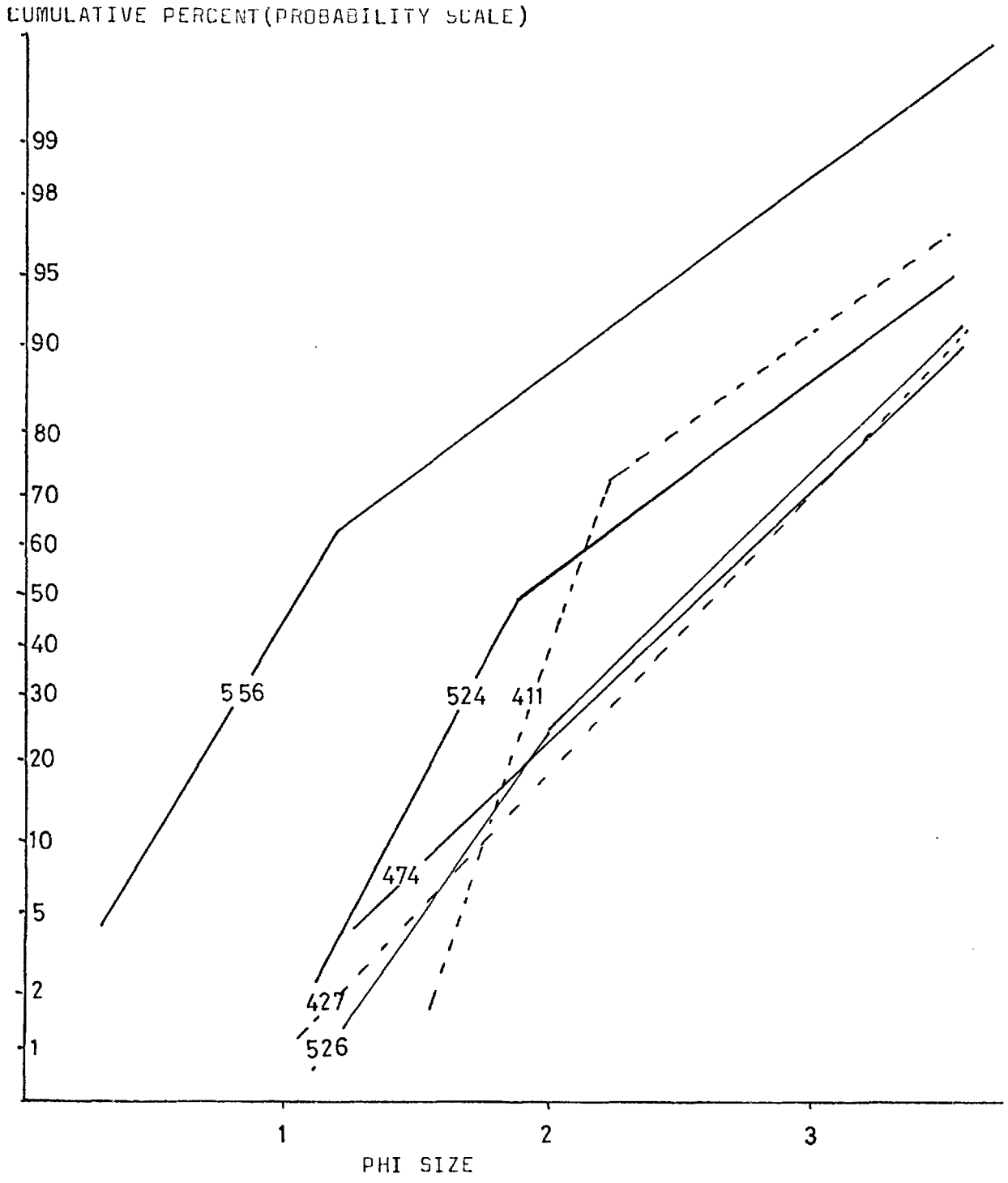


Figure 5.7 Cumulative grain size curves for selected samples from Naxos and Kithnos.

samples seem to be bimodal and consist of a mixture of two of the three sub-populations listed above. Both the bioclastic sands (I) and the calcareous muds have a sand fraction consisting of sub-populations (2) and (3). Some of the bioclastic sands (I) (e.g. 474 and 526) appear to be unimodal with a broad peak. They are thought to be similar to 427 from Kithnos which also appears to be unimodal (figure 5.7), but is, in fact, bimodal (section 2.4.2b), and consists of sub-populations (2) and (3). Bioclastic sands (II), like their counterparts at Kithnos, have a sand fraction dominated by sub-population (4) with a mode in the medium to coarse sand range (e.g. 556, figure 5.7).

The distribution of the four major sub-populations are shown in figures 5.8 (mud), 5.9 (very fine sand), 5.10 (fine sand) and 5.11 (medium to coarse sand). The muds and very fine sands are thought to represent 'modern' sediments (see section 2.4.2d for a detailed discussion) and both have broadly similar distributions (compare figure 5.8 and 5.9) strongly related to the seafloor topography. Both are most abundant in two zones - nearshore, close to the probable alluvial source of the fine-grained material, and in depressions on the shelf. Such depressions often act as sinks for fine-grained material on continental shelves (see McCave 1972). Topographic highs and shoals mark the areas of low mud and very fine sand accumulation - either energy levels are greater, thereby preventing accumulation, or they are isolated from the dispersal paths of the fine-grained material (see section 2.4.3).

Much of the material is probably flushed into the area following the onset of the winter rains, but aeolian material may also be important, especially during the dry summer season. The significance of this alternative source of terrigenous material is not known.

Bioclastic material is the second major 'modern' component of the sediments and this generally forms the coarser sub-population (4). It tends to be abundant on shoals and topographic highs (compare figures 5.2 and 5.11) where fine-grained terrigenous sediment accumulation is least and where small coralline algal reef assemblages may occur on exposed rock outcrops.

Sub-population (3) (fine sand) is dominant where the contribution of both the 'modern' components is least. Sample 524 is the best example at Naxos and it is very similar to sample 411 from Kithnos

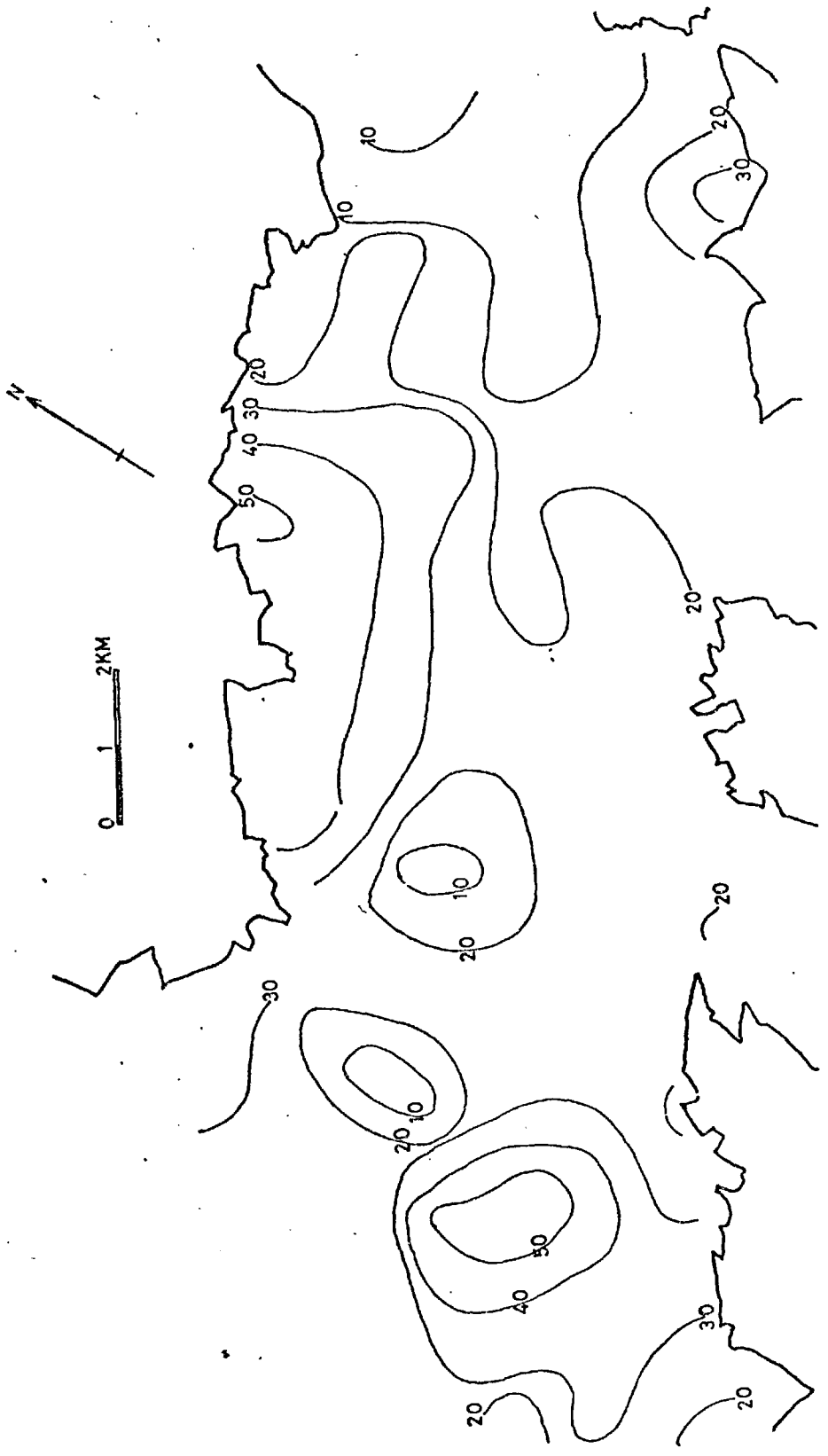


Figure 5.8 Distribution of mud as a percentage of that fraction of the sediment finer than 2mm.

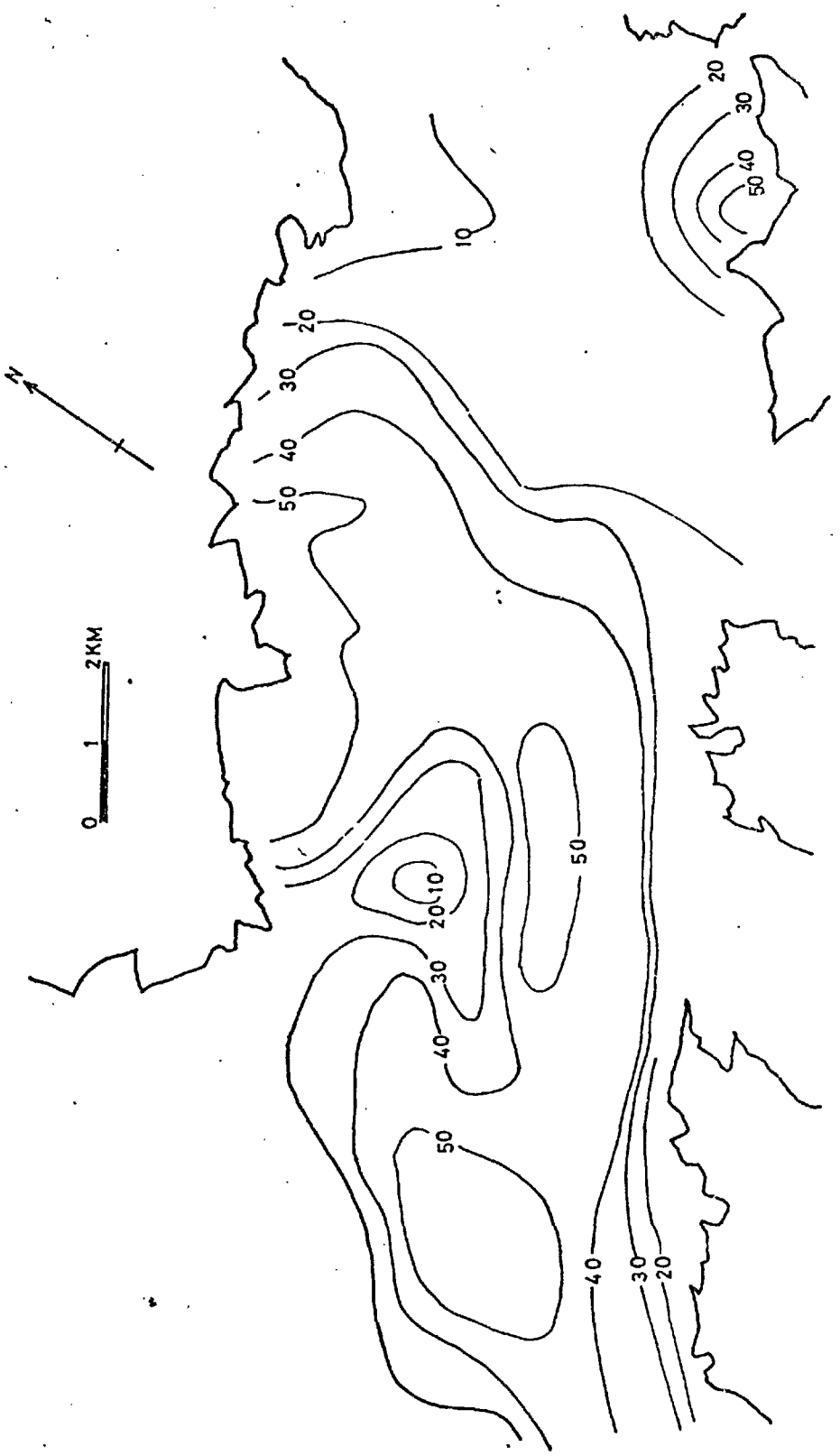


Figure 5.9 Distribution of sub-population 2 (2.5phi to 4.0 phi)as a percentage of the sand fraction.

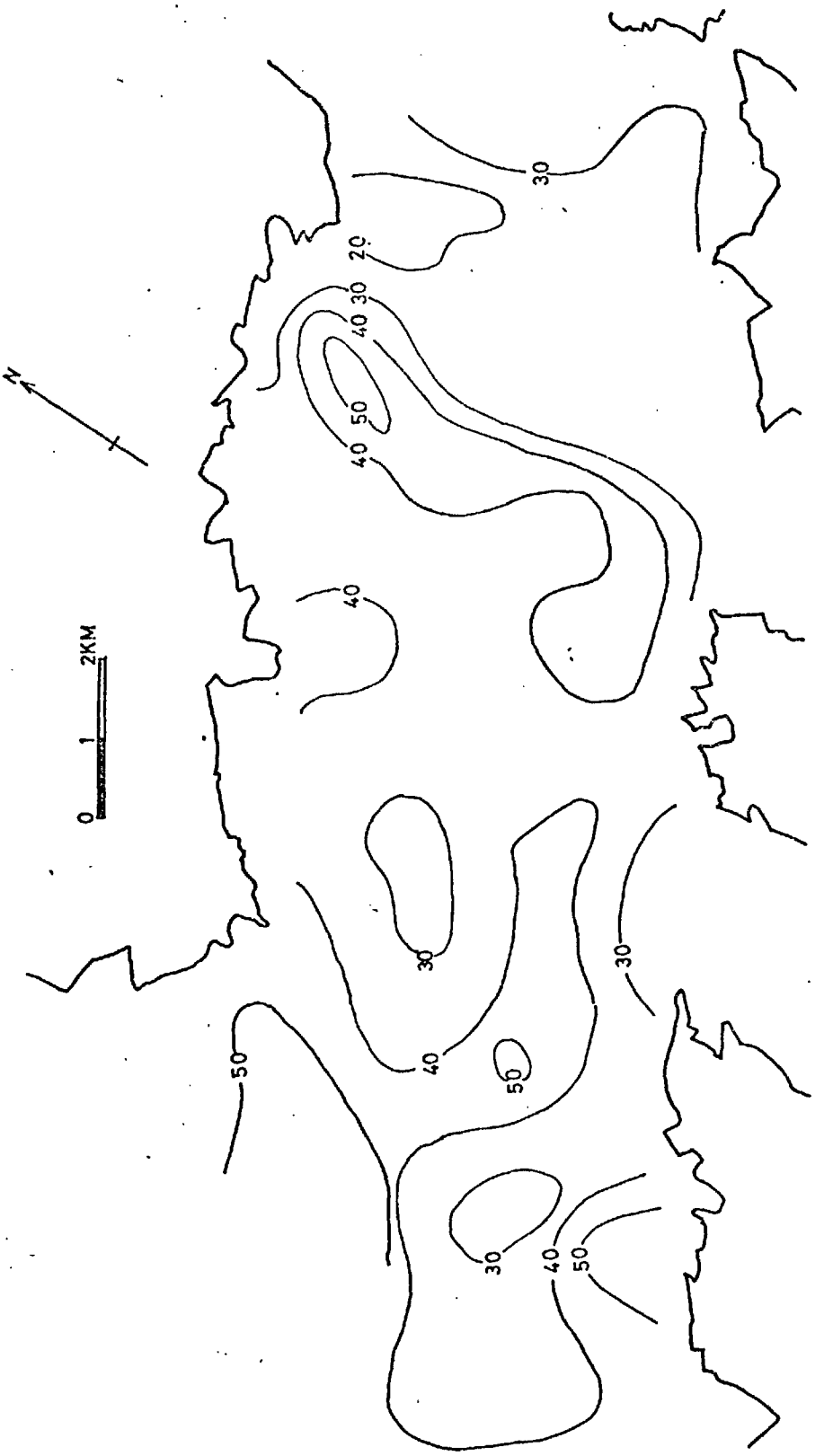


Figure 5.10 Distribution of sub-population 3 (1.5phi to 2.5phi)(% of sand fraction).

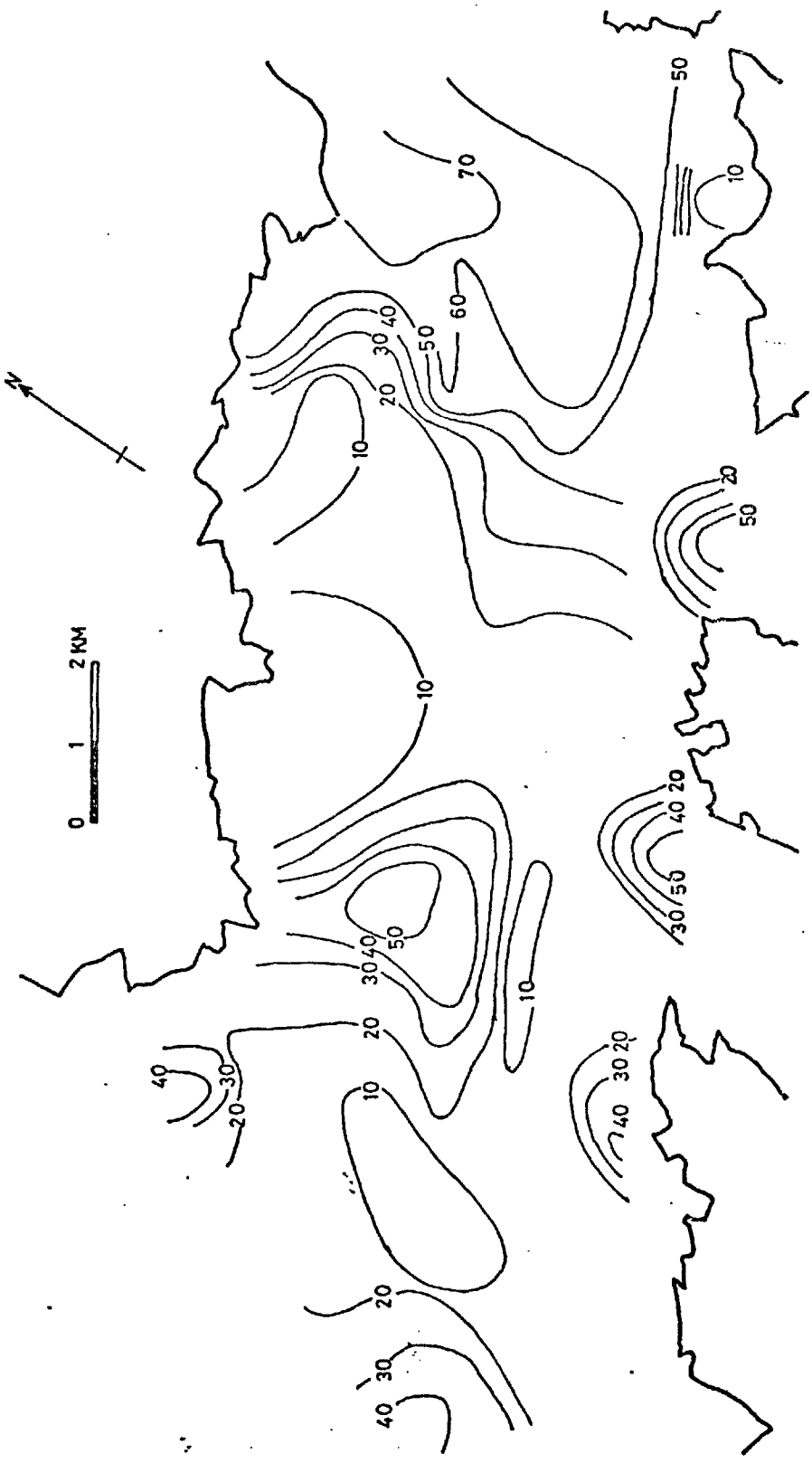


Figure 5.11 Distribution of sub-population 4 (coarser than 1.5phi)(% of sand fraction).

(see figure 5.7). It is a significant component of most of the Naxos samples but is particularly abundant in the north-west, and on the flanks of the shallow area to the east of the survey area (figure 5.10). On all the shelves described thus far, this sub-population (i.e. fine sand with a mode between $1\frac{1}{2}$ and $2\frac{1}{2}$phi) is an important component of the sediments and is thought to represent the Holocene transgressive sand sheet with which 'modern' sediments are subsequently mixed. Such may be the case at Naxos but, because depths are generally less than elsewhere, sub-population (3) may also contain a substantial 'modern' component.

Although the textural parameters and constituent sub-populations are generally similar to samples from Kithnos and elsewhere, the Naxos samples are different in certain respects. At Kithnos, Serifos and Andros the calcareous muds accumulate in the deeper water offshore and not on the shelf proper. In contrast, the calcareous muds at Naxos are strictly shelf deposits and, although given the same classification because of the similarity of their Ca and mud contents, they are different types of deposits in several respects. First of all, the mud sub-population for the deeper water deposits has a mode in the fine silt range. In contrast, the mode for the mud sub-population for the Naxos samples is the same as that found for shelf deposits elsewhere i.e. coarse silt. Five samples (477, 488, 519, 526 and 565), covering the major sediment types, were analysed by pipette techniques and the mode for the mud sub-population in all cases was found to lie in the coarse silt range. This feature is not reflected in the textural parameters because the technique for calculating them does not take into account the differences in the mode of the mud sub-population (see appendices).

Secondly, detrital sands are not found at Naxos but this could be a problem of classification rather than sedimentology, particularly as many of the bioclastic sands (I) are the textural equivalents of the detrital sands from Kithnos. For example, both the size distribution of the sand fraction (figure 5.7) and the proportion of mud in samples 474 (from Naxos) and 427 (from Kithnos) are very similar. The different nomenclature for texturally similar deposits may result from much of the terrigenous very fine sand and coarse silt being calcareous and derived from erosion of the marbles, rather than, for example, the 'chlorite-mica' group of minerals derived from erosion of schists. The greater abundance of terrigenous Ca causes

the samples to be classified as bioclastic rather than detrital sand. Resolving the problem of assessing the significance of terrigenous carbonates must await a more detailed microscopic examination of the Naxos samples.

To summarise, the distribution of facies on the Naxos continental shelf (see figure 5.12) reflects the admixture of three major components:-

(1) a fine bioclastic sand primarily consisting of reworked and 'modern' components;

(2) 'modern' silts and very fine sands deposited during the allochthonous regime post-dating the Holocene transgression and (3) coarse to medium 'modern' bioclastic sands.

Although these components are common to sediments from all the areas studied so far, the deposits from the shallower waters off Naxos differ from those from other areas in two respects:-

(1) obviously, deposits characteristic of shelf edge and deeper environments are not found, particularly the relict bioclastic sands and the deep water calcareous muds;
and (2) 'modern' terrigenous components are more extensive, especially the mud sub-population with a mode in the coarse silt range.

5.5 GEOCHEMISTRY OF THE SEDIMENTS

5.5.1 Introduction

The main reasons for determining the chemical composition of the sediments from Naxos are to establish the general levels of selected elements and, at the same time, to assess the influence of a marble dominated provenance on the chemical composition.

Discussion is primarily based on a comparison with the composition of sediments from the areas examined in previous chapters. Although the simple classification scheme based on the percentage of total Ca and mud is not entirely satisfactory for a comparison of textural parameters, it is still appropriate for geochemical comparisons because the terrigenous $CaCO_3$, like the bioclastic $CaCO_3$, dilutes the dominant element-bearing phases.

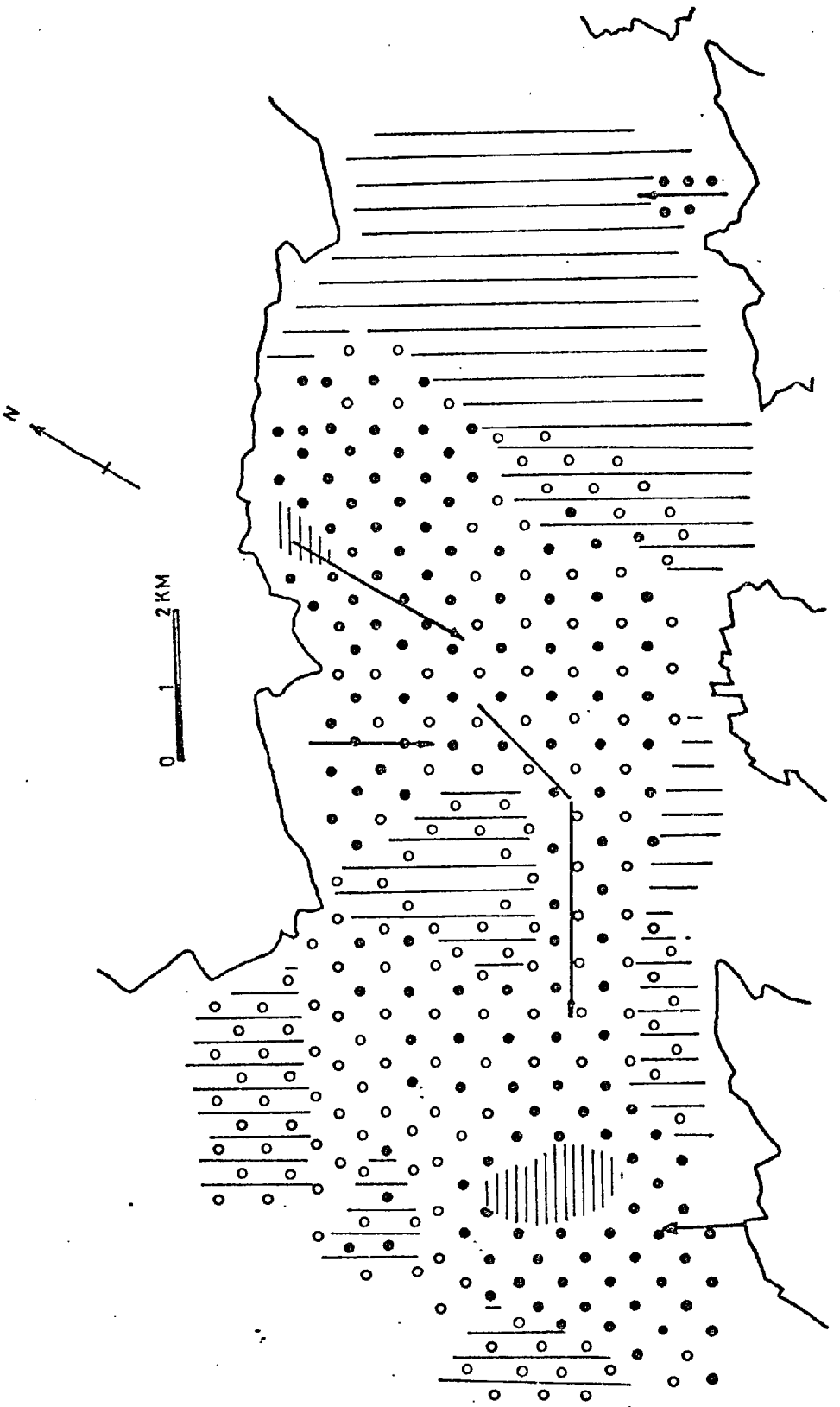


Figure 5.12 Distribution of sedimentary facies off Naxos(see figure 2.14 for key).

5.5.2 Bulk Composition

The average and range of concentration of each element for each sediment type is given in table 3. The most distinctive feature of the chemical composition of the Naxos samples is that the calcareous muds are markedly depleted in Fe, Mn, Mg, Zn and Ni, compared to their counterparts from Andros, Kithnos and Serifos. The same elements are also depleted in the bioclastic sands but not to the same extent. In contrast, Al and Ti abundances are similar to those found elsewhere.

Within the Naxos survey area the range in chemical composition of the major sediment types is smaller than that found at Kithnos, Andros and Serifos. The bioclastic sands have an almost identical composition to the calcareous muds (table 3). Obviously, the relative proportions of mud has little influence on the chemical composition.

5.5.3 Composition of the Detrital Fraction

Ten samples (471, 472, 473, 474, 475, 476, 478, 516, 517, 518), chosen to cover the range of sediment types, were leached with acetic acid and the residues analysed. The partial chemical composition of each sample is given in table 4, together with the percentage contributed by the 'detrital' fraction to the total element abundance. The composition of the 'detrital' fraction of samples from Andros, Kithnos and Serifos falls into two distinct groups - sandy sediments (427, 411, 357, 373) and muddy sediments (445, 448, 432, 435, 365, 367) (N.B. 416 and 453 are excluded because they include an authigenic iron phase). The range in element abundances for each group are displayed in table 8, together with the range in the Naxos data, to aid comparison of the composition of the detrital fractions.

At Naxos the range in composition of the 'detrital' fraction is comparatively small and, for all the elements except Ca and Mg, the samples have a similar composition to the 'sandy' group (table 8). Like the Naxos samples (5.3.4), the 'sandy' sediment mineralogy is dominated by quartz and feldspar, and the 'chlorite-mica' group are a minor component (see section 6.6.4 for further discussion).

Calcium and, to a lesser extent, Mg enrichment in the 'detrital' fraction is testimony to the presence of dolomite in the Naxos

TABLE 8 Range of element concentrations in the detrital fraction of the sediment samples from the Aegean Sea.(Ca,Fe,Al,Ti,Mg,and K are given in percent,the remaining elements are given in ppm.Summarised from table 4.)

	Sands (1)	Muds (2)	Naxos	Sounion Group A(3)	Sounion Group B(4)
Ca	0.80-1.40	1.40-2.35	2.35-4.10	1.06-1.60	1.60-1.70
Fe	2.70-3.90	5.20-5.80	2.60-4.00	3.96-5.10	2.20-3.75
Al	4.82-5.94	6.25-7.42	4.40-6.25	3.50-4.46	3.02-3.60
Ti	.27-.50	.46-.50	.27-.37	.22-.29	.26-.31
Mg	1.45-1.90	2.30-2.80	1.55-2.68	1.41-1.80	1.50-2.00
K	1.40-1.90	2.05-2.80	1.30-2.40	1.20-1.60	1.50-2.00
Mn	255-300	420-1480	240-400	230-270	240-400
Cu	17-21	40-53	15-30	20-27	26-41
Zn	58-103	109-120	55-75	129-292	440-547
Ni	53-105	143-220	28-85	63-95	105-145
Cr	160-200	240-290	110-168	168-198	230-260
Pb	7-16	17-35	11-32	39-63	105-128

Notes:-

(1) Sandy sediments from Kithnos,Serifos and Andros - 357,373,411,427.

(2) Muddy sediments from Kithnos,Serifos,and Andros - 365,367,432,435,445,448.

(3) Group A samples - 327,328,329,341,344,347.

(4) Croup B samples - 349,350,351.

samples (see 5.3.4).

The 'detrital' fraction contribution to the total element abundance also follows a similar patter to that found elsewhere, and decreases in the order:-

Fe, Al, Ti, Ni, Cr, (c.90%)> Mn, Zn, Cu (c.50%)
> Mg, Pb (c.30%)> Ca (c. 4%).

5.5.4 General Discussion and Conclusions

One aspect of the differing provenance of the terrigenous component of the sediments from Naxos, the relative paucity of the 'chlorite-mica' group of minerals, has a marked influence on the chemical composition of the sediments. Because the 'chlorite-mica' group tend to be preferentially concentrated within the finer sizes, calcareous muds are generally enriched in the elements found in this group of minerals (e.g. Fe, Mg and the trace elements). At Naxos, the lack of the 'chlorite-mica' group means that a similar enrichment in the finer fraction of the calcareous muds does not occur and they are, therefore, depleted in Fe, Cu, Zn and Ni (ie. those elements enriched in the chlorite-mica group).

A second feature of the differing provenance is that the additional terrigenous $CaCO_3$ reduces the general level of element abundance in the sandy deposits. The most obvious effect is elemental abundances less than those found in the texturally similar detrital sands elsewhere.

A result of the differing sedimentological environments is the absence of a significant manganese oxide component in the calcareous muds. Manganese oxides tend to be more important in areas of low sediment accumulation. The calcareous muds on the shelf at Naxos probably accumulate at a greater rate than the equivalent deposits found in deeper waters of Andros, Kithnos and Serifos. Neither is authigenic iron found in the samples because the relict bioclastic sands, which provide the necessary environment for the formation of such minerals, occur in depths greater than those found in the Naxos survey area.

About half of the total abundance of Mn, Cu, Zn and Pb is provided by the 'non-detrital' fraction but, even so, the concentration of the 'non-detrital' fraction is still low for these elements. Consequently, the carbonate component of the sediment could account for much of the 'non-detrital' contribution

as well as the soluble Mg.

To conclude, the major factor governing the chemical composition of the sediments at Naxos is simply calcium carbonate dilution of a 'detrital' fraction depleted in the 'chlorite-mica' minerals because of a differing provenance to that of deposits from Kithnos, Andros or Serifos. Moreover, the greater accumulation rates of 'modern' sediment also reduces the significance of the manganese 'oxides'.

5.6 GENERAL SUMMARY

(1) Although the constituent textural sub-populations are similar to those found elsewhere on the continental shelves of the Aegean, the nature and distribution of the sediment facies differ in several respects:-

(a) relict bioclastic sands are not found because they occur at greater depths;

(b) the calcareous muds are strictly shelf deposits and have a finer sand mode and a coarser silt mode

and (c) the 'fine-sand' sub-population, with which the 'modern' components are mixed, may also contain a substantial 'modern' component (whereas elsewhere this sub-population is thought to be relict, or to be part of the transgressive sand sheet).

(2) The chemical composition of the samples from Naxos is more uniform than that found elsewhere and is simply equivalent to carbonate dilution of a relatively uniform 'detrital' mineralogy because:-

(a) a marble-dominated 'provenance' means that the terrigenous component lacks the 'chlorite-mica' group and, hence, the elements which tend to be concentrated in these minerals (e.g. Fe, Cu, Zn, Ni);

(b) manganese oxides are not a significant component because accumulation rates are greater;

and (c) the absence of major deposits of relict bioclastic sands means that suitable environments for the formation of authigenic iron minerals are not available.

CHAPTER 6 SOUNION

6.1 INTRODUCTION

Sounion lies at the southern tip of the Attica Peninsula, approximately 45km to the south-east of Athens (figure 1.1). It forms the southern half of the Laurium mining district which has been famous since ancient times for the production of lead, silver, zinc and mixed sulphides. Waste dumps are widespread throughout the area, especially close to the shoreline around Mikri Skala and Asprolithari. It follows that mine waste dispersed into the adjacent marine environment will influence the composition of the sediments. Additionally, of all the areas studied in this investigation, Sounion has the greatest potential for offshore mineral deposits. Not only are the onshore deposits of Pb and Zn more extensive than elsewhere in the southern Aegean, but also their general trend is north-south which indicates they might extend onto the continental shelf.

In the context of this investigation into aspects of the applied geochemistry of continental margin sediments from the southern Aegean, therefore, the area off Sounion is of obvious interest. Accordingly, it was initially surveyed during the reconnaissance survey aboard the R.R.S. SHACKLETON in November, 1972. Chemical analysis of the 20 samples recovered established that concentrations of Pb and Zn are markedly enhanced in sediments off Sounion (Smith and Cronan, 1975a) and so the area was surveyed in greater detail aboard the Hellenic Ship PLIAS in September and October 1973, during a joint cruise between the Applied Geochemistry Research Group and the Greek Institute of Oceanographic and Fishing Research. An additional 85 grab samples from off Sounion and Laurium Harbour, and 19 beach samples from Sounion, were collected at this time. The location of all the samples used in this study are given in figure 6.1.

6.2 GEOLOGICAL SETTING AND HISTORY OF MINING

Marinos and Petrascheck (1956) provide a comprehensive account of both the geology and mining history of the Laurium district and

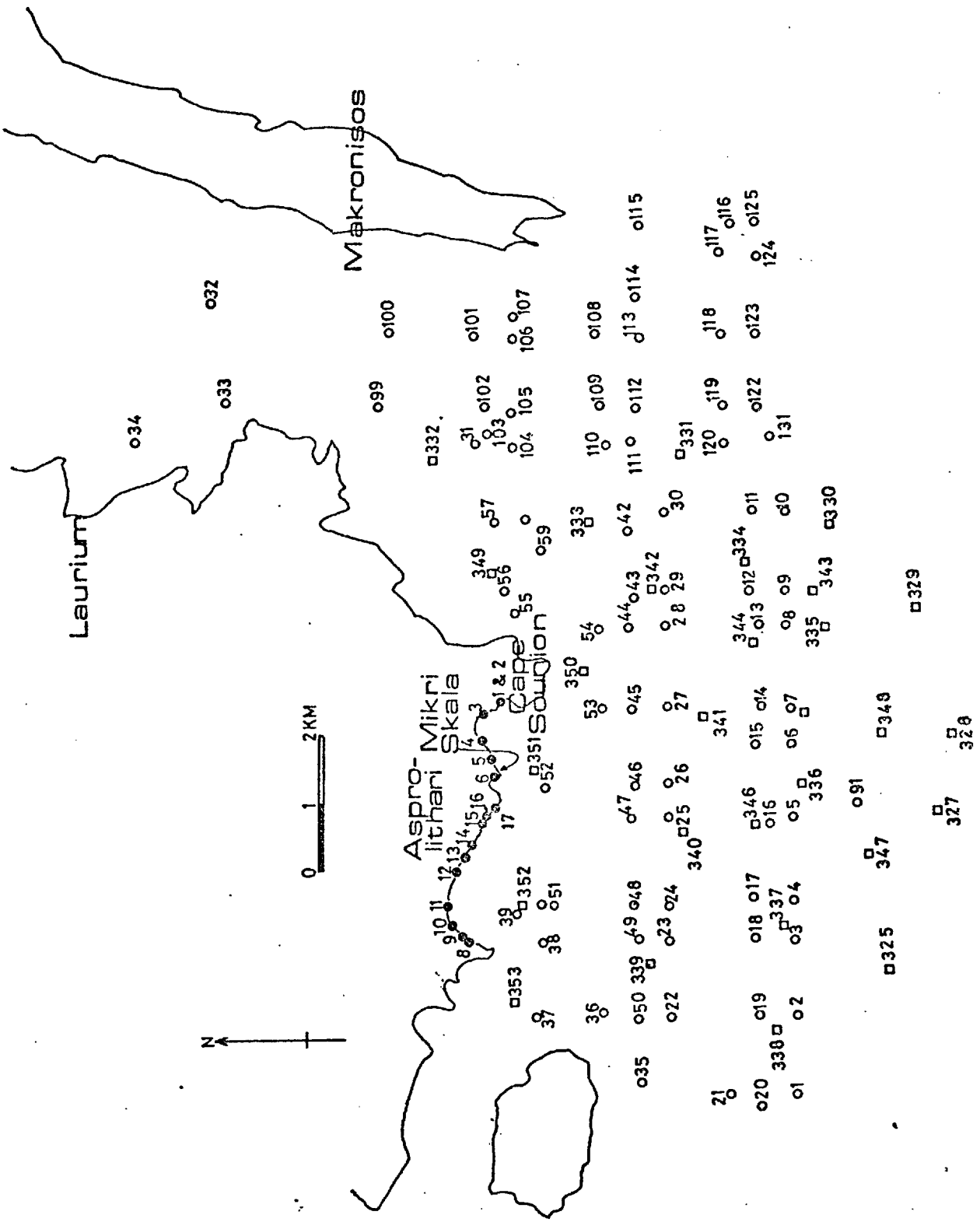


Figure 6.1 Sample locations at Sounion: ● beach samples; □ 1972 grab samples; ○ 1973 grab samples.

much of the following, plus the simplified geological map shown on figure 6.2, is based on this work. Like the islands of the Cyclades examined so far, the rocks found at Laurium are part of the metamorphic Attic-Cyclades massif. They may be divided into two units - an autochthon consisting of marbles, dolomites and mica-schists, and an overthrust nappe comprising phyllites, marbles, prasinite (metamorphosed basic rocks) and serpentine. Intersecting both units are granodiorite dykes.

Hydrothermal mineralisation is associated with the granodiorite intrusions but is partly post-magmatic with the latest phase occurring in the Miocene. A mixed sulphide assemblage of galena, sphalerite, and pyrite are the primary ores but these form secondary minerals, particularly cerussite and smithsonite. Mixed sulphides tend to be confined within the marbles of the autochthon but often occur at the contact between the marbles and the schists. North-south is the general trend of the orebodies (figure 6.2) which suggests that they could well extend onto the continental shelf. Iron-manganese ores, comprising ankerite and rhodochrosite, with associated barite, fluorite and quartz, occur in both the nappe and autochthon.

Exactly when mining began at Laurium is not known but it was probably before 1000 B.C. The peak of activity, however, coincided with the development of the Athenian state (483 B.C. and onwards). At this time the mines were of great importance - silver from Laurium, for example, apparently paid for the fleet used to defeat the Persians. Eventually the rich deposits of silver-bearing galena were exhausted and so mining declined and stagnated during the middle ages. Nevertheless, large reserves of poorer ore remained. In the latter half of the nineteenth century, therefore, mining revived and continues today.

Testimony to the remarkable skills of the ancient miners are the 1000 or more mine shafts, a large number of open-cuts, and the remains of extensive metallurgical plants, all of which are still evident today throughout the Laurium district. Unfortunately, a further legacy of this intensive activity are the huge waste dumps which, in combination with additional waste from modern operations, provide an abundant source of potentially toxic material for subsequent wind - or water-borne transport to the adjacent marine environment, particularly where dumps occur close to the shoreline (e.g. Mikri Skala and Laurium Harbour). Furthermore, tailings from

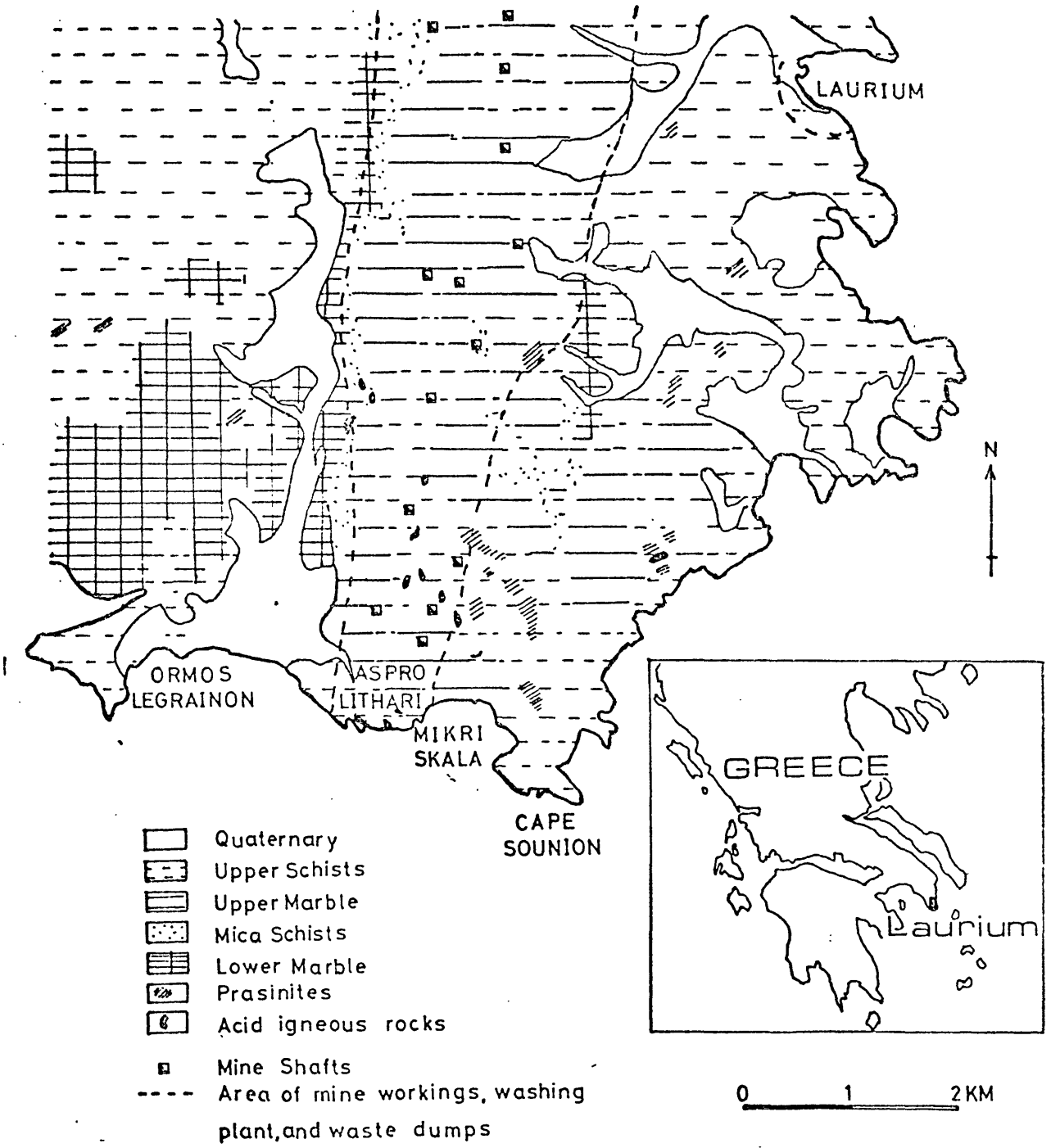


Figure 6.2 Geological outline of the southern half of the Laurium mining district showing the main area of mine workings and waste dumps.(Modified from Marinos and Petrascheck,1956.)

operations close to the coast may have been dumped directly into the sea. This practice is not unusual (Down and Mills, 1978) and may have taken place around Mikri Skala. Mine waste reaching the sea may also be indirectly related to the development of the tourist industry because local mine waste may have been used as fill material in the extensive construction work around the Sounion shoreline.

6.3 SHELF TOPOGRAPHY

A bathymetric map of the Sounion survey area is shown in figure 6.3 and is based on P.D.R. traces obtained during the 1972 survey. In general there are four depth zones which tend to be laterally continuous across the survey area.
These are:-

(1) a gently sloping 'inner shelf' shorewards of about the 55m isobath;

(2) a 'mid-shelf' slope between 60m and 100m, with steeper gradients (although to the south of Cape Sounion the generally continuous slope is interrupted by a flatter area between 70m and 80m)and which is often associated with very irregular, perhaps rocky, outcrops on the P.D.R. traces;

(3) a gently sloping 'terrace' between 100m and 120m;

and (4) the 'shelf edge' seawards of the 120m isobath and which is characterised by steeper gradients and a complex, relict topography resembling alternating headlands and embayments. The 'shelf break' occurs at approximately 130m.

6.4 THE NATURE AND DISTRIBUTION OF THE SEDIMENTS

6.4.1 Sediment Distribution

Following the scheme of Folk (1954), the sediments have been classified according to the relative proportions of mud, sand and gravel. For the 1973 samples the amount of gravel has been measured but the sand/mud ratio is based solely on visual comparison with 1972 samples. A map of the resulting sediment distribution is shown in figure 6.4.

Two broad zones with distinct characteristics of sediment distribution are evident from figure 6.4. Most of the area to the east of an imaginary line drawn from Cape Sounion to the south-east

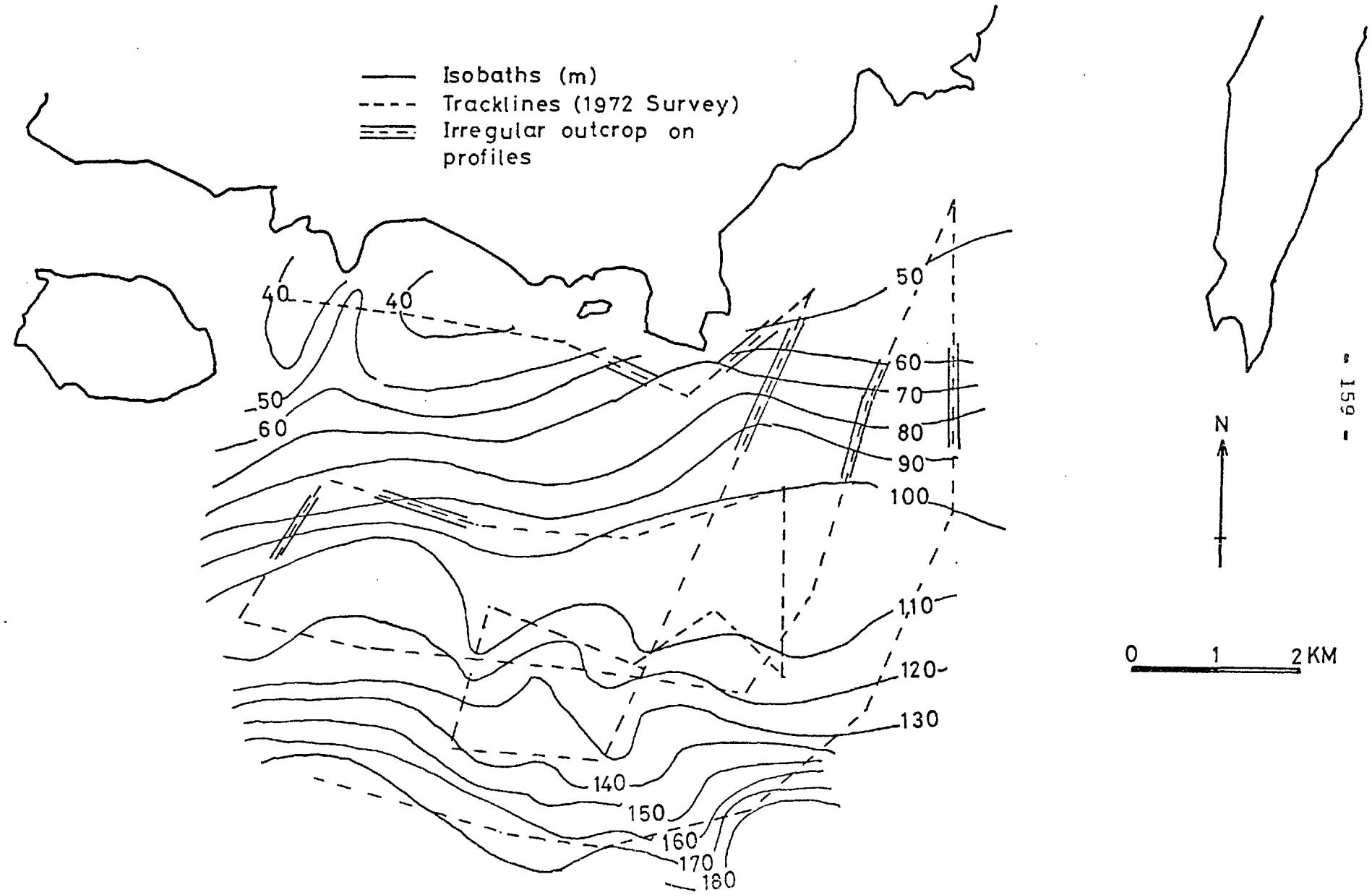


Figure 6.3 Bathymetry of the Sounion survey area.

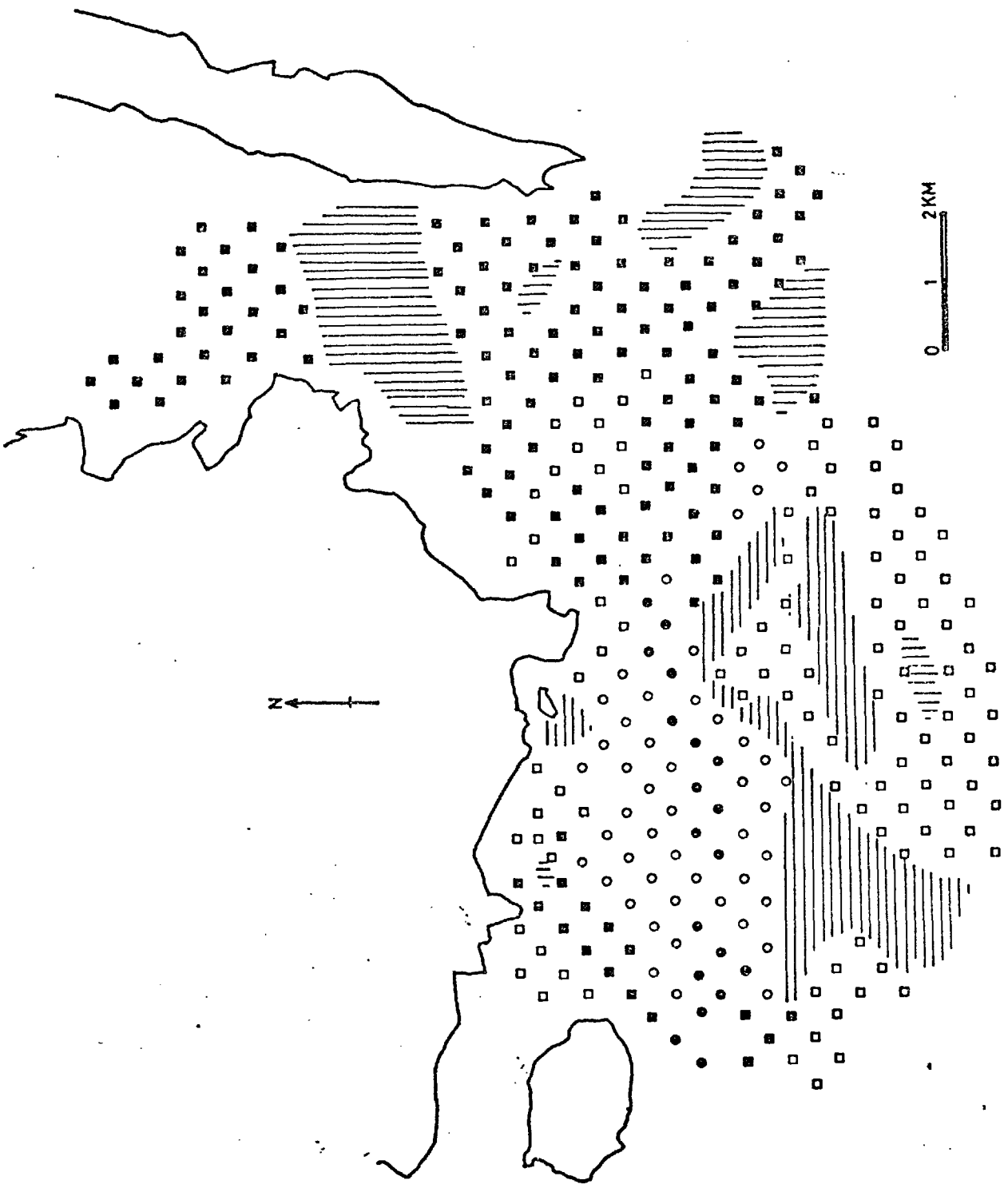


Figure 6.4 Distribution of the main sediment types off Sounion (classified according to the scheme of Folk,1954).(See figure 2.2 for key.)

is covered in gravelly-sands. Above the 50m, and below the 90m, isobath, coralline algal debris (maerl) is the most conspicuous component but between these depths the sediments are much more shelly. Patches of sandy gravels are particularly abundant between 90m and 130m but also occur between Makronisos and the mainland. Once again, coralline algae are the major components of the gravel and include both the encrusting and nodular forms. Algal nodules are, nevertheless, the most abundant type which indicates a certain amount of bottom instability (see 2.3.2). Finally, mantling the 'mid-shelf slope', to the east of Cape Sounion, is a patch of very shelly sand.

To the west of this imaginary line the sediments are more sandy. A marked feature, however, is the belt of sandy-gravels coincident with the steep, irregular 'mid-shelf slope' and comprising both the encrusting and nodular forms of coralline algae. Sandy sediments surrounding the gravels also contain abundant algal debris, whereas the sands and muddy sands seawards include little gravel and a larger proportion of shelly, molluscan material.

Perhaps the most distinctive feature of the deposits found in the western sector is the greater proportion of mud - many of the samples have the 'muddy' prefix. The gently sloping 'shelf' seawards of the 'mid-shelf slope' seems to be the major zone of mud accumulation in the western sector (fig. 6.5a). Furthermore, seaward lobes in the 'mud' isolines correspond to the embayments in the 'shelf edge' topography and may indicate dominant dispersal paths of fine-grained material. The paucity of mud in samples from less than 50m in the western sector, or in most samples from the eastern sector, may reflect greater bottom current activity which, in turn, limits the accumulation of mud. The dominance of nodular algal in the eastern sector supports this contention. Such currents in the eastern sector could relate to the funnelling affect of the channel between Makronisos and the mainland.

6.4.2 Calcium Carbonate

Leaching of selected samples shows that generally more than 98% of the total Ca is soluble in 25% acetic acid (see table 1 and section 6.6.4) and probably occurs, therefore, as calcium carbonate. How much of this carbonate is biogenous or terrigenous is impossible to say at this stage although visual examination suggests the former

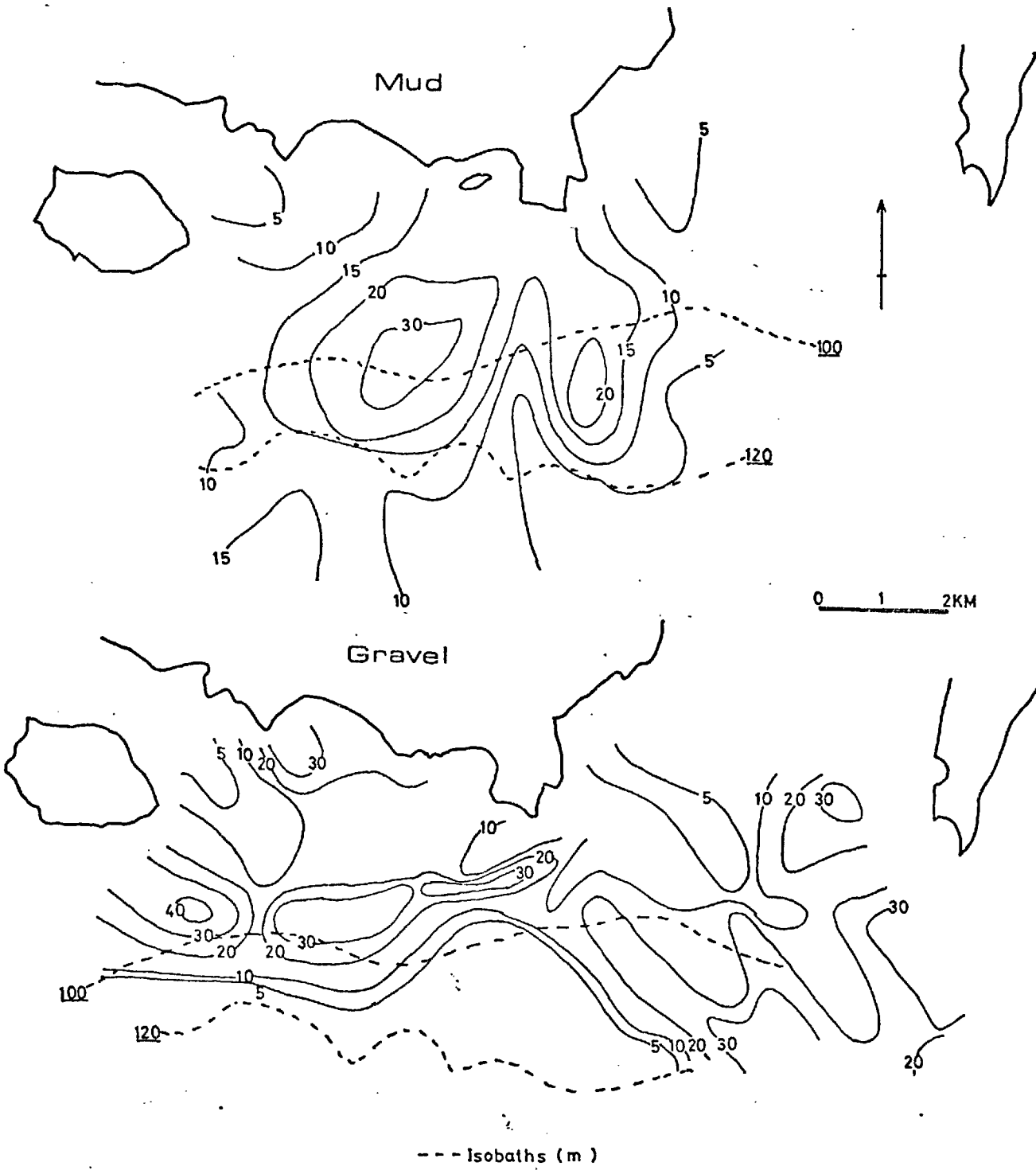


Figure 6.5 Distribution of mud(% of the fraction finer than 2mm) and gravel (1973 samples).

to be the most important. Whatever its' origins, the lateral changes in the abundance of $CaCO_3$ parallel the changes in total Ca (figure 6.6). All Sounion samples contain more than 50% $CaCO_3$ (or 20% Ca_{tot}) (except the beach sands - section 6.6.3) but in the western sector $CaCO_3$ is generally less than 75% (i.e. 30% Ca_{tot}) whereas in the eastern sector it generally exceeds this value. If, as seems likely, the $CaCO_3$ abundance is mainly an inverse function of the accumulation of modern, detrital material, it follows that detrital accumulation is greatest in the western sector and in three zones in particular:-

(1) close to the shore to the south-west of Mikri Skala (N.B. the adjacent beach sands are rich in detrital material - section 6.6.3);

(2) seaward of the 'mid-shelf edge' to the south-west of Cape Sounion;

and (3) the embayment in the 'shelf edge' in the south-western corner of the survey area. The overlap between the latter two zones with the major zones of mud accumulation (compare figure 6.5a and 6.6) supports the hypothesis that fine-grained detrital accumulation is greatest in these zones. In the nearshore zone coarser detrital material may be accumulating.

6.4.3 Reclassification of the Sediments

Because the gravel fraction of the sediments is removed prior to the geochemical and textural analyses, the Folk classification scheme is inappropriate for comparison of the characteristics of the major sediment types between the areas studied. Instead, a simple scheme based on the proportions of total Ca (as an estimate of $CaCO_3$) and mud is used (2.3.4). Elsewhere this scheme seems to be reasonable for geochemical comparisons but textural comparisons may be limited, especially if the terrigenous component contains carbonate minerals (5.3.3). Textural analyses have not been conducted on the 1973 samples and so comparisons between Sounion and the other areas is based solely on the 1972 samples. Of these, most (23 samples) contain more than 27% total Ca and less than 30% mud and are accordingly classified as bioclastic sands (II). Two samples (325 and 341) are bioclastic sands (I) and only one sample (340) is a calcareous mud.

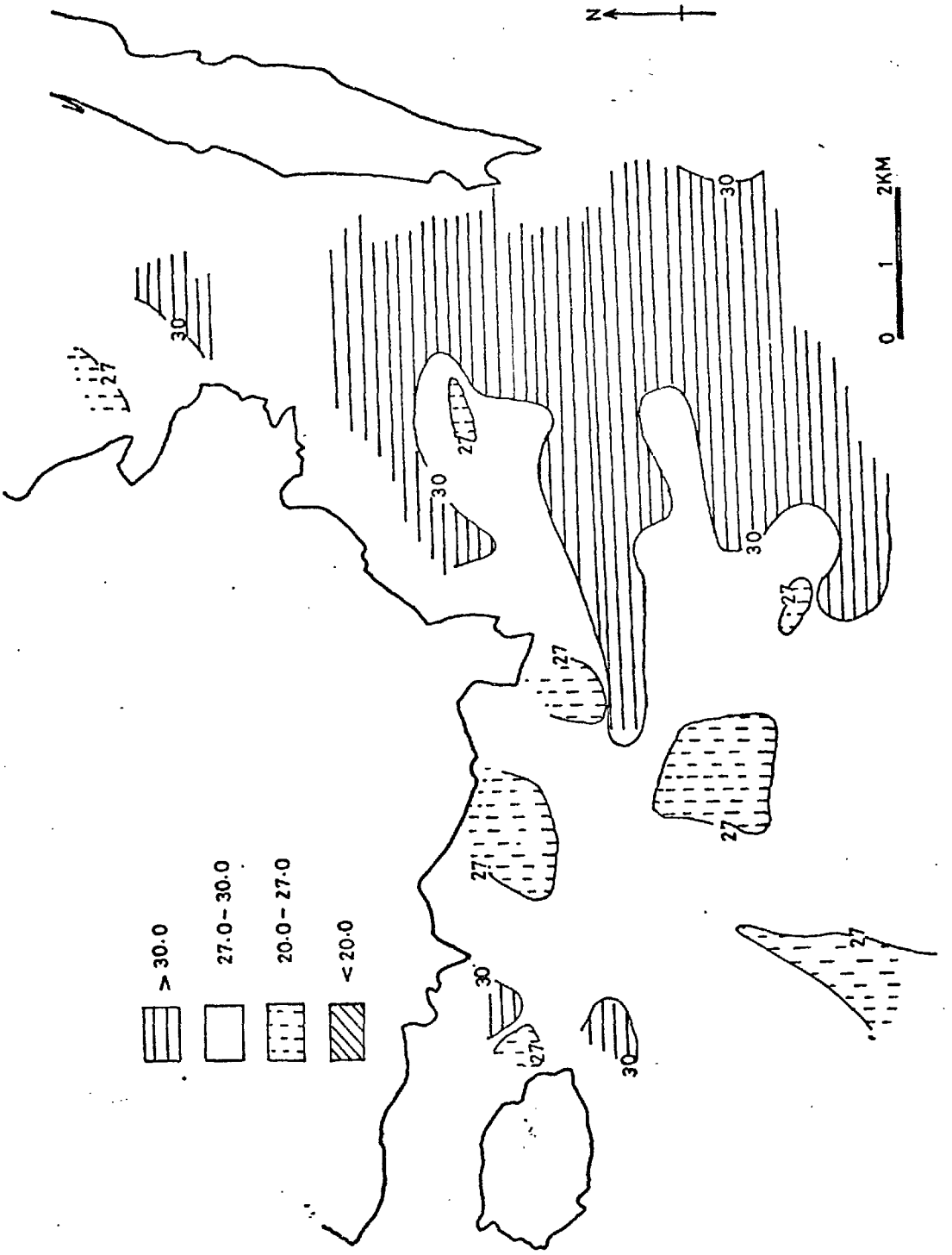


Figure 6.6 Distribution of total calcium (%) in samples from Sounion.

6.4.4 Mineralogy of the Detrital Fraction

Based on the qualitative X.R.D. examination of the acetic-acid residues of seven samples (327, 328, 329, 341, 347, 350 and 351) from Sounion, the detrital fraction appears to have a common mineral assemblage comprising quartz, feldspar, the chlorite-mica group and dolomite. Such an assemblage is consistent with a local geology which includes both marbles and schists. Compared to the detrital fraction of samples from other areas, the relative proportion of quartz appears to be greater in the Sounion samples.

6.5 TEXTURAL ANALYSIS AND SHELF SEDIMENTATION

6.5.1 Sediment Texture

Most of the samples from Sounion are bioclastic sands (II) and from table 2 it is evident that they have a wide range of textures. On average, however, they are broadly similar to the equivalent deposits in other areas except Andros, although they do have a slightly finer average median size and are slightly better sorted. The two bioclastic sands (I), like their counterparts at Naxos, are texturally closer to the detrital sands from Kithnos and Serifos. The calcareous mud (340) falls into the coarser end of the spectrum of sizes for this group.

Figure 6.7, the scatter plot of mean size against sorting, illustrates the range in textural characteristics of the Sounion samples. Once again it is the relative proportions of sand and mud, combined with changes in the dominant modal size of the sand fraction, which govern the texture (see 5.4.1). Samples 344 and 352, for example, have a similar sand fraction size distribution but widely different amounts of mud (22.0% and 6.1% respectively). For a given sand mode, an increase in the proportion of mud is matched by a decrease in the mean size and an increase in the sorting coefficient (2.4.3) and consequently 344 is finer and more poorly sorted than 352 (figure 6.7).

Superimposed on this trend is the influence of the range in size of the major sand modes. Samples 343 and 345, for example, both contain about 3% mud but different sand modes (i.e. between 2 and 2½phi for 343, and between 1 and 1½phi for 345). For a given

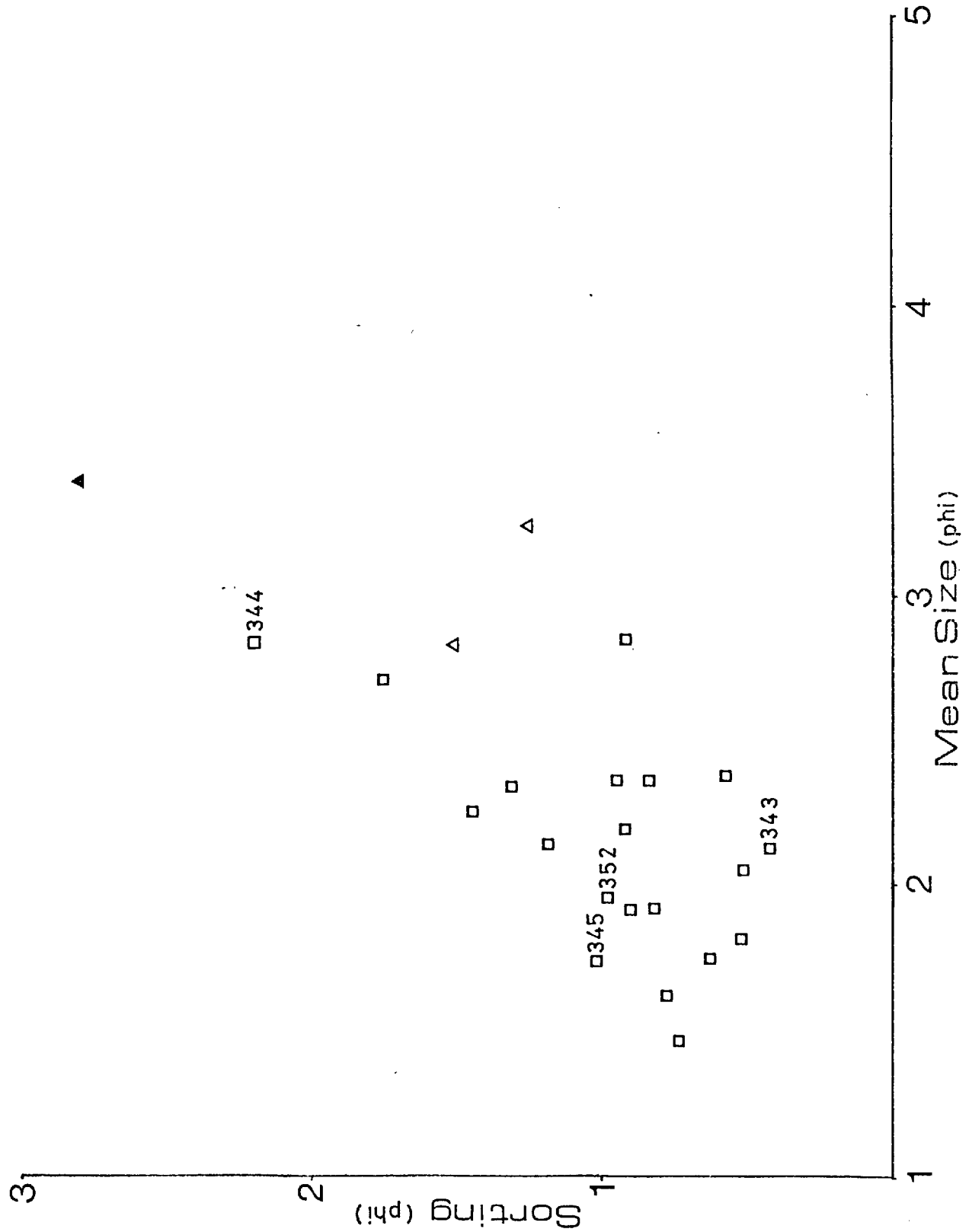


Figure 6.7 Sorting against mean size for Sounion samples:
▲ calcareous mud; △ bioclastic sands I; □ bioclastic sandsII.

amount of mud, an increase in the size of the major sand mode is matched by an increase in both the mean size and sorting coefficient and accordingly 345 is coarser and more poorly sorted than 343 (figure 6.7). Sand fraction size distributions for the major types of deposit found at Sounion are shown in figure 6.8. Also illustrated, for comparison, are selected examples from Kithnos.

The textural characteristics of the deposits from Sounion may, like their counterparts elsewhere, be described in terms of the mixing of four sub-populations.

These are:-

(1) mud;

(2) very fine sand with a mode around 3 phi;

(3) fine sand with a mode around 2 phi;

and (4) medium/coarse sand with a mode coarser than $1\frac{1}{2}$ phi (section 2.4.3).

The largest group of bioclastic sands (II)(327, 331, 332, 333, 335, 339, 342, 344, 352 and 353) are mixtures of sub-populations 4 and 3, with the former, coarser sub-population being dominant (e.g. 344, 352 - figure 6.8). Where sub-population 4 is particularly large the sand fraction appears almost unimodal (e.g. 332 - figure 6.8) and very similar to Group E deposits found at Kithnos (e.g. 404 - figure 6.8, see section 2.4.2c). A second group of bimodal bioclastic sands (II) (338, 345, 350) also have a major mode corresponding to sub-population 4 (i.e. coarser than $1\frac{1}{2}$phi) but the minor mode is finer and corresponds to sub-population 2. The sand fraction of the calcareous mud (340) also falls into this category.

The distribution of sub-population 4 is shown in figure 6.9a and it mainly comprises bioclastic material. Although abundant in most deposits shorewards of the 110m isobath, like gravel, it is most abundant close to the mid-shelf slope and in the eastern sector of the survey area (compare figure 6.9a and 6.6b), close to the coralline algal biocoenoses.

Many samples in the deeper waters of the survey area, particularly to the south of Cape Sounion, appear unimodal and consist almost entirely of sub-population 3 (fine sand) (330, 334, 343, 347, 348, 349 - e.g. 343 figure 6.8). They are texturally equivalent to the well-sorted bioclastic sands found at similar depths off Kithnos (Groups B and C - section 2.4.2c, e.g. 412 - figure 6.8). At Sounion, as in the other areas of the southern Aegean, sub-population 3

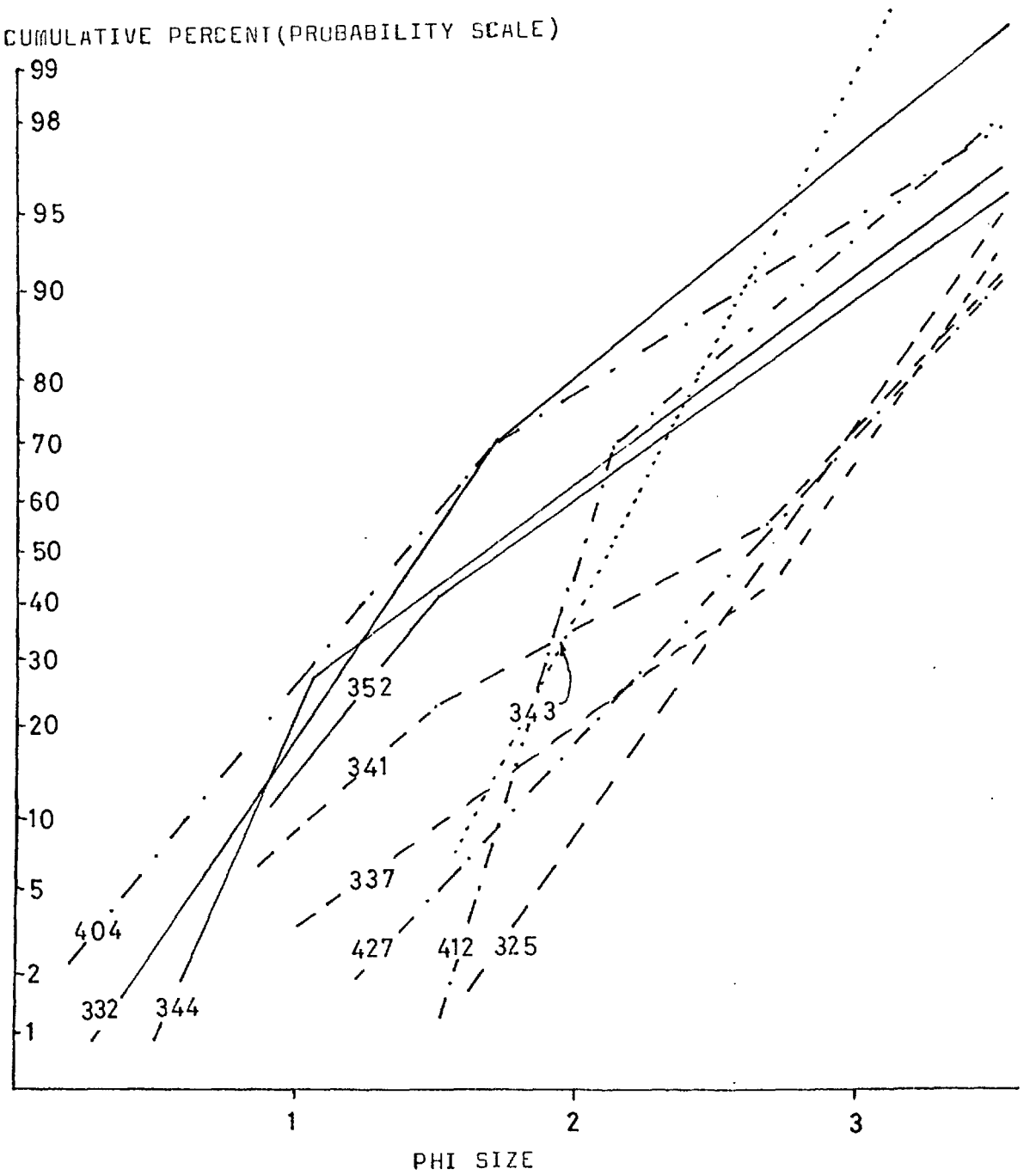


Figure 6.8 Cumulative grain size curves for selected samples from Sounion and Kithnos.

is thought to mainly comprise relict material which, in deposits at depths less than 120m, has been reworked during the Holocene transgression to form a 'framework' deposit, equivalent to the Holocene transgressive sand sheet found on other shelves of the world (Curray, 1965), with which 'modern sediments are subsequently mixed. It is evident from figure 6.9b that this sub-population is a prominent fraction of all samples but is most abundant on the shelf edge south of Cape Sounion where the material is predominantly relict, and on that part of the 100m-120m terrace where the accumulation of 'modern' components (i.e. coarse bioclastic and fine-grained terrigenous material) is least. Iron-staining is particularly evident in the latter samples and this is testimony to their relict origin and previous sub-aerial exposure.

In contrast, samples from the 'inner shelf' (e.g. 349) containing a large sub-population 3, may include a substantial amount of modern bioclastic fine sand, or terrigenous fine sand, which has managed to escape the nearshore zone (normally considered to be a sink for material of this size).

In the remaining bioclastic sands (325, 336, 337, 341 and 351) the dominant sub-population is sub-population 2 (very fine sand) (e.g. 325, 337 and 341 - figure 6.8). Although these samples generally contain less mud than the detrital sands from Kithnos, their sand fractions are similar texturally (compare with 427 - figure 6.8). Either the terrigenous component of sub-population 2 contains a greater proportion of calcium carbonate (as is thought to be the case in similar deposits from Naxos - see section 5.4), or fine-grained bioclastic material (e.g. Foraminifera, ostracods) is more abundant in this sub-population than in equivalent deposits elsewhere. Several features of the distribution of sub-population 2 (figure 6.9c - represented by the amount of the sand fraction falling between $2\frac{1}{2}$ and $3\frac{1}{2}$phi) suggest, however, that in common with the other areas studied it does contain a substantial 'modern', terrigenous component.

These features are:-

(1) a similarity between the distribution of mud and very fine sand (compare figures 6.6a and 6.9c) - mud is the most likely modern terrigenous component (section 2.4.3);

and (2) seawards of the 'mid-shelf slope', zones of least $CaCO_3$ (i.e. zones where detrital accumulation may be greatest) broadly

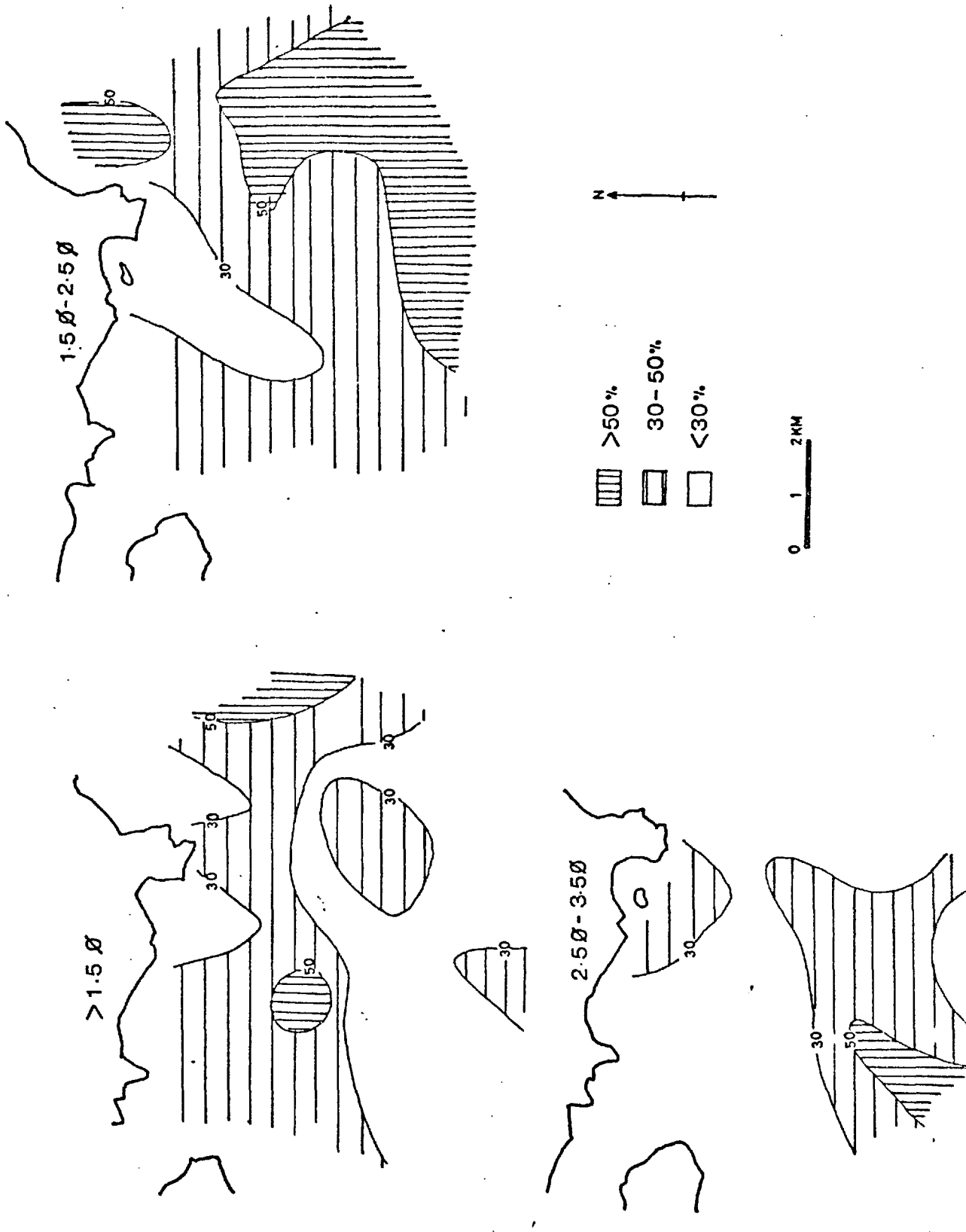


Figure 6.9 Distribution of sub-populations 2 (2.5phi to 3.5phi), 3 (1.5phi to 2.5phi), and 4 (coarser than 1.5phi) (% of sand fraction).

correspond to zones where the abundance of sub-population 2 is greatest (compare figures 6.7 and 6.9c), indicating a possible correlation between the accumulation of terrigenous material and sub-population 2.

6.5.2 Shelf Sedimentation

Controls on the nature and distribution of the major facies (see figure 6.10) on the Sounion continental margin are similar to those considered to be important elsewhere (see e.g. section 2.4.5). As on many continental margins of the world, the surface sediments are mixtures of relict, reworked and modern components. Shelf edge deposits seawards of the 120m isobath mainly comprise relict material deposited during, or prior to, the last low-stand of the sea-level. During the Holocene transgression that followed pre-existing sub-aerial deposits were reworked and redistributed to form a transgressive sand sheet across the shelf. Products of modern processes have been subsequently mixed with this transgressive fine sand.

There are two main sources of 'modern' material - terrigenous and biogenous. Once again, the accumulation of fine-grained material (very fine sand and mud) appear to be related to 'modern' terrigenous sedimentation, although a proportion of the coarser sand found in nearshore samples may also have a similar origin. On the assumption that fine-grained terrigenous material present in pre-existing unconsolidated deposits would be unlikely to survive reworking by a transgressing shoreline and would therefore be removed and redeposited seawards, all that can be said about the origin of this fraction in sediments from depths less than 130m is that it was deposited after the passage of the shoreline. It could derive from the reworking of shallower deposits, more recent allochthonous sedimentation, or, as seems more likely, a combination of the two. Modern bioclastic material is an important component of most samples on the shelf particularly around the coralline algal 'biocoenoses' present on the 'mid-shelf slope' and in the deeper waters of the eastern sector. Elsewhere mulluscan infauna and Foraminifera are important contributors of modern bioclastic material.

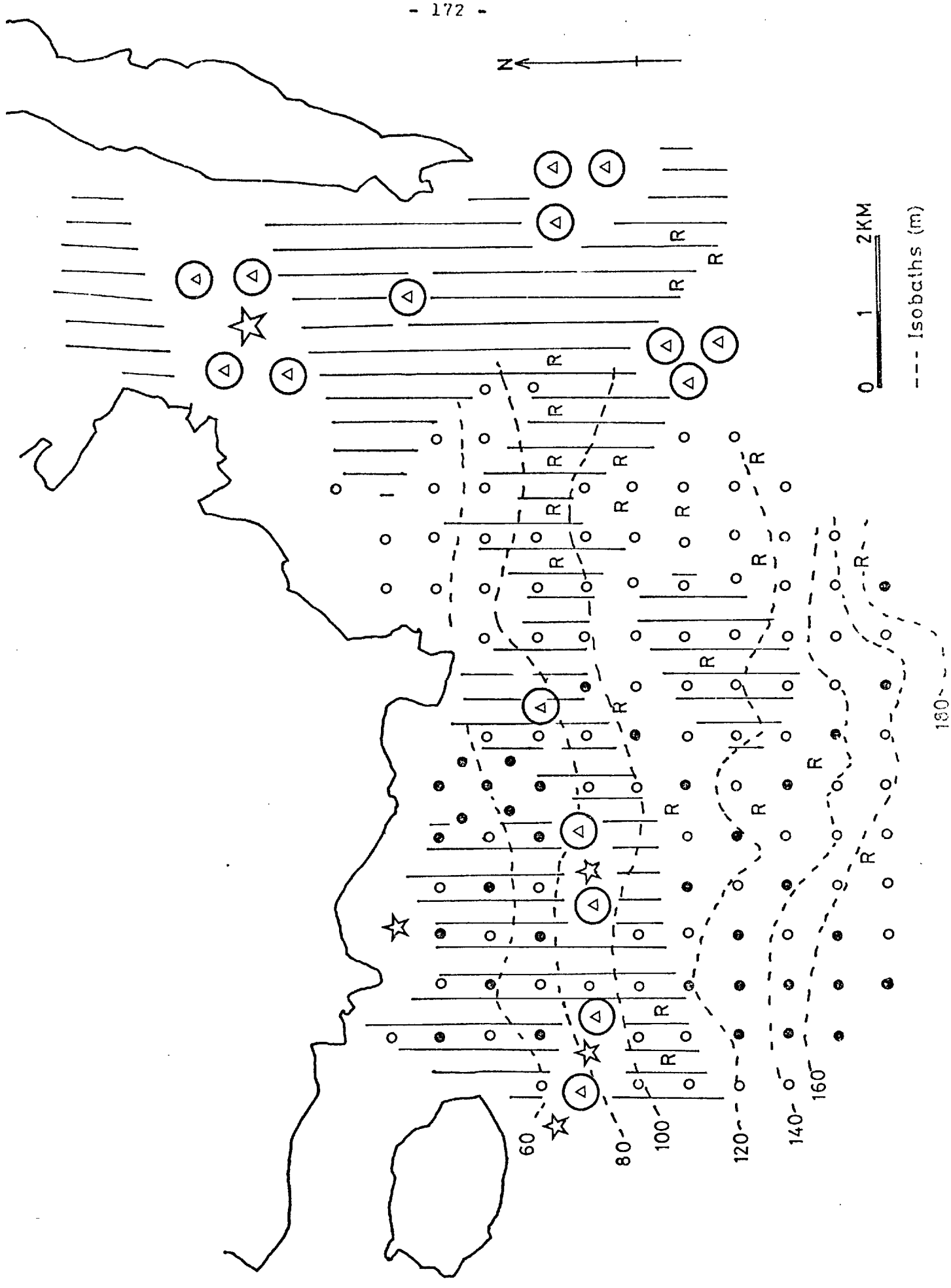


Figure 6.10 Distribution of sedimentary facies off Sounion (see figure 2.14 for key).

6.6 GEOCHEMISTRY OF THE SEDIMENTS

6.6.1 Introduction

Sounion samples are of geochemical interest for two reasons. Firstly, the dispersal of mine waste during a long history of lead mining close to the coast will influence the composition of the adjacent marine sediments to some extent. Secondly, the general trend of the mineral deposits suggests they may extend offshore. Accordingly, samples were collected off Sounion during the 1972 reconnaissance survey, and their analysis established that the concentration of Pb and Zn are much higher than elsewhere (Smith and Cronan, 1975a). Therefore a further detailed survey was conducted during the 1973 expedition to the Aegean Sea.

Much of the following discussion is based, therefore, on two sets of samples. 1972 samples alone are used to compare the average partial composition of the major sediment types found at Sounion with the equivalent deposits from other areas. Both the 1972 and 1973 samples are combined to assess the major controls on the composition of the sediments and the geographic distribution of element concentrations.

Important questions considered in this section include:-

(1) "what are the major factors governing the composition of the sediments?";

(2) "what influence does the accumulation of mine waste have on the chemical composition of the sediments?";

(3) "what do geochemical studies of the sediments reveal about the potential toxicity of the Pb and Zn?";

and (4) "what does the geographic distribution of Pb and Zn reveal about the nature of 'modern' sedimentation?" - the mine waste (and associated anomalous levels of Pb and Zn) is a known 'modern' component of the sediment and may be used, therefore, as a natural 'tracer'.

6.6.2 Bulk Composition

Most Soumion samples are bioclastic sands (II) and undoubtedly the most significant differences between the average composition of this group and their counterparts elsewhere are the much greater

abundance of Pb and Zn. On average Pb is five times, and Zn three times, more abundant (table 3). In view of previous comments on the local mining history, this enrichment of Pb and Zn is not surprising. It seems, however, that the influence of the mine waste on the composition is restricted to these two elements because the average concentrations of the other elements at Sounion are broadly similar to those found in equivalent deposits elsewhere (table 3).

Small differences in the average composition of the bioclastic sands (II) include, for example, a small depletion in Al (table 3) which is consistent with a greater quartz abundance at Sounion (6.4.4). Furthermore, despite the presence of dolomite in some of the samples (section 6.4.4) Mg, like Al, is slightly depleted. This could reflect the greater proportion of quartz relative to the magnesium - rich 'chlorite-mica' group but other factors may be equally or more significant. An interesting possibility, discussed later, is that differences in the mineralogy of the bioclastic component may account for the depletion in the average concentration of Mg at both Naxos and Sounion.

Although limited in number, comparing the two bioclastic sands (I) and the one calcareous mud with the equivalent deposits elsewhere reveals similar differences in composition to those found for the bioclastic sands (II), but the degree of enrichment of both Pb and Zn is even greater.

Charts of element distribution within the Sounion area are based on both the 1972 and 1973 samples. As expected, the predominantly ' detrital' elements Al, Fe, Cr, Ni and Ti (e.g. Al-figure 6.11) have distributions broadly antipathetic to Ca (c.f. figures 6.6 and 6.11). Particularly evident is the broad division in abundance between the eastern and western halves of the survey area. A similar division was found for Ca (section 6.4.2) but in the opposite sense (i.e. in the eastern half Ca is highest but Al lowest). Once again this illustrates the importance of carbonate-dilution as a control on element abundance. Nevertheless, although it is probably the major control, carbonate-dilution does not totally account for the distribution of the 'detrital' elements and mineralogical factors are also likely to be important, particularly the relative proportions of quartz and the alumino-silicates within the 'detrital' fraction (i.e. equivalent to the

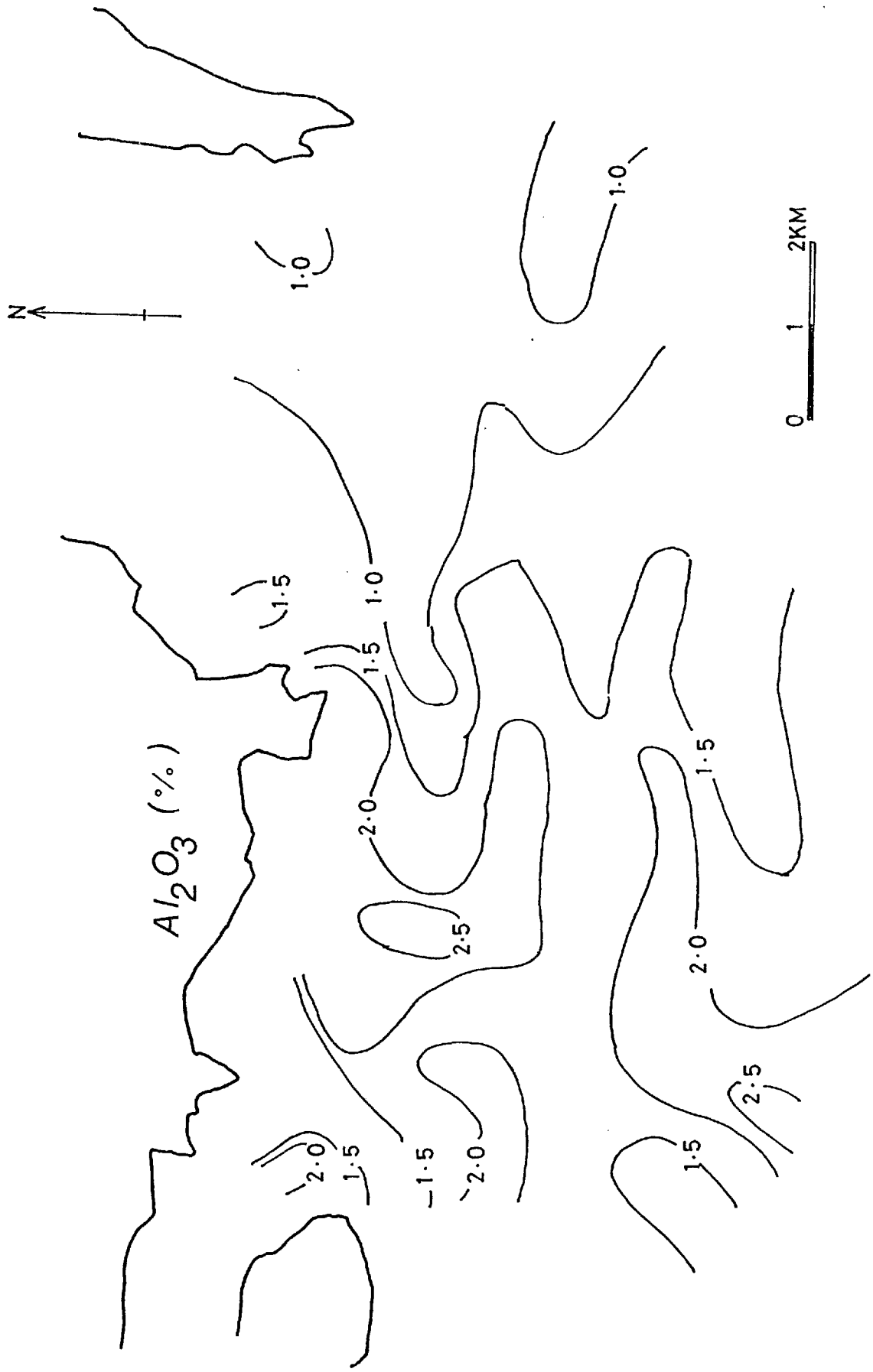


Figure 6.11 Distribution of Aluminium.

'aluminosilicate' factor found at Kithnos - section 2.5.4, see also section 6.6.4).

Interestingly, both Mg and Mn (figure 6.12 and 6.13 respectively) have similar distributions characterised by a belt of high values broadly corresponding, in the western sector, to the 'mid-shelf slope', and extending into deeper water in the eastern sector. These same characteristics also apply to the distribution of gravel (c.f. figures 6.5b and 6.12) which, in turn, is probably related to the predominance of coralline algal material in the deposits. There is, therefore, an association between Mg and the abundance of coralline algae. This is consistent with the latter consisting primarily of magnesian calcite, whereas molluscan and foraminiferal fragments (the other major bioclastic components) mainly comprise calcite or aragonite (Milliman, 1974). A major control on the abundance of Mg is, therefore, the relative proportions of the major bioclastic components, which may also account for the regional differences in the average Mg concentrations of the bioclastic sands (table 3). These are highest at Kithnos, Serifos and Andros where the deposits contain a larger proportion of algal material. At Sounion and Naxos, in contrast, molluscan debris is more abundant overall.

For Mn, however, the simplest interpretation of the higher concentrations approximately coinciding with the 'mid-shelf slope' is that the accumulation rate of that fraction of the sediment smaller than 2mm is lower in this zone than elsewhere on the shelf. Lowest levels of Mn occur in shallower water (figure 6.13) where sediment accumulation rates, either bioclastic or terrigenous, are probably greater. Other factors, such as the availability of appropriate nucleii and the Eh of the depositional environment, may also control the accumulation of manganese 'oxides' but their importance is difficult to assess at this stage.

Although the range in Cu concentration is small (8ppm - 20ppm, excluding P34 off Laurium Harbour), the Cu distribution (figure 6.14) indicates that the higher values correspond to those samples with either a lower Ca (i.e. $CaCO_3$) or higher Mn concentration, suggesting that the abundance of Cu in Sounion deposits is mainly governed by the combined influence of manganese 'oxide' scavenging and the dilution, by $CaCO_3$, of 'detrital' Cu. Similar factors govern the abundance of Cu at Kithnos and elsewhere. Only in one sample (sample 34 off Laurium Harbour - 50ppm Cu) does mine waste appear to significantly influence the amount of Cu in the deposit.

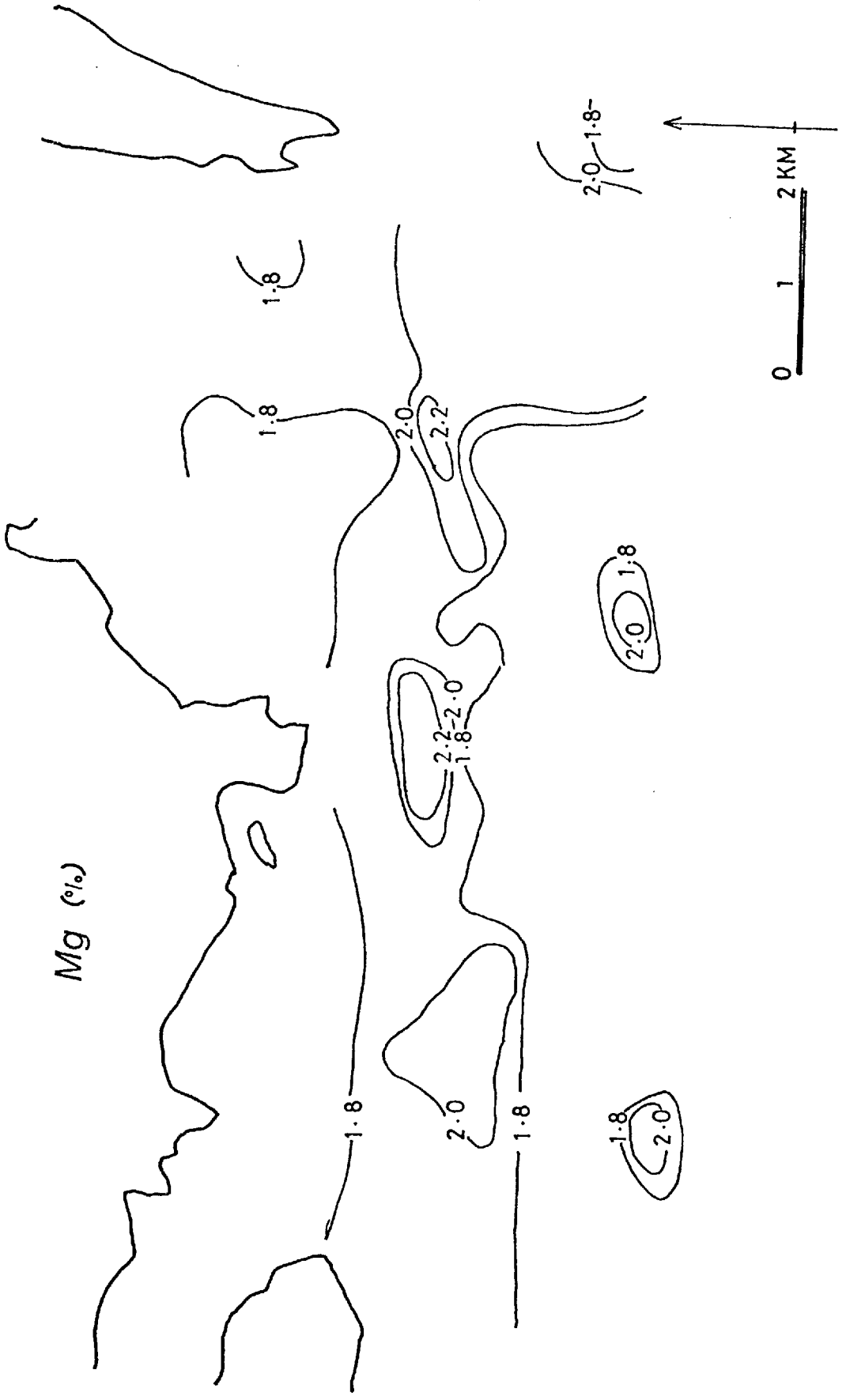


Figure 6.12 Distribution of Magnesium.

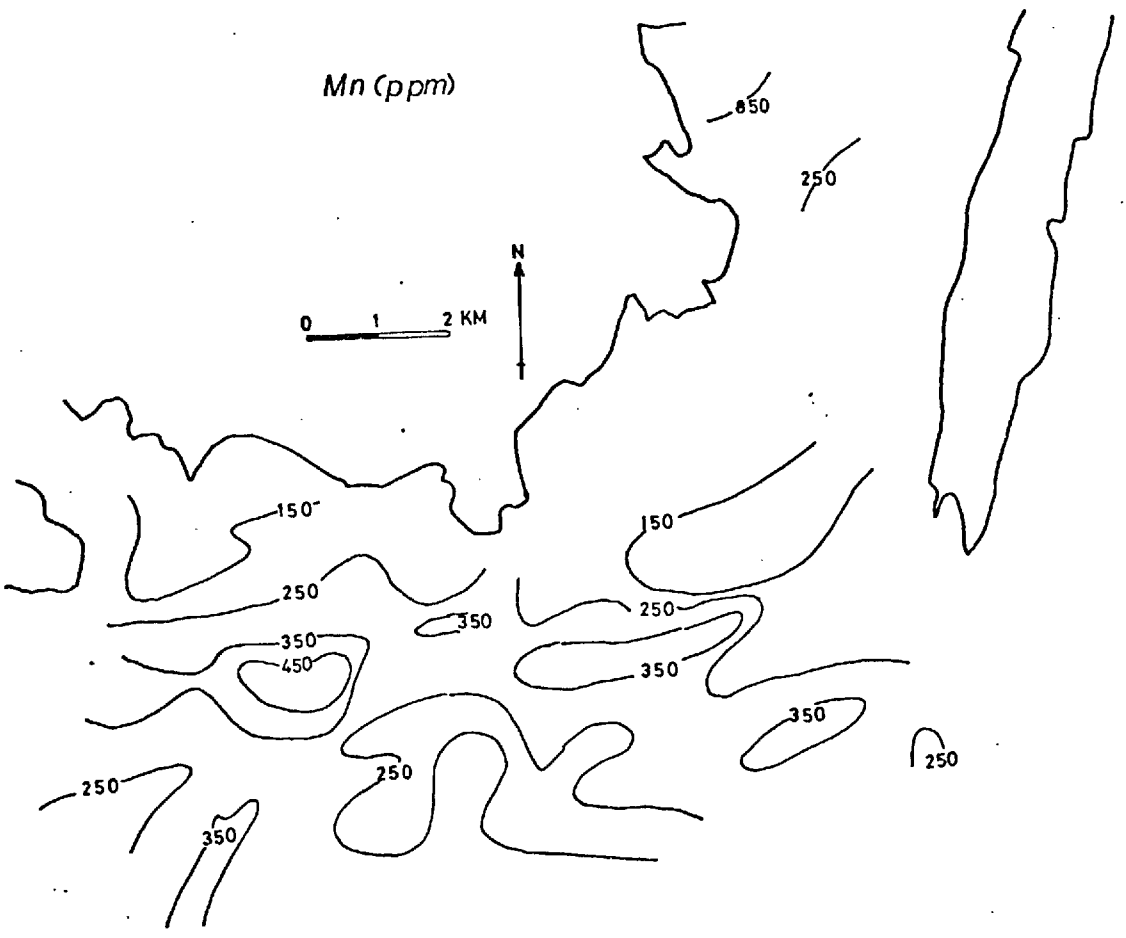


Figure 6.13 Distribution of Manganese.

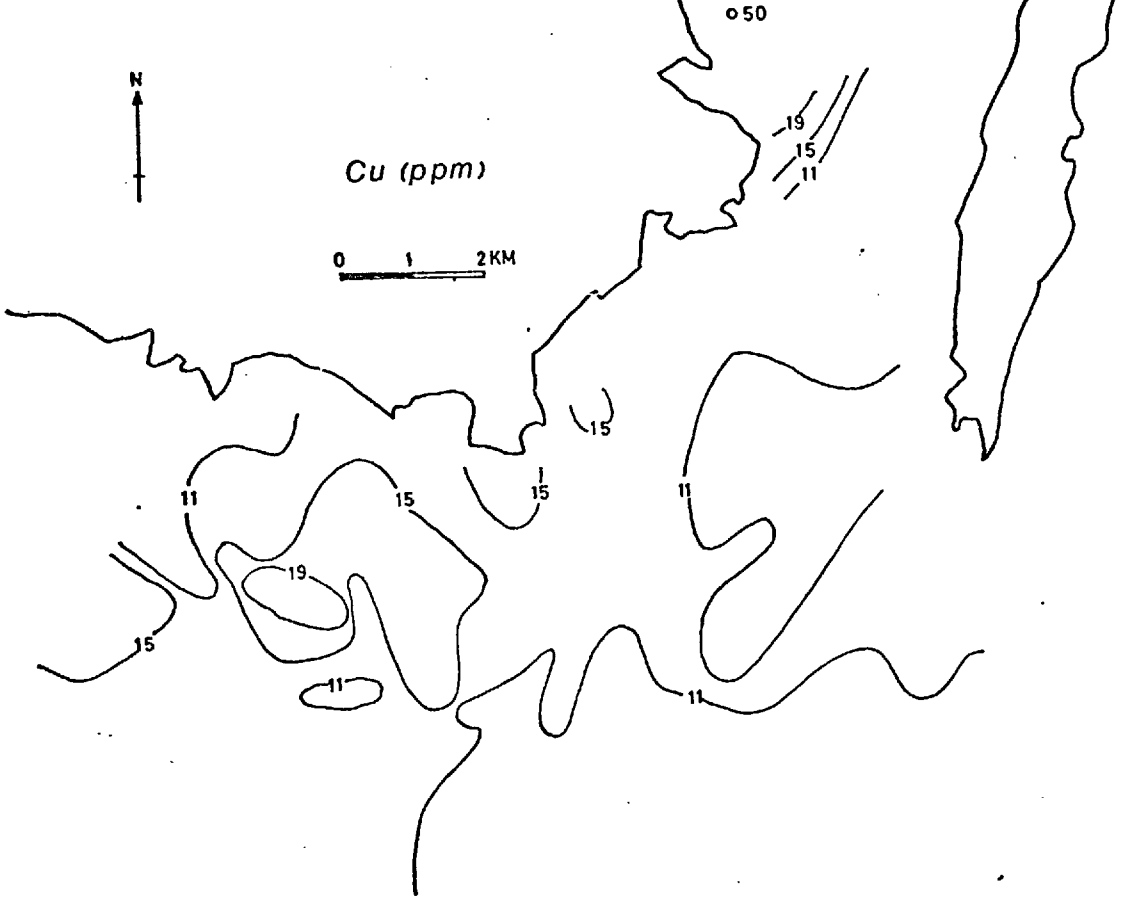


Figure 6.14 Distribution of Copper.

Highest levels of Pb and Zn in the offshore deposits occur off Laurium Harbour where sample 34, for example, contains 1340ppm Zn and 1540ppm Pb. In the main part of the survey area, however, the most distinctive feature of the distribution of both Zn and Pb (figures 6.15 and 6.16 respectively) is the gradual decrease in concentration with distance away from the shoreline. Off Asprolithari (figure 6.1), Zn and Pb reach 322ppm and 425ppm respectively, but decrease to less than 40ppm and 50ppm respectively on the shelf edge. Such concentration gradients are characteristic of 'modern' terrigenous sedimentation. Superimposed on the overall trend is the movement of Pb and Zn, as part of the 'modern' terrigenous component of the sediment, along preferred dispersion pathways. In the western sector, in particular, lobes in the concentration isolines (e.g. 100ppm Zn - figure 6.15) coincide with valleys in the shelf edge topography. Some possible dispersion pathways are shown in figure 6.15 and 6.16.

6.6.3 Composition of the Beach Sands

Beach samples were collected along the Sounion shoreline for the following reasons:-

(1) to assess the influence of local mining activity on the composition of the beach sands;

and (2) to pinpoint sources of contaminating material through longshore changes in composition.

Table 9 summarizes the chemical composition of the beach sands. The 'general' category refers to the majority of samples and includes BS1, BS3 and all of the samples from Ormos Legrainon (figure 6.1). BS4 and BS5 are considered separately because of their anomalous composition.

All samples fall into the category of 'detrital sands' but compared to their offshorecounterparts they contain much less $CaCO_3$ (c.f. tables 3 and 9). Furthermore, the 'general' group appear to be rich in quartz because, despite less diluting $CaCO_3$, the average concentrations of Fe and Al remain lower than their offshore counterparts (c.f. tables 3 and 9). Another diluting component must be present in greater quantities than that found in offshore detrital sands and the most likely candidate is quartz. The most distinctive feature of the 'general' group, however, is the marked enrichment of Pb and Zn. Concentrations are as high as 1125ppm Pb and 1060 ppm Zn,

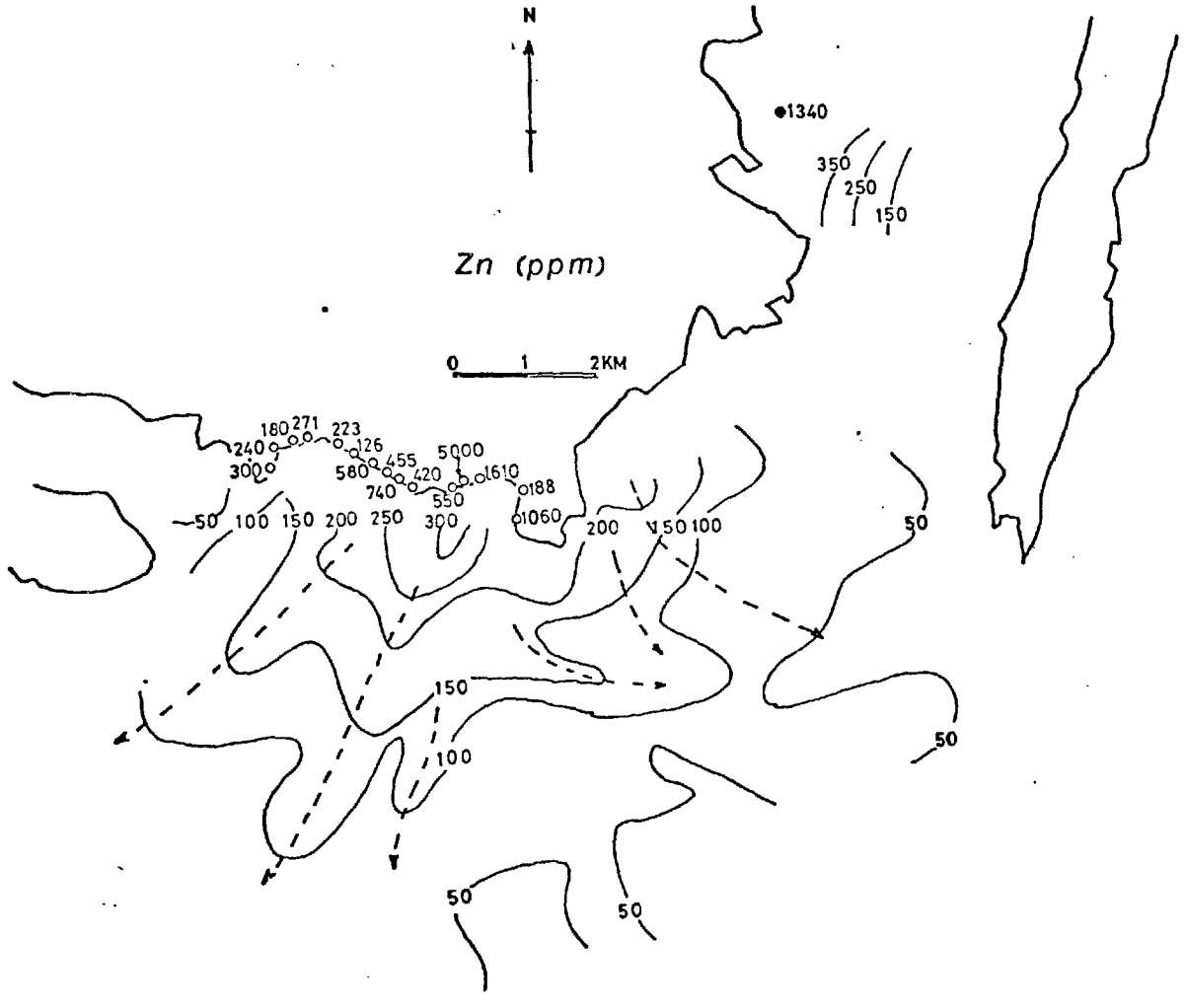


Figure 6.15 Distribution of Zinc. Possible dispersion pathways are indicated by the broken arrows. (o beach samples, • sample 34 off Laurium Harbour.)

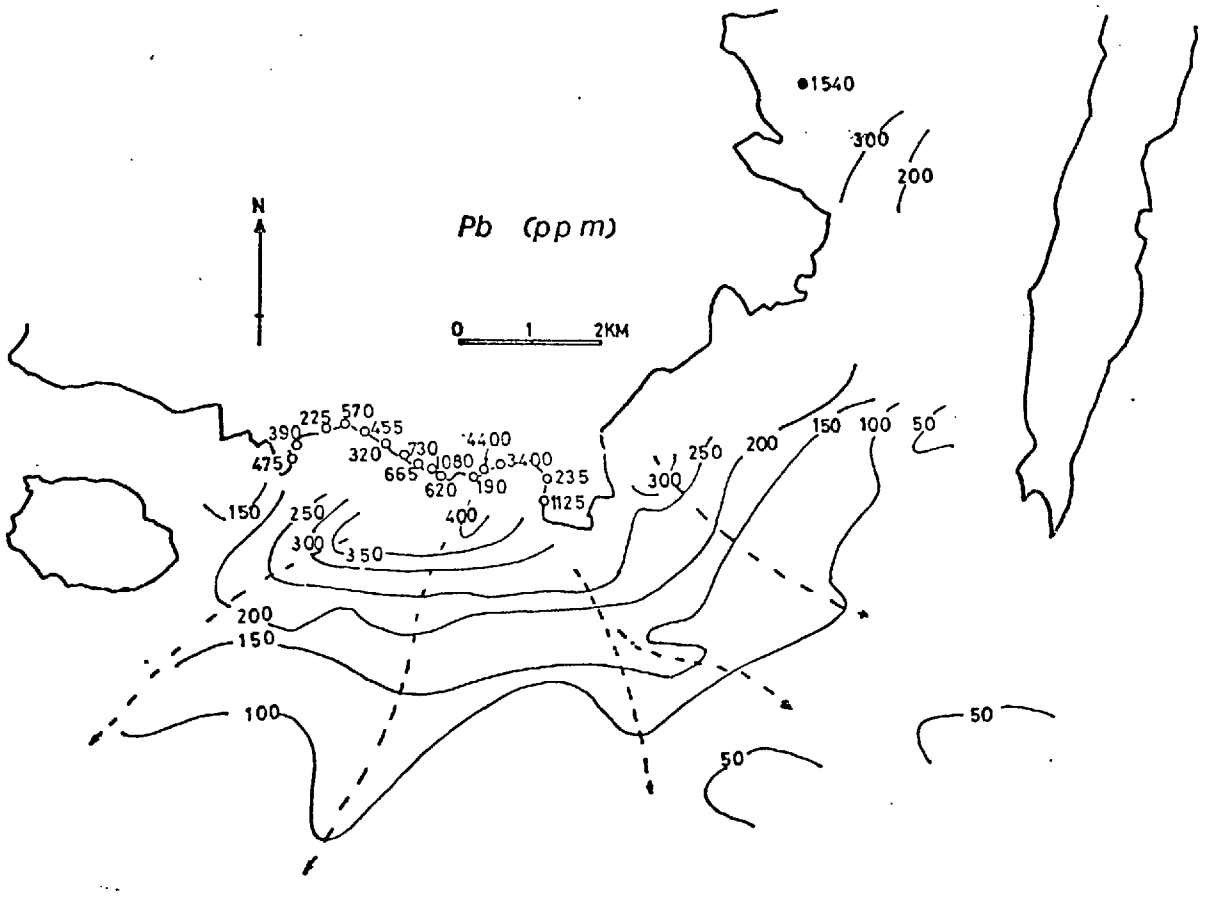


Figure 6.16 Distribution of Lead. Possible dispersion pathways are indicated by the broken arrows. (O beach samples, ● sample 34 from off Laurium Harbour.)

TABLE 9 Average and range of the partial chemical composition of beach sands at Sounion(Ca,Mg,Al,Fe in percent, the remaining elements in ppm).

	General	B.S.4	B.S.5
Ca	9.7 5.2-12.5	5.9	14.0
Mg	1.49 0.92-1.90	1.05	2.70
Al	2.22 1.38-2.75	2.70	1.22
Fe	1.72 1.07-2.60	4.25	6.90
Mn	435 260-860	1290	1540
Pb	605 125-1125	3400	4400
Zn	410 119-1060	1610	5600
Cu	19 11-29	140	360
Cr	118 20-170	290	180
Number of samples	17		

N.B. 'General' composition refers to most of the beach samples (B.S.) from the area and includes B.S.1,B.S.3 and all the samples from Ormos Legrainon.B.S.4 and B.S.5 have a distinctive composition and were collected from beaches around Mikri Skala.

but all samples are enriched to some extent suggesting that mine waste pervades the entire shoreline.

Lead and zinc concentrations as high as 4400ppm and 5600ppm respectively, (table 9) obviously suggest that beach samples 4 and 5 (figure 6.1) contain a larger proportion of mine waste. Under these circumstances, the anomalous levels of Fe, Mn and Cu (table 9) indicate that the influence of the mine waste on the composition of the beach samples is not restricted to Pb and Zn but also includes these elements. In most deposits (except those off Laurium Harbour), however, the relative amount of mine waste is small and it's influence masked therefore by 'normal' controls on the abundance of Fe, Mn and Cu.

Figures 6.15 and 6.16 also show the longshore trends in the amounts of Zn and Pb, respectively, in the beach deposits along the Sounion shoreline. Concentrations of both elements are highest in samples collected from the vicinity of Asprolithari and Mikri Skala (figure 6.1). Highest concentrations of Zn and Pb in the offshore deposits, apart from those close to Laurium Harbour, also occur off Asprolithari. Considering the extent of past mining activity and present construction work in this area (see section 6.2), it was anticipated that much of the mine waste in both the beach and offshore deposits would derive from the Asprolithari and Mikri Skala districts and this is confirmed by the distribution of Pb and Zn.

6.6.4 Composition of the 'Detrital' Fraction

Nine samples from Sounion (327, 328, 329, 341, 344, 347, 349, 350 and 351) were leached with acetic acid and the residues analysed. Table 4 gives the partial composition of each sample and table 8 summarises the range in concentration for each element. Compared to the sandy samples from other areas, the Sounion samples have higher concentrations of Pb and Zn but the contrast is particularly marked in Group B samples (349, 350 and 351) from closer to the shoreline. The same group are also slightly enriched in Mn, Cu, Ni and Cr. Al and Ti depletion is common to both groups of Sounion samples, reflecting the quartz-rich nature of the deposits. Group A samples (327, 328, 329, 341, 344 and 347), from seawards of the mid-shelf slope, are characterised by a greater abundance of Fe.

Before accounting for the composition of the Sounion samples, it is useful at this stage to review the relationship between the mineralogical and chemical composition of the detrital fraction. Two diagrams are used to accomplish this task. Figure 6.17 shows part of the detrital Mg-Fe-Al ternary diagram which reveals differences in the relative proportions of feldspar, the 'chlorite-mica' group, dolomite and authigenic iron minerals, but not quartz. The influence of quartz is shown by the relationship between detrital Fe and Al (figure 6.18). The proposed compositional trends related to mineralogical change are illustrated in figure 6.19.

At Kithnos, Serifos and Andros, mica-schists dominate the local geology and the relative proportions of quartz, feldspar, the 'chlorite-mica' group, and authigenic iron minerals in some samples, controls the composition of the detrital fraction. Calcareous muds found seawards of the shelf edge in these areas are relatively rich in the fine-grained 'chlorite-mica' group (muddy samples, e.g. 435 - figure 6.17). (Because they group together in the centre of figure 6.17, all changes in composition subsequently discussed are considered in relation to the muddy samples - see figure 6.19). However, simply increase the relative proportion of quartz and the chlorite-mica/feldspar ratio remains constant (hence the samples plot in the same place as the 'muddy' group in the Mg-Fe-Al ternary diagram - figure 6.17) but the abundance of detrital Fe and Al decrease. The change in composition from sample 435 to 427 is thought to illustrate this trend (trend 1 - figures 6.18 and 6.19). In contrast, increasing the relative proportions of quartz and feldspar reduces the chlorite-mica/feldspar ratio (hence the samples plot towards the Al apex of the Mg-Fe-Al diagram), the Fe/Al ratio, and the abundance of detrital Fe and Al. This trend (trend 2 - figures 6.18 and 6.19) is illustrated by the change in composition from sample 435 to 411 and 357. A third possibility is the addition of authigenic iron minerals to a muddy assemblage. Under these circumstances, samples (e.g. 416) plot towards the Fe apex of the Mg-Fe-Al diagrams (figure 6.17) and the Fe/Al ratio increases (trend 3 - figures 6.18 and 6.19).

At Naxos, marbles are much more significant and the consequence is that dolomite, feldspar and quartz are the major minerals within the detrital fraction, whereas the 'chlorite-mica' group are, at

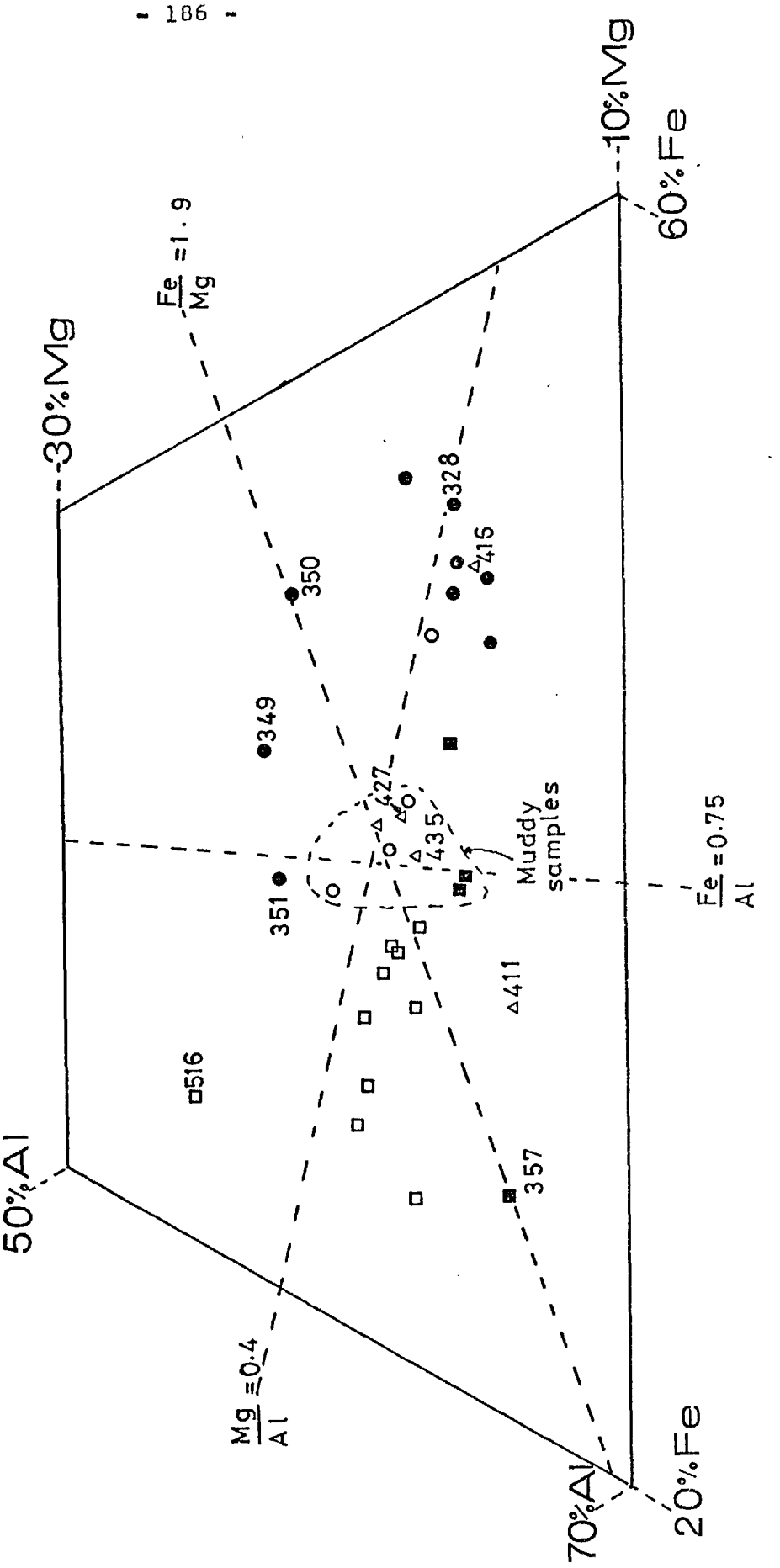


Figure 6.17 Part of the Mg - Al - Fe ternary diagram for analyses of the detrital fraction of selected samples from all areas: ● Sounion; ■ Andros; △ Kithnos; ○ Serifos; □ Naxos.

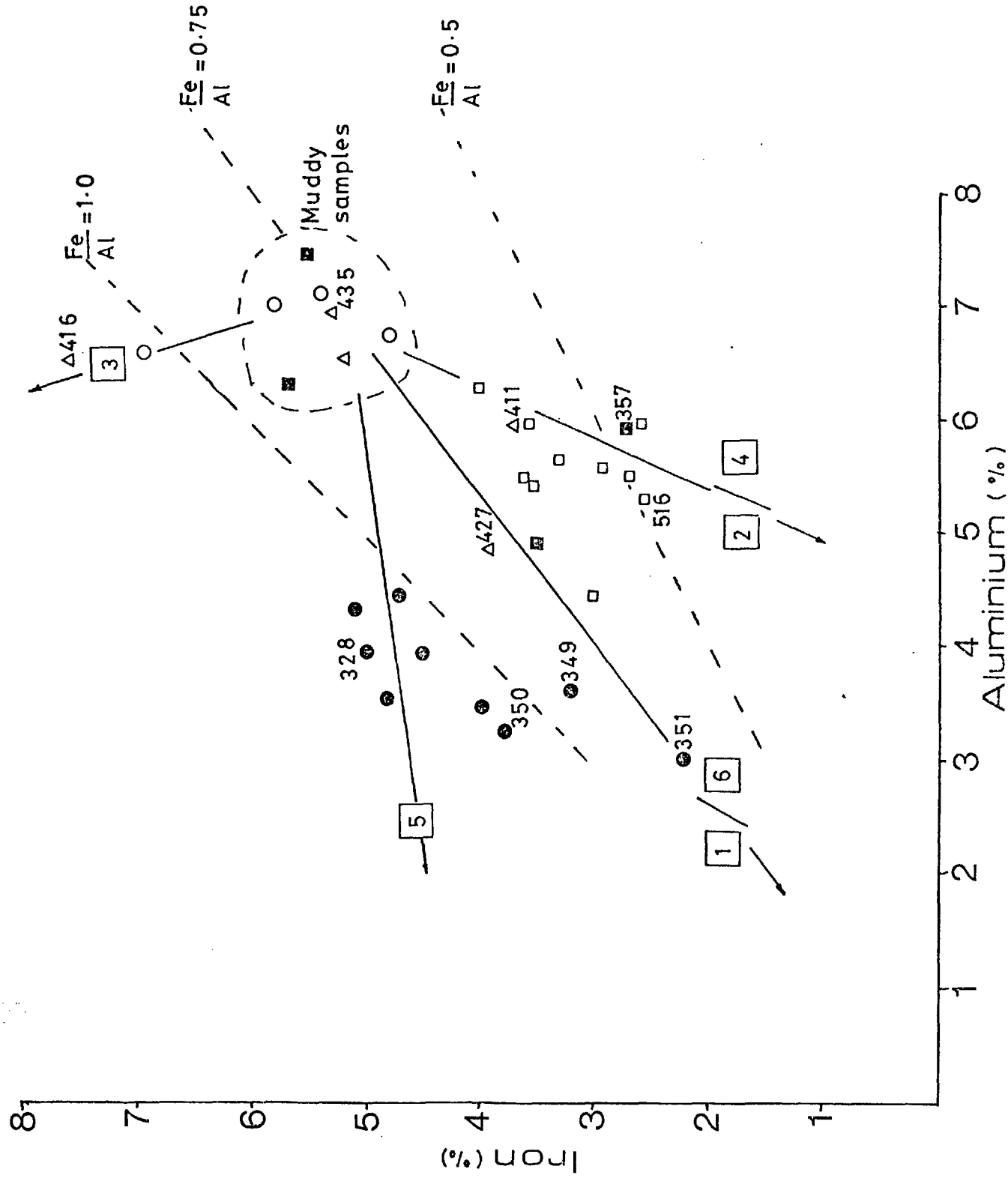


Figure 6.18 Iron against aluminium for the detrital fraction of selected samples from all areas. The figures in squares refer to the compositional trends (see figure 6.19).

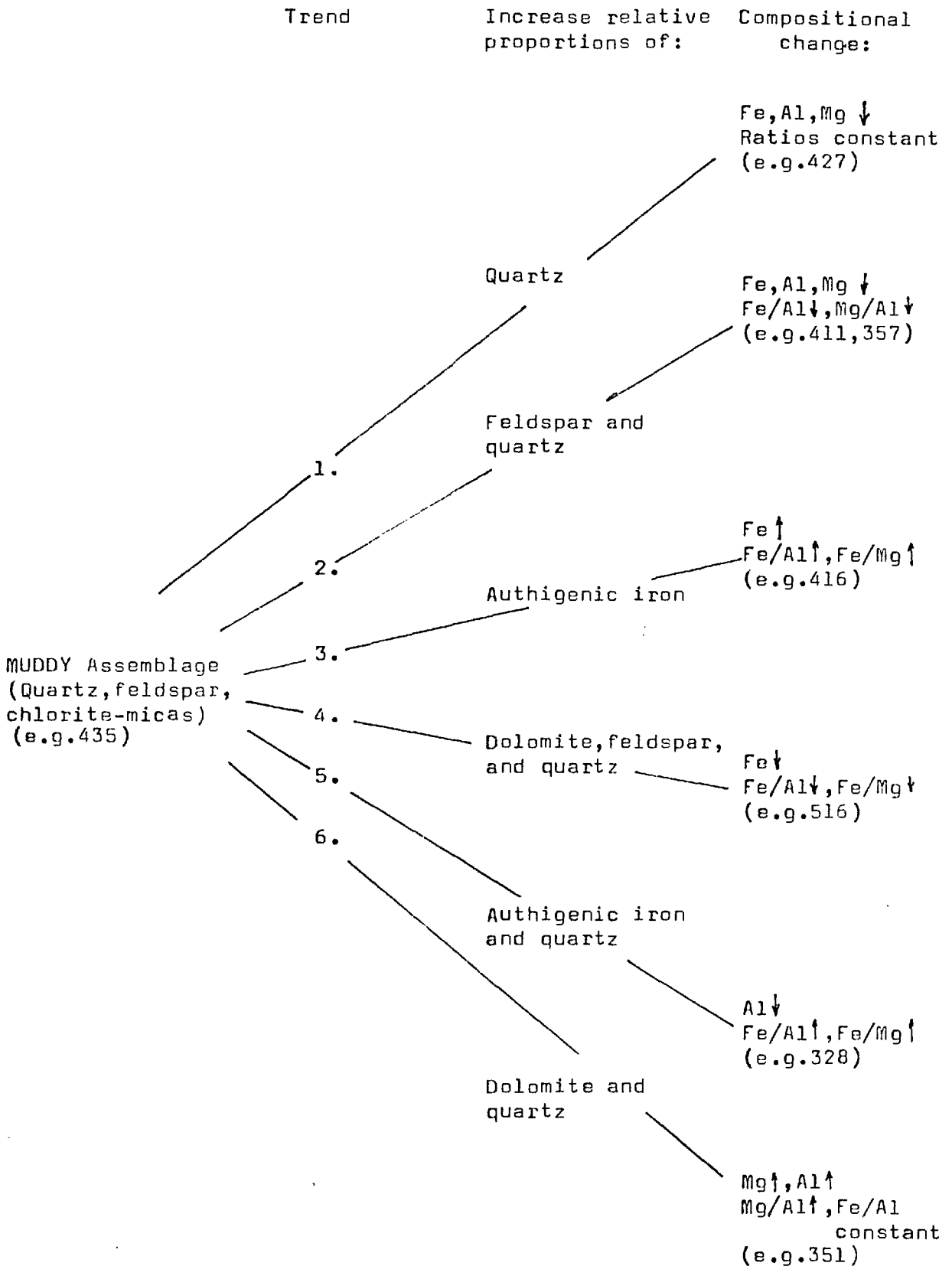


Figure 6.19 Compositional trends related to changes in the mineralogical composition of the detrital fraction. Arrows indicate an increase or decrease in the relative abundance of an element or the ratio.

most, minor. Relative to the 'muddy' samples, therefore, the amount of Fe relative to Mg and Al decreases and samples plot towards the Mg-Al baseline (e.g. Naxos samples - figure 6.17, trend 4 - figure 6.19). Their position relative to the Mg and Al apices depends upon the relative abundance of dolomite and feldspar; sample 516, for example, appears to be rich in dolomite and plots towards the Mg apex (figure 6.17). In figure 6.18, the additional quartz and dolomite simply decreases the abundance of detrital Fe and Al, whereas the greater proportion of feldspar relative to the 'muddy' samples causes the composition of the Naxos samples to appear along trend 2.

As noted earlier, and as is evident from figure 6.17, the Sounion samples fall into two distinct groups. All group A samples cluster around sample 416 which suggests that they, like 416, contain a greater proportion of iron. As all group A samples are from seawards of the 'mid-shelf slope' they may include a substantial relict bioclastic component with the associated authigenic iron minerals. Although the Fe/Al ratio is similar, the amounts of Fe and Al are less than in other samples with an authigenic iron component (figure 6.18), indicating that group A samples are also rich in quartz. Trend $\underset{\sim}{5}$ (e.g. 435 - 328, figure 6.18) represents, therefore, an increase in the relative proportions of quartz and authigenic iron (figure 6.19) and characterises group A samples from Sounion.

Two features characterise the group B samples. Firstly, the relative amount of Mg is larger (figure 6.17), reflecting the presence of dolomite in the two group B samples analysed by X.R.D. (350 and 351). Group A samples only contain, at most, a trace of dolomite. Secondly, the lower abundance of Fe and Al (figure 6.18) suggests that the group B samples are also relatively rich in quartz. Therefore trend 6 (e.g. 435 - 351, figure 6.18) represents an increase in the relative proportions of quartz and dolomite (figure 6.19).

To summarise, the chemical composition of the 'detrital' fraction of Sounion samples suggest they are richer in quartz than deposits elsewhere, supporting observations based on the bulk composition of the beach and offshore samples and limited mineralogical data. Authigenic iron minerals appear to be a prominent component of samples from deeper waters (see later), whereas the presence of mine waste seems to influence the composition of the 'detrital'

fraction in samples from closer to the shoreline.

The contribution made by the 'detrital' fraction to the total abundance of the elements follows a similar pattern to that found elsewhere (table 4). Overall Al, Fe, Ti, Ni and Cr are 'detrital'; Cu and Zn have approximately equal contributions from 'detrital' and 'non-detrital' sources; and Mn, Mg, Pb and Ca are predominatly 'non-detrital'. The order, in more detail, is:- Fe, Al, Ti, Ni, Cr (>75%)> Cu, Zn (37% - 67%)>Mn (16% - 42%), Mg (17% - 26%)> Pb (8% - 23%)>Ca (2%)

Anomalous concentrations, a general decrease in concentration seawards and strong covariance (figure 6.20), confirm that Pb and Zn derive from mining waste. Nevertheless, despite occurring within the same component of the deposits, the amounts of Pb and Zn soluble in acetic acid differ, reflecting, perhaps, differences in the relative proportion of primary sulphide (insoluble in acetic acid) and secondary carbonate (soluble) minerals within the mining waste for each element. About 90% of the Pb is soluble in acetic acid (figure 6.20) and mainly occurs, therefore, as a carbonate (cerussite?) with only small amounts of galena. In contrast, Zn may occur as both sulphide (sphalerite) and carbonate (smithsonite) because only about 50% is soluble in acetic acid (figure 6.20).

6.6.5 General Discussion

6.6.5a Controls on the Chemical Composition of the Sediments

From the preceding discussion it is evident that for most elements the main controls on element abundance are similar to those found elsewhere, namely:-

(1) dilution of detrital elements by bioclastic carbonates;

(2) the range in mineral composition of the detrital fraction;

(3) the amount of hydrogenous manganese 'oxides' and their associated scavenging of copper;

(4) authigenic iron minerals present in the relict components of the sediment; and

(5) for magnesium, the range in mineralogical composition of the bioclastic component.

Only the amounts of Pb and Zn are markedly affected by the presence of mine waste in the deposits.

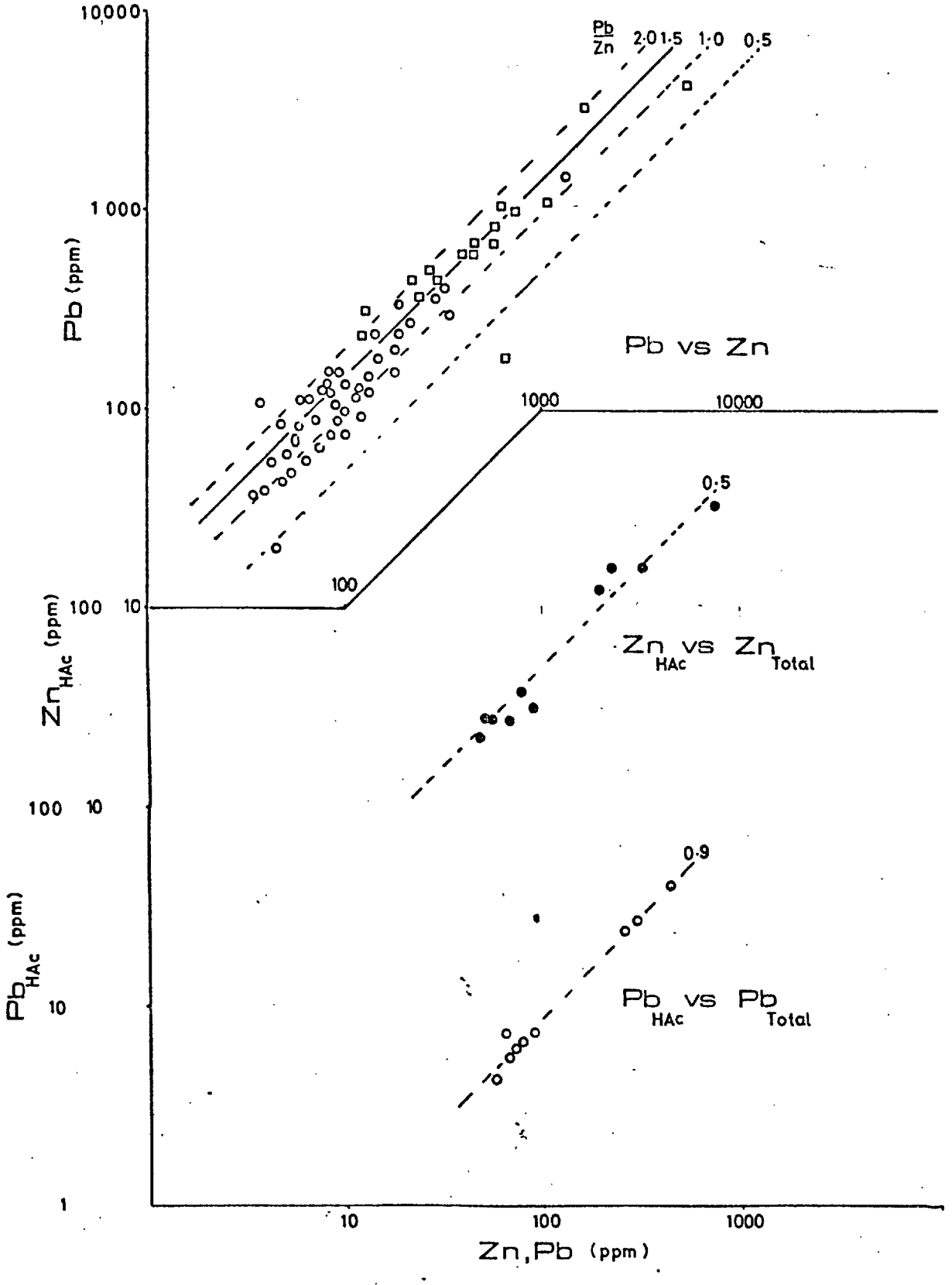


Figure 6.20 Relationships between total lead and total zinc, Zn_{HAc} and Zn, and Pb_{HAc} against Pb.

'Carbonate-dilution' governs the overall chemical composition although the Sounion deposits appear to be richer in quartz than their counterparts studied elsewhere in the Aegean (sections 6.4.4, 6.6.2, 6.6.4). Also more evident at Sounion is the influence of carbonate mineralogy on the Mg concentration; it is more abundant in samples with a larger proportion of coralline algae (relative to molluscan or other bioclastic material) and, therefore, magnesian calcite (relative to either calcite or aragonite) (section 6.6.2).

The wide range in the concentration of Mn is partly attributable to differences in the amount of hydrogenous manganese 'oxide' in each sample. In turn, this is mainly considered to be an inverse function of the rate of accumulation of that fraction of the sediment smaller than 2mm. On this basis accumulation rates are highest in shallower waters (less than 60m) where the accumulation of bioclastic and coarser terrigenous material is probably greatest; and lowest around the base of the 'mid-shelf slope' and in the deeper part of the eastern sector (section 6.6.2).

Based on the chemical composition of the detrital fraction, samples from deeper water off Sounion seem to contain an 'excess Fe' over that held within the detrital minerals. This is confirmed by the distribution of the bulk Fe/Al ratios (figure 6.21) which reveals that most samples seawards of the 80m isobath have an Fe/Al ratio greater than 1.0 (i.e. an 'excess Fe'), whereas shorewards (apart from Laurium Harbour where mine waste may be contributing iron) ratios generally are less than 1.0 (i.e. the iron is simply attributable to detrital minerals present). (See also section 3.5.3). Because the samples with an 'excess Fe' occur deeper than 80m and often show replacement textures (particularly of foraminiferal tests), the 'excess Fe' is thought to be held in authigenic iron minerals formed in certain relict bioclastic fragments. Nevertheless, iron-staining could be an additional source of 'excess Fe', especially in those samples from depths between 80m and 120m which may have suffered sub-aerial exposure during the last low-stand of the sea level.

6.6.5b The Nature, Source, and Dispersion into the Adjacent Marine Environment of Waste Material derived from Coastal Lead Mining

Undoubtedly the most important effect of the accumulation of

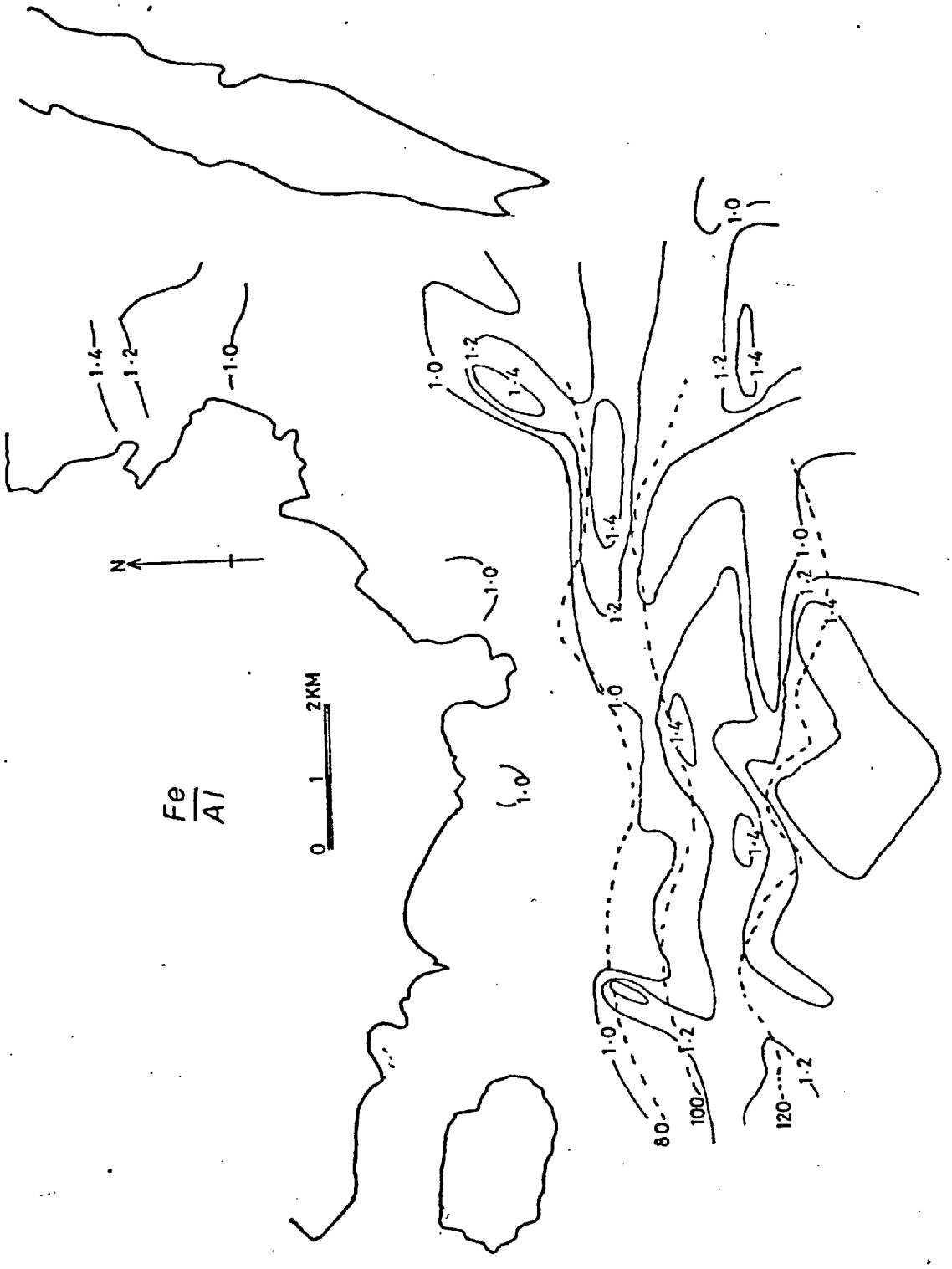


Figure 6.21 The distribution of the Fe/Al ratio in the bulk samples from Sounion. A value greater than 1.0 may indicate the presence of authigenic iron minerals in the relict component of the sediment.

mine waste offshore is the marked enrichment of both Pb and Zn off Sounion (up to 435ppm Pb and 322ppm Zn - approximately equivalent to 1000 and 800ppm on a carbonate-free basis). At the entrace to Laurium Harbour the concentrations found are even higher (1540ppm Pb and 1340ppm Zn, approximately equivalent to 4000 and 3000ppm respectively on a carbonate-free basis). In the waste material from the mine dumps, Pb and Zn occur either as sulphides or secondary carbonates. Consequently, they are likely to be in a similar form in the deposits offshore. Nevertheless, their solubility in acetic acid suggests that Pb mainly occurs as a carbonate (about 90% of the Pb is soluble), whereas Zn probably occurs in both forms (only 50% soluble) (section 6.6.4). For the other elements the influence of mine waste on their composition seems small which, in turn, suggests that it only forms a small proportion of the bulk sample.

Trends in the distribution of Pb and Zn offshore (section 6.6.2) and alongshore (section 6.6.3) confirm that a major source of the waste material is the area around Asprolithari and Mikri Skala. This is not surprising: the area has a long history of mining activity and, more recently, construction work close to the shoreline. How the material reaches the marine environment is difficult to establish in this essentially 'static' study but the limited scale of stream input into the nearshore zone implies that wind-borne transport may be a quantitatively significant process, especially during dry periods. In addition, it would not be surprising to discover that material also derives from direct dumping onto the beach or into the nearshore zone, either as part of the extensive construction work or by the deliberate marine disposal of mine tailings.

Although samples from closer to the shoreline have the highest concentrations, those from deeper water, particularly in the south-western sector, are also enriched in Pb and Zn (N.B. the maximum values found in sandy deposits elsewhere are 57ppm Zn and 45ppm Pb - tables 3) (see figures 6.15 and 6.16). Only a few samples from the south-eastern corner have concentrations of Pb and Zn similar to those found in other parts of the Aegean. Therefore, it appears that the waste material can reach even the deepest parts of the continental margin. Lobes in the concentration contours of Pb and Zn indicate, furthermore, that the dominant dispersion pathways into deeper water follow the valleys in the shelf topography.

Sedimentologically these observation are of general significance because they confirm that 'modern', terrigenous material is not confined to the shallower parts of the shelf and may reach depths greater than 110m (see e.g. off Kithnos).

6.6.5c Lead and Zinc Pollution of the Marine Environment?

Mine waste reaching coastal waters, whether through deliberate disposal at sea or, as is more likely in this situation, dispersal from onshore mining activity, potentially pollutes the marine environment in a variety of ways. The main problems are:-

(1) the large scale dumping of material which may destroy benthic habitats and upset spawning and predation; and

(2) toxic trace metals entering and accumulating in the food chain through uptake by marine biota (see Down and Mills, 1978; Owen, 1977). Although the concentrations of Pb and Zn are high off Sounion and Laurium, the actual quantity of waste in the deposits is small. The most likely form of 'pollution' off Sounion, therefore, is the uptake of the potentially toxic elements Pb and Zn, particularly through ingestion of solid particles by bottom and filter-feeding organisms.

Whether or not a pollution problem exists is difficult to assess simply from the composition of the sediments. In a comprehensive review of the problems involved in identifying trace metal pollution in coastal waters, Phillips (1977) points out "..... it is conceivable that even in a situation where metal concentrations in sediments are very high, little metal is available to the biota .....". Two factors govern the availability of a metal. Firstly, the solid particle has to be an appropriate size for ingestion. Unfortunately, individual size fractions have not been analysed and so the predominant size range of the waste material reaching a given point on the shelf is not known. In the nearshore zone some material may be too coarse, but, since it reaches most parts of the shelf, much of the waste material is likely to be fine-grained and available, therefore, for ingestion. Further studies on the composition of individual size fractions would test this assumption. Secondly, even if the organism ingests the particulate or solid matter, the chemical bonding of the metal may inhibit or prevent uptake. To take an extreme case, metals easily chelatable are likely to be more available than the same metals held within the detrital silicates.

Obviously, bulk analyses will shed little light on this problem.

Nevertheless, useful information may be gleaned from the sediments by leaching them with a weak, organic chelating agent. Although any chemical reagent is limited in it's capacity to predict 'availability', at least this approach reveals the degree to which metals are bound in the sediment and improves on bulk analysis as a means of predicting 'availability'. Accordingly, selected samples have been leached with 0.05M E.D.T.A. (Ethylenediaminetetracetic acid) for five minutes, filtered and the solutions analysed for Pb, Zn and Cu.

The results, summarised in table 10, reveal some interesting features:-

(1) 40% of total Pb (Pb_{tot}) but only 10% of the total Zn (Zn_{tot}) is soluble in E.D.T.A. ($Zn_{EDTA} = 0.1\ Zn_{tot}$; $Pb_{EDTA} = 0.4\ Pb_{tot}$ - figure 6.22);

(2) Pb_{EDTA} and Zn_{EDTA} covary, indicating that both occur in the same component (i.e. the mine waste), but the amount of Pb available is approximately four times the amount of Zn (i.e. $Pb_{EDTA} = 4.Zn_{EDTA}$ - figure 6.22), even though total Pb is only 1.5 times total Zn (figure 6.20);

and (3) as expected, the amount of available Cu is exceedingly small. Consequently, a potential pollution problem exists off Sounion, not because of the high total levels of Pb and Zn but because a substantial proportion of the Pb is readily extractable from the sediment and may therefore be in a form suitable for uptake by marine biota. Conversely Zn may be less of a problem.

At Sounion, analysis of the sediment only indicates that a problem may exist. The next step must be to sample and analyse the marine biota. Phillips (op. cit.) suggests that the filter-feeding bivalve molluscs and the macroalgae are appropriate to assess the uptake of metals from solids and solution respectively. Such knowledge is vital if the impact of mine waste on the marine environment is to be understood. Moreover, such a study would be timely in view of the renewed interest in the disposal of tailings at sea (see the review by Down and Mills, 1978) and the potential development of offshore mining (see the review of the potential environmental impact by Owen, 1977).

TABLE 10 Range of E.D.T.A. soluble Pb,Zn,and Cu in sediment samples from Sounion(in ppm).

	General Range	P34	B.S.16b	B.S.8
Pb	18-112	720	400	240
Zn	3.4-27.4	224	76	50
Cu	1.4-3.2	11.9	1.8	1.8
Number of samples	42			

N.B. The general range refers to the bulk of offshore samples; P34 was collected just off Laurium harbour;and B.S.16b and B.S.8 are two beach samples analysed.

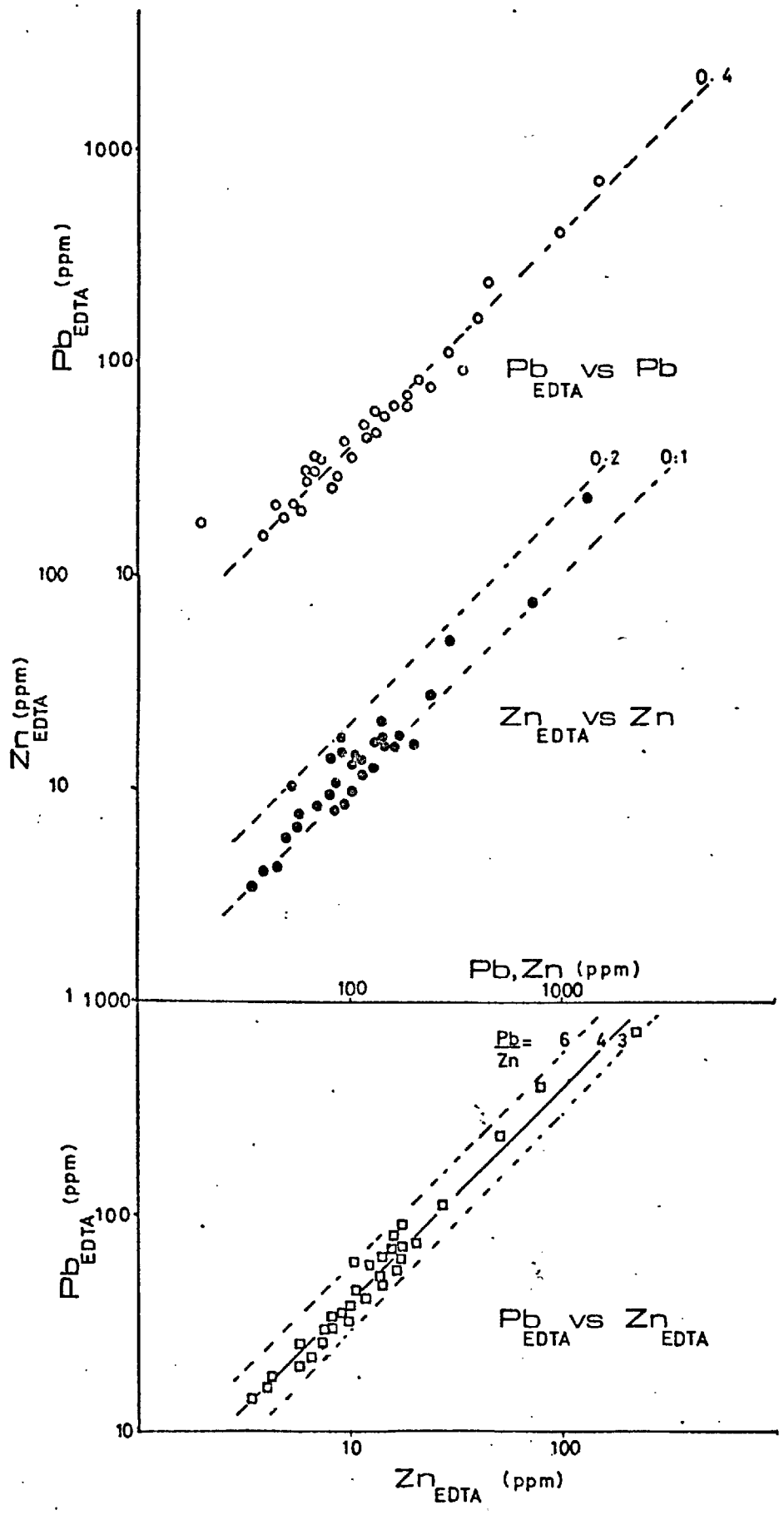


Figure 6.22 The relationships between Pb_{EDTA} and Pb,Zn_{EDTA} and Zn, and Pb_{EDTA} against Zn_{EDTA}.

6.7 GENERAL SUMMARY

(1) Although the constituent textural sub-populations are broadly similar to those elsewhere, the nature and distribution of sedimentary facies at Sounion differ in several respects, namely:-

(a) the 'fine sand' sub-population in samples from depths of less than 60m is probably the 'modern' equivalent of the relict or reworked 'fine sand' sub-population found in deeper waters at both Sounion and elsewhere;

(b) to account for the textural similarity between detrital sands from Kithnos and Serifos and certain bioclastic sands from Sounion and Naxos, the 'very fine sand' sub-population in samples from the latter two areas probably contains a larger proportion of terrigenous calcium carbonate;

(c) based on the distribution of sedimentary facies, there are two distinct zones within the Sounion survey area, namely:-

(i) a current-swept eastern zone comprising bioclastic sands and gravels, very small amounts of terrigenous mud, and a depth zonation in the distribution of the sedimentary facies -

less than 60m	- 'maerl' sands and gravels, algal nodule deposits and reefs, rock outcrop
60m to 100m	- shelly bioclastic sands
greater than 100m	- 'maerl' sands and gravels, algal nodule deposits (all with a substantial relict or reworked component);

(ii) a western zone, also comprising bioclastic sands, but with a larger amount of fine-grained, terrigenous material (particularly seawards of the mid-shelf slope), and a distinctive depth zonation -

less than 60m	- shelly bioclastic sands (some with a large proportion of terrigenous? very fine sand)

60m to 100m - 'maerl' sands and gravels, algal reefs

greater than 100m - bioclastic sands, muddy bioclastic sands (all with a large relict or reworked component).

(2) The major controls on the chemical composition of the Sounion deposits are similar to those found elsewhere, with the exception that:-

(a) mine waste reaching the marine environment results in very high concentrations of Pb and Zn;

(b) the detrital fraction is richer in quartz;

and (c) the range in mineralogical composition of the bioclastic components has a more marked influence on the concentrations of Mg.

(3) (a) Offshore gradients in the concentration of Pb and Zn, and lateral trends in the beach deposits confirm that the area around Mikri Skala and Asprolithari is a major source for the mine waste reaching the marine environment to the south of Sounion;

(b) selective leaching with acetic acid and an organic chelating agent (E D.T.A.) indicates that:-

(i) Pb mainly occurs as a secondary carbonate, whereas Zn is in the form of both carbonate and sulphide and in approximately equal proportions;

(ii) a substantial amount of the Pb (but only a small amount of Zn) may be available for uptake by marine biota and there is, therefore, a potential pollution problem off Sounion.

(4) Using the mine waste as a natural tracer of 'modern', terrigenous sedimentation confirms that:-

(a) modern, terrigenous material reaches most parts of the continental shelf,

and (b) the dominant dispersion pathways offshore follow valleys in the shelf topography.

CHAPTER 7 - SANTORINI

7.1 INTRODUCTION

Santorini is well-known as a centre of active volcanism and, as such, is included in this study because both the solid products from eruptions and the dispersal of precipitates from the submarine hydrothermal activity will influence the chemical composition of the sediments from the southern Aegean, particularly in and around the caldera. Furthermore, the geochemical study of the iron-rich sediments, presently forming close to the fumaroles on the volcanic islands in the centre of the caldera, contributes to the Applied Geochemistry Research Group's wider investigation of metalliferous sediments from the worlds' oceans. This work extends the coverage to include an island arc tectonic environment and the associated shallow, submarine hydrothermal activity. Finally, ancient volcanogenic exhalative deposits have much in common with those forming at Santorini. This detailed study may help, therefore, to clarify the processes involved in the formation of the ancient deposits. Particular emphasis is placed on the extensive ferruginous horizons and the associated metal zoning which is also often found around stratiform massive sulphide deposits.

The framework for much of the discussion is the five bathymetric zones identified by Smith and Cronan (1975b), each of which has distinctive sedimentological and geochemical characteristics. Initially, the sedimentological and physico-chemical characteristics of the zones are reviewed to provide a framework for the detailed geochemical studies which follow.

7.2 GEOLOGICAL SETTING

As a site of active volcanism, Santorini is of obvious interest to the geologist and, accordingly, has been the subject of volcanological research for more than a century. The attempts by Pègues (1842) to unravel the chronology of the historical eruptions and the first geological description of the island by Fouqué (1878), have been followed by the works of Ktenas (1925), Oekonomidis (1932), Reck (1936), Georgalas and Papastamatiou (1951), and many others. More recent interest in the extrusive volcanic rocks stems from their postulated relationship to an active subduction zone (Nicholls, 1971a

and b; Ninkovich and Hays, 1972; Pichler and Kussmaul, 1972; and Pichler et al., 1972).

Santorini lies on the southern Aegean volcanic arc (see Chapter 1) and the islands of the archipelago mainly comprise Pliocene to Recent calc-alkaline (Nicholls, 1971a) lavas and pyroclastics (including agglomerates, tuffs, pumice and ash). These rocks are best exposed in the walls of the caldera (figure 7.2). Basement rocks cropping out on Thera include Triassic (Papastamatiou, 1958) limestones and marbles forming high ground to the south-east of the island, and Eocene (Tataris, 1964) phyllites exposed in the caldera wall to the south-east of Nea Kameni (figure 7.2). The phyllites have been locally altered and impregnated by hydrothermal solutions, resulting in the accumulation of lead, zinc and copper sulphides but only in sub-economic quantities (Murad and Hubberten, 1975). Covering most of the archipelago, however, is the "upper" pumice layer derived from the major eruption in about 1400 B.C.

Pichler et al.(1972) have constructed a geological history of Santorini and Ninkovich and Heezen (1965) described the chronology and scale of eruptions that have lead to the formation of extensive tephra layers in sediments of the eastern Mediterranean. It seems that during the volcanic history of Santorini there have been three major pumice eruptions culminating in the 'Minoan' eruption in about 1400 B.C. During this eruption the centre of the large volcanic island of Stronghyli collapsed forming the present caldera, and all that remains of the original volcano are the islands of Thera, Therasia and Aspronisi. Since Minoan times submarine eruptions in the centre of the caldera resulted in the appearance of the Kameni Islands in 197 B.C. There have been a large number of sub-aerial and shallow submarine eruptions since that time (see Ninkovich and Heezen, op.cit.), including the Kolomvos eruption in 1650 A.D. to the north-east of Santorini.

7.3 BATHYMETRIC ZONES

The Santorini Archipelago is situated on the Cyclades volcanic arc in the southern Aegean Sea, approximately 130km north of Crete (figure 1.1). Morphologically, it consists of a fractured caldera open to the sea through channels between the islands of Thera, Therasia, and Aspronisi (figure 7.1). In the middle of the caldera

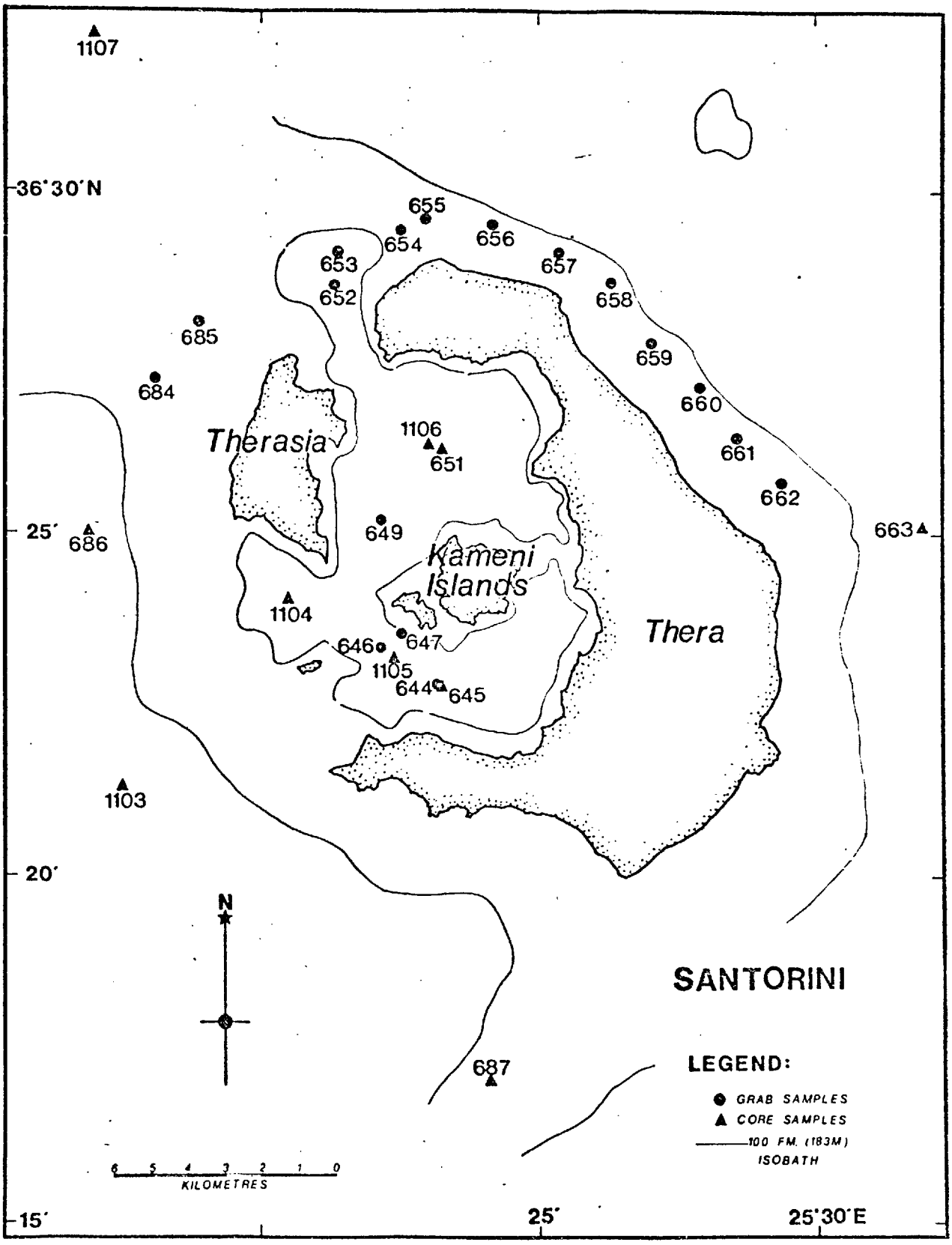


Figure 7.1 Sample locations in and around the Santorini archipelago.

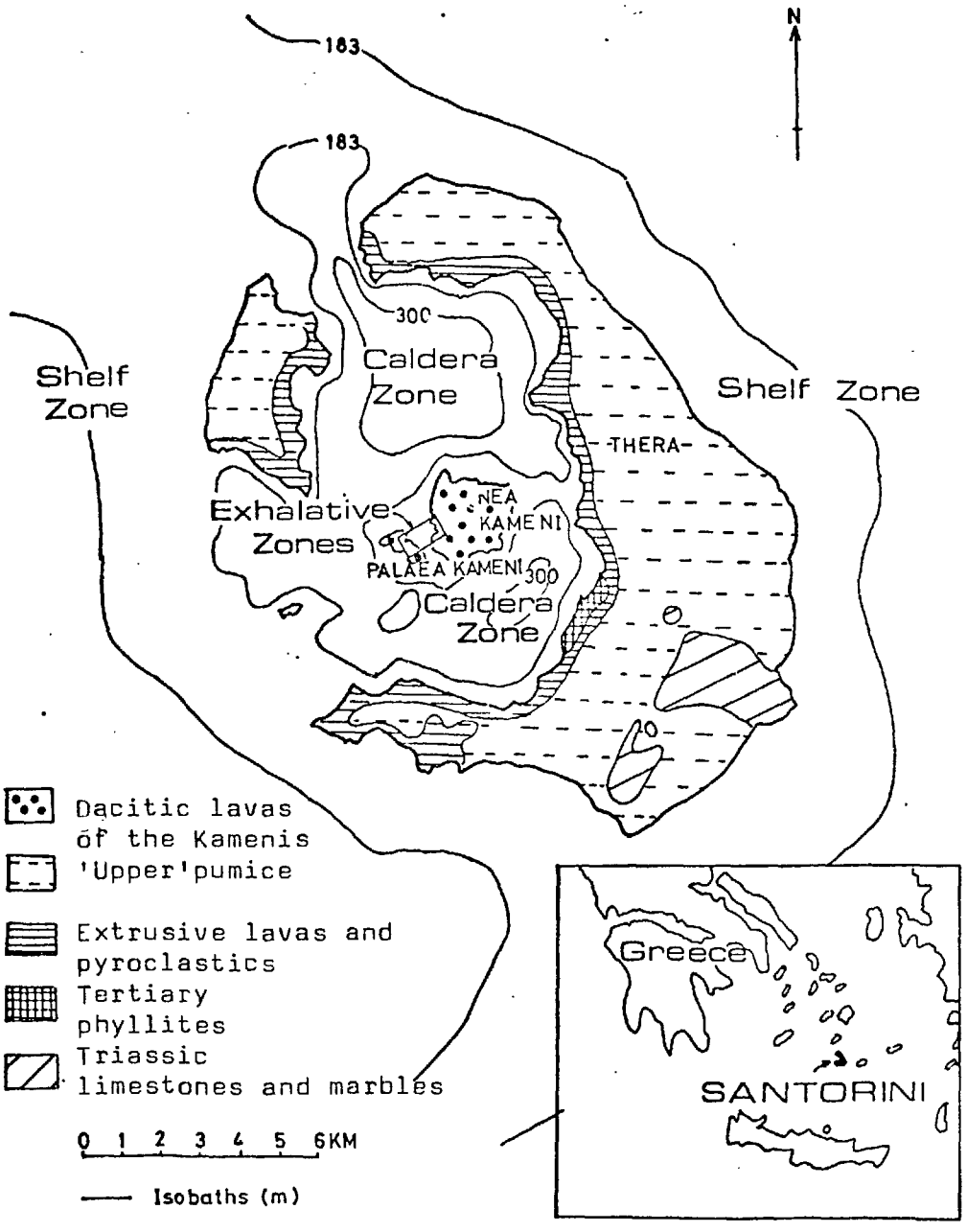


Figure 7.2 Simplified geological map of Santorini (modified from Pichler et al.,1972)which also shows the bathymetric zones.

are the islands of Palaea and Nea Kameni, the centres of volcanic exhalative activity of interest in this investigation.

Much of the collapsed seafloor of the caldera is at a depth greater than that of the surrounding continental shelf, especially in several basins where depths exceed 200fm (365m). The northern basin is the most extensive (figure 7.2), with a maximum depth of approximately 400m. Smaller basins characterize the southern half of the caldera sea floor (figure 7.2).

High cliffs, lining the inner shores of the caldera, continue beneath sea-level resulting in steep depth gradients from the shore. Similarly, depths shoal rapidly between the basins and the open sea, particularly in the south-western channel where a shallow sill occurs at an approximate depth of 10fm (18m). In contrast, no such sill occurs in the north-western channel where depths shoal rapidly, but only to the depth of the adjacent continental shelf (100fm, 180m).

Around the perimeter of the islands of Nea and Palaea Kameni are a series of small embayments, generally developed between diverging lava flows. Most of the shallow samples examined in this investigation were collected from two such embayments, one on Nea Kameni and one on Palaea Kameni (figure 7.3), either side of the channel between the two islands. Depths in the channel are generally in excess of 30m, but the embayments may be divided into two depth zones. Firstly, an inner zone of depths less than 3m and separated from the outer zone by a shallow sill. Outer zone depths range between 4m and 30m, intermediate between the shallow inner zone and the deeper channel. The topography of the exhalative zones is shown in figure 7.2. Although giving the general seafloor topography it is only approximate as depths are based solely on "wire out" measurements at sampling stations. The results, however, generally agrees with depths given on Admiralty Chart 2043.

The caldera and adjacent continental shelf are separated into several distinct bathymetric zones, each possessing distinct physical and chemical characteristics (Smith and Cronan, 1975b).
These zones are as follows:-

(1) Exhalative Zones are so called because much of the sediment (particularly the abundant iron minerals) is derived from volcanic exhalations. "Exhalative" is generally included in the description of the environment of such deposits as long as exhalatives are considered to include both springs and vapours (White, 1968; Ferguson et.al., 1974). Some authors (e.g. Bäcker, 1973) prefer to

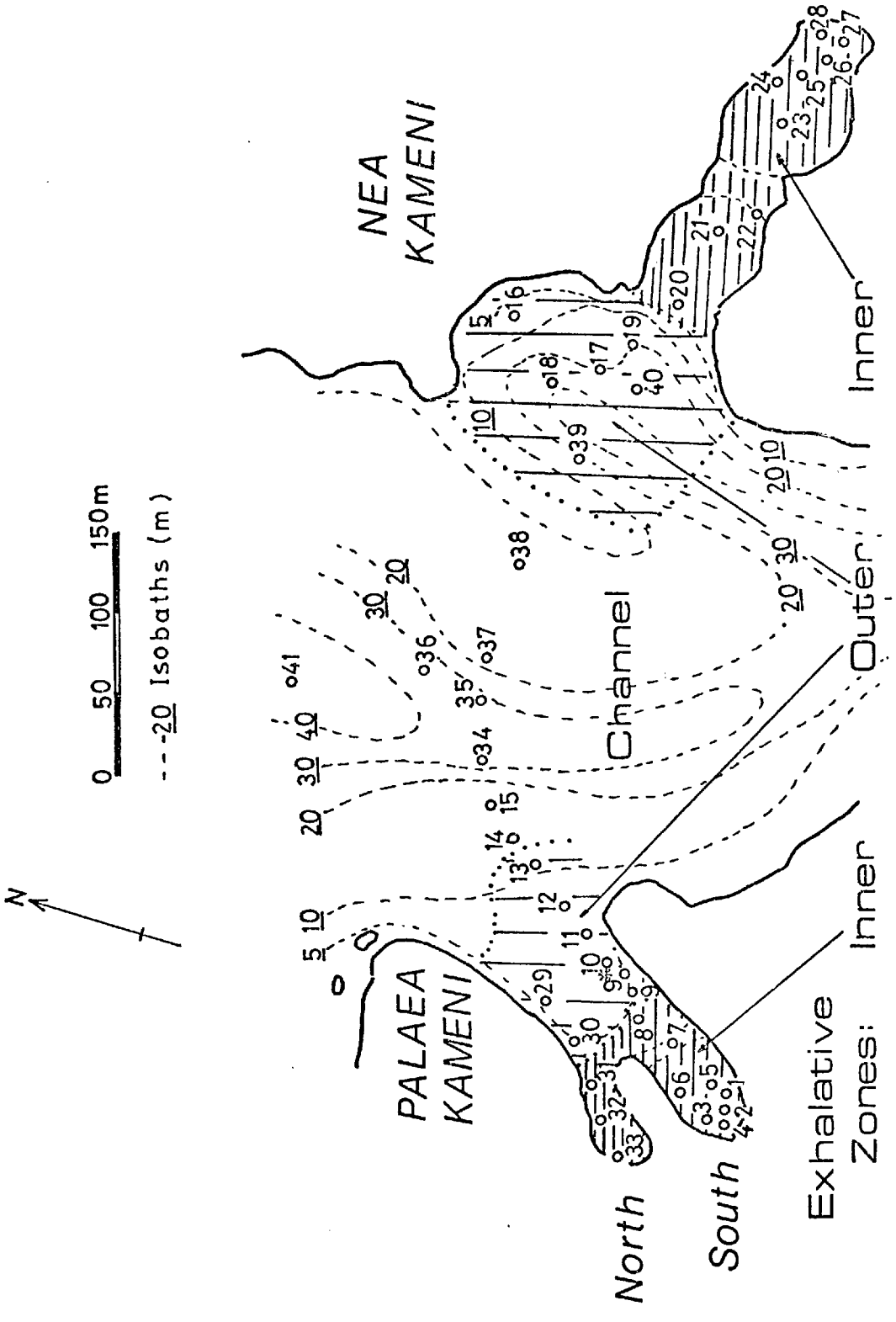


Figure 7.3 Sample locations and bathymetry within the exhalative and channel zones.

call such deposits, where solutions rather than vapours dominate, 'hydrothermal'. As "exhalative" is more specific, and more widely used in the discussion of volcanic - sedimentary environments, it is maintained in this investigation.

(a) Inner Exhalative Zones are the shallow, landward sections of the embayments on the islands of Nea and Palaea Kameni, where depths are generally less than 5m and where water circulation is restricted by shallow sills between the inner and outer zones. Infra-red studies (Puchelt, 1972) revealed a high, continuous heat flow in these embayments. Temperatures up to 35°C have been recorded close to the fumaroles (Puchelt, 1972; Butuzova, 1966) but decrease towards the open sea. Temperatures recorded during this investigation confirmed the previous observations. Close to the fumaroles temperatures of 28°C and 30°C were recorded in the Palaea Kameni and Nea Kameni embayments respectively, and these decreased to normal sea-water temperatures (19°C) in the 'outer exhalative' zones.

Eh and pH determinations were not made as part of this investigation but data from Puchelt (1972) and Puchelt, et al. (1973) indicate that the pH of the surface sediments in the inner exhalative zone of Palaea Kameni (south) is approximately 6.0 and between 5.0 and 6.0 in the cores. Eh readings are available from one core in this zone. Surface sediments, with an oxidation potential of + 100mv, are mildly oxidising but, locally in the core, strongly reducing conditions are present, apparently caused by the action of sulphate reducing bacteria. Local patches of surficial sediment are also reducing for similar reasons (Puchelt, 1972). For Nea Kameni, Butuzova (1966) reports an upper oxidised layer with an Eh between 260 and 270mv and a mildly lower layer with Eh of-40mv. Both layers have a pH of 5.2.

To summarize, the 'inner exhalative' zones are characterized by warm, shallow waters, restricted circulation, and where the environment of the surficial sediments is mildly oxidising, (although locally reduced) and slightly acidic.

(b) 'Outer Exhalative' zones cover depths ranging between 4m and 40m, and are subject to wave action and an open seawater circulation. The bright orange colour of the surface iron-rich sediment suggests a highly oxidising environment where the pH is probably closer to that of normal sea water (i.e. alkaline). Pushkina (1967) reports a pH close to that of seawater for the waters of the outer exhalative zone.

(2) The Channel Zone with depths generally in excess of 30m, lies between the two islands and is probably subject to both current and wave action. Bottom conditions, again from the nature of the sediment, appear to be oxidising.

(3) The Caldera Zone is characterised by deeper waters, generally exceeding 300m, where more quiescent conditions prevail. To be more specific, the 'Caldera Zone' is that area of the seafloor where depths exceed 100fm (182m).

(4) Finally, the Shelf Zone, although covering a range of environments including the volcanic sands of the beaches of the outer shoreline of the archipelago and offshore biogenic sediments, has a distinct physico-chemical environment, different from the previously described zones. For the purpose of this investigation, therefore, it is treated as a single bathymetric zone.

7.4 SAMPLING

As part of the Applied Geochemistry Research Group cruise to the Aegean Sea in 1972, thirty nine Shipek grab samples and five gravity cores were recovered in the vicinity of Santorini. The locations of samples used in this investigation are presented in figure 7.1. Sample sites were chosen to assess the influence, if any, of the fumarolic activity off the central islands on the geochemistry of sediments of the caldera basins.

Analysis of the 1972 cores from Santorini indicated that the fumarolic activity appeared to have some influence on the caldera sediments. Accordingly Santorini was revisited in 1973 as part of a joint venture between the Applied Geochemistry Research Group and the Greek Institute of Oceanographic and Fishing Research. Originally it was planned to sample both deep and shallow sediments but, unfortunately, the weather prevented the Greek minesweeper being used from visiting Santorini and so the sampling programme concentrated on the shallow sediments of the exhalative zones. This was achieved using a fishing boat with a shallow draught and sampling with a hand held snapper grab. This proved to be an efficient means of sampling in the shallow exhalative zones but little sediment was recovered in the channel zone. Sediment cover could have been thin due to the action of currents, but it was also difficult to 'feel bottom' with the light grab in depths in excess of 40m. Water samples and temperatures were obtained using N.I.O.

bottles on hand held lines.

Figure 7.3 provides the sample locations within the exhalative and channel zones. Traverses from source fumaroles to the channel zone were sampled to provide as complete a coverage as possible of the dispersion of elements in the exhalative zones. As the embayment on Palaea Kameni includes two traverses, they are designated as Palaea Kameni (north) and (south) (for convenience PK (N) and PK (S) respectively).

Finally, in 1974, an opportunity occurred to revisit the volcanic arc and Santorini during a University of Cambridge cruise to the eastern Mediterranean, aboard the RRS SHACKLETON. This allowed the completion of the deep-water sampling that was not possible in 1973. Six gravity cores were recovered (figure 7.1) improving the coverage of the caldera and continental shelf.

7.5 SEDIMENTS - THEIR NATURE AND DISTRIBUTION

7.5.1 Caldera and Shelf Zones

7.5.1a Previous Work

Characteristics of the sediments from the Caldera and Shelf zones have been studied in considerable detail by Butuzova (1969) and investigators from the Laboratorium for Sedimentforschung, University of Heidelberg (Petersen and Muller, 1974; Petersen, 1975; Raab and Stoffers, 1975). Butuzova (1969) concentrated on the general characteristics of the surficial sediments; Petersen and Muller (1974) examined the mineralogy, petrology, and tephrochronology; Petersen (1975) provided a detailed textural account of sediments from cores in the vicinity of Santorini; and Raab and Stoffers (1975) investigated the concentration of heavy minerals in the nearshore zone off the south coast of Thera.

Butuzova (1969, figures 7,8,9 and 10) and Petersen and Muller, (1974, figure 4), broadly agree on the textural variation in surficial sediments. It is evident (from Petersen and Muller, Figure 4) that the percentage of mud (that fraction finer than 0.063mm) increases with increasing depth, both on the shelf and within the caldera. Beach and shallow water sediments are predominantly sands and gravels, whereas, below 180m, silt becomes the dominant grain size (Petersen, 1975). Indeed, clay is a minor

component in all sediments, only averaging 8% in the muds of the caldera basins.

From the detailed study of the textural parameters of sediments from the Santorini, Petersen (1975) recognised five distinct sediment types:

(1) Normal sediment deposited in still water conditions and with a mean size varying between 4phi and 7phi. This type occurs both within and outside the caldera, but typical examples are the fine-grained sediments of the caldera basins.

(2) Current influenced sediments characterize the shallow waters of the channel entraces and the nearshore zones of the exposed outer shoreline, including the heavy mineral sands of the south coast described by Raab and Stoffers (1975). Mean sizes vary between 2phi and 4phi and may include some silt but no clay.

(3) Tephra - mixed layers in which the black tephra sands are intermixed with the silt-sized white to grey pumice mud.

(4) Subaqueous deposited tephra layers with "doubly graded" bedding.

(5) Slumped sediments occur close to the inner and outer shores of the caldera and also exhibit graded bedding where pumice fragments increase in size upwards. They are distinguished from tephra layers by a variety of features including mixtures with biogenic carbonate components; convolute bedding; rounded grains of pumice and lava derived from the beaches; and mud intraclasts present within the sands.

Pumice, derived from the rapidly eroding upper pumice strata, is the main constituent of most sediments (Petersen and Muller, 1974). Generally a glass of rhyolitic to rhyodacitic composition, it often contains inclusions of plagioclase feldspar, hypersthene, augite and magnetite. In the shallow water sediments off the south coast it forms the dominant constituent of the coarser fractions (Raab and Stoffers, 1975) but in most sediments it occurs in all sizes ranging from the fine-grained pumice muds to the pebble sized layers of lapilli pumice.

High concentrations of heavy minerals occur in the beach and nearshore sands around the outer perimeter of Santorini. Off the south coast, Raab and Stoffers (1975) report 35.4% magnetite in one sample, but heavy minerals also include hypersthene, augite, and hornblende. These heavy minerals of volcanic origin are also

evident in other sediments of the area, but so also are epidote, glaucophane, and tourmaline, derived from the metamorphic basement rocks (Petersen and Muller, 1974).

Lighter minerals include feldspars and quartz. The former are derived from the pumice fragments and often exhibit an halo of glass around the outer margin (Raab and Stoffers, 1975). Quartz is dominantly of eolian origin (Petersen and Muller, op.cit.) possibly derived from North Africa.

Clay minerals in the <2 micron fractions of the sediment are mainly montmorillonite, chlorite, and illite (Petersen and Muller, 1974). Although Bonatti, Joensuu, and Wanless (1972) report kaolinite and montmorillonite in bottom sediments of the Caldera, Peterson and Muller were only able to find kaolinite in one sample from outside the Caldera and then only in almost insignificant amounts. They also attribute the clay minerals to a terrigenous source, whereas Bonatti, Joensuu, and Wanless suggest that montmorillonite in the caldera sediments is formed by reaction of the volcanic material with seawater.

Variation in the carbonate content of the surficial sediments is also recorded by Petersen and Muller (1974) and Butuzova (1969). Shelf sediments exhibit a carbonate distribution similar to that of muds in that it increases with increasing depth of water. Close to the shore, where volcanic sands are dominant, the carbonate content is lowest and often less than 2%. Offshore the content exceeds 50% and is as high as 90% locally.

Similarly, within the caldera shallow water sediments around the shoreline have low carbonate concentrations (less than 5%) but so also do deeper water sediments from the south eastern sector of the caldera. Pyroclastic sedimentation rates are probably much higher in this zone than in other basins, due to the proximity of the eroding pumice layers forming the adjacent cliffs. In the remaining basins the carbonate concentration ranges between 7% and 14%.

Coccolithophorids and red algae are the main carbonate producing organisms but the sediments may also include pelecypods, bryozoa, gastropods, brachiopods, echinoderms, and Foraminifera. In the nearshore sediments off the south coast, Raab and Stoffers (1975) report that fragments of mollusc and gastropod are the major carbonate components in the coarser fraction and Foraminifera in the 125-63 micron size range.

To summarize, most of the sediments in and around Santorini are mixtures of redeposited pyroclastic material with biogenic and terrigenous components (tuffites - Petersen and Muller, 1974), with the intercalation of tephra layers. Particular aspects of the work of previous investigators summarised above are relevant to the subsequent discussion of the geochemistry of the sediments, including:-

(1) most samples are pumiceous (rhyolitic or rhyodacitic glass);

(2) most fine grained samples are silt-rich with only minor quantities of clay-sized material;

and (3) individual minerals are dominantly feldspars and pyroxenes although heavy minerals (e.g. magnetite) are important locally.

7.5.1b Description of Samples (present investigation)

Four possible sediment types based on colour variation can be recognised and all are dominantly fine-grained (silty - Petersen and Muller, 1974). Figure 7.4 illustrates the variation in the sediment types within cores from the caldera and shelf zones. Varying proportions of lapilli-sized pumice fragments, biogenic fragments, black sands, lava fragments, and organic debris are also evident.

At the top of each core within the caldera (645, 651, 1104, 1105, 1106) is a layer of "brown mud". The thickness of this layer varies between 1cm in 1104 to more than 10cm in 645 and 1106. Only in core 645 is the sediment type evident at depth. Interspersed within the "brown muds" are subordinate amounts of lapilli pumice, black sands, and, in 1104, shell debris.

"Grey pumice mud" appears to be the most abundant sediment type, with intercalations of both lapilli pumice and black sand layers. On the shelf, however, the proportion of lapilli pumice increases substantially and are similar to the tephra layers described by Petersen and Muller (1974).

A third sediment type is apparent in cores from the caldera zone - "olive muds". They occur both intercalated with the "grey pumice muds" and transitional between the "grey pumice muds" and the surface layer of "brown mud".

Finally, "beige muds" form the surface layers of the cores 1103 and 663 of the shelf zone. Lapilli pumice fragments are also

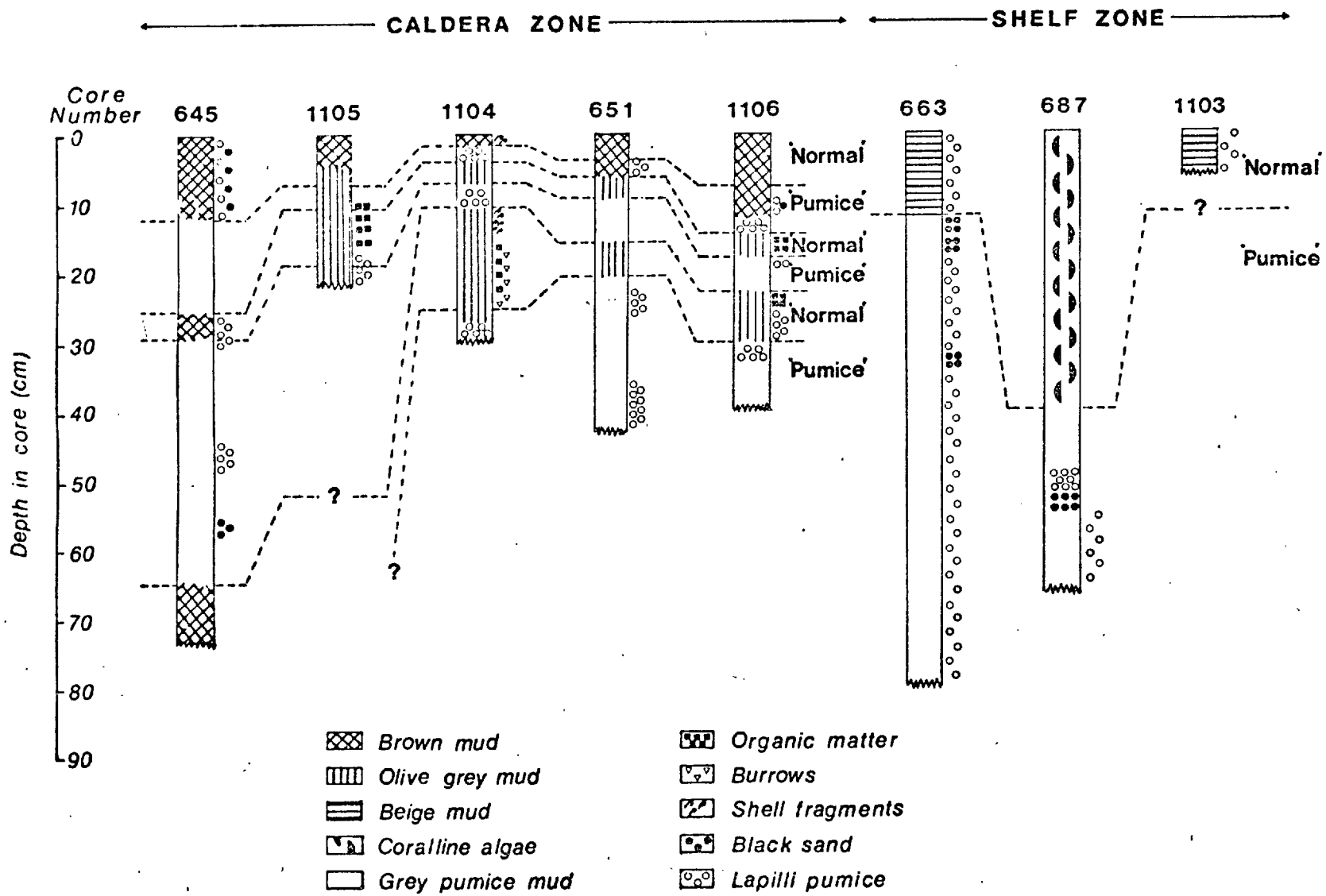


Figure 7.4 Lithology of cores from the caldera and shelf zones.

intermixed with this sediment type.

Biogenic carbonate is evident in two cores. In 1104, recovered from a basin close to the south western entrance of the caldera, shell debris occurs at several horizons. Overlying tephra sediments in core 687 is almost 40cm of calcareous algae intermixed with pumice mud.

Visual evidence for organic matter was not apparent in cores recovered during the 1972 cruise (645, 651 etc.) as these were stored frozen prior to analysis. However, cores from the 1974 cruise were not frozen and so reduced patches were able to develop in the presence of abundant organic matter. This is particularly evident in comparing 651 and 1106, both recovered from a similar location in the northern basin. In 1106 a dark, anoxic layer occurs between 22cm and 26cm and is obviously rich in organic matter. Correlation evidence presented in the following discussion suggests that this layer is equivalent to the olive mud of 651 between 15cm and 20cm. Perhaps olive muds deposited in the northern basin are generally rich in organic matter. In addition to organic matter, the lower half of 1104 is characterised by abundant worm burrows.

7.5.1c Discussion

Dating of strata within cores studied by Petersen and Muller (1974) was achieved by comparing the refractive indices of pumiceous glass. Both the Kolomvos eruption of 1650 A.D. and the Santorini eruption of 1400 B.C., ejected material with a different, but characteristic R.I. By determining this parameter in samples of the rhyolitic pumice Petersen and Muller (op.cit.) were able to recognise these events and so allow the determination of a chronostratigraphic correlation between cores and the estimation of accumulation rates. Within the caldera the post Kolomvos accumulation rate was estimated to be 8cm/100 years (Petersen and Muller, op.cit.).

It was not necessary to determine refractive index in the present investigation as Petersen and Muller suggested a further method of correlation based on total carbonate content of the strata. Carbonate content has not been measured but can be estimated from total Ca determinations. Pumice has an approximate Ca/Al ratio of 0.3 (Puchelt and Schock, 1972). The concentration of Al is not much greater than 7.0% in the core samples and so pumice calcium is unlikely

to exceed 2%, based on the above Ca/Al ratio. Obviously this figure will vary, but a Ca concentration substantially in excess of 2% is probably attributable to carbonate calcium.

Total calcium profiles of caldera cores and a total carbonate profile of core C13 from Petersen and Muller (1974) (also from the northern basin of the Caldera) are illustrated in figure 7.5. The profiles for C13 and 1106 are almost identical. A surface layer Ca maximum of 6% suggests approximately 4% carbonate Ca, equivalent to 10% $CaCO_3$ and compares well with a surface total carbonate of 10% determined by Petersen and Muller (op.cit.).

Of particular interest is the carbonate minimum at 25cm in core C13. According to Petersen and Muller, this carbonate minimum corresponds to the Kolomvos eruption of 1650 A.D. As this minimum is distinct in core 1106 it is possible to use this event as a chronological marker for the present investigation. For core 651, the Ca profile is very similar to 1106 and C13 but the strata seem to be compressed. This feature could be due to a sedimentological phenomenon but could equally be caused by the sampling technique because gravity coring often compresses sediments.

Post - Kolomvos sedimentation in the northern basin is characterised by"brown muds" at the surface in both 651 and 1106. Carbonate concentration appears to be relatively high and the presence of iron oxides is indicated by the colouration of the sediment. Both these features point to a relatively low detrital accumulation rate, increasing the relative proportions of the two components. At the base of the "brown muds" there is a slight Ca minimum, but Ca increases again to surface levels in the"olive mud" (c.f. figures 7.4 and 7.5). In 1106 this horizon shows evidence of a relatively high organic content. Olive (651) and greenish grey (1106) muds may well be very similar in mineralogy and organic content but at different oxidation states (see later discussion). The relatively abundant carbonate and organic material again indicates a relatively low detrital accumulation rate for the "olive muds".

At the base of the olive mud, the Ca concentration decreases to the first major minimum marking the Kolomvos event. Both the carbonate and apparent organic contents are lower in the "grey pumice muds" marking the Kolomvos minimum, and this suggests that the accumulation rates of the pumice muds are relatively high.

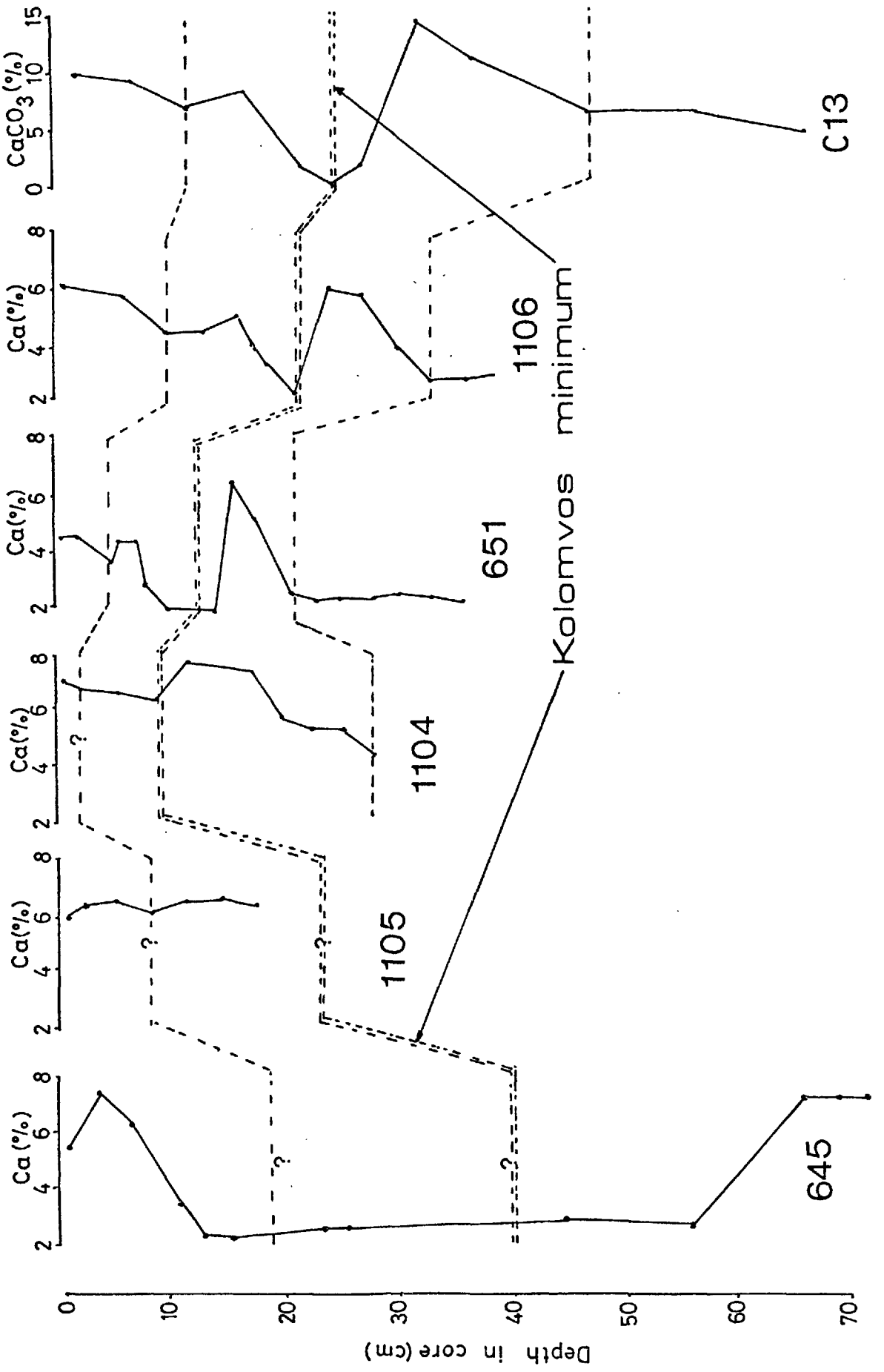


Figure 7.5 Calcium profiles with depth in cores from the caldera. The proposed stratigraphic correlation between cores is shown by the broken lines. Core C 13 is taken from Petersen and Müller, 1974.

Before the Kolomvos eruption, accumulation rates were again relatively low and characterised by the organic-rich, high carbonate "olive muds". In turn, pre-Kolomvos muds were also preceded by a period of rapid pumice sedimentation, perhaps related to earlier eruptions of the Kameni volcano.

Using the Kolomvos event as a chronostratigraphic marker it is possible to estimate the accumulation rates at each location. In 1106, there is 22cm of sediment above this marker, giving an average rate of 7cm/100 years, very close to the 8cm/100 years estimated by Petersen and Muller. Core 651 gives a lower figure of 4cm/100 years but it has been noted that this core may have been compressed during coring. In both cores the sediment above the Kolomvos marker includes some rapidly deposited pumice and so "normal" accumulation rates may be slightly lower. Furthermore, core 1106 may also be slightly compressed compared to the piston cores of Petersen and Muller, once again giving a lower estimate. An accumulation rate between 7 and 9cm/100 years appears to be realistic for normal conditions in the northern basin. Even this "low" rate of accumulation is very high compared to the "millimetres per thousand years" (Arrhenius, 1963) characteristic of pelagic sedimentation, an aspect of some importance when considering the possible formation of authigenic minerals in the deeper basins of the caldera.

To summarize, the vertical succession of sediment types within the northern basin reflects a distinctive alternation between rapid deposition of pumice muds at times of volcanic disturbance and the deposition of organic and carbonate-rich muds under quiescent conditions. In both types of sediment, silt-sized pumice fragments are the dominant component, which during quieter conditions were derived from the normal erosion of the terrestrial pumice strata rather than from eruption. In the former case (i.e. the pumice muds) the volcanic disturbance may cause increased rates of terrestrial erosion, slumping of sediment on the seafloor, the deposition of pyroclastic fallout, or a combination off all three.

As other basins may have slightly different sedimentological regimes, it is not surprising that the Ca profile of other cores are not easily correlatable with those of the northern basin. However, it is reasonable to expect that extended periods of "normal" sedimentation in one basin of the caldera would be paralleled in other basins. Similarly, at times of volcanic activity, rapid sedimentation of pyroclastics would also be expected in all basins.

Therefore, the alternation of sediment types characteristic of the northern basin should be evident elsewhere, but modified by local conditions. If this assumption is valid, then it is possible to provide a broad correlation between the sediments of each basin. Proposed stratigraphic correlations between the caldera samples are illustrated in figure 7.4 and the basis for the correlations are considered in the following discussion.

Like cores 651 and 1106, core 645 exhibits two distinctive carbonate maxima, one at the surface, and one at depth in the core (figure 7.5). However, the carbonate minimum extends over 45cm between the two maxima, compared with only a few centimetres in cores 651 and 1106. The basal high carbonate layer of 645 may well represent the pre-Kolomvos episode of normal sedimentation. Between 25 and 27cm, in 645, is a narrow layer of brown sediment which is not reflected in the Ca profile but may represent the onset of post-Kolomvos normal sedimentation, only to be closely followed by another period of rapid sedimentation of grey pumice mud. This later event may be a larger expression of the small minimum superimposed on the high carbonate surface layer evident in 651 and 1106. If the small layer of brown mud at 26cm does represent the onset of the post-Kolomvos "normal" sedimentation, then the Kolomvos event in itself is represented by 35cm of pumice mud in 645 compared to only a few centimetres in the northern basin. Certainly, the suggested structure of core 645 fits well with the sequence of Ca maxima and minima of the northern basin but implies that pumice mud sedimentation rates at times of volcanic activity are in excess of those in the northern basin. Evidence from the surficial distribution of carbonate (from Petersen and Muller, 1974) supports this conclusion - the south eastern sector of the caldera is generally low in carbonate, implying rapid terrigenous sedimentation. The extent of post-Kolomvos brown muds in 645 is approximately 15cm, giving accumulation rates of the order of 5cm/100 years, which is consistent with previous estimates.

Variation in the Ca profile for 1105 is very slight and remains within the range of 6% to 7%, suggesting approximately 10% $CaCO_3$. It seems most likely that this zone has been influenced by similar conditions as elsewhere but that the gravity corer has only penetrated the post-Kolomvos layer of high carbonate brown to olive muds. If the pumice horizon at the base of core 1105 does coincide with the Kolomvos eruption, a sedimentation rate of 6cm/100 years

is indicated, again similar to estimates elsewhere.

Certain unique characteristics are evident in core 1104. Shell debris is present at several horizons, as are abundant animal burrows and organic debris in the lower half of the core. All of these features may be related to the proximity of very shallow water at the sill marking the outer perimeter of the caldera between the islands of Therasia and Aspronisi. The Ca concentration is fairly high throughout the length of the core but a possible pre-Kolomvos Ca maximum occurs between 12cm and 17cm. Post-Kolomvos points are less distinctive but a combination of possible maxima and minima of the Ca profiles and an examination of the general characteristics of the core suggest the possible correlation illustrated in figure 7.4.

Critical to the interpretation of depth-related geochemical profiles is the oxidation state prevailing in the sediment. Anoxic patches have been noted in several of the unfrozen cores. Organic matter is certainly present but the highly reducing conditions are probably due to post-recovery changes. A truer reflection of the in situ conditions may be preserved in the frozen cores but interpretation depends on colour variation and this is not particularly reliable. However, such variation may provide certain clues, particularly in contrasting cores 645 and 651.

In core 645 both the pre and post - Kolomvos "normal" brown muds retain a similar brown colour throughout the core. Moreover, the pumice muds are distinctively light grey. The general appearance is consistent with oxidising conditions throughout the core.

In contrast, only the surface layer of 651 retains an oxidised brown colour. At depths, "normal" sediments are olive and apparently rich in organic matter. Iron contents of both the surface and lower layers are similar and so a lack of iron does not account for the colour variation. What is most likely is that the layers are compositionally similar but that the deeper sediments are at a lower Eh. Pumice muds in 651 are also much darker than in 645, again consistent with less oxidising conditions.

Hence it appears that distinct differences exist in the chemical environments between sediments at depth in the northern basin (651, 1106) and in one of the southern sector basins (645). The latter core was recovered from a shallower depth and in a zone of higher pumice mud sedimentation rate (low organics) and consequently oxidising conditions appear to have been preserved throughout the core. In the northern basin, pumice muds were deposited at a lower rate and mildly

reducing conditions appear to have developed post-depositionally.

Outside of the caldera, in the shelf zone, the cores exhibit a lower tephra layer with a surface layer of beige muds or calcareous algae (figure 7.4). Petersen and Muller believe the tephra layers to be derived from the Santorini eruption of 1400 B.C. and were subsequently deposited either by slumping or subaqueous deposition of the pyroclastic fallout. Core 663 occupies a similar location to a core described by Petersen and Muller in which it was proposed that the lower tephra layer was derived from subaqueous deposition. If this is the case then the top of the layer can be dated at approximately 1400 B.C., giving an average sedimentation rate for the beige mud of 3cm/1000 years - an order of magnitude less than the fine grained caldera sediments. This is a minimum value. If the sediments were slumped at a later date, then the actual sedimentation rate may approach other values reported for the southern Aegean, i.e. between 4cm and 20cm per thousand years (Opdyke et al., 1971; Wong and Zurudzski, 1969; Pastouret, 1970).

Further testimony to the low sedimentation rate is the presence of abundant calcareous algae in the upper layer of 687. Shallow depths (of the order of 100m) around the outer shoreline of the island may be characterised by coralline algal reefs, as are other islands of the Aegean (see previous sections).

7.5.2 Exhalative and Channel Zones

7.5.2a Previous Work

Much of the emphasis in previously published papers on sediments from the exhalative and channel zones has been on the nature and origin of the iron deposits. Behrend (1936) presented some of the first published analyses, and since then several investigators have assessed the major characteristics of the deposits to provide a key to the interpretation of possible ancient analogs. Puchelt (1972) and Puchelt et al. (1973) describe the deposits on Palaea Kameni (equivalent to the inner exhalative zone of PK(S)) and Butuzova (1966),(1969) provides a similar description of sediments from Nea Kameni (inner exhalative zone of NK). Harder (1960,1964) and Chukrov (1973) present data on iron deposits from other locations around Nea Kameni, as do Bonatti and co-workers but more in the context of modern metalliferous sediments. Bonatti et al. (1972a) compare Santorini deposits with other iron rich

deposits from the Mediterranean, and Bonatti et al. (1972b) compare them with metalliferous sediments from the world oceans.

Further studies have assessed the role of bacteria in the deposition of iron minerals (Hanert, 1973) and the possible sources of the iron in the mineralising solutions (Shorin, 1972).

7.5.2b Sample Description (present investigation)

(1) Inner Exhalative Zone surficial sediments are mainly orange, brown and greenish black muds. Organic debris is more evident in samples from PK(N) which are generally much darker than samples in other embayments. Near to the beaches, at the landward ends of each inner exhalative zone, lapilli sized pumice fragments are abundant.

Description of cores recovered by Butuzova, and Puchelt and co-workers, (Butuzova, 1966; Puchelt, 1972 and Puchelt et al. 1973) show the vertical stratification of sediments within the inner exhalative zone. In Nea Kameni, between 24 and 40cm of orange/red mud overlies a greenish black mud (Butuzova, 1966). Orangey-brown mud also forms the upper layer of the sediment in Palaea Kameni, but they are underlain by olive to dark grey sediments with only local patches of greenish-black sediment (Puchelt, 1972; Puchelt et al.,1973).

(2) Outer Exhalative Zone surficial sediments are generally orange to orange/brown muds with varying amounts of black volcanic sand.

(3) Channel Zone surficial sediments consist of varying proportions of shell, organic detritus, and volcanic sand. Unlike the exhalative zone deposits, they are dominantly sands with only a minor mud component.

7.5.2c Nature and Origin of the Iron Rich Deposits

Iron deposits, containing up to 40% Fe, are limited to the inner exhalative zones where shallow sills at the seaward end prevent the escape of the bulk of precipitated iron minerals. Volcanic gases, mainly CO_2 (Butuzova, 1966; Puchelt, 1972), and solutions enter the embayment either at the landward ends, as in Palaea Kameni, or around most of the perimeter, as in Nea Kameni. Associated with the submarine fumarolic activity is a high heatflow (Puchelt, 1972) and sea water temperatures as high as 35°C (see section 7.3).

Leaching of volcanic rocks by circulating meteoric and seawater appears to be sufficient to supply the iron and associated metals in the hydrothermal solution (Puchelt, 1972; Bonatti et al., 1972a; Puchelt et al., 1973; Chukrov, 1973) without needing recourse to a magmatic source (Harder, 1964). Both Chukrov (1973) and Harder (1964) emphasise the carbonate-rich nature of the circulating solutions. In addition, Puchelt (1972) recognises an increase in the SO_4/Cl ratio at the base of certain cores which he attributes to the sulphuric acid content of the solution. As a possible mechanism of metal leaching, Puchelt (1972) and Puchelt et al., (1973) cite the evidence of Shorin (1972), which showed that H_2SO_4 at a pH1 and at 100°C could preferentially leach iron and manganese from volcanic rocks of Santorini.

Whatever the nature of the circulating solutions, as they enter seawater a combination of rapid increase in redox potential and pH cause the ferrous iron in solution to be oxidised to form ferric hydroxide gels (ferric hydroxide - Butuzova, 1966; Harder, 1964; Puchelt, 1972; poorly developed, cryptocrystalline goethite - Bonatti et al., 1972; ferrihydrite and goethite - Chukrov, 1973). Hanert (1973) also proposes that the iron oxidising bacterium Gallionella ferruginea contributes substantially to this oxidation process. Experiments by Hanert provisionally indicate two major zones of iron oxidation. By placing glass slides, on which the iron precipitates, throughout the water coloumn, he has found that oxidation occurs at the seawater/air interface and the sediment/water interface (Hanert, personal communication). At the former site, what might be termed "normal" oxidation of the ferrous iron occurs in the presence of atmospheric oxygen. In contrast, at the sediment/water interface the iron bacterium Gallionella ferruginea is present in abundance. The upper layer of ferric hydroxide gels is therefore a mixture of flocculated and sedimented ferric hydroxide precipitated at the water/air interface, combined with ferric hydroxide partially precipitated by bacteria at the sediment/water interface.

Beneath the upper layer of ferric hydroxide in PK(S), siderite becomes the dominant component (Puchelt, 1972; Puchelt et al., 1973). In some cores it persists throughout the length of the core, but in others the dominant mineral in the lowest layers becomes ferrous hydroxide (Puchelt, 1972; Puchelt et al., 1973). Locally, in layers where sulphate reducing bacteria have been found, iron sulphides form (Puchelt, 1972; Puchelt, et al., 1973).

Mineralogically, the lower greenish-black layer in Nea Kameni appears similar to the lowest layer of certain cores from Palaea Kameni, in that the dominant iron phase is ferrous hydroxide (Butuzova, 1966) with only minor siderite. Other iron phases include hydrotroilite, vivianite, and pyrite. Butuzova (1966) suggests that fumarolic H_2S plays an important role in the development of this lower layer. She proposes that there are two types of spring based on their gaseous composition - one with "the acid reek of hydrogen sulphide" and another with a high CO_2 component "secreting a fine, rusty-brown ferruginous suspension". It is not clear whether evidence exists for both types within the Nea Kameni embayment, but Butuzova believes that the volcanic H_2S from one type of spring reacts with the ferric hydroxide secreted from the other, thereby reducing it to ferrous hydroxide. However, Bonatti et al. (1972a) suggest that the lower layer in Nea Kameni may represent a more extensive horizon of sulphate reducing bacterial activity, as noted locally in Palaea Kameni. Certainly sulphate reducing bacteria may play an important part in the formation of the local sulphides, but volcanic H_2S cannot be ruled out, especially as abundant sulphur occurs around the subaerial craters on Nea Kameni.

Therefore, ferric oxides occur at the oxidised surface, ferrous carbonates or hydroxides at a lower Eh within the sediments, and ferrous sulphide locally at the lowest Eh. In iron rich deposits generally, James (1966) describes an exactly similar facies sequence of oxide, carbonate and sulphide, characteristic of a decreasing redox potential during formation. According to Garrels and Christ (1965) the relative abundance of iron minerals is a function of Eh, pH and the concentration of carbonate and sulphide ions. Below the highly oxidising surficial layer a slightly positive to negative Eh range and low sulphide ion concentration is suitable for the formation of ferrous hydroxide or siderite, depending on the carbonate ion concentration. Where sulphide ion concentration is locally high, then sulphides form.

Other components of the iron deposits include volcanic rock fragments and pyroclastics derived from the surrounding volcanic strata, authigenic vivianite, and opaline silica. The opaline silica is derived from one or more of the following sources:- halmyrolysis of pumice; tests of siliceous organisms; and derivation from hydrothermal solutions. Pushkina (1967) found silica in hydrothermal solutions entering the embayments. Like Bonatti (in Bonatti et al.,

1972a), we also observed "white, snow like flocculating particles, probably silica "being formed in the Nea Kameni embayment.

7.5.3 Summary

(1) Inner exhalative zone sediments are the major iron deposits and include a surface layer of ferric hydroxide mud overlying ferrous carbonate (siderite) and hydroxide muds with varying amounts of pumice, vivianite, and opaline silica. Iron and associated elements in the hydrothermal solutions are derived by the leaching of volcanic rocks by heated, circulating, meteoric and sea water. On entering the marine environment, a combination of the increase in pH, redox potential, and the action of iron oxidising bacteria, cause the precipitation of hydrated ferric oxides. Local patches of sediment with negative redox potentials occur where sulphate reducing bacteria are active, and/or volcanically derived H_2S is present.

(2) Outer Exhalative Zone sediments reflect the decreasing influence of hydrothermal activity and the increasing contribution of detrital volcanic phases. Accordingly sediments are an admixture of ferric oxides and volcanic sands.

(3) Channel Zone sediments are deposited in a comparatively high energy environment dominated by strong currents. Components include bioclastic debris, organic detritus, volcanic sands and lapilli pumice.

(4) Caldera Zone sediments reflect the alternation in sedimentation rate between the rapid deposition of pumice muds at times of volcanic activity and the "pre-" and "post-volcanic" deposition of "normal" sediments. Brown muds forming the surface layer in all caldera cores are typical of "normal" sediments. Local modification of this pattern includes bioturbation; post - depositional development of mildly reducing conditions; and higher than average rates of pumice mud sedimentation.

(5) Shelf Zone sediments exhibit a succession from nearshore volcanic sands, through offshore coralline algal reefs to beige muds of deeper water. Underlying these surficial deposits are extensive tephra layers derived from the 1400 B.C. eruption of Santorini, either by slumping from shallow waters nearer the shore or by the subaqueous deposition of ash and lapilli sized pyroclastics.

7.6 GEOCHEMICAL INVESTIGATIONS

7.6.1 Introduction

To assess the major dispersion pathways of the heavy metals, and the conditions under which they are deposited, chemical analyses have been conducted on sediment and water samples collected on detailed traverses from the fumarolic metal sources to the open sea (sample locations - figure 7.3).

Preceding sections have outlined how the distinctive sedimentological and mineralogical characteristics of sediments in the five zones reflect their physico-chemical environments. Preliminary investigation of these deposits reported by Smith and Cronan (1975b) also indicate that the bathymetric zones are distinct geochemically, particularly when considering the variation in Fe and Al - two major elements that reflect the hydrothermal and detrital components respectively. Consequently, much of the subsequent discussion is within the framework of the bathymetric zone classification scheme.

Initially, the average bulk chemical composition of sediments from the different zones are considered. More deteiled investigation of caldera and shelf zone sediments establish the nature of the detrital controls on element abundance and reveal the extent of hydrothermal influence on the outer zones. The abundance of selected elements in water samples provide an estimate of the volcanic contribution and the dispersion gradients in solution of the elements concerned. Trends in the data are also assessed to aid in interpreting element relationships, but they are also useful in the context of geochemical exploration which often utilizes consistent trends to pinpoint targets. Finally, partition studies are aimed at elucidating element associations and the fraction in which each element occurs.

7.6.2 Average Composition of Surficial Sediments

7.6.2a Introduction

Full details of the analytical techniques, precision, and accuracy are given in the appendices. In general, bulk analyses for the elements Al, Ti, Ca, Mg, Cu, Zn, Fe and Mn are based on digestion in hydroflouric, perchloric, and nitric acids, followed by analysis, in duplicate, by atomic absorption spectrophotometry. Abundances of

the elements Pb, Mo, V, Co, Ni, Cr, Ga, Sr, Ba, K, Li, Si and Sc were also determined in duplicate but by a rapid, semi-quantitative, direct reading emission spectrographic technique (DR).

7.6.2b Results and Discussion

Average concentrations of the elements determined in sediments from the five bathymetric zones are presented in table 11. Also included are the average crustal abundances of the elements (Mason, 1966); the analysis of a latite - andesite sampled from a lava flow on Nea Kameni (Puchelt et al., 1973); data on a sample of the upper pumice strata on Santorini (Thera) - a major contributor to the sediments (Puchelt et al., 1973); three analyses of iron deposits from Santorini reported by Bonatti et al. (1972a), Butuzova (1966) and Puchelt et al., (1973) (equivalent to deposits from the inner exhalative zones); and average values of elements from the caldera and shelf zone from Butuzova (1969).

Average abundances of elements in the Santorini zones determined in this work appear to be consistent with those reported by other authors. Only the Ti in the inner exhalative zone of Puchelt et al., (1973) appears to be different, being an order of magnitude higher than that found during this present investigation or by Bonatti et al., (1972a).

Comparison with average crustal abundances is made to pinpoint possible enrichment and depletion processes. Not surprisingly, of the major elements only Fe is substantially enriched in the exhalative zones, although Mn is moderately enriched in the outer exhalative and caldera zones. The greater amount of calcium carbonate in the channel, caldera, and shelf sediments is reflected in the enrichment of Ca in these zones. Otherwise, the major elements are generally depleted in all zones because they occur in phases other than the major iron and carbonate minerals.

Enrichment of minor elements in the iron deposits is restricted to Mo, Hg and possibly Zn and V in the outer exhalative zones. The well known association between Sr and carbonates on the sea floor is apparent in the enrichment of Sr in the high carbonate zones. Co, Ni and Cr are distinctly depleted in the exhalative zones and only approach average crustal abundances in the shelf zone.

Comparison of abundances between zones is limited by the small number of samples from each zone. Nonetheless, certain distinct

TABLE 11 Partial chemical composition of surface sediments from in and around the Santorini caldera (Si to Sr in percent, Cu to Sc in ppm, and Hg in ppb).

	1	2	3	4	5	6	7	8	9	10	11	12	13
Si	9.10	6.50	6.10	11.1	19.4	14.5	29.8	-	20.1	-	30.0	30.6	27.7
Al	1.10	0.30	0.30	0.22	4.58	4.50	6.76	-	5.35	-	7.66	7.90	8.13
Ca	1.09	0.66	0.91	1.60	2.55	14.0	6.20	-	13.6	-	-	2.60	3.63
Mg	0.95	0.83	0.63	1.47	1.02	1.85	1.29	-	1.61	-	-	0.78	2.09
K	0.69	0.43	0.49	0.25	1.53	1.57	2.10	-	1.87	-	-	1.85	2.59
Fe	32.6	27.0	37.1	31.3	17.7	4.00	4.20	6.00	2.65	2.40	-	3.87	5.00
Mn	0.03	0.20	0.01	0.03	0.17	0.09	0.16	0.35	0.07	0.10	0.10	0.15	0.10
Ti	0.04	0.01	-	0.26	0.31	0.28	0.41	0.38	0.30	0.23	-	0.51	0.44
Sr	0.04	-	-	-	0.03	>0.1	0.04	-	>0.1	-	0.01	0.02	0.04
Cu	34	9	-	18	26	18	30	48	19	31	21	14	55
Zn	63	-	-	57	105	74	87	-	68	-	112	88	70
Pb	13	-	-	-	17	20	23	-	12	-	15	11	12
Mo	29	-	-	35	17	4	<2	-	<2	-	3	2	2
V	66	30	-	65	172	26	101	155	42	58	80	53	135
Co	<1	<5	-	17	4	<1	8	18	7	18	-	-	25
Ni	5	<5	-	-	7	6	14	22	52	54	-	-	75
Cr	5	<5	-	10	14	6	24	31	52	56	7	3	100
Ga	3	-	-	-	10	21	17	-	18	-	-	-	15
Ba	103	80	-	-	232	334	285	-	377	-	517	410	425
Li	3	-	-	-	23	48	25	-	38	-	-	-	11
Sc	14	<3	-	-	8	4	7	-	4	-	12	14	22
Hg	179	-	-	-	65	37	37	-	-	-	-	-	80

Notes: Al, Ca, Mg, Fe, Mn, Ti, Cu, and Zn were analysed by A.A.S.; Si, K, Sr, Pb, Mo, V, Co, Ni, Cr, Ga, Ba, Li, and Sc by D.R.; and Hg by flameless A.A.S.

1 - average composition of inner exhalative zone samples (17 samples for A.A.S., 15 for D.R., and 5 for Hg).

2, 3, 4 - inner exhalative zone analyses from Bonatti et al. (1972a), Butuzova (1966), and Puchelt et al. (1973) (core 25) respectively.

5 - outer exhalative zone (12 samples A.A.S., 11 for D.R., 3 for Hg).

6 - channel zone (4 for A.A.S., 2 for D.R., 1 for Hg).

7 - caldera zone (10 for A.A.S, 2 for D.R., 2 for Hg).

continued ....

TABLE 11 (continued)

8 - caldera sediment analysis from Butuzova(1969).

9 - shelf zone (based on 10 samples for A.A.S.elements,and 3 for D.R.).

10 - shelf sediment analysis from Butuzova(1969).

11 - analysis of the upper pumice from Puchelt et al.(1973).

12 - analysis of a latite-andesite from the Kameni Islands (in Puchelt et al.,1973).

13 - average abundance of the elements in the Earth's crust (Mason,1966).

differences do exist. As might be expected from the very nature of the deposit, iron is highest in the inner exhalative zones (32.6%) but also exceeds 15% (iron rich sediments - James, 1966) in the outer exhalative zones (17.7%). Also highest in the inner exhalative zone are the minor elements Hg, Sc, Mo and Cu, (179ppb, 14ppm, 29ppm, and 34ppm respectively) but, in the case of Cu, the difference between here and the other zones is small.

In the outer exhalative zone V and Zn are highest (172ppm and 105ppm respectively). Average Mn is also highest in this zone (0.17%). Calcium, Mg, and Sr, elements with strong carbonate affinities, are highest (14.0%, 1.85%, greater than 0.1% respectively) in the channel and shelf zones. Also included in this group are the elements Li, Ba and Ga, with maximum average concentration of 48ppm and 377ppm and 21ppm respectively. In contrast, elements with strong ditrital affinities, namely Al, Si, K and Ti, are highest (6.76%, 29.8%, 2.1% and 0.41% respectively) in the caldera zone, although only the inner exhalative zone sediments, with average concentrations of 1.1% Al, 9.1% Si, 0.69% K, and 0.04% Ti, are markedly depleted in this group of elements. Pb (23ppm) and Co (8ppm) are also highest in the caldera zone but variation in Pb is not significant and Co elsewhere is close to the detection limit. Finally, Ni and Cr are highest in shelf sediments (both at 52ppm). In other zones the average concentration of these two elements is less than half that of the shelf abundance. This trend in Ni and Cr is also supported by the data of Butuzova, (1969).

The average bulk composition of sediments from the different zones reflects the dominant depositional processes. The characteristics of the surficial sediments from each zone may be summarised as:-

(1) Inner Exhalative Zones: high in iron and low in other major elements and characterised by the highest concentration of Hg, Sc and Mo.

(2) Outer Exhalative Zone: moderate iron, moderate Al, Si and Ti, and low in carbonate associated elements. Characterised by high Mn, V and Zn.

(3) Channel Zone: dominated by carbonate and detritally associated elements.

(4) Caldera: detritally associated elements are dominant but Mn is also abundant.

(5) Shelf zone: carbonate and detritally associated elements dominate but also highest in Cr and Ni.

7.6.3 Bulk Geochemistry of Sediments from the Shelf Zone

7.6.3a Introduction

Butuzova (1969) made a comprehensive study of the geochemistry of the elements Fe, Mn, Ti, V, Cr, Ni, Co and Cu in the shelf sediments around Santorini. Average abundances from Butuzova (1969) are presented in table 11 to enable comparison with average abundances determined in this investigation. There is close agreement in all elements between the two investigations.

According to Butuzova, the hydrothermal influence on Shelf Zone sediments is so low as to be undetectable. The volcanic influence is limited to the solid products of volcanism, particularly close to the archipelago where pyroxene and magnetite result in the enrichment of Fe and Ti. Sedimentological investigations (reviewed in section 7.5.1), particularly those of Raab and Stoffers (1975), support this conclusion. Butuzova (op.cit.) notes that with increasing distance from Santorini normal sedimentological factors, including granulometry, composition, biogenic processes, and adsorption on clays, become more important than the volcanic influence.

7.6.3b Results

In general, two distinct facies are present in most cores. The upper horizon represents conditions of "normal" sedimentation and includes, from the shoreline seawards, volcanic sands through coralline algae to beige muds consisting of calcium carbonate, pumice silt eroded from the Santorini pumice strata,and minor quantities of terrigenous clay material. Underlying the surficial deposits are extensive pumice horizons, probably derived from the 1400 BC eruption of Santorini, either by slumping from shallow water or by the sub-aqueous deposition of pyroclastic falls. In most cases the following discussion will refer simply to the "normal" and "pumice" horizons.

Table 12 summarises the range of element abundance found within the two horizons. "Normal" sediments straddle the average bulk composition for shelf sediments given in table 11, whereas "pumice" sediments have a composition very similar to that of a sample of pumice from the Upper Pumice Strata on Santorini (Puchelt et al., 1973, see table 11). Only the Ba appears to be depleted compared to

TABLE 12 Range of element concentrations in cores from the caldera (645 and 651)and shelf zones (Si,Al,Ca, Mg,K,Fe,and Ti are in percent,the remaining elements in ppm).

	Caldera		Shelf	
	Normal	Pumice	Normal	Pumice
Si	22.0-35.0	32.0-40.0	8.40-26.5	30.0->40.0*
Al	6.7-7.8	5.7-7.5	3.0-6.6	7.0-7.8
Ca	3.0-8.0	1.0-3.5	10.0-24.0	4.3-5.7
Mg	1.0-1.5	0.6-1.2	1.7-2.0	1.1-1.6
K	1.7-2.3	1.9-2.2	1.4-2.2	2.1-2.3
Fe	4.0-5.4	2.8-4.0	1.4-3.5	3.8-4.4
Ti	.38-.48	.35-.50	.17-.36	.44-.46
Mn	1000-5400	890-1060	395-1060	825-990
Sr	155-605	85-155	520-2450	140-230
Cu	23-39	12-26	17-30	21-28
Zn	80-98	80-98	50-88	81-130
Pb	13-27	8-20	9-15	9-13
Mo	< 2	< 2	< 2	< 2
V	68-123	28-60	<2-68	48-127
Co	7-10	4-9	3-9	9-12
Ni	10-23	3-12	42-71	5-9
Cr	17-33	4-25	24-84	18-27
Ga	9-23	13-18	16-21	16-25
Ba	210-440	180-285	360-490	220-360
Li	15-29	9-16	26-53	9-14
Sc	3-8	3-7	2-5	6-8

* exceeds calibration range

the upper pumice strata.

When compared, the "pumice" sediments are enriched in Al, Si, Fe and Ti, whilst the "normal" sediments have higher concentrations of Ca, and Mg. Of the minor elements, Zn, V, Sc and possible Co are enriched in the pumice sediments, whereas Ba, Li, Cr, Ni and Sr are enriched in the "normal" sediments. Cu, Mn, Ga, K, Pb and Mo appear to be similar in both groups.

7.6.3c Discussion

From the lithological point of view both the "normal" and "pumice" sediments have certain characteristics in common. The most abundant component in both is pumice. Moreover, the pumice probably has a common origin in that the lower pumice horizons are derived from some form of subaqueous deposition from the 1400 B.C. erupted material, and the pumice component of the "normal" sediment is derived from the erosion of pumice on land from the same eruption.

During the differing processes of erosion and sedimentation, mineral assemblages would be expected to remain the same but differing in the relative proportion of the three main pumice components - rhyolitic glass, feldspars, and pyroxenes. In addition to pumice in the "normal" sediments we have a variable carbonate, and a minor clay, component. Organic matter may also be present.

It might be expected, therefore, that although sedimentologically distinct, compositionally the sediments may be considered as occurring at some point on a carbonate - pumice end member system. Only in the sediments with dominant pumice and minor diluting carbonate would variation in pumice mineralogy play a significant role in influencing composition. This feature (the carbonate - pumice relationship) is well illustrated by the relationship between Ca and Al (figure 7.6), representative of the carbonate and pumice components respectively. The carbonate - pumice line is constructed such that at the origin for Al, Ca is 40%, representing approximately 100% $CaCO_3$. This point is joined to four upper pumice analyses taken from Puchelt and Shock, (1972).

Data points for both grab and core samples straddle the carbonate - pumice line indicating that varying proportions of the pumice and carbonate end members constitute the shelf sediments. Elements, therefore, with a strong pumice control would be expected to have a

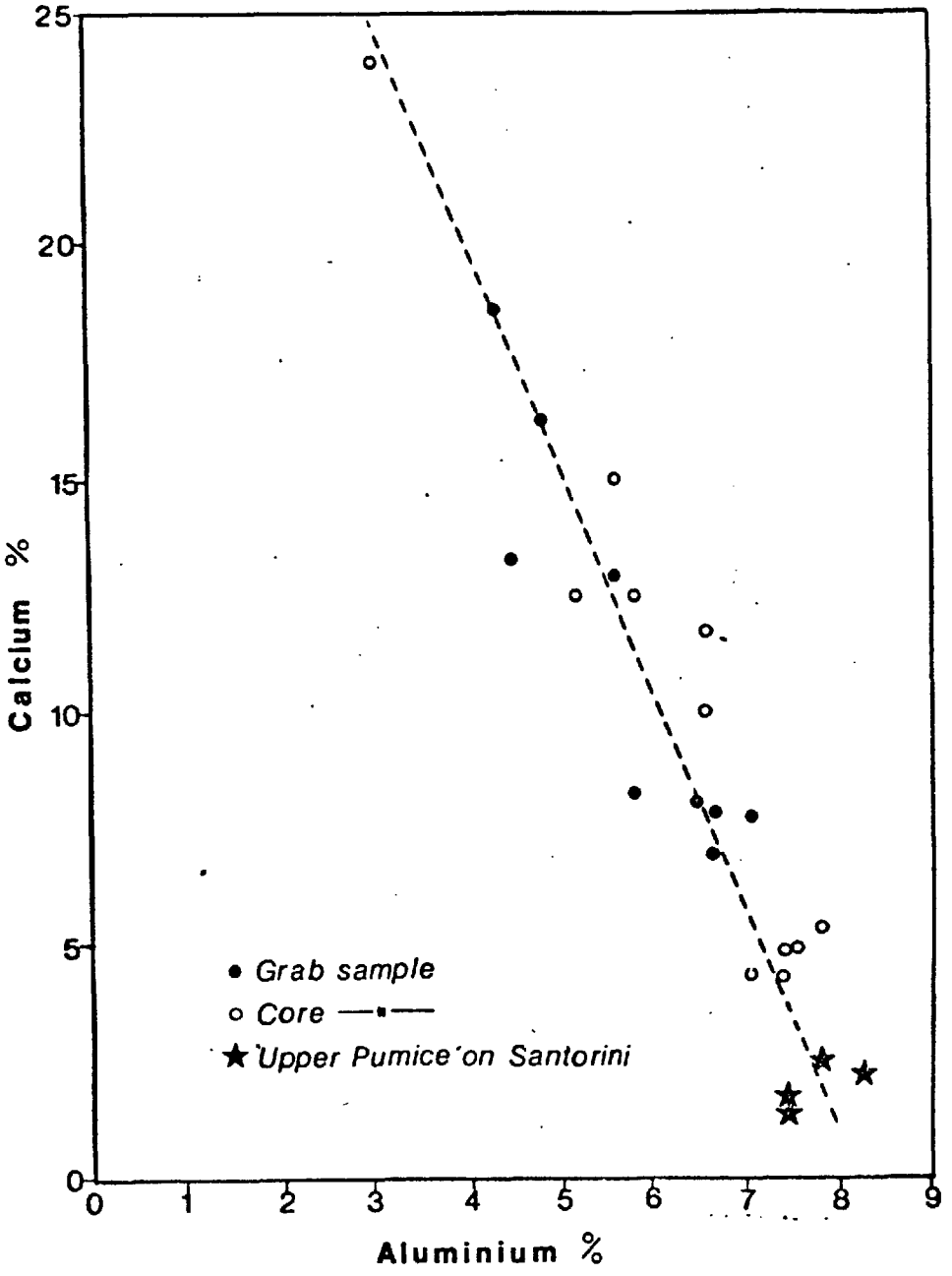


Figure 7.6 Calcium against aluminium for samples from the shelf zone. ('Upper' pumice data are from Puchelt and Schock, 1972.)

direct relationship with Al, and elements in phases which serve to dilute the pumice will have an inverse relationship to Al.

A positive relationship is observed between Fe and Al (figure 7.7) and Ti and Al (figure 7.8). Minor elements enriched in the "pumice" sediments, such as Sc, V and Zn, also show a generally positive relationship to Al (e.g. Sc and Zn - figure 7.9). Fe, Ti, Sc, V and Zn are considered, therefore, to be mainly pumice controlled.

Although Mn also shows a direct relationship with Al, data points are much more scattered (figure 7.10). To a certain extent this could reflect a similar variation found by Puchelt and Schock (1972) in the Mn abundance in samples from the upper pumice strata on Santorini but there are certain features which indicate an additional control superimposed on the pumice Mn. Certain grab samples, and the surface layers from cores 1103, 686 and 663, have the highest Mn/Al ratios. In contrast, Mn/Al ratios in lower horizons of the "normal" sediments (686/2, 663/2) are significantly less even though lithologically they are similar to the upper layers, reflected in the equal abundances of Al. Remobilisation of Mn from the lower to the upper layers of the "normal" sediments (Lynn and Bonatti, 1965) could account for this increase in the Mn/Al ratio.

Cu also shows a positive relationship with Al (figure 7.11) but with a greater scatter of points. Pumice is thought to be the dominant control on Cu abundance but it seems that, for a given Al abundance, "normal" sediments (e.g. 1103/1, 663/1) are enriched in Cu compared to the "pumice" sediments (e.g. 663/3). An additional contributor of Cu is indicated by the apparent enrichment but it is not possible to be more specific from the evidence available, except to suggest that it may be related to the unidentified "terrigenous" component which appears to cause the enrichment of several other minor elements in the "normal" sediments (see later).

Li, Ba, Cr and Ga are a group of elements with an apparently inverse relationship to Al (figure 7.12.) and which are enriched in "normal" sediment. This indicates that the pumice component acts as a diluent of the phases containing these elements. There is also limited evidence (sample 687/2 - high in carbonate) that the carbonate component also dilutes these phases, although this is not so apparent for Li. These elements may be associated with an unidentified terrigenous component which could derive from other parts of the Cyclades where it is known that the fine-grained

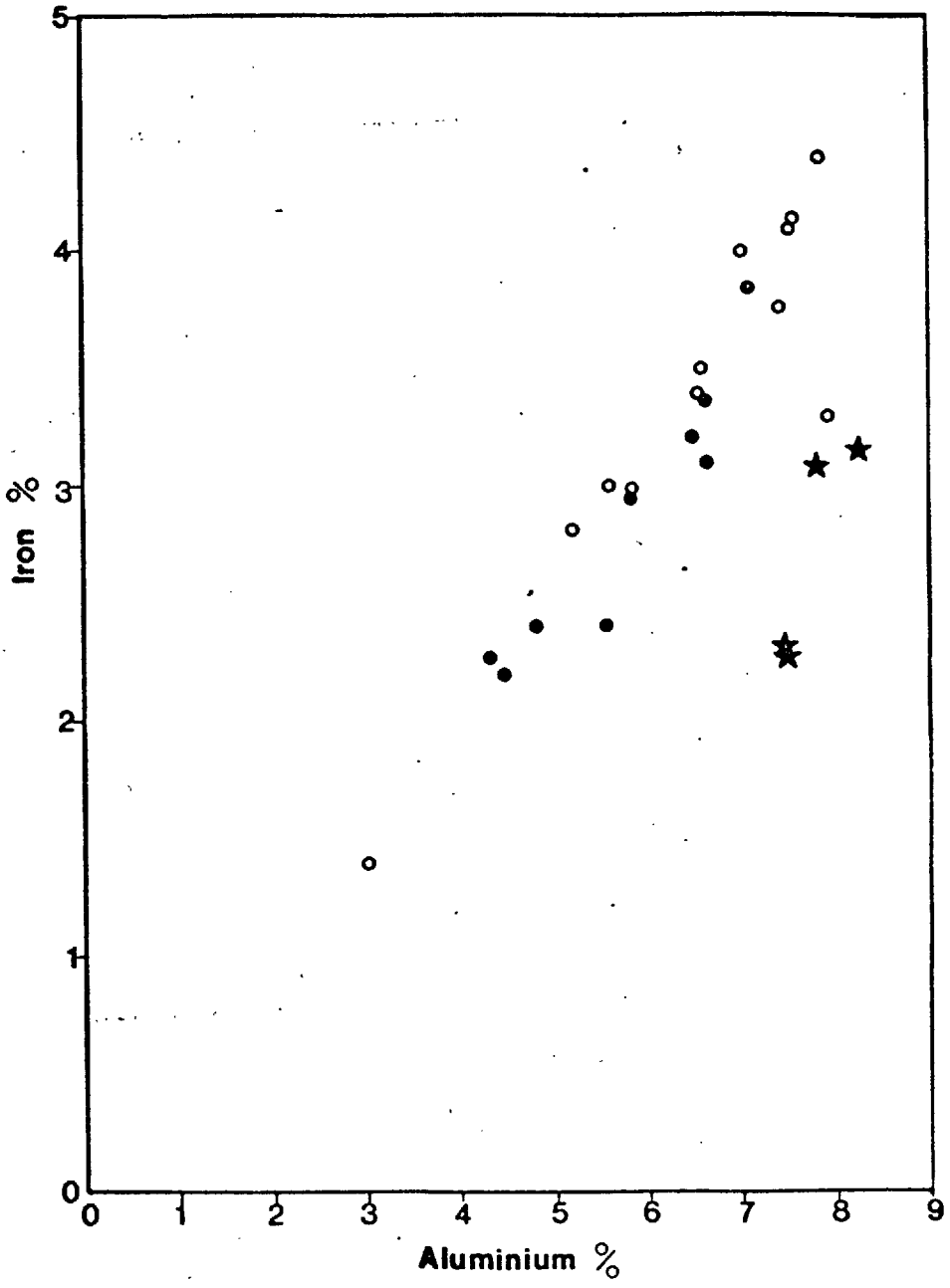


Figure 7.7 Scatter plot of iron against aluminium for samples from the shelf zone. (See figure 7.6 for key.)

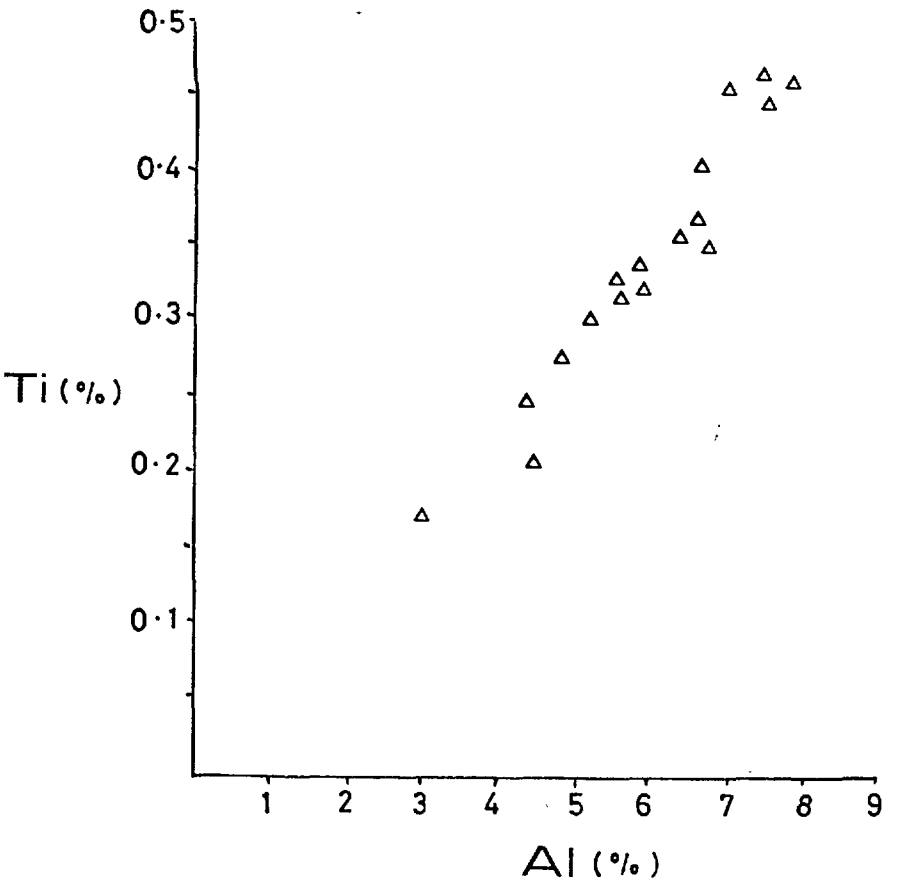


Figure 7.8 Scatter plot of titanium against aluminium for shelf zone sediments.

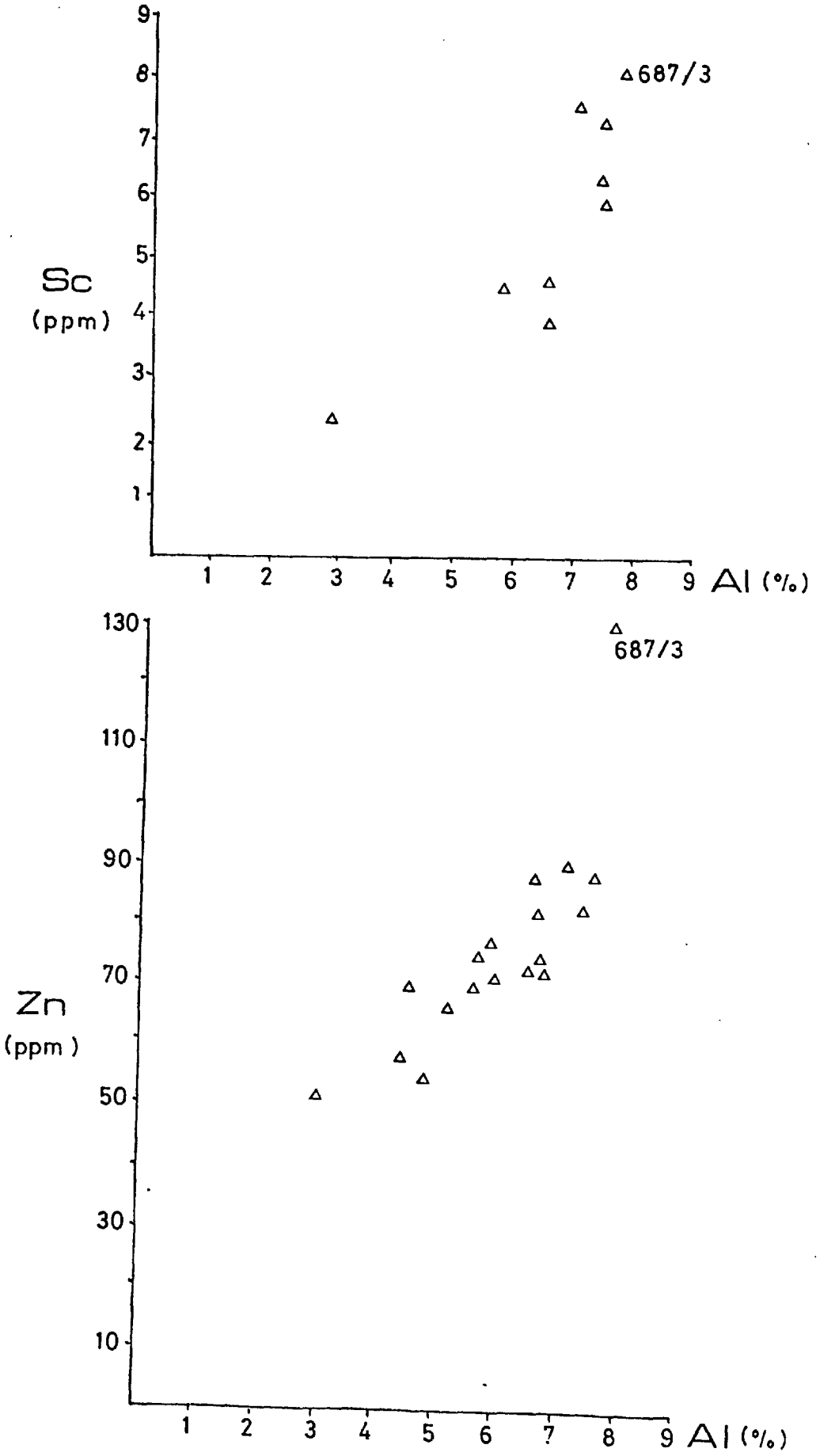


Figure 7.9 Scatter plots of scandium and zinc against aluminium for shelf zone samples.

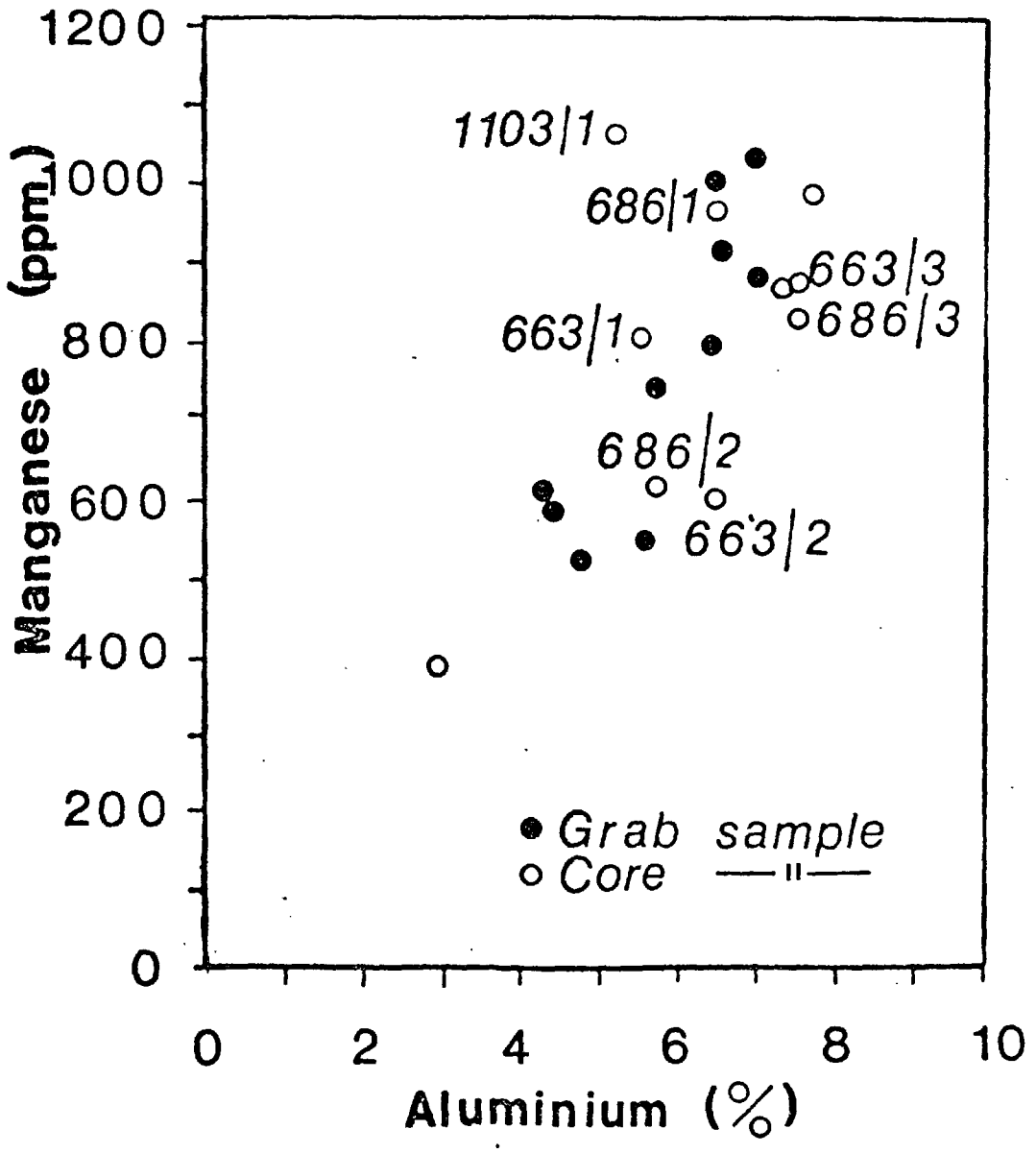


Figure 7.10 Scatter plot of manganese against aluminium for shelf zone samples.

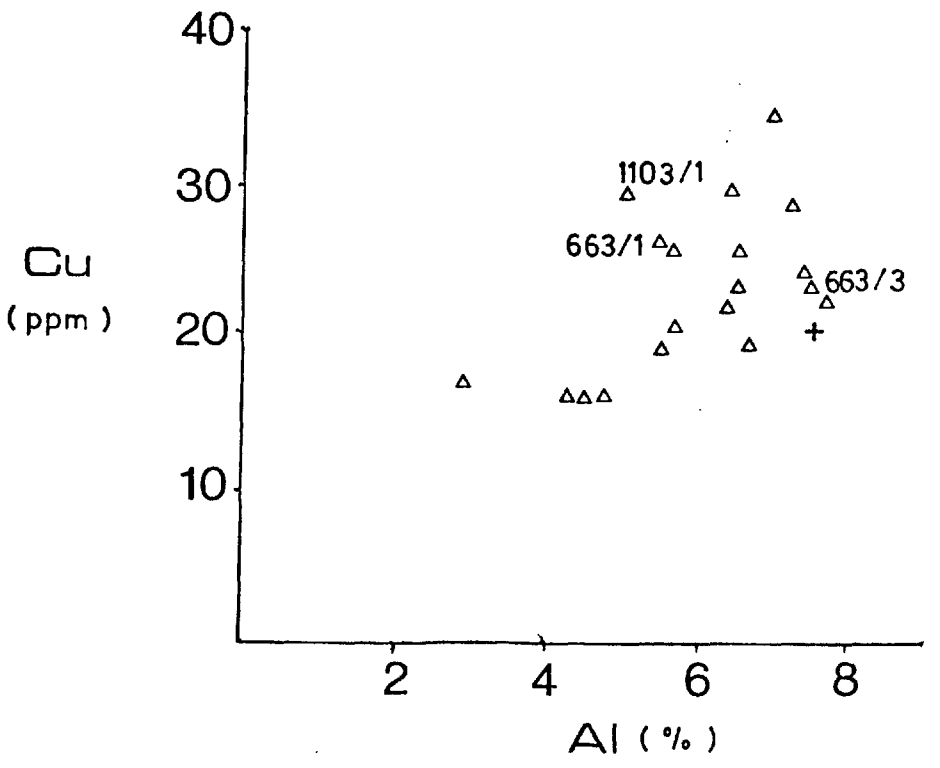


Figure 7.11 Scatter plot of copper against aluminium for shelf zone samples(+ 'upper' pumice from Puchelt and Schock,1972).

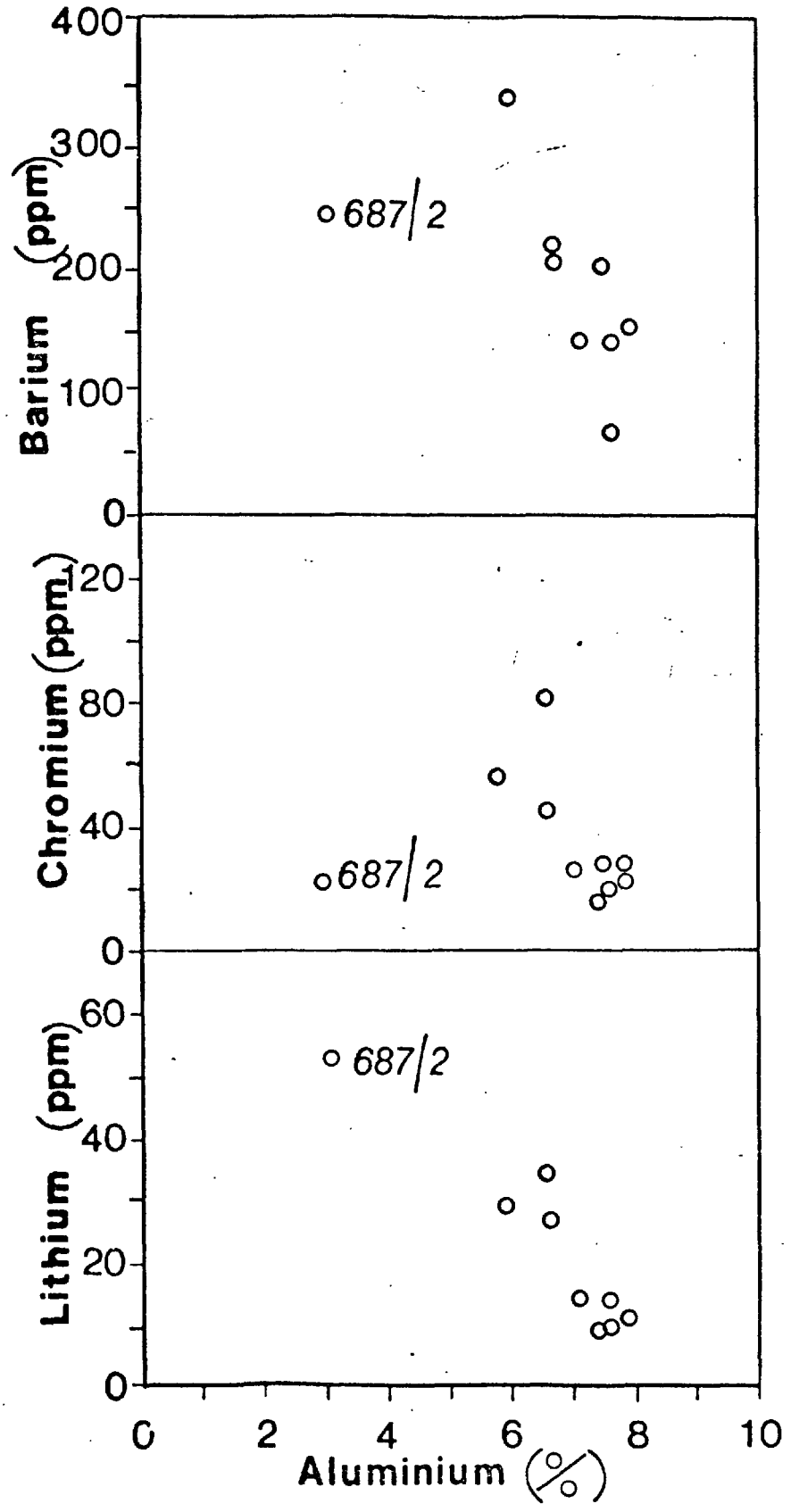


Figure 7.12 Scatter plots of barium, chromium, and lithium against aluminium for shelf zone samples.

detrital minerals are enriched in elements such as Ni and Cr (Chapters 2 to 6).

Although an inverse relationship exists between Mg and Al, there is a wider scatter of data points than that exhibited by Ca and Al. The Ca/Mg scatter plot (figure 7.13) provides a clearer picture of the Mg behaviour. In the "pumice" samples a good correlation between Mg and Ca is apparent. Samples with a Ca abundance in excess of 6% also show a direct relationship between Ca and Mg which is attributable to the carbonate component but in which the Mg/Ca ratio is much less than that in the detrital pumice samples. It is apparent that although Mg has a significant carbonate association the pumice contribution to this element is also large. Sr also has a strong positive relationship with Ca which is consistent with the well-known substitution of Sr in carbonates (Turekian, 1964).

7.6.3d Conclusions

Relationships of various elements to Al suggest that the abundance of elements in sediments from the shelf zone are controlled by the relative proportions of three end members - pumice, carbonate and an unidentified terrigenous component. To summarise, the dominant phase/element associations are as follows:-

(1) Al, Fe and Ti are controlled by the pumice, Ca by the carbonate and Mg reflects variation in both these phases;

(2) V, Zn, Cu, Sc and Ga are mainly governed by the pumice phase, possibly within the ferromagnesian minerals;

(3) Sr is directly related to the carbonate phase;

(4) Ni, Cr and Ba are related to one or more unidentified terrigenous components of the "normal" sediments, and which may also contribute some Cu and Ga;

(5) Mn has a direct relationship with the pumice phase but superimposed on this is the possible remobilisation of Mn in the "normal" sediments, resulting in enrichment in the surface layers.

7.6.4 Bulk Geochemistry of Caldera Zone Sediments

7.6.4a Introduction

The aim of this section is to establish the factors controlling

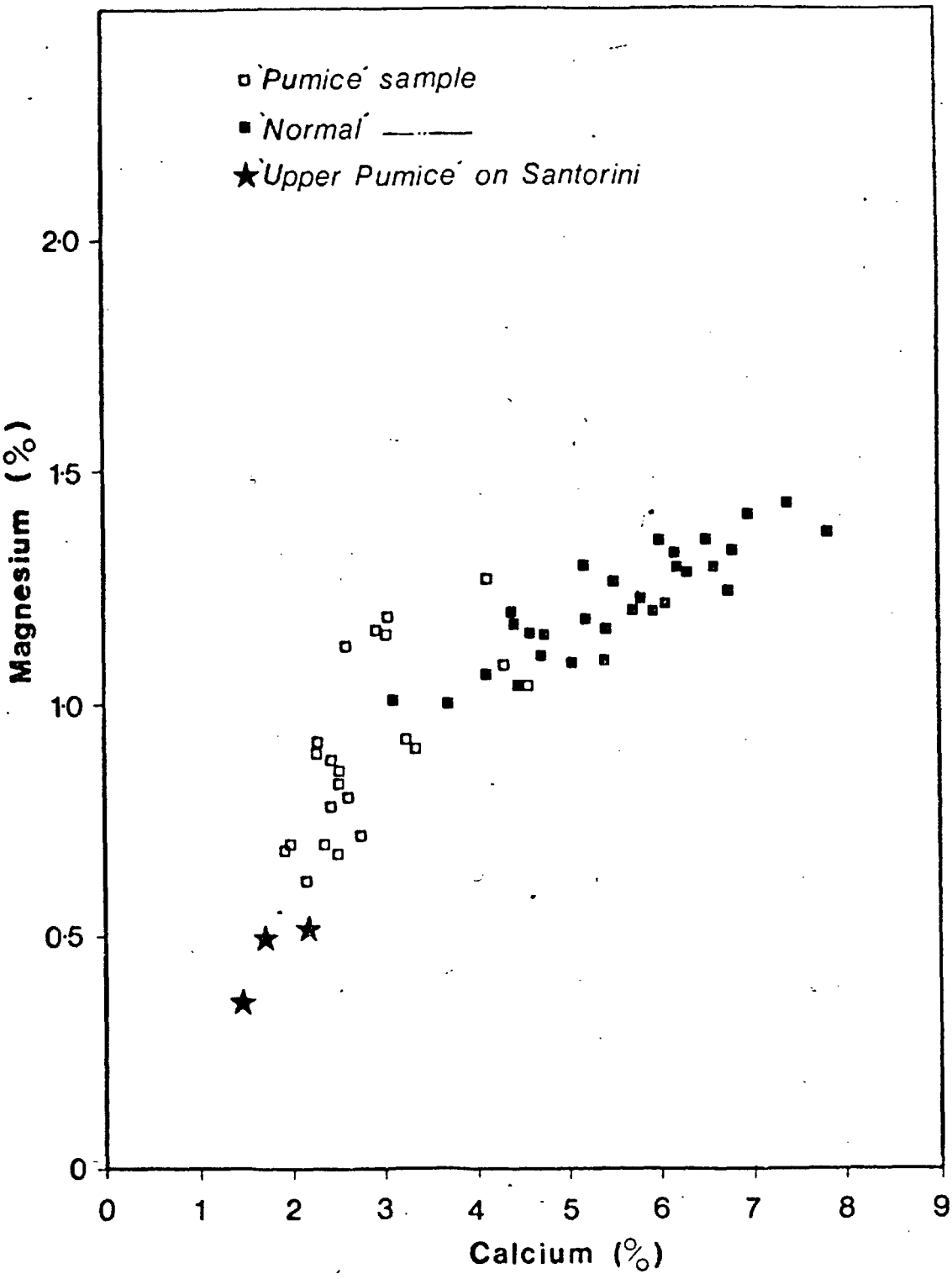


Figure 7.13 Scatter plot of magnesium against calcium for shelf zone samples ('upper'pumice data from Puchelt and Schock,1972).

element abundance in the caldera zone sediments and, in particular, any metal contribution from hydrothermal sources. Butuzova (1969) believed there to be four main components in these sediments - a direct, volcanic hydrothermal influence on the abundance of Fe and Mn; an indirect influence on the abundance of V and Cu due to the scavenging action of hydrothermally derived particulate ferric hydroxides; the solid products of volcanic activity influencing the concentration of Ti, V, Cr, Ni, Co and Cu and the biogenic influence providing $CaCO_3$, organic carbon, and possibly silica.

Based on the general lithological character, and, in particular, the variation in carbonate with depth in the sediment, two major facies have been identified (Section 7.5.1, figures 7.4 and 7.5). A "normal" facies which represents sedimentation during relatively quiescent periods. Characteristic of the "normal" facies are fine grained sediments (dominantly silt) enriched in calcium carbonate, iron oxides, and minor amounts of clay minerals, including montmorillonite (Bonatti et al., 1972; Petersen and Müller, 1974). Organic matter is locally present producing mildly reducing conditions at depth in some cores, particularly in the northern basin.

Intercalated with the "normal" facies is the "pumice" facies deposited at times of volcanic disturbance and characterised by more or less extensive pumice horizons, with a low carbonate content. Unlike the "normal" facies from both the caldera and the shelf and the "pumice" facies from the shelf, the pumice component of the "pumice" facies in the caldera may also be derived from eruptions post-dating the 1400 B.C. eruption of Santorini.

7.6.4b Results and Discussion

Variation in the range of elements within each major facies is presented in table 12 for cores 651 and 645. Locations of core and grab samples used in this investigation are indicated in figure 7.1. Both Ca and Mg are highest in the "normal" facies and lowest in the "pumice" facies. Ca and Mg also covary but, as with the shelf facies (compare figures 7.13 and 7.15), this is not a simple direct relationship. The Mg/Ca ratio for the "pumice" field is higher than that for the "normal" field and represents the variation in Ca and Mg within the "pumice" samples. In a similar fashion to the shelf facies, the addition of carbonate Ca and Mg results in a decreased

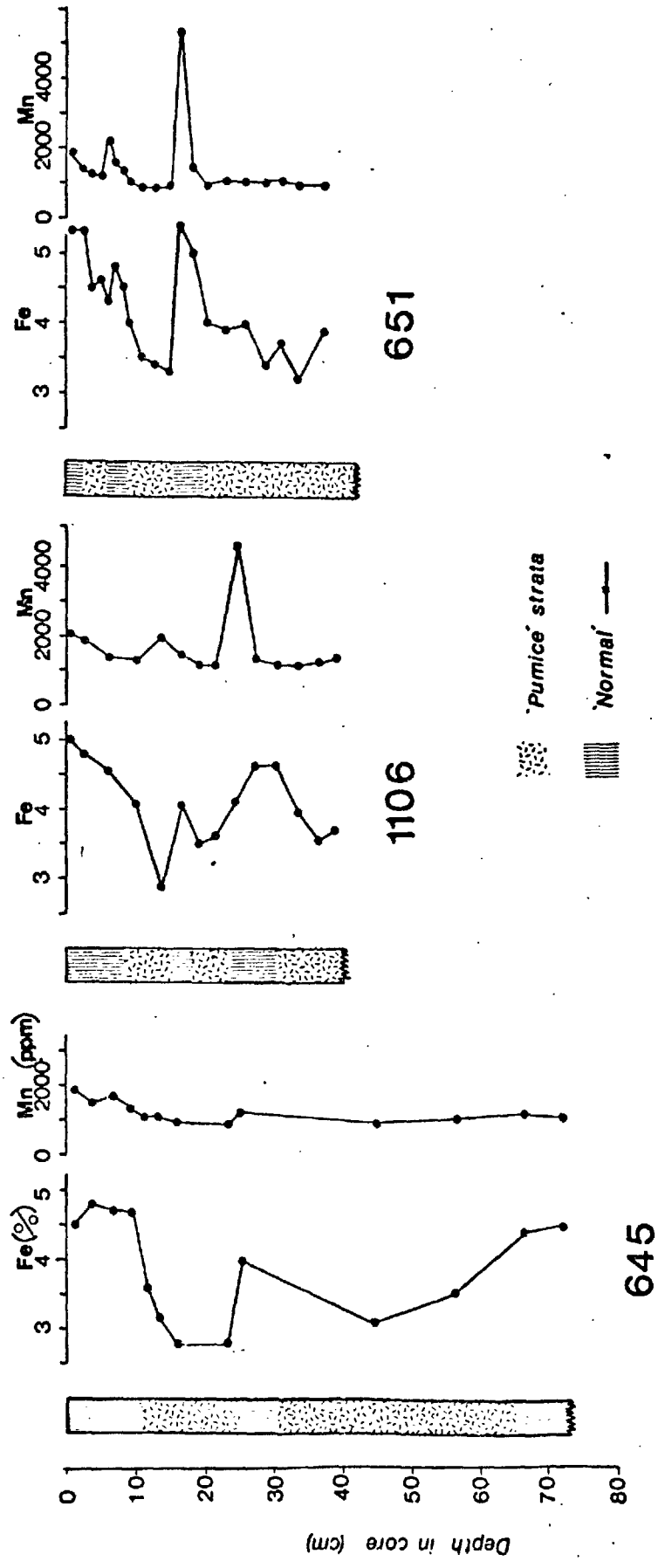


Figure 7.14 Iron and manganese profiles in cores from the caldera zone.

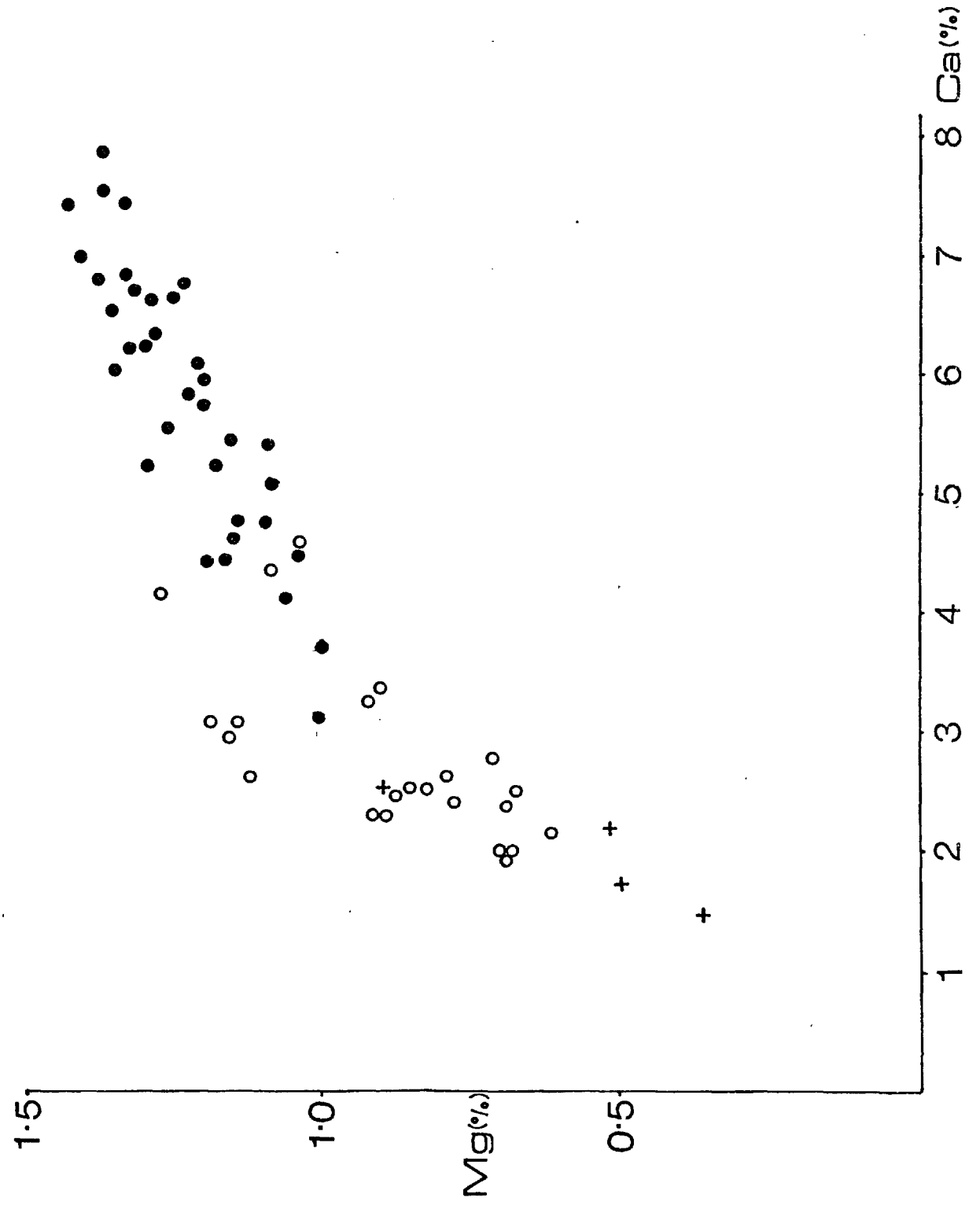


Figure 7.15 Scatter plot of magnesium against calcium for samples from the caldera zone (o pumice, ● normal, + 'upper'pumice from Puchelt and Schock,1972).

slope of the Mg/Ca relationship.

Aluminium has a narrow range in abundance (table 12) but is, on average, higher in the "normal" facies (figure 7.16). In contrast, Si is higher in the "pumice" facies (table 12, figure 7.16). From figure 7.16 it is also seen that the "pumice" facies have a Si/Al ratio close to 6, whereas the "normal" facies samples have a Si/Al ratio scattered around 4 and similar to the Si/Al field for 'upper pumice' analysed by Puchelt and Schock (1972). It seems that the 'pumice' samples are more rhyolitic (quartz-rich) in composition than the pumice component of the 'normal' facies.

Ti abundance varies between 0.38% and 0.50% in cores 651 and 645, but there is little distinction in abundance between "normal" and "pumice" sediments (table 12).

Fe is enriched in the "normal" facies of the caldera, varying between 4.0% and 5.4%, compared to a range between 2.8% and 4.0% for the "pumice" facies (table 12). Iron profiles with depth in the sediment (figure 7.14) illustrate the enrichment in the "normal" horizons.

To provide an assessment of the 'excess' Fe due to hyrothermal activity, Butuzova (1969) compared the Fe and Ti relationships for the shelf and caldera. A similar approach is used in the present investigation but the relationship between Fe and Al is used instead (figure 7.17). In agreement with the results of Butuzova, an excess Fe over the detrital component (represented by the detrital Fe to Al regression line) is apparent in the "normal" sediments of the caldera. Using the average Fe/Al ratio for detrital sediments (i.e. the "pumice" facies from the caldera and shelf plus the "normal" facies to the shelf) an "excess Fe" between 0.15% and 2% is indicated for the caldera "normal" facies. This may not seem particularly large but Butuzova (1969) reported Fe concentrations up to 17% in the northern basin. This level of Fe has not been found but sample density is low compared to that of Butuzova (1969).

An interesting difference exists in the Mn profiles between cores from the northern basin (651 and 1106) and core 645 from a smaller southern basin. In all cores manganese appears to be enriched in the "normal" sediments but the abundances reached in the northern basin (up to $\frac{1}{2}$%) are much higher than in core 645 (less than 0.2%). Closer inspection of the pre-Kolomvos "normal" sediments in 651 and 1106 reveal that the high Mn contents are limited to the uppermost sample of the horizon, unlike the iron

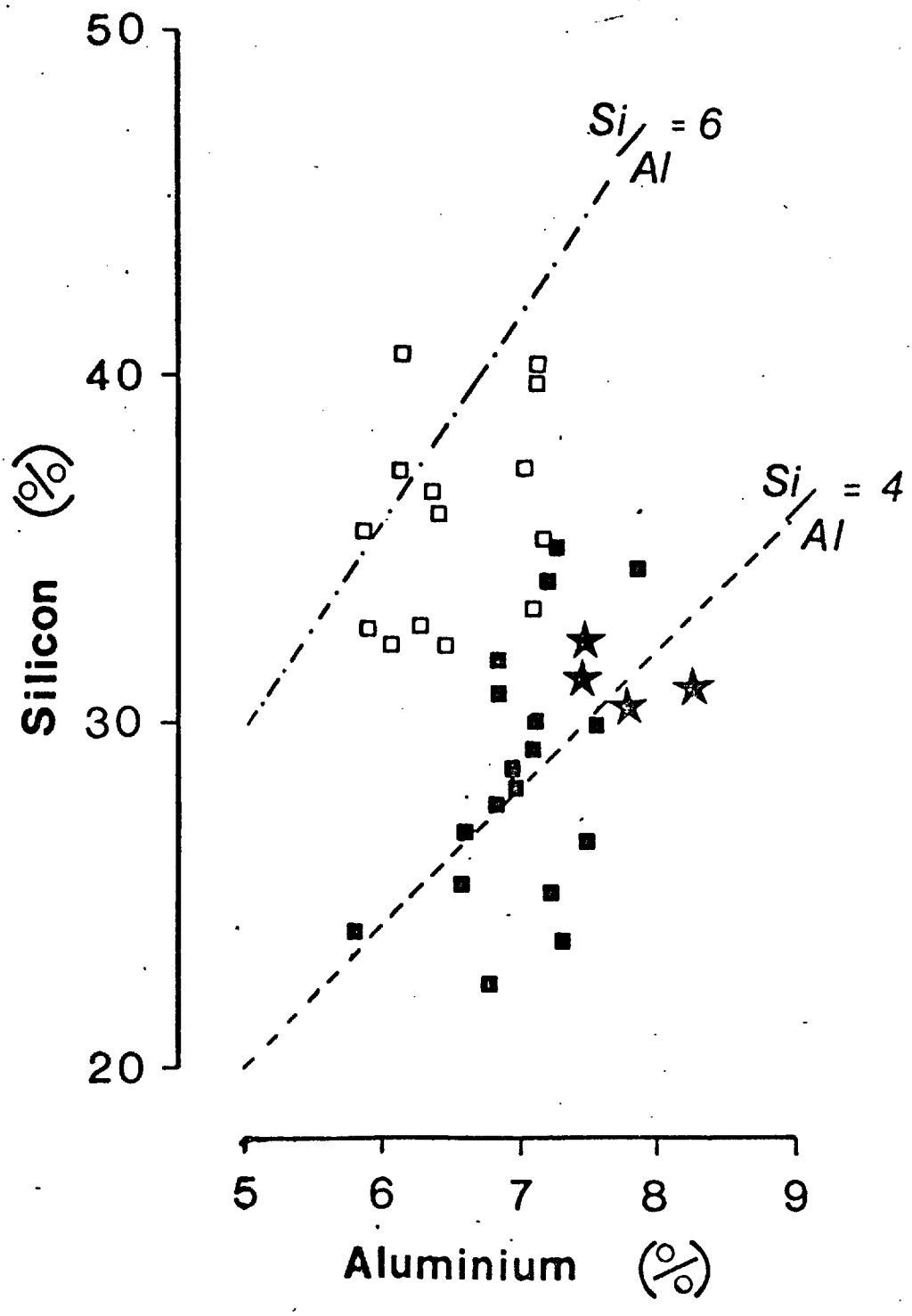


Figure 7.16 Scatter plot of silicon against aluminium for samples from the caldera zone (□ pumice, ■ normal, ★ 'upper' pumice from Puchelt and Schock,1972).

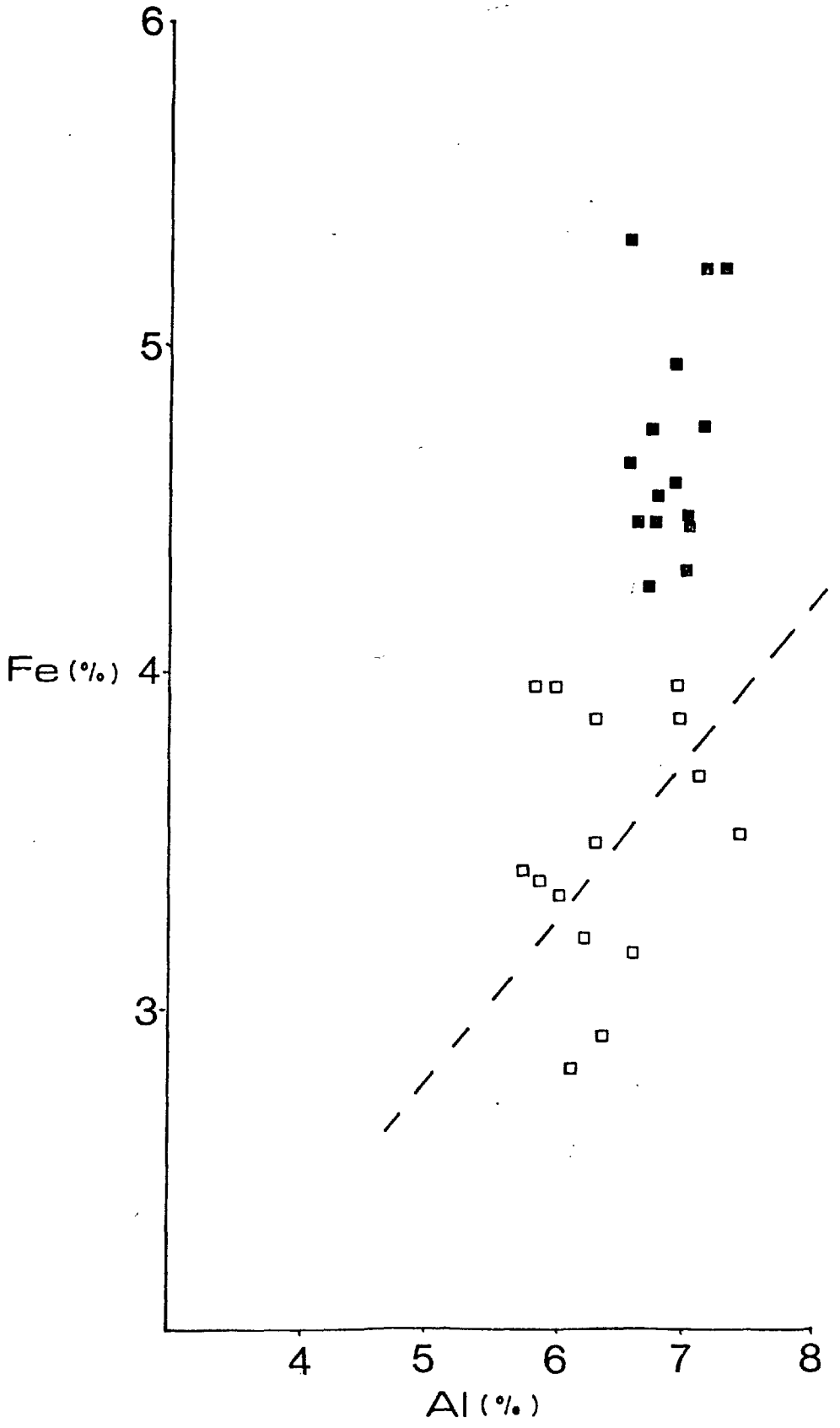


Figure 7.17 Scatter plot of iron against aluminium for caldera samples(see figure 7.16 for key).The broken line represents an approximate pumice Fe/Al regression line.

which is uniformly distributed within the "normal" horizons. A high manganese content at the oxidised surface layer, and which decreases with depth in the core, is a characteristic of the post depositional migration of Mn (Lynn and Bonatti, 1965). It is a well known feature in marine sediments in which mildly reducing conditions develop within the sediment column, thereby causing a reduction of the Mn to the soluble divalent state and enriching Mn in the pore waters of the reduced sediment. Due to the concentration gradient developed in the pore waters, there is an upward flux of Mn through ionic or molecular diffusion (Lynn and Bonatti, 1965). Mn subsequently reprecipitates in the oxidised zone at the interface between the "normal" horizon and the overlying "pumice" horizon.

It is important to note that none of the trace elements covary with manganese. Had the high Mn abundances at the tops of each "normal" horizon precipitated from seawater under abnormally quiescent conditions, positive trace element - manganese relationships would be expected because 'hydrogenous' manganese normally has a significant trace element signature (Bonatti et al., 1972c). This feature lends further support to 'diagenetic remobilisation' of Mn because it is characterised by a low trace element signature (Bonatti et al., 1972c) since the post-depositional mobility of the transition elements, such as Ni, Cu, Co, V and Cr, is much less than that of Mn (Bonatti et al., 1971).

In discussing the redox potential of cores 651 and 1106, in section 7.5.1c, it was suggested that conditions were mildly reducing, especially within the pre-Kolomvos "normal" horizon in which the high concentrations of Mn are observed. Conditions are suitable, therefore, for Mn remobilisation. Precipitation of the Mn in the upper most layer of the "normal" facies could be caused by more oxidising conditions existing in the overlying "pumice" horizon. In the younger horizons, Mn enrichment is not so well developed, probably because reducing conditions are not so well established. Even so, there is still evidence for a decreasing Mn gradient with depth in each "normal" horizon.

To summarize, during the quiescent conditions of "normal" facies accumulation, mildly reducing conditions develop in the lower layers of the "normal" facies horizon. Mn is remobilised and migrates upwards to a more oxidising environment. Rapid sedimentation of pumice, low in organics, at times of volcanic disturbance, interrupts

the "normal" sedimentation and results in an oxidising "pumice" horizon overlying the "normal" horizon. This oxidising layer effectively seals the underlying "normal" sediments, preventing remobilisation and migration of the Mn into younger strata. Consequently, the classic "remobilised Mn" profile is preserved.

In contrast, conditions in core 645 are considered to have been more oxidising throughout (section 7.5.1c). Admittedly, this assessment is only based on qualitative evidence but the lack of apparent Mn remobilisation, particularly in the pre-Kolomvos "normal" horizon, is consistent with this belief.

The "excess Mn" in the "normal" facies can be derived from several sources. Halmyrolysis of volcanic ash and lava has been suggested as a possible contributor of Mn to the oceans (Wilkness et al., 1971; Elderfield, 1972; Elderfield, 1976). There is little evidence of depletion in Mn in the pumice horizon of the cores and so this is considered to be an insignificant source in caldera zone sediments. In some way, therefore, the "excess Mn" derives from the column of seawater above the sediments. There are several possible alternatives:-

(1) Mn coprecipitated with the particulate iron oxides in the inner exhalative zone and subsequently dispersed into the caldera zone;

(2) Mn scavenged by particulate iron oxides during passage through the water column from the inner exhalative zone to the caldera floor;

(3) resuspended and dispersed particulate manganese oxides originally precipitated in the outer exhalative zone;

(4) hydrogenous manganese precipitated directly from the caldera water column;

and (5) as soluble, divalent Mn escaping from the exhalative zones and precipitating within the caldera.

Which of these is significant is difficult to assess. There is certainly sufficient "excess Fe" to support (1) and (2). Butuzova (1966) cites concentrations of Mn exceeding ½% in the caldera zone as evidence to support alternative (5). Bonatti et al., (1972a) also suggest the possibility of hydrothermally derived Mn precipitating in the caldera zone. However, this investigation shows that high levels of Mn are more likely to result from remobilisation and migration and the outer exhalative zone is considered to be the main zone of Mn precipitation. Alternative (4) may provide MnO_2

to the sediments but sedimentation rates are high compared to normal pelagic sediments and so this is probably a minor contribution. Alternative (3), in which particulate MnO_2 is dispersed from the outer exhalative zone, combined with alternatives (1) and (2), is the most likely source of excess Mn.

Trace element profiles in cores 651 and 645 (table 12 and figure 7.18) reveal that "normal" sediments are enriched in Sr, Cu, Pb, V, Ni, Cr, Ba and Li. From table 12, Zn does not appear to be enriched but the profile of Zn in core 651 (figure 7.18) reveals that some of the highest concentrations of Zn occur in the "normal" facies, particularly in the top half of the core. Distinct differences between the lithologies of the "pumice" and "normal" facies may account for the enrichment of trace elements in the latter. Firstly, although pumice is the dominant constituent of both facies, the mineralogical (and, hence, chemical) composition of the pumice in each facies may differ because of a different source and depositional history. Secondly, compared to the "pumice", the "normal" facies contains more biogenic carbonates, organic matter, fine-grained terrigenous material, and iron and manganese oxides, all of which could enrich the "normal" sediments in a range of trace elements.

Although, at first sight, the range in pumice mineralogy may be sufficient to explain the range of V, closer inspection, particularly of the scatter plot of V against Al (figure 7.19), suggests that additional factors could be important. From figure 7.19 a distinct grouping of samples is evident. Caldera "pumice" samples range between 30ppm and 50ppm, whereas "normal" samples have a V range between 70ppm and 120ppm. Also shown in figure 7.19 is an approximate regression line between V and Al for pumice alone. Although there is a certain amount of overlap with the shelf "pumice" samples, the "normal" group lie on the "excess" vanadium side of the regression line. Butuzova (1969) also noted an apparent excess of vanadium in the caldera sediments which she attributed to the scavenging capabilities of iron oxides (Krauskopf, 1956). According to Butuzova (op.cit.), the contribution of V by organic carbon is minor. It seems, therefore, that the abundance of V is controlled by two factors - the mineralogy of the pumice fraction and scavenging by particulate iron oxides as they pass through the water column.

By analogy with vanadium, Cu, Pb, Ni, Cr and Li may also be scavenged from seawater by particulate iron (or manganese) oxides.

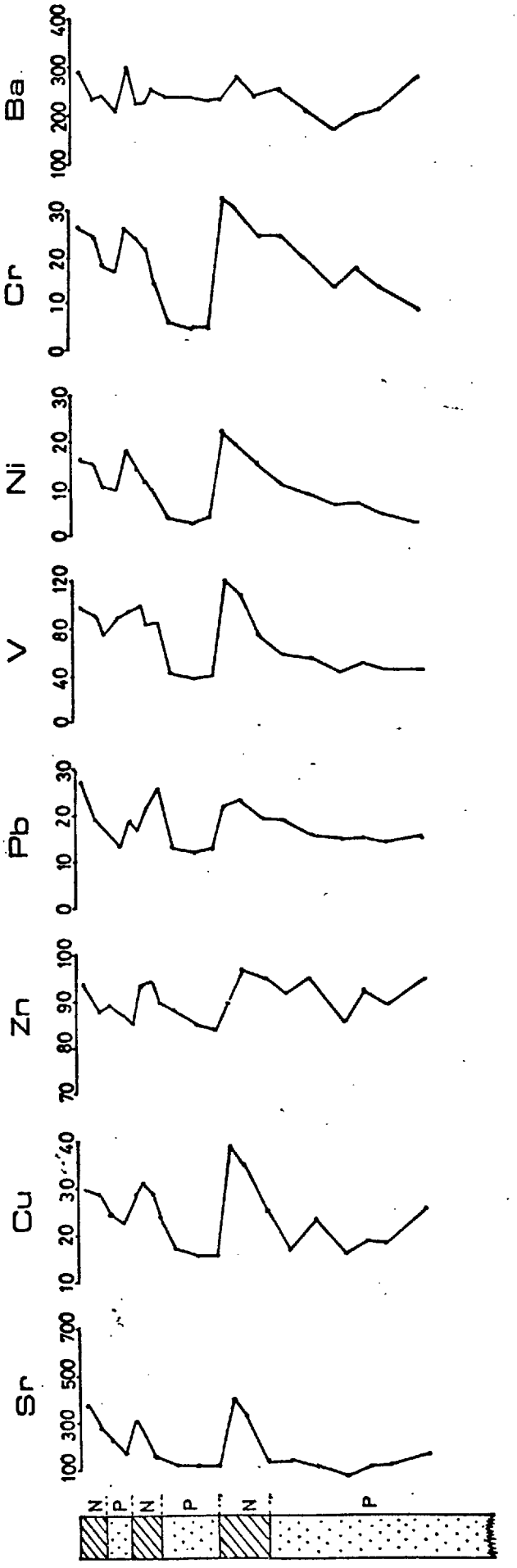


Figure 7.18 Trace element profiles for core 651 from the caldera. (values in ppm)

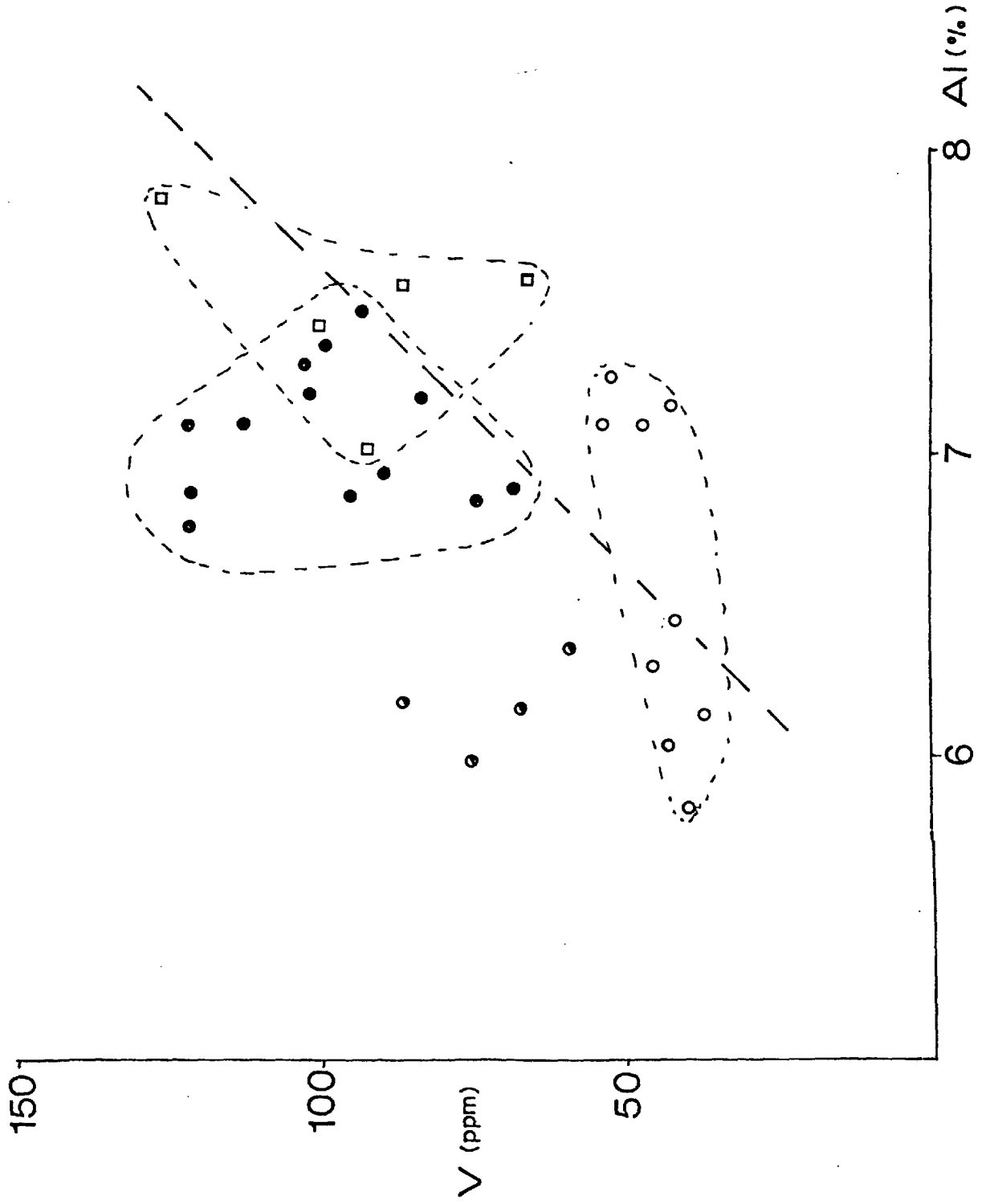


Figure 7.19 Scatter plot of vanadium against aluminium for samples from the caldera zone(◒ samples from the boundary between the normal and pumice samples, ● normal, pumice-caldera ○ , □ pumice-shelf, - - - approximate V/Al regression line for pumice).

Scatter plots of these elements against Al reveal a similar grouping of samples as that found for V (e.g. Cu - figure 7.20, Ni - figure 7.21). Excess in these elements is, however, less than that for V but is of the same order as the pumice contribution. An alternative source of these elements, particularly Ni and Cr, could be any terrigenous material within the "normal" sediments. An unspecified terrigenous component, or components, was invoked to account for the enrichment of Ni, Cr, Ba and Li in the surface sediments from the shelf zone. Possible sources of this material include the local metamorphic rocks on Santorini or fine-grained material transported from more distant parts of the southern Aegean. The latter are known to have relatively high abundances of Ni and Cr (Smith and Cronan, 1975a; see earlier chapters).

Enrichment of Ba and Zn in the "normal" sediments, although present, is not marked (figure 7.18). The Ba and Zn to Al scatter plots reveal little variation of either Ba or Zn with Al, and sample fields generally overlap. Iron or manganese could be scavenging these elements from seawater, but the contribution from this or other sources is masked by the contribution from the pumice.

For Sr, amounts in excess of 200ppm are attributable to a phase other than the pumice and the most likely candidate is the biogenic carbonate component enriched in the "normal" sediments. It is possible that a limited amount of Sr could be scavenged by the iron oxides but this is not thought to be significant.

For K, Co, Ga and Sc, the difference between strata is too small to assess the dominant control, but the general levels indicate pumice to be the major component contributing these elements to the sediments.

Molybdenum is close to, or below, the detection limit (2ppm) for all caldera samples.

7.6.4c Summary

(1) Dispersion of particulate iron oxides from the exhalative zones appears to enrich the caldera sediments in this element.

(2) Hydrothermal activity does not contribute Mn directly to the caldera sediments but indirectly through the dispersion of particulate phases. It is subsequently remobilised to give horizons of high Mn content.

(3) The abundances of V, Cu, Pb, Ni, Cr, Li, Ba and Zn appear to reflect the combined influence of pumice and scavenging by iron and/or

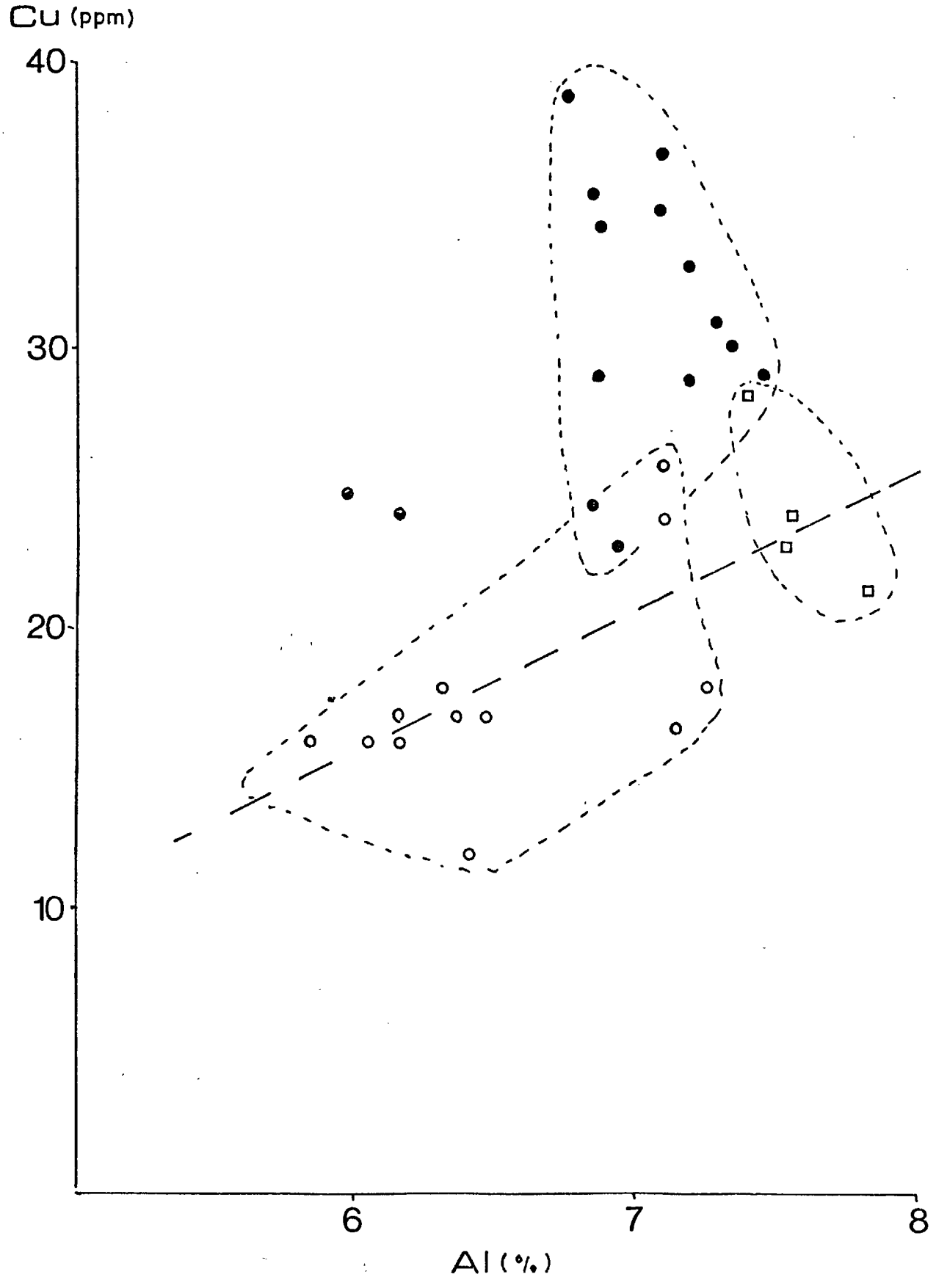


Figure 7.20 Scatter plot of copper against aluminium for samples from the caldera zone(see figure 7.19 for key).

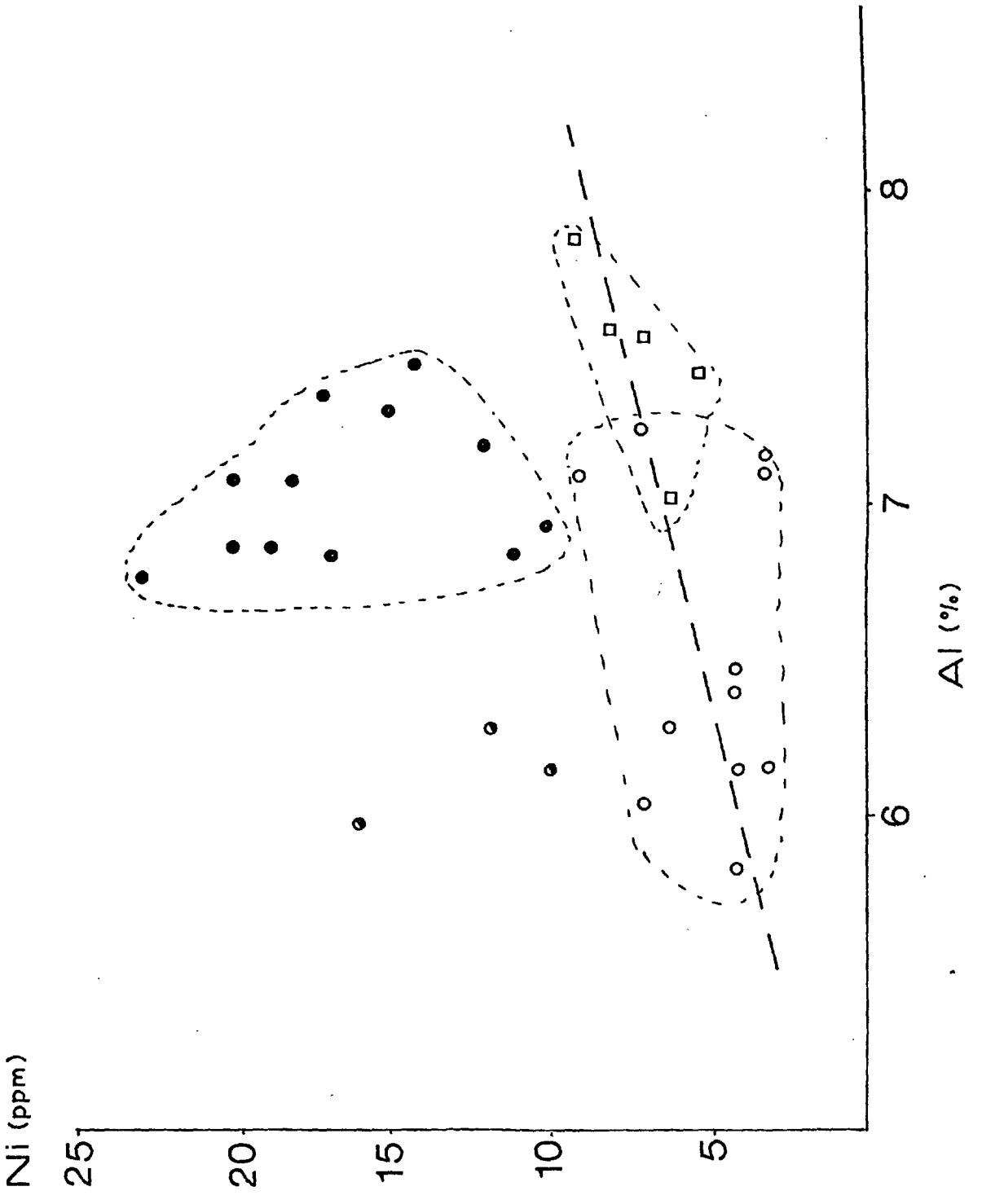


Figure 7.21 Scatter plot of nickel against aluminium for caldera zone samples (see figure 7.19 for key).

manganese oxides. Further study is required, however, to confirm these tentative conclusions. Partition studies might clarify the relative significance of the iron oxides, pumice and terrigenous material but the role of organic matter also deserves further investigation.

(4) Biogenic carbonates are the major control on the abundance of Ca, Mg and Sr but the pumice contribution is also significant.

7.6.5 The Composition of Waters from the Exhalative and Channel Zones

7.6.5a Introduction

Before considering the geochemistry of the sediments from the exhalative and channel zones, it is appropriate to assess the hydrothermal influence on the composition of the water column. Relating water composition to sediment geochemistry is often difficult because the composition and structure of the water mass is highly variable and depends upon the intensity of hydrothermal activity and the prevailing oceanographic and meteorological conditions. In contrast, the composition of the hydrothermally derived sediment reflects the average conditions of the water mass over the period of accumulation. Nevertheless, there are certain general conclusions that may be drawn from a study of the water samples and which may then be applied to the study of the sediments. For example, it may help to answer such questions as "what elements are contributed by the hydrothermal solution?"; "do these elements disperse in solution or in particulate form?" and "is there any evidence for the differential mobility of elements derived from the hydrothermal solution?".

Accordingly, water samples were collected along a series of traverses away from the source fumaroles (figure 7.3). Pushkina (1967, 1968) also provides useful additional information on the composition, and physico-chemical characteristics, of the waters around Nea Kameni, including the embayment examined here.

As soon as possible after sampling, the waters were filtered through a 0.45 micron millipore filter and acidified. Subsequently samples were analysed for Fe, Mn, Zn, Cu and Pb by atomic absorption spectrophotometry after preconcentration by solvent extraction techniques (see appendices). Because water samples were collected at the same time as the sediment samples, a certain amount of

resuspension of the bottom material was unavoidable, therefore, the particulate phases (0.45 microns) have not been analysed. Some colloidal material might also derive from the resuspended sediment but this is unlikely to mask the overall pattern.

7.6.5b Results

Thirty-seven samples were analysed for the elements Fe, Mn, Zn, Cu and Pb. Data for selected samples collected close to the fumaroles at the landward end of each embayment are given in table 13. For comparison, table 13 also shows the composition of a sample from the inner exhalative zone of Nea Kameni (Pushkina, 1967, 1968), and the analyses of water samples from other areas of submarine hydrothermal activity. Figure 7.22 illustrates the lateral variation in the abundance of Fe, Mn and Zn in the waters from the exhalative and channel zones.

In the inner exhalative zone, 'soluble' Fe, much of which is probably colloidal and not in true solution, reaches a maximum of 13.7mg l^{-1} at the landward end of Nea Kameni but is generally between 1mg l^{-1} and 7mg l^{-1}. This represents about a thousand - fold enrichment over normal seawater (average Fe in seawater is about 0.003mg l^{-1} - Riley, 1971). Pushkina (1967) found similar levels of Fe in Nea Kameni (table 13). Concentrations of Fe in waters from certain other volcanic areas are also similar to those found at Santorini (e.g. Rabalankaia shore - Ferguson and Lambert, 1972 and table 13; Lake Ove, Simbo Island, British Solomon Islands - Taylor, 1976), but at least an order of magnitude less than the Fe concentrations found in other areas (e.g. Atlantis II deep - table 13). Between the landward and seaward ends of the inner exhalative zones, Fe decreases rapidly until, at approximately the boundary of the inner and outer exhalative zones, it reaches a level similar to that of normal seawater (0.003mg l^{-1})(see figure 7.22).

Manganese also decreases in abundance from an almost thousand - fold enrichment in the inner exhalative zones (1.4mg l^{-1} for sample 28 compared to an average of 0.002mg l^{-1} for normal seawater) to normal channel levels (0.002mg l^{-1}) in the outer exhalative zones, but the rate of decrease, particularly for Nea Kameni, is apparently less (see figure 7.22) than for Fe. Normal seawater concentration for Fe are reached at the boundary between the inner and outer exhalative zones whereas, for Nea Kameni at least, normal seawater

TABLE 13 Analyses of selected water samples from the inner exhalative zones.For comparison,data for normal seawater and water samples from other areas of submarine hydrothermal activity are included.

	1	2	3	4	5	6	7	8	9	10
t^oC	0-25	30	33	22	27	20	65	85	56	340
pH	8.3	-	6.0	-	-	-	3.7	6.1	5.3	5.2
Cl	19.0	-	21.5	-	-	-	22.5	18.0	163	155
Ca	0.40	-	0.54	-	-	-	0.39	1.03	5.40	28.0
Mg	1.35	-	1.43	-	-	-	1.34	1.37	0.79	.054
Fe	0.3	115	200	68	730	0.2	9700	350	5900	229000
Mn	0.2	107	159	8	43	0.2	11100	270	7200	140000
Zn	0.5	20	50	4	40	0.3	2530	30	2500	540000
Cu	3	1	2.5	1.3	5.5	3	50	50	800	8000
Pb	.03	7	-	4	4	4	90	70	120	102000

1 - Composition of average seawater(Riley,1971).
2 - Sample 27 from close to the landward end of the Nea Kameni inner exhalative zone.
3 - Water sample from the inner exhalative zone of Nea Kameni from Pushkina (1967,1968)(point III at the surface).
4 - Sample 33 from the inner exhalative zone of Palaea Kameni(N).
5 - Sample 2 from the inner exhalative zone of Palaea Kameni(S).
6 - Sample 35 from the channel zone.
7 - Tavurvur Shore springs from Ferguson and Lambert(1972).
8 - Rabalankaia Shore springs from Ferguson and Lambert(1972).
9 - Atlantis II deep,Red Sea from White(1968).
10 - I.I.D. No.1,Salton Sea from White (1968).

N.B. For inner exhalative zone samples and normal seawater Cl, Ca, and Mg are in gl^{-1},Fe and Mn in $mgl^{-1} \times 10^2$,and Zn,Cu and Pb in $mg\ l^{-1} \times 10^3$.For the other areas the data are in ppt,ppm$\times 10^2$, and ppm $\times 10^3$ respectively.

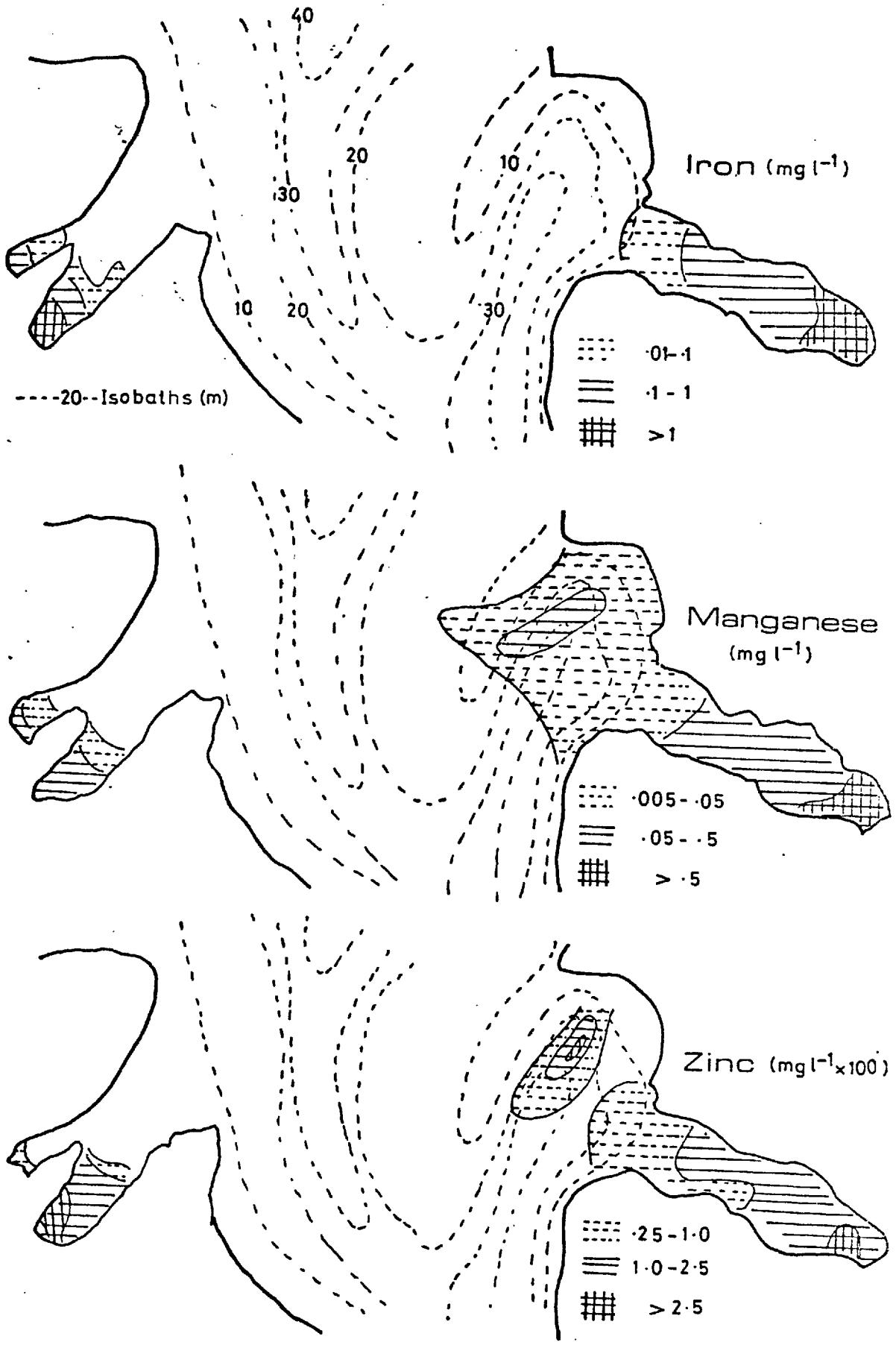


Figure 7.22 The concentrations of Fe, Mn, and Zn, in seawater from the exhalative and channel zones.

concentration of Mn are not reached until the outer edge of the outer exhalative zone. Manganese abundance in the waters close to the fumaroles is similar to that reported by Pushkina (1967) for the same zone (table 13) and to other volcanic areas, especially Rabalankaia shore springs (table 13), Crater Lake on Deception Island (upto 2.4mg l^{-1} - Elderfield, 1972) and Lake Ove (upto 2mg l^{-1} - Taylor 1976). Like Fe, however, Mn is markedly depleted compared to areas such as Tavurvur Shore springs (also at Matupi Harbor, like Rabalankaia shore - see table 13), Atlantis II deep and the Salton Sea brine.

A further interesting feature of the Mn distribution (figure 7.22) is the enrichment of Mn in the adjacent samples 18 and 39 (about 0.07mg l^{-1} compared to 0.002mg l^{-1} for the channel) in the outer exhalative zone of Nea Kameni. 'Soluble' Fe in both samples is low and close to that of normal seawater (0.006mg l^{-1} and 0.002mg l^{-1} respectively). Fumarolic activity occurs around the whole perimeter of the Nea Kameni embayment and so the Mn is not necessarily derived from the inner exhalative zone. It does illustrate, however, that selective separation of iron and manganese is taking place and that the waters of the outer exhalative zones, under certain conditions, are enriched in Mn.

Relative to Fe and Mn, Zn enrichment in waters from the inner exhalative zones is less, but still represents more than a one hundred-fold enrichment over average seawater. The maximum Zn concentration found was almost 0.1mg l^{-1}, although the average found for samples close to the fumaroles was approximately 0.03mg l^{-1}. Once again, this concentration of Zn is similar to that reported by Pushkina (1968) and that found for the Rabalankaia shore springs (table 13) but substantially less than for Altantis II Deep, Tavurvur shore springs and the Salton Sea brine (table 13). Interestingly, samples 18 and 39 are also enriched in Zn as well as Mn (figure 7.22). Selective separation of Zn and Fe, as well as Mn and Fe, also appears to occur under certain conditions, thereby enriching the waters of the outer exhalative zone in Zn.

For copper there is only slight evidence for any enrichment over normal seawater (0.0055mg l^{-1} compared to 0.003mg l^{-1}). Pushkina (1968) also concluded that there was no evidence of Cu enrichment in the inner exhalative zone of Nea Kameni. Similarly for Pb, there is only slight evidence for any enrichment (0.007mg l^{-1} compared to 0.004mg l^{-1} for the channel).

7.6.5c Discussion and Conclusions

The above results confirm the observations of Pushkina (op.cit.) that the hydrothermal solutions contribute moderate amounts of Fe, Mn and Zn. They may also contribute some Cu and Pb but only to a very limited extent. The general order of abundance is:-
Fe > Mn > Zn > Cu and Pb.

A variety of factors govern the composition of the hydrothermal fluids that mix with the overlying seawater including:-

(1) the nature and composition of the host rocks through which the fluids pass;

(2) the physico-chemical characteristics and, hence, the leaching and transporting capacity of the fluids;

and (3) the fate of the fluids before they reach the waters of the exhalative zones.

A combination of (1) and (2), in particular, could account for the differences in the hydrothermal influence on seawater composition between Santorini and other volcanogenic exhalative environments such as the Atlantis II deep, Tavurvur shore, and the Salton Sea brine. The relative abundance of Fe, Mn, Zn, Cu and Pb in the hydrothermal fluids reaching the waters of the inner exhalative zones parallels the relative abundance reported for a sample of lava from Nea Kameni (Puchelt et al., 1973). Furthermore, the Fe/Mn ratios for the water samples close to the fumaroles (between 10 and 20) are similar to the surrounding lava (about 26-Puchelt et al., 1973). The slightly lower ratios for the water samples may be due to the selective precipitation of iron before the sampling points. The Zn/Cu and Cu/Pb ratios are also similar to those given by Puchelt et al., (op. cit.) for the local lavas. It would seem, therefore, that the relative abundances of Fe, Mn, Zn, Cu and Pb in the hydrothermal fluids may simply reflect the composition of the lava through which they circulate.

The nature of the host rocks will also influence the degree of enrichment of elements in the hydrothermal fluids - certain minerals or components are more resistant to leaching than others. In addition, the leaching and transporting capacity of the fluids is obviously very important. Based on the similarity in abundance of the prinicipal cations and anions (except HCO_3) of water samples close to the fumeroles and normal seawater (see table 13), Pushkina (1967) concluded that the springs entering the embayments are low temperature carbonic acid springs and comprise seawater and CO_2.

Rabalankaia shore springs are also low temperature, carbonic acid springs and the composition of the waters close to the hydrothermal outlets at both Santorini and Rabalankaia are remarkably similar (see table 13). Perhaps moderate amounts of Fe, Mn and Zn are typical of environments where seawater rich in CO_2 circulates through volcanic rocks and then flows onto the sea floor. In contrast, both the Atlantis II and Salton Sea samples (table 13) derive from solutions containing large amounts of chlorine and which may carry large amounts of metal as chloride complexes (White, 1968). These differences in the nature of solvents could account for differences in the degree of enrichment of elements in hydrothermal solutions but brine formation may not be a prerequisite (Cronan, 1976b). The Tavurvur shore springs, Matupi Harbor, for example, have a chlorinity close to that of normal seawater and yet contain concentrations of Fe, Mn and Zn similar to the Atlantis II sample (table 13). Furthermore, experimental data show that leaching of basalt with normal seawater can achieve a similar degree of enrichment (Seyfried and Bishoff, 1977).

It is interesting to note that Ferguson and Lambert (op.cit.) attribute the greater abundance of Fe, Mn and Zn in the Tavurvur shore springs to the presence of H_2S, which is also found in and around Nea Kameni (Butuzova, 1966 and section 7.5.2b). Perhaps hydrothermal solutions of a similar composition are possible at Santorini.

On the basis of differences in their lateral distribution in the waters of the exhalative zones, Mn and Zn seem to be more mobile than Fe. At the time the samples were collected the 'soluble' Fe decreased rapidly to reach normal seawater levels at the boundary between the inner and outer exhalative zone of Nea Kameni. In contrast, the Mn concentration gradient was less and normal seawater levels were not reached until the outer margins of the outer exhalative zones. This is evidence for a greater Mn mobility. Separation of Fe from Mn and Zn is also illustrated by the composition of samples of the outer exhalative zone - samples 18, for example, is enriched in Mn (0.07mg l^{-1}) and Zn (0.03mg l^{-1}) but Fe (0.006mg l^{-1}) is close to normal seawater concentrations (0.003mg l^{-1}).

Undoubtedly the most important requirement for the observed separation of Fe and Mn is the gradual change from acid and mildly oxidising to alkaline and highly oxidsing conditions (Krauskopf, 1957). The confined nature of the embayments and the restricted

circulation, allows just such a gradient to develop. Accordingly, Pushkina (1967) invokes such a mechanism to account for the separation of Fe and Mn in Nea Kameni. In the acid (Pushkina, op.cit.) and mildly oxidising waters of the inner exhalative zone, Fe is oxidised and begins to precipitate as soon as the hydrothermal fluids mix with the seawater. Manganese, however, can remain in solution until the more alkaline conditions of the outer exhalative zone are reached.

Interestingly, Pushkina (1967) also found that the waters of Nea Kameni were stratified and this may also contribute to the mobility of manganese. Because the hydrothermal solutions are less dense than the seawater they form a surface layer of warmer, acid waters extending almost to the outer exhalative zone. The extent of such stratification is unlikely to be constant and will depend upon the composition and temperature (i.e. density) of the hydrothermal solutions and the degree of mixing with seawater. In turn, the degree of mixing depends upon the hydrodynamic conditions and the intensity of hydrothermal activity. Under unusually calm conditions and intense activity the acid surface waters may even extend into the outer exhalative zone. In these circumstances the advective component within the hydrothermal plume of water may aid particulate iron dispersion, whereas the preservation of acid conditions into the outer exhalative zone would increase Mn mobility.

For Zn, simple solubility constraints are unlikely to control its mobility; even the highest values found are an order of magnitude less than the saturation level in seawater (see Krauskopf, 1966). Instead, scavenging by iron and/or manganese oxides is more likely to control the mobility of Zn but, for some reason, the precipitating iron oxides are unable to scavenge all of the hydrothermal Zn in the inner exhalative zone. Zn, therefore, has a greater mobility than iron. Several factors could account for the limited scavenging of Zn by iron oxides in the inner exhalative zone:-

(1) the rate of iron precipitation and accumulation may be too great to allow the complete scavenging of the Zn through co-precipitation, for example;

(2) the scavenging efficiency may be pH dependent and limited under acid conditions;

(3) manganese oxides may control the solubility of Zn rather than iron oxides and Zn mobility follows Mn mobility therefore (but evidence from the partition studies suggests this mechanism is not important here).

Scavenging by iron oxides in the inner exhalative zone seems more than capable of removing any hydrothermal Cu and Pb. Consequently, Cu and Pb mobility is severely limited. The problems of element mobility are discussed further in section 7.6.7a.

7.6.5d Summary

(1) Hydrothermal fluids contribute Fe, Mn, Zn and smaller amounts of Cu and Pb, to the waters of the inner exhalative zones.

(2) Mn and Zn are more mobile than Fe and Cu.

(3) Any iron passing out of the inner exhalative zone is probably in a 'particulate' form whereas Mn could be 'soluble'. Any Mn passing out of the outer exhalative zone is probably in 'particulate' form.

7.6.6 Geochemical Investigation of Sediments from the Exhalative and Channel Zones

7.6.6a Introduction

Previously described investigations of sediments from the Caldera and Shelf Zones, have established the controls on element abundance in the absence of extensive hydrothermal influence. In the light of this work, it is possible to investigate the hydrothermal deposits themselves as the likely detrital contribution of the minor elements, and the degree to which elements such as Zn, Cu, Pb, Fe and Mn are contributed by the volcanic solutions, is known.

7.6.6b Trends of Element Concentration in Sediments from the Inner Exhalative to the Channel Zone

Average abundance is useful for illustrating the overall geochemical characteristics of the five zones and for a preliminary indication of element inter-relationships, but they mask important trends between samples from each of the source to channel traverses. Consequently trends of element concentration away from the fumarolic source are illustrated in figures 7.23 to 7.26 for the three bays.

Comparison of the element distribution patterns reveals that groups of elements have distinctive characteristics. Each group behaves differently but within each group element trends are very similar and consistent throughout the three traverses.

Iron and scandium are highest in the inner exhalative zone and gradually decrease in concentration towards both the outer exhalative and channel zones, and, in the opposite direction, towards the coarse pumice beaches at the landward ends of PK(S) and NK (figure 7.23). Only PK(N) lacks a back beach of pumice, and so a landward decrease is not apparent. Mo shows a similar pattern of enrichment in the inner exhalative zone in NK and PK(N) but in the innermost samples of the outer exhalative for PK(S). Interpretation of the Mo profiles is hampered by the depressing effect of high concentrations of Fe (see appendix), which may contribute to the difference for PK(S). It is also possible that Mo control is not as simple as direct association with Fe and that further controls result in a more irregular distribution. Hg also appears to be concentrated in the inner zone (table 11). Only limited analyses were made for Hg and so it is not possible to fully assess its distribution.

Aluminium, Si, Ti, K, Ga and Co are a group of elements which are enriched in the outer exhalative zone and decrease towards both the inner exhalative and channel zones (figure 7.24 - Co not shown). The well known association of these elements with detrital minerals, and the antipathetic relationship with Fe would seem to suggest a detrital control on these elements. This would also be consistent with data on caldera and shelf sediments in which abundances of these elements are dominantly a function of the relative abundance of pumice and diluting phases such as carbonate. The trends observed reflect the decreasing influence of hydrothermal iron accumulation away from the source fumeroles and the greater proportion of biogenic carbonates in the deeper waters of the channel.

Although Si and K generally follow Al, they appear to be slightly enriched in the inner exhalative zones. The Si/Al ratio in the inner exhalative zones averages about 10 compared to about 6 for pumice from the caldera (figure 7.16). Both Bonatti *et al.* (1972a) and Puchelt *et al.* (1973) report the presence of opaline silica in sediments from the inner exhalative zones (see section 7.5.3) and Pushkina (1967) found substantial quantities of Si in the hydrothermal solutions entering the embayments. The volcanic silica

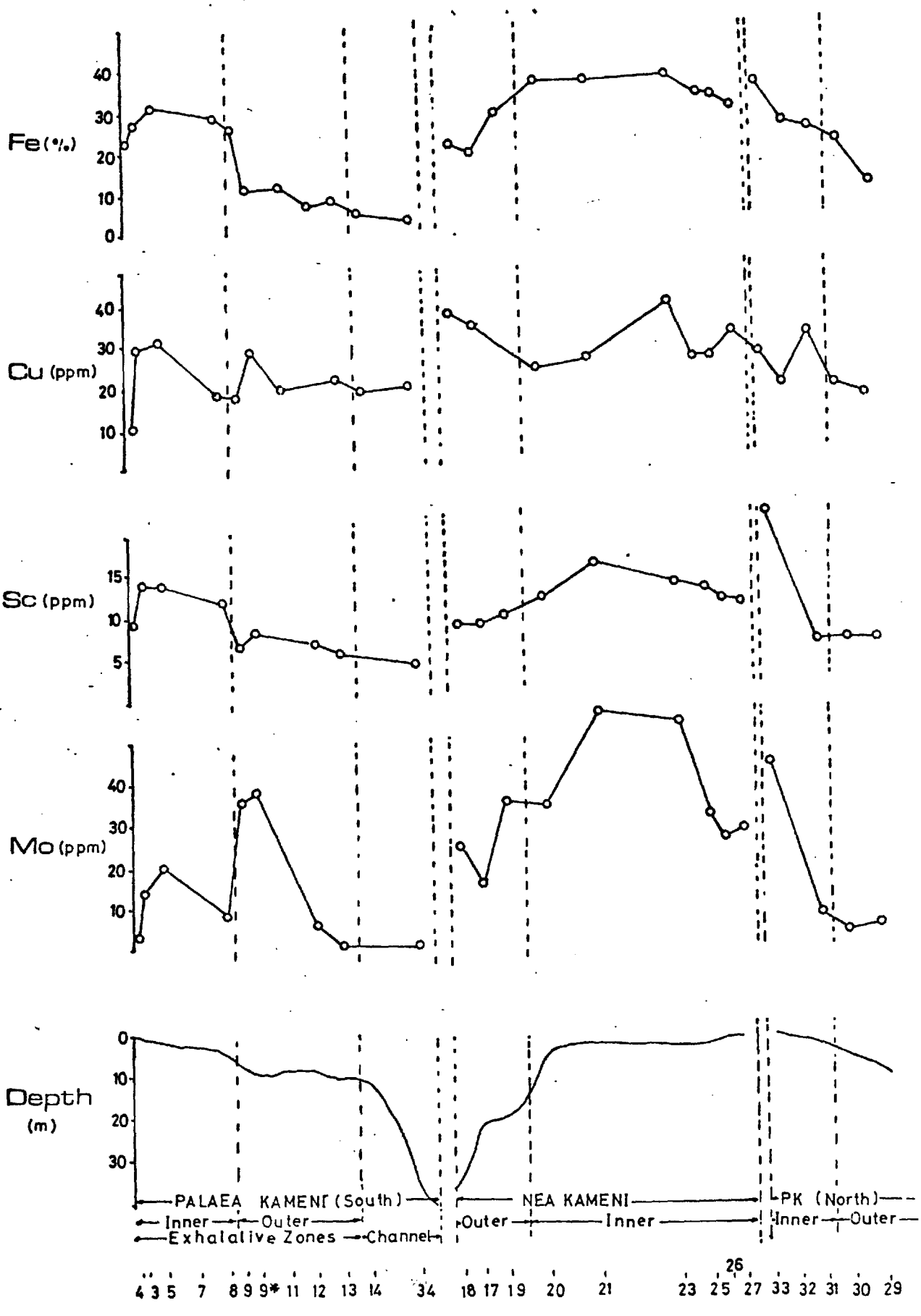


Figure 7.23 Trends in the concentration of Fe, Cu, Sc, and Mo, in samples from the exhalative and channel zones.

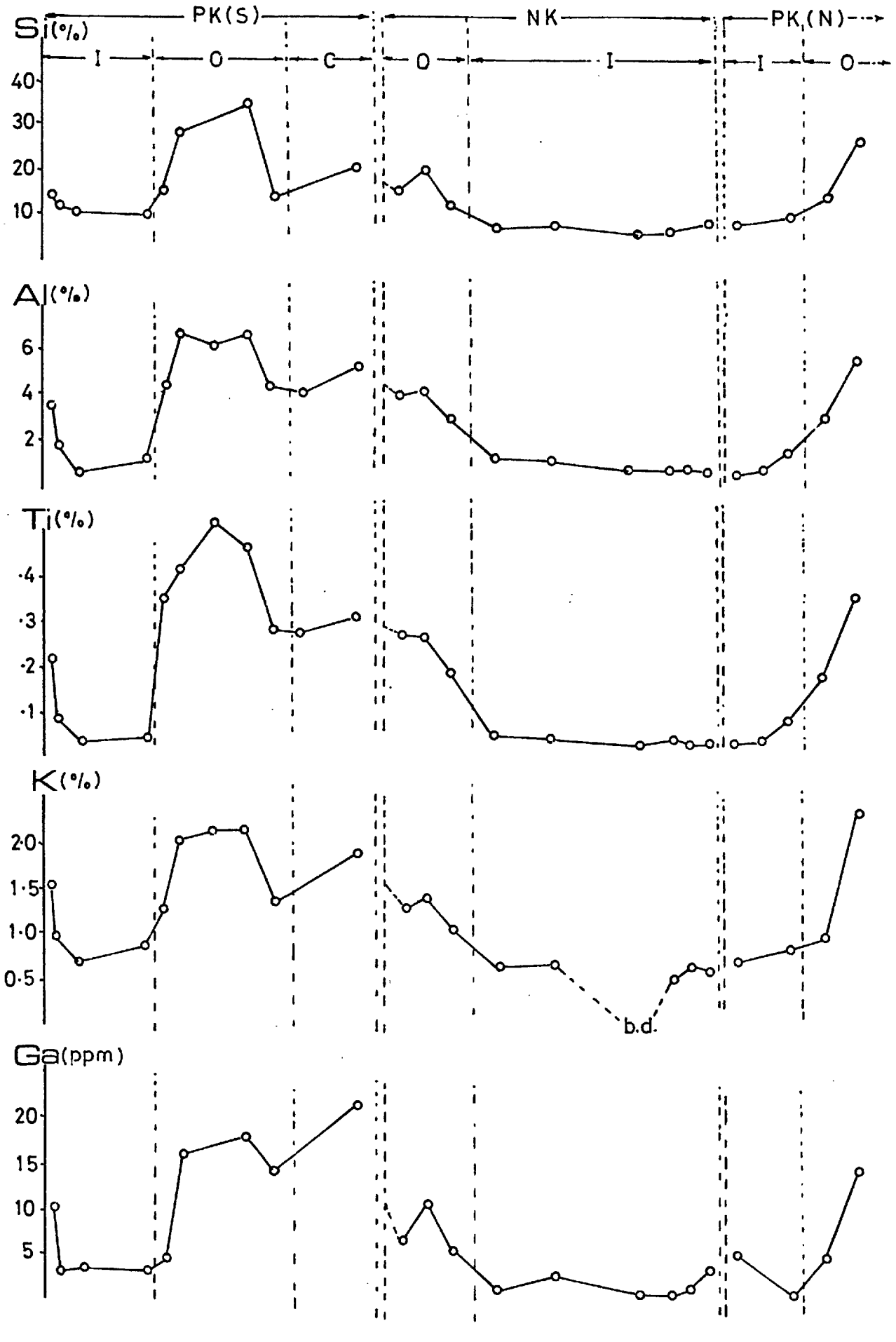


Figure 7.24 Trends in the concentration of Si,Al,Ti,K,and Ga, in the exhalative (I - inner,O - outer)and channel(C) zones.

enters the sediment through either the utilization by organisms (Butuzova, 1966; Pushkina, 1967; Puchelt, et al., 1973) or precipitation due to the rapid decrease in temperature (Bonatti et al., 1972a). Excess K in these deposits is probably due to evaporate minerals.

Vanadium, Cr and Zn show a broadly similar trend to the previous group (figure 7.25) (i.e. lowest in the inner exhalative, highest in the outer exhalative, and intermediate in the channel zone), but there are certain differences. In PK(S), for example, sample 9 has the greatest abundance of V but sample 12 has the greatest abundance of Al. Similar differences between the vanadium and aluminium groups are found in other traverses. Furthermore, the element to Al ratios of the vanadium group (V, Zn, Cr) in the outer exhalative zone are greater than those found in pumice samples elsewhere. It seems that an additional factor to the pumice is required to account for the abundance of the vanadium group in the outer exhalative zone.

Manganese has a most distinctive trend being generally low in the inner exhalative and channel zone sediments but with pronounced highs in the outer exhalative zones, especially in Palaea Kameni (S), where sample 9* has a value greater than 0.5% Mn (figure 7.25). Again the pattern is consistent throughout the three traverses but, unlike the vanadium and aluminium groups which also have peaks in the outer exhalative zones but with broader distributions, the peaks are more pronounced. This zoning of manganese may reflect it's greater mobility compared to iron and subsequent deposition in the more oxidising and alkaline outer exhalative zone (Smith and Cronan, 1975b) as a distinct Mn phase (see section 7.6.5).

Because other elements do not appear to have a distinct relationship to Mn, it is unlikely that they are greatly influenced by the manganese phase. Adsorption onto Mn phases, however, may play a subordinate role in determining their distribution.

Calcium, Mg and Sr have a similar trend (figure 7.26). Calcium carbonate, in the form of biogenic debris, is the dominant component in which these elements are concentrated but there may be a substantial pumice contribution, especially in the outer exhalative zone.

The remaining elements - Ni, Cu, Pb, Li and Ba - have a variable and indistinct distribution.

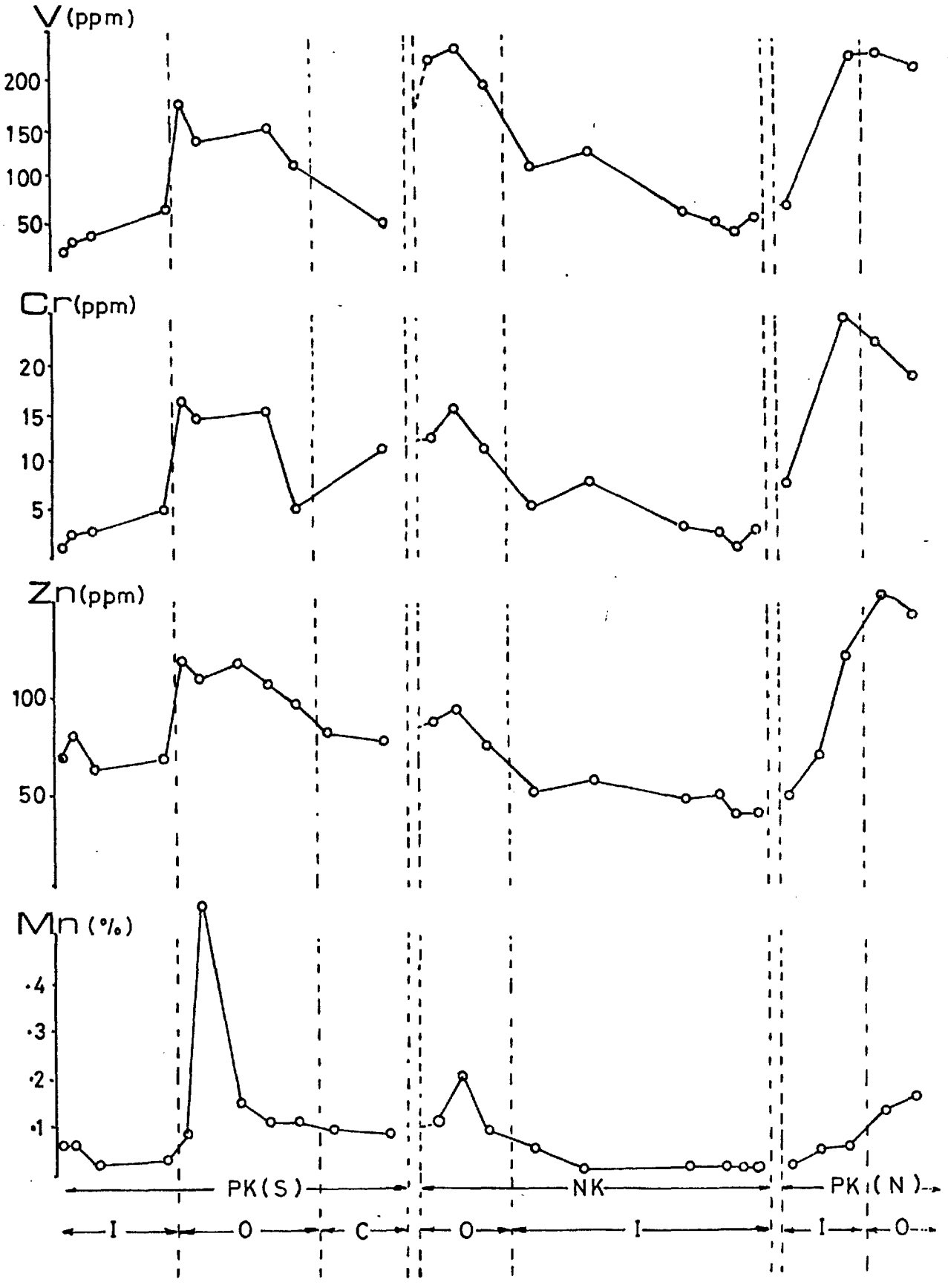


Figure 7.25 Trends in the concentration of V,Cr,Zn,and Mn,in sediment samples from the exhalative (I- inner, O - outer)and channel (C) zones.

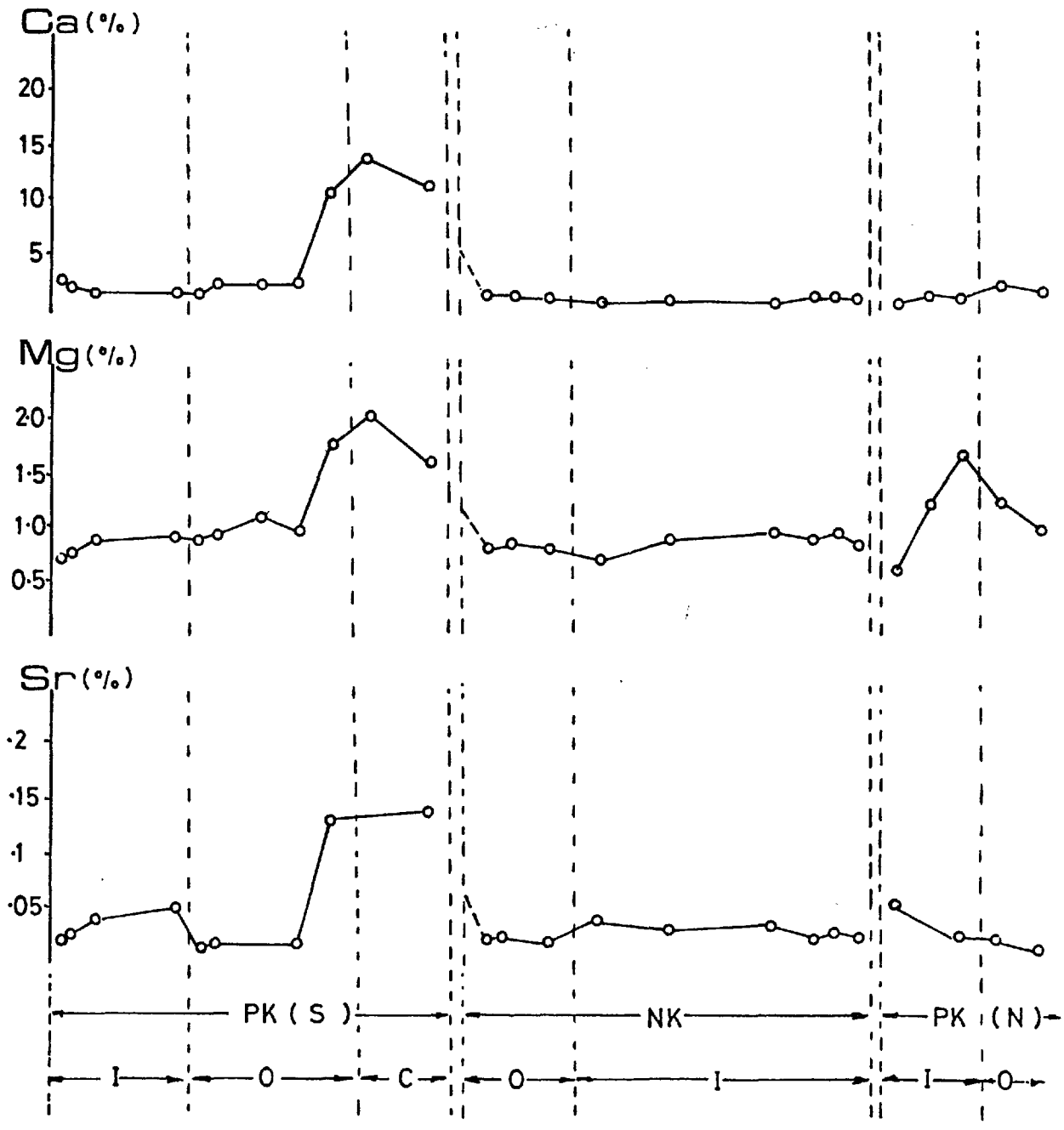


Figure 7.26 Trends in the concentration of Ca, Mg, and Sr in the inner exhalative (I), outer exhalative (O), and channel (C) zones.

To summarise, trends in elemental abundance have pinpointed certain distinct associations which may be tentatively ascribed to particular components within the sediment. These associations are summarised below:-

(1) Fe, Sc, Hg and Mo - hydrated iron oxides;

(2) Al, Si, Ti, K, Ga and Co - detrital minerals, particularly pumice (including volcanic sand);

(3) Si - hydrothermally derived silica in the inner exhalative zones, otherwise pumice;

(4) K - evaporate minerals in the inner exhalative zones;

(5) V, Zn and Cr - detrital minerals (pumice) and a further, unidentified, phase in the outer exhalative zones;

(6) Mn - detrital minerals and Mn oxides;

(7) Ca, Mg and Sr - biogenic carbonates;

(8) Ni, Cu, Pb, Li and Ba - a range of controls and no distinct association evident.

7.6.6c Partition of Elements in the Sediments of the Exhalative and Channel Zones

Although the trend relationships of elements were useful in pinpointing distinct associations between groups of elements, they also posed certain questions. Particular samples were distinctively high in Mn in the outer exhalative zone and yet the remainder were generally much lower. Do the Mn-rich samples contain a different Mn phase to the others? V, Cr and Zn have distributions similar to the detrital components and yet appeared to be in excess of that predicted from studies of the detrital components from the shelf and caldera. Partial association with iron oxides is possible but an obvious relationship with iron is not seen. Finally, it was difficult to establish any particular association for Ni, Cu, Pb,Li and Ba. In order to better understand the distribution of these elements, and to provide some answers to the questions posed, this section examines the partition of the elements between particular fractions of the sediments.

A range of chemical attacks have been used by earlier workers to assess the partition of elements in sediments. Hirst and Nicholls (1958) and Chester (1965) used acetic acid to assess the partition of trace elements in carbonates. Pelagic sediments have been examined by a variety of techniques including combined dialysis

and EDTA (Goldberg and Arrhenius, 1958); 1M hydroxylamine, originally used by Arrhenius and Korkish (1959) to separate the major fractions of Mn - nodules and subsequently used by Lynn and Bonatti (1965) to study the partition of Mn in marine sediments; and acetic acid hydroxylamine hydrochloride (Chester and Hughes, 1967). In this investigation a modification of the methods suggested by Chester and Hughes (1967) and Cronan and Garrett (1973) is employed (see appendices). The acetic acid (HAc) soluble fraction includes carbonates, loosely sorbed ions (Chester and Hughes, 1967) and interstitial water evaporates (Cronan, 1976a). This fraction may also include some colloidal iron (Chester and Hughes, 1966). The 'hydroxylamine' soluble fraction is that amount of an element solely attributable to removal by a combined acid - reducing agent: acetic acid hydroxylamine hydrochloride. Mn oxides, if present, will mainly occur in this fraction. That fraction of an element removed solely by hot 50% HCl is termed the HCl-soluble fraction and will include all components of the sediment except the resistant detrital minerals (Cronan and Garrett, 1973). "Detrital" is used to describe the residues insoluble in HCl. It should be borne in mind that partition data are based on the analysis of residues and not the leach solutions (see appendices for further details). Although this is not as precise or as accurate as analysis of the leach solutions, it is not thought to mask the important features of element partition between phases.

Average partition of the elements in each zone are given in table 14. Each of the elements studied are considered below.

Iron

In the exhalative zones the dominant iron-bearing fraction of the sediments is that soluble in HCl. This is consistent with the nature of the deposits - they mainly consist of hydrated iron oxides. The bulk of the Fe in basal metalliferous sediments from the Paciffic also occur in the HCl-soluble fraction (Cronan and Garrett, 1973; Cronan, 1976a). HAc-soluble Fe is also important in the exhalative zones and this is attributable to the presence of colloidal iron (Chester and Hughes, 1967). In the channel, detrital iron is more important than in the other zones.

Manganese

In the outer exhalative zones, where the total concentrations of Mn are greatest, on average the "hydroxylamine"-soluble fraction of the sediment contributes the most Mn. Other fractions, however,

TABLE 14 Average partition of the elements in sediments from the inner exhalative, outer exhalative, and channel zones. Fe, Al, Ti, Si, K, Ca, and Mg are in percent, the remaining elements in ppm.

Zone		Fe	Al	Ti	Si	K	Ca	Mg
INNER EXHAL.	Acetic acid soluble	7.6	.2	.01	.46	.36	.58	.66
	'Hydroxylamine' soluble	.7	.05	.005	.06	.07	.11	.01
	Hydrochloric acid soluble	24.9	.2	.01	2.41	.17	.38	.13
	Detrital	.3	.4	.02	6.56	.10	.12	.03
	Total	33.5	.8	.04	9.49	.70	1.19	.83
OUTER EXHAL.	Acetic acid soluble	2.7	.5	.01	*	.37	1.55	.48
	'Hydroxylamine' soluble	.4	.05	*	*	.10	.03	.01
	Hydrochloric acid soluble	11.6	.2	.1	*	.05	.23	.18
	Detrital	1.4	3.9	.19	23.1	1.23	1.25	.37
	Total	16.1	4.6	.29	23.1	1.75	3.06	1.04
CHANNEL	Acetic acid soluble	.5	.7	.01	*	.6	14.08	1.39
	'Hydroxylamine' soluble	*	.2	*	*	*	.08	.01
	Hydrochloric acid soluble	1.5	*	.1	*	*	.67	.14
	Detrital	1.2	3.4	.16	20.6	1.3	.56	.31
	Total	3.2	4.3	.27	20.6	1.9	15.39	1.85

* - below determination

continued .....

TABLE 14(continued)

Mn	Sr	Cu	Zn	Pb	Mo	V	Co	Ni	Cr	Ga	Ba	Li	Sc
90	268	10.3	15.7	2.5	5.3	13.3	*	1.3	.5	1.8	42	*	6.8
7	11	3.6	1.1	4.1	4.1	6.9	*	.7	.5	.1	3	*	1.0
167	4	14.8	29.4	7.0	16.8	23.7	*	2.7	1.9	1.2	35	*	7.0
40	6	3.6	6.3	.6	3.7	1.0	*	.6	.3	.7	22	*	.4
304	326	32.3	52.5	14.2	29.9	44.9	< 1	5.3	3.2	3.8	102	< 3	15.2
334	264	6.0	17.4	2.0	4.4	17	.3	.8	.7	1.2	34	14	.8
575	12	4.4	6.7	5.1	2.2	37	.2	.9	1.6	1.4	24	20	1.4
405	54	7.3	42.3	4.4	13.0	108	1.4	5.2	9.0	*	27	3	2.2
491	64	7.2	40.3	5.0	1.7	13	3.1	.4	3.7	10.4	167	9	3.5
1805	394	24.9	106.7	16.5	21.3	175	5.0	7.3	15.0	13.0	252	46	7.9
284	1300	6.2	16.6	11.8	*	*	*	2.1	*	11.0	162	22	1.2
12	*	2.1	13.0	2.7	*	*	*	*	1	*	*	5	*
119	52	4.8	6.8	2.7	.2	33.5	*	3.9	5	*	79	*	.7
423	48	5.5	33.7	5.3	1.3	14.5	*	*	5	10	135	8	2.8
838	1400	18.6	70.1	22.5	1.5	48.0	< 1	6.0	11	21	374	35	4.7

contribute similar amounts of Mn (table 14). In fact, the averaging process masks a much wider range in Mn partition. For most samples the Mn occurs in both the HCl-soluble and detrital fractions but, in those samples with the highest concentrations of Mn (i.e. those with more than about 1500ppm Mn, e.g. 9*, 17 and 29), the "hydroxylamine"-soluble Mn is much more important. In sample 9*, in particular, total Mn exceeds ½%, of which about 70% is held in the "hydroxylamine"-soluble fraction. Discrete manganese oxide minerals probably account for this fraction of the Mn (see Chester and Hughes, 1967).

In the inner exhalative zones, Mn occurs in both the HCl and HAc soluble fractions but, on average, HCl soluble Mn is the largest. Both are probably associated with the dominant component soluble in the same solvents, namely the hydrated iron oxides. The physico-chemical environment of the inner exhalative zones (acid pH, low to moderate Eh) is unsuitable for the precipitation of discrete manganese minerals. Instead, Mn in the sediments from the inner exhalative zones may derive from co-precipitation with the hydrated iron oxides.

In the channel zone, the detrital fraction is the most significant source of Mn although HAc-soluble (hydrogenous) Mn is also important. The latter could be associated, in some way, with the bioclastic fragments - either as coatings on the fragments or lattice-held within the carbonate minerals.

From the above discussion it seems that the total abundance of Mn is governed by the relative proportions of four Mn-bearing phases:-

(1) "detrital" Mn in the outer exhalative and channel zones;

(2) "hydrogenous" Mn in the channel zone;

(3) Mn co-precipitated with, or scavenged in some other way by, the hydrated iron oxides;

and (4) discrete Mn minerals in the outer exhalative zones.

Aluminium, Titanium and Silicon

In all three zones the major proportion of these elements occurs in the "detrital" fraction of the sediments, thereby confirming previous observations based on the antipathetic distribution of these elements with the iron and carbonate phases, and to their association in "pumice" sediments in the caldera and shelf zones. However, as noted earlier, sediments in the inner

exhalative zones have derived some of their silicon from hydrothermal solutions.

Calcium, Magnesium and Strontium

Not surprisingly, Ca, Mg and Sr exhibit similar behaviour in the partition studies. In all zones these elements occur dominantly in the acetic acid-soluble fraction probably as carbonates, especially in the outer exhalative and channel zones.

Potassium

Partition data support the conclusions based on the trends in the bulk data. In the outer exhalative and channel zones, K is mainly concentrated in the "detrital" fraction. In the inner exhalative zone the HAc-soluble is the largest. As the salt in the samples was not removed prior to analysis, evaporate minerals could account for the HAc-soluble K in this zone.

Copper

In the inner exhalative zones, where the average total abundance is greatest, the bulk of the Cu occurs in the HCl- and HAc-soluble fraction of the sediments. The major phase in these two fractions is the hydrated iron oxide. Consequently, Cu is probably co-precipitated with the hydrated iron oxides in the inner exhalative zone. Although the absolute levels of HCl- and HAc-soluble Cu decrease in the outer exhalative and channel zones they are still important, but detrital Cu increases.

Lead

Like Cu, the bulk of the Pb in the inner exhalative zone occurs in that fraction of the sediment soluble in HCl and is, therefore, probably associated with the dominant iron phases. In the outer exhalative zone there is a significant 'hydroxylamine' fraction but examination of individual samples indicates that this component is not associated with the Mn oxide phase. In the channel zone, Pb is concentrated in the HAc-soluble fraction which suggests association with either the 'hydrogenous' Mn or the carbonate minerals.

Molybdenum

In both the inner and outer exhalative zones Mo is most abundant in the HAc- and HCl- soluble fractions of the sediment which suggests that, in both zones, the Mo is co-precipitated with the iron oxides. The 'detrital' fraction is the major source of Mo in the channel zone.

Scandium

Like Cu, Pb and Mo, the HCl- and HAc-soluble fractions contain most of the Sc from the inner exhalative zone. "Detrital" Sc is more important in the outer exhalative and channel zones.

Vanadium

In a similar manner to Cu, Pb, Mo and Sc, V is most abundant in the HCl soluble fraction of the sediments from the exhalative zones. In contrast to Cu, however, the absolute abundance of HCl soluble V is greatest in the outer exhalative rather than the inner exhalative zone (24ppm in the inner zone compared to 108ppm in the outer zone). The V is still probably associated with the dominant iron phases but an additional mechanism is required to account for the apparent enrichment in the outer exhalative zone.

Zinc

For Zn the pattern of partition is very similar to that of V but the 'detrital' contribution in the outer exhalative and channel zones is much larger.

Barium

The partition of Ba throughout the phases is highly variable. The "detrital" fraction is a major contributor to all zones, but with a major HCl fraction in the inner exhalative zone, similar to other elements, and a major HAc-soluble fraction in the channel zone.

Lithium

Lithium is the only element to occur in the "hydroxylamine" fraction of sample 9* (high "hydroxylamine" soluble Mn) but this association is limited to one sample and so firm conclusions cannot be drawn. Otherwise, Li values are too low to clarify it's partition.

Gallium

According to the trends in the bulk data, Ga appeared to be associated with the Al/detrital group of elements. 'Detrital' Ga is particularly evident in the outer exhalative and channel zones but in the latter an hydrogenous component is also significant.

Chromium, Nickel and Cobalt

Generally Cr, Ni and Co concentrations are too low to draw any firm conclusions but in the outer exhalative zones the HCl soluble fraction seems to be important for Cr and Ni, whereas Co is dominantly "detrital".

To summarise, the abundances of the elements in the sediments from the exhalative and channel zones are governed by the relative proportions of five major components:-

(1) hydrated iron oxides;

(2) manganese oxides;

(3) detrital components (mainly pumice);

(4) carbonate minerals (biodetrital);

and (5) an unspecified "hydrogenous" component in the channel zone.

The following element - component associations are proposed:-

(1) Inner Exhalative Zone

Hydrated iron oxides - Fe, Mn, Cu, Zn, Pb, Mo, V, Sc and Ba

Detrital - Al, Ti and Si (including hydrothermally derived Si)

(2) Outer Exhalative Zone

Hydrated iron oxides - Fe, Mn, Zn, Mo and V

Manganese oxides - Mn

Detrital - Al, Ti, Si, K, Ca, Mg, Mn, Zn and Ba

Carbonate - Ca, Mg and Sr

(3) Channel Zone

Detrital - Al, Ti, Si, K, Mn, Zn, Mo, Ga and Ba

Carbonate - Ca, Mg and Sr

Hydrogenous (unidentified) - Mn, Pb, Ga, Ba and Li

The inner exhalative zone is dominated by the precipitation of iron oxides derived from hydrothermal activity. The outer exhalative zone is also influenced by iron oxide accumulation but the detrital contribution is greater and, significantly, manganese oxide minerals precipitate. The latter, however, do not seem to affect the distribution of the other elements to any noticeable extent. Abundances of elements in the channel zone are governed by the relative proportions of the carbonate, detrital and unidentified 'hydrogenous' components.

Although limited to a few samples, the occurrence of a distinct Mn phase confined to the outer exhalative zone is important. It confirms observations based on the analysis of water samples that Mn is more mobile than Fe and illustrates the often described phenomenon of the separation of Fe and Mn, formulated by Krauskopf (1957) and since proposed by many authors to explain

distinct iron and manganese horizons in both ancient and modern volcanogenic sedimentary-exhalative deposits. Manganese compounds are more soluble than iron compounds under naturally occurring conditions of Eh and pH. Iron is,therefore, more easily oxidised and precipitated than manganese. At Santorini, consequently, iron compounds precipitate in the inner exhalative zone, whilst the more mobile manganese does not precipitate until it reaches the more oxidising and alkaline conditions of the outer exhalative zone (section 7.6.5). Rarely has a modern deposit exhibited the phenomenon of iron/manganese separation so well, except, perhaps, in the Red Sea. Both Butuzova (1966, 1969) and Pushkina (1967) arrived at a similar conclusion but failed to recognise that the major zone of accumulation of discrete manganese oxide minerals was the outer exhalative zone rather than the caldera.

7.6.7 The Mechanisms of Dispersion of Elements In and Around the Caldera

7.6.7a Introduction

Core profile comparisons and inter-element relationships in the caldera and shelf zone sediments have identified certain controls on element abundance. Similarly, for the exhalative and channel zones, comparison of lateral trends in element abundance reveal particular element associations which have been partly clarified by partition studies. For those elements apparently associated with the iron phases, however, the situation is not straight-forward. Before summarising the major controls on the dispersion of the elements, this section examines the apparent anomalies in the iron association in more detail.

7.6.7b Controls on the Abundance of Elements in the Exhalative Zones Related to Hydrothermal Activity

The anomalies referred to above are found in the exhalative zones where HCl-soluble fractions of Mn, V, Zn, Mo, Cu, Sc, Pb and Cr (Mn_{HCl}, V_{HCl}, etc.) occur in association with the major component of the HCl-soluble fraction - the hydrated iron oxides.

There is no evidence that the HCl has leached the pumice component to any significant extent nor of further HCl-soluble components other than the hydrated iron oxides. It is proposed, therefore, that the HCl-soluble fraction of each element is contributed to the sediments of the exhalative zones through the scavenging action of the hydrated iron oxides. ('Scavenging' covers any mechanism by which the hydrated iron oxides remove the trace elements from the water column and could include coprecipitation, surface adsorption or any other form of occlusion within, or reaction with, the iron oxides.) Despite the common association with the iron phases, Cu_{HCl}, Mo_{HCl}, Sc_{HCl}, and Pb_{HCl} are concentrated in the inner exhalative zone, whereas Mn_{HCl}, V_{HCl}, Zn_{HCl} and Cr_{HCl} are concentrated in the outer exhalative zone (table 14 and see figure 7.33).

Interestingly, on the basis of the analysis of water samples two of the elements enriched in the outer exhalative zone, Zn and Mn, appear to be more mobile than iron, whereas two of the elements concentrated in the inner exhalative zone, Cu and Pb, have a very limited mobility (see section 7.6.5). Ferguson and Lambert (1972) reported a very similar situation within the Tavurvur gully, Matupi Harbor, New Britain. Mn and Zn, both enriched in the hydrothermal solutions, increase in abundance within the iron phase with distance away from the hydrothermal conduit, but Cu and Pb, both depleted in the solutions relative to Mn or Zn, do not increase in the same way. Element mobility, it seems, is an important contribution to the development of element zoning. Other factors are involved, however, and the relationship between scavenging, element mobility and zones of enrichment is discussed below.

Because the scavenging action of the hydrated iron oxides contributes, to the sediments, that fraction of the total trace element concentration related to hydrothermal activity (Me_H), it follows that this fraction (Me_H) is given by the product of (a) the abundance of the accumulating iron oxides (i.e. the scavenging phase) in unit weight of sediment (Fe_H), and (b) the scavenged element to scavenging phase ratio, $\frac{(Me)}{(Fe)S}$, that is:

$$Me_H = Fe_H \cdot \frac{(Me)}{(Fe)_S} \qquad \text{--- (1)}$$

The HCl-soluble fraction of the sediments contains the bulk of the elements related to the hydrothermal activity therefore the above equation may be represented by:

$$Me_{HCl} = Fe_{HCl} \cdot \frac{Me_{HCl}}{Fe_{HCl}} \quad \text{--- (2)}$$

The zoning of the HCl-soluble fraction of the elements, therefore, is a function of the factors which govern (a) and (b) above. Hydrated iron oxide accumulation is not considered further here but is discussed throughout this chapter and reviewed in section 8.3.2. More important at this stage is the scavenging ratio $(Me/Fe)_S$. From equation (1) it follows that, for a given scavenging iron profile (Fe_H), the development of zoning related to hydrothermal activity through the scavenging action of the hydrated iron oxides is a function of the change in this ratio.

The types of ratio change fall into three categories which appear to be dependent upon the degree of hydrothermal influence on the abundance of a particular element in the seawater above the exhalative zones:

(1) Where there is no hydrothermal influence, the composition of the waters is close to that of normal seawater and relatively constant throughout the zones. Under these circumstances it seems that scavenging ratio $(Me/Fe)_S$ increases with increasing depth (or distance) away from the hydrothermal source. Cr is thought to fall into this category; the Cr_{HCl}/Fe_{HCl} and Cr_{HCl} profiles with depth are shown in figure 7.27. Because each embayment has different characteristics there is a scatter of points; nevertheless, Cr_{HCl}/Fe_{HCl} clearly increases between the inner exhalative zone and the caldera. (The ratio for the caldera shown in figure 7.27 is only an estimate of the scavenged element to scavenging phase ratio and is based on the approximate 'excess' Cr divided by the approximate 'excess' Fe - see section 7.6.4).

In this case the seawater abundance of Cr is thought to be relatively constant and so the change in the ratio is simply governed by the change in the scavenging ability of the iron oxides. Several factors could affect this scavenging ability including a change in:-

(a) the rates of precipitation, aggregation and sedimentation of the scavenging phase which, inturn, govern the contact time between the scavenging phase and the scavengeable elements;

(b) the mineralogy, crystallinity and speciation of the scavenging phase;

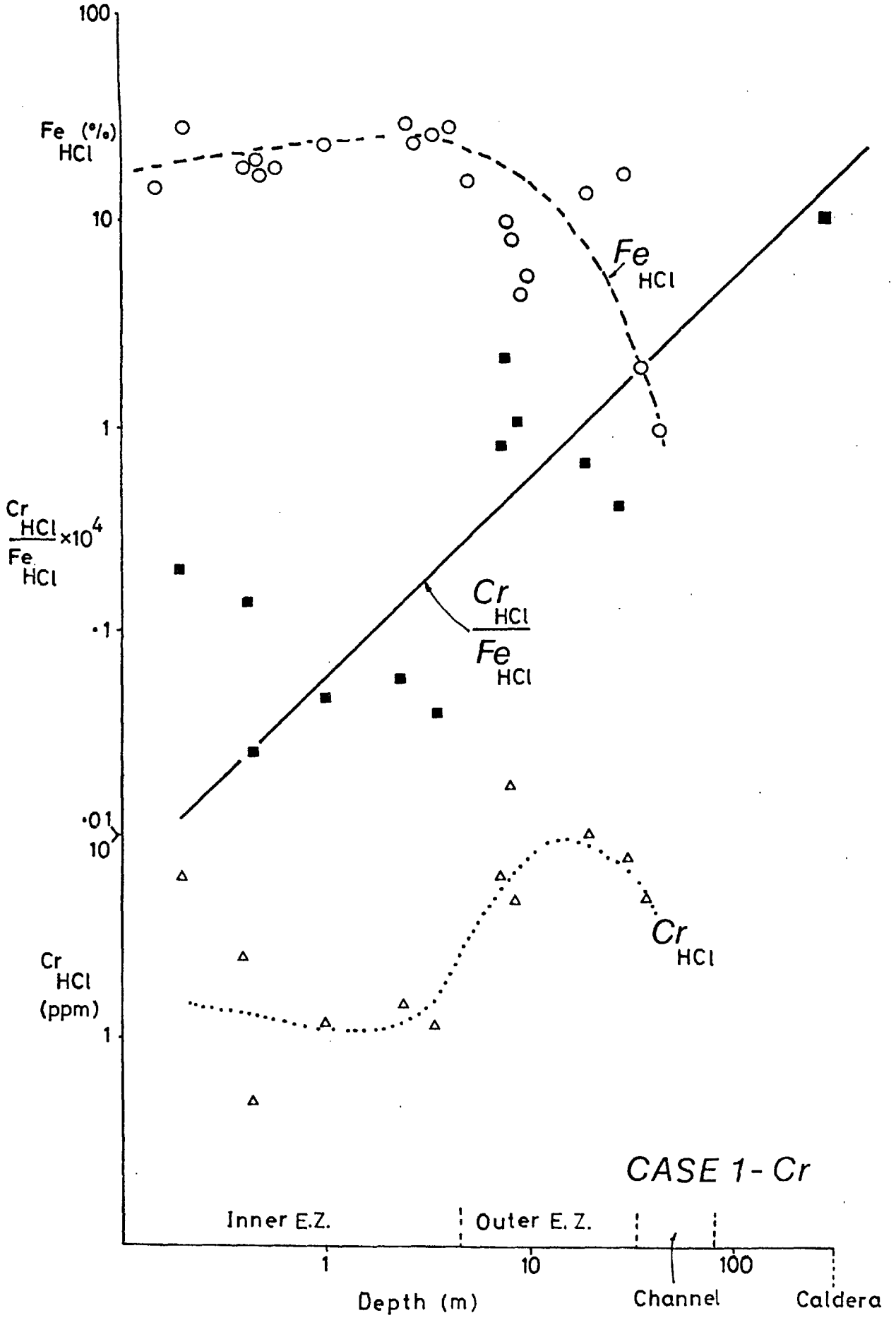


Figure 7.27 Case 1 - Chromium.Profiles of HCl-soluble Fe,Cr,and Cr/Fe ratio with depth (E.Z. - exhalative zone).

and (c) the nature of the reaction between the scavenged element and the scavenging phase.

At Santorini the major difference between the zones seems to be the sedimentation rates of the hydrated iron oxides. In the inner exhalative zone the rapid precipitation, aggregation and sedimentation of the iron oxides limits the contact time between the scavenging phase and the scavengeable element (scavenging time), and this, in turn, limits the scavenging capacity of the scavenging phase (Goldberg, 1954). With increasing depth or distance from the fumeroles, however, the scavenging time and, hence, scavenging increases. The result is a scavenging ratio which is low in the inner exhalative zone but which increases with increasing distance away from the hydrothermal source.

Other mechanisms may contribute to the increased scavenging ability of the hydrated iron oxides away from the fumaroles but their significance is difficult to assess. The acid conditions of the inner exhalative zone, for example, may limit the scavenging ability. At Tavurvur gully, Ferguson and Lambert (op.cit.) attribute the increasing ability of the iron oxides to scavenge the mobile elements to the changing physico-chemical environment, particularly the change in pH from 3 to 5. The age of the hydrated iron oxides could also affect their scavenging ability and 'aged', or more crystalline, iron oxides may have a greater scavenging ability than the initial amorphous forms. More crystalline forms may have developed by the time the particulate iron phases accumulate in the outer exhalative zone. Element speciation is not thought to be an important factor because Krauskpopf (1956) showed that elements with theoretically different speciations (e.g. Zn and V) are equally well scavenged from seawater by iron oxides.

Whatever the mechanism, the scavenging ratio $(Me/Fe)_S$ for elements derived simply from seawater increases with depth because of the increase in the scavenging ability of the iron oxides. The product, therefore, of the concentration of the scavenging phase (e.g. Fe_{HCl}) and the scavenging ratio (e.g. Cr_{HCl}/Fe_{HCl}) is enrichment of the scavenged element in the outer exhalative zone (see figure 7.27).

(2) Certain elements (e.g. Cu) are supplied by the hydrothermal solutions but only in relatively small amounts. Their mobility is limited because the hydrated iron oxides are able to remove the

hydrothermal contribution of these elements entirely within the inner exhalative zones. Abundances in the waters of the outer exhalative zones are, therefore, close to normal seawater (see section 7.6.5). Consequently the hydrothermal influence is restricted to the inner exhalative zone. The scavenging ratio (e.g. Cu_{HCl}/Fe_{HCl}) for these elements is, therefore, much higher in the inner exhalative zone than for elements derived simply from seawater (figures 7.28 and 7.29), but is of a similar order of magnitude in the outer exhalative and deeper zones.

The outcome is that the Cu_{HCl}/Fe_{HCl} ratios, for example, are approximately constant throughout the exhalative zones (figure 7.28). Cu_{HCl} appears to follow Fe_{HCl}, therefore, with enrichment in the inner exhalative zone.

Other category (2) elements (i.e. those with a small hydrothermal contribution but limited mobility and enrichment in the inner exhalative zone) include Pb, Mo, Sc and possibly Hg.

(3) For those elements with a moderate hydrothermal contribution (e.g. Mn and Zn), the scavenging ratio (e.g. Mn_{HCl}/Fe_{HCl} and Zn_{HCl}/Fe_{HCl}) increases with distance (depth) away from the fumaroles (Mn - figure 7.32, Zn - figure 7.30). Like Cu, the hydrothermal contribution increases the ratio in the inner exhalative zone above that due to simple scavenging from seawater. Unlike Cu, however, Mn and Zn are more mobile (section 7.6.5) and are able to pass into the outer exhalative zone in solution. Distinct Mn phases in the sediments of the outer exhalative zones support this hypothesis. Excess metals over normal seawater in the outer exhalative zone are, therefore, available for further scavenging by the particulate iron oxides. In this way the scavenging ratio for the outer exhalative zone is greater than that for scavenging from normal seawater (figure 7.29).

The product of the concentration of hydrated iron oxides (Fe_{HCl}) and the scavenged Zn to scavenging iron oxide ratio (Zn_{HCl}/Fe_{HCl}) is a slight enrichment of Zn_{HCl} in the outer exhalative zone (figure 7.30). Similarly, examination of individual embayments, Nea Kameni for example, reveals a positive relationship between Mn_{HCl}/Fe_{HCl} and depth and distinct enrichment of Mn in the outer exhalative zone.

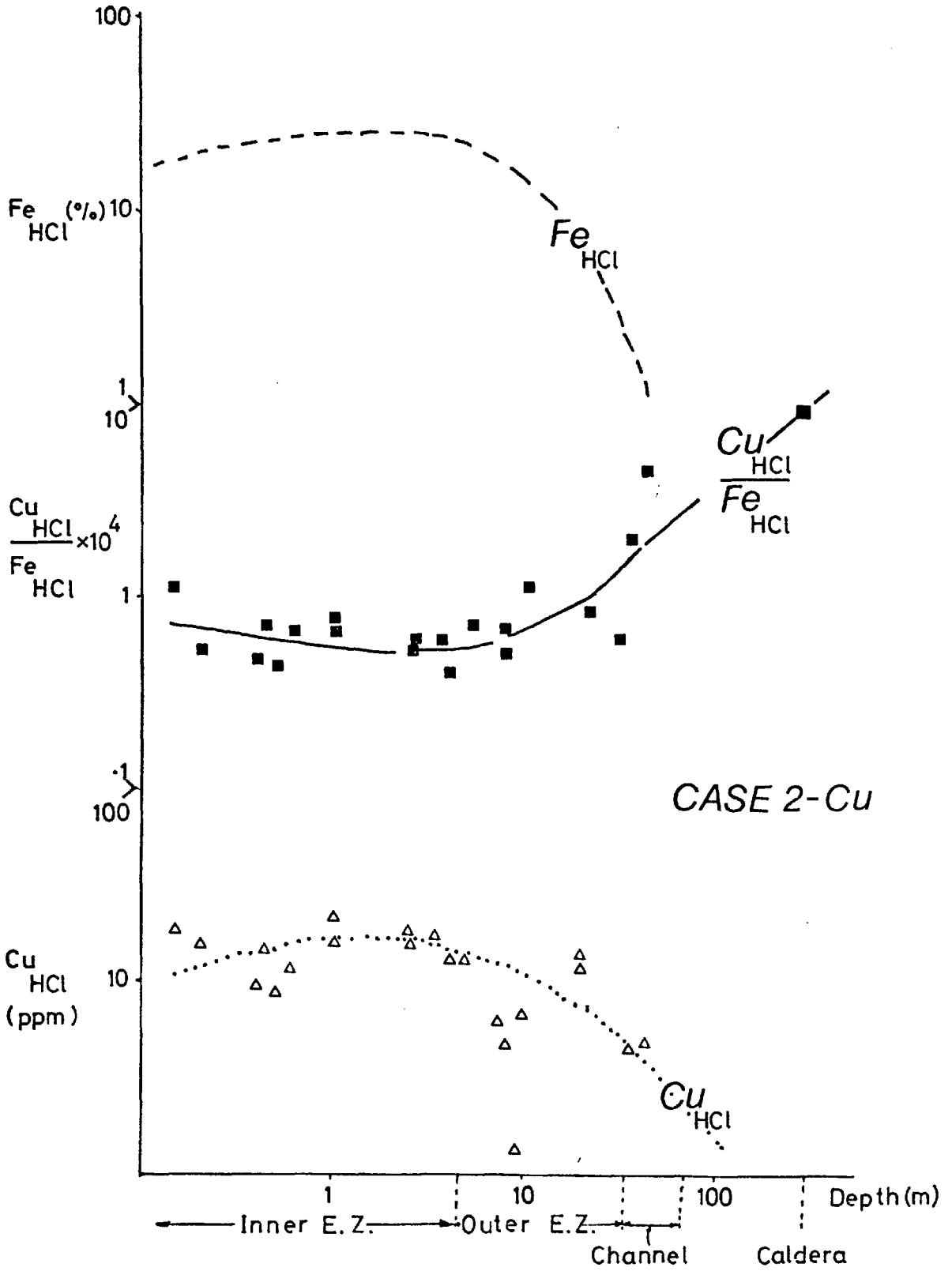


Figure 7.28 Case 2 - Copper. Profiles of HCl-soluble Fe(see figure 7.27),Cu,and the Cu/Fe ratio with depth.

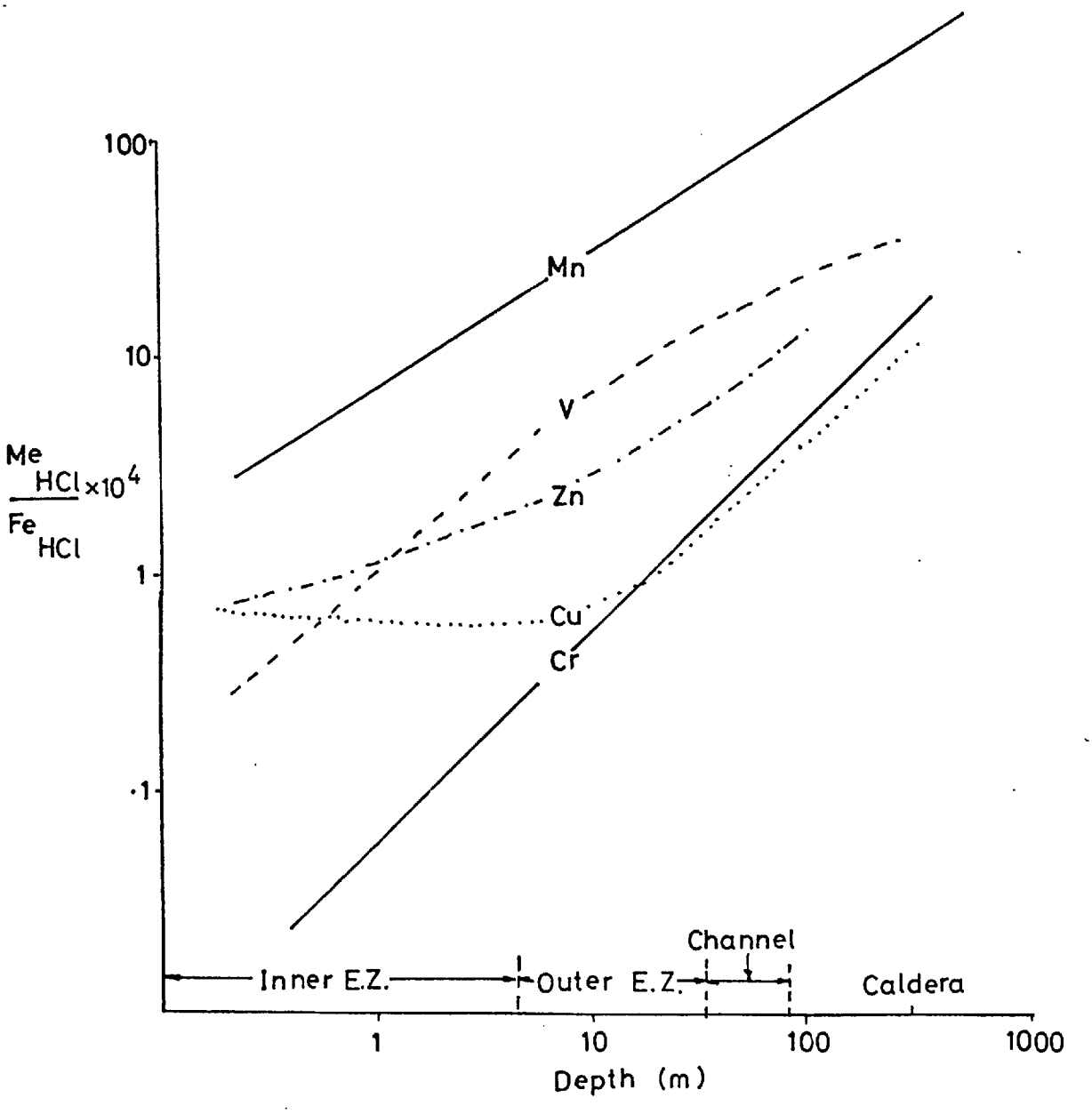


Figure 7.29 A comparison between the HCl - soluble element (Me_{HCl}) to HCl-soluble Fe profiles with depth.

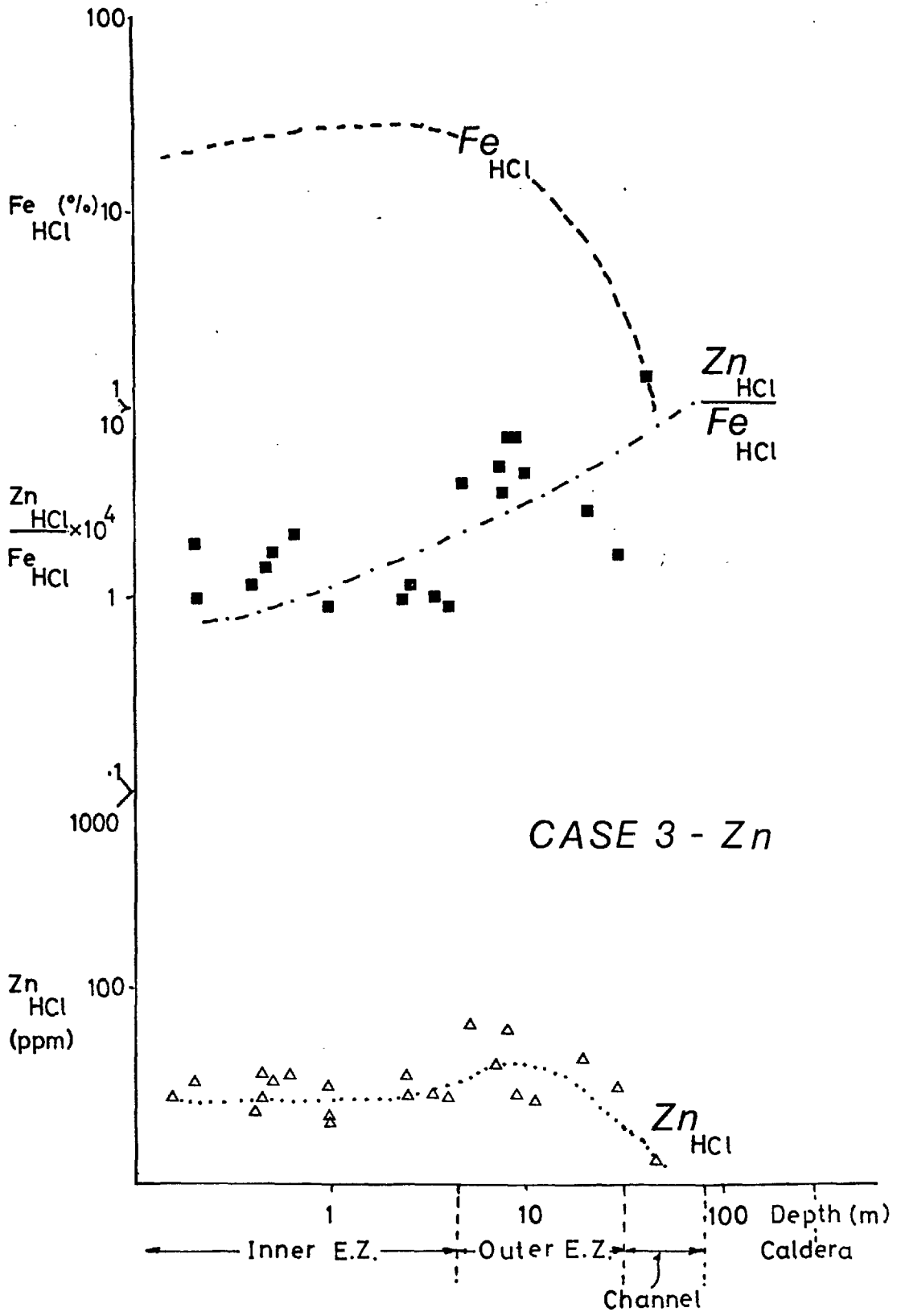


Figure 7.30 Case 3 - Zinc.Profiles of HCl-soluble Fe(see figure 7.27),Zn,and the Zn/Fe ratio with depth.

HCl-soluble vanadium behaves in a very similar way to Zn and has a most distinctive enrichment in the outer exhalative zone (figure 7.31). This profile could be achieved through simple scavenging from seawater (see Cr - category 1) but the similar concentrations of V and Zn suggest otherwise, that is V is also contributed by the hydrothermal solutions. Pushkina (1968) and Butuzova (1969) found no evidence for a hydrothermal contribution of V but it would not be inconsistent with previously reported data on other similar areas. Zelenov (1964), for example, reports concentrations of V in deposits from Banu Wuhu of the order of tenths of a percent, and Ferguson and Lambert (op.cit.) report up to 180ppm V in recent surficial sediments from Matupi Harbor. Valette (1972) also suggests a similar, fumarolic source for V in sediments around Volcano Island.

The distributions of the HCl-soluble fractions resulting from the interaction between iron oxide accumulation and the change in the scavenging ratio are shown in figure 7.33. The significance of this zoning of trace elements related to hydrothermal activity is discussed in section 8.3.4.

To summarise, from the discussion in this section it seems that the development of trace element zoning related to hydrothermal activity through the scavenging action of the hydrated iron oxides is a function of the concentration of the scavenging phase (i.e. the iron oxides) in the sediments and the change in the scavenged element to scavenging phase ratio away from the fumaroles. For a given scavenging phase profile, therefore, it is the ratio that is critical and this is governed by (a) the scavenging capacity of the scavenging phase and (b) the abundance of the scavengeable elements in the water column. The scavenging capacity of the scavenging phase improves with distance away from the fumaroles because of a concomitant increase in the contact time between the scavenging and scavenged phases. Three categories of element behaviour are recognised:-

(1) no hydrothermal influence on the abundance in seawater and so simple scavenging results in a gradual increase in the ratio and enrichment of these elements in the outer exhalative zone (Cr,Ni);

(2) a small hydrothermal influence but a limited mobility results in an approximately constant ratio in the exhalative zones and enrichment in the inner exhalative zone (Cu, Mo, Pb, Sc, Hg);

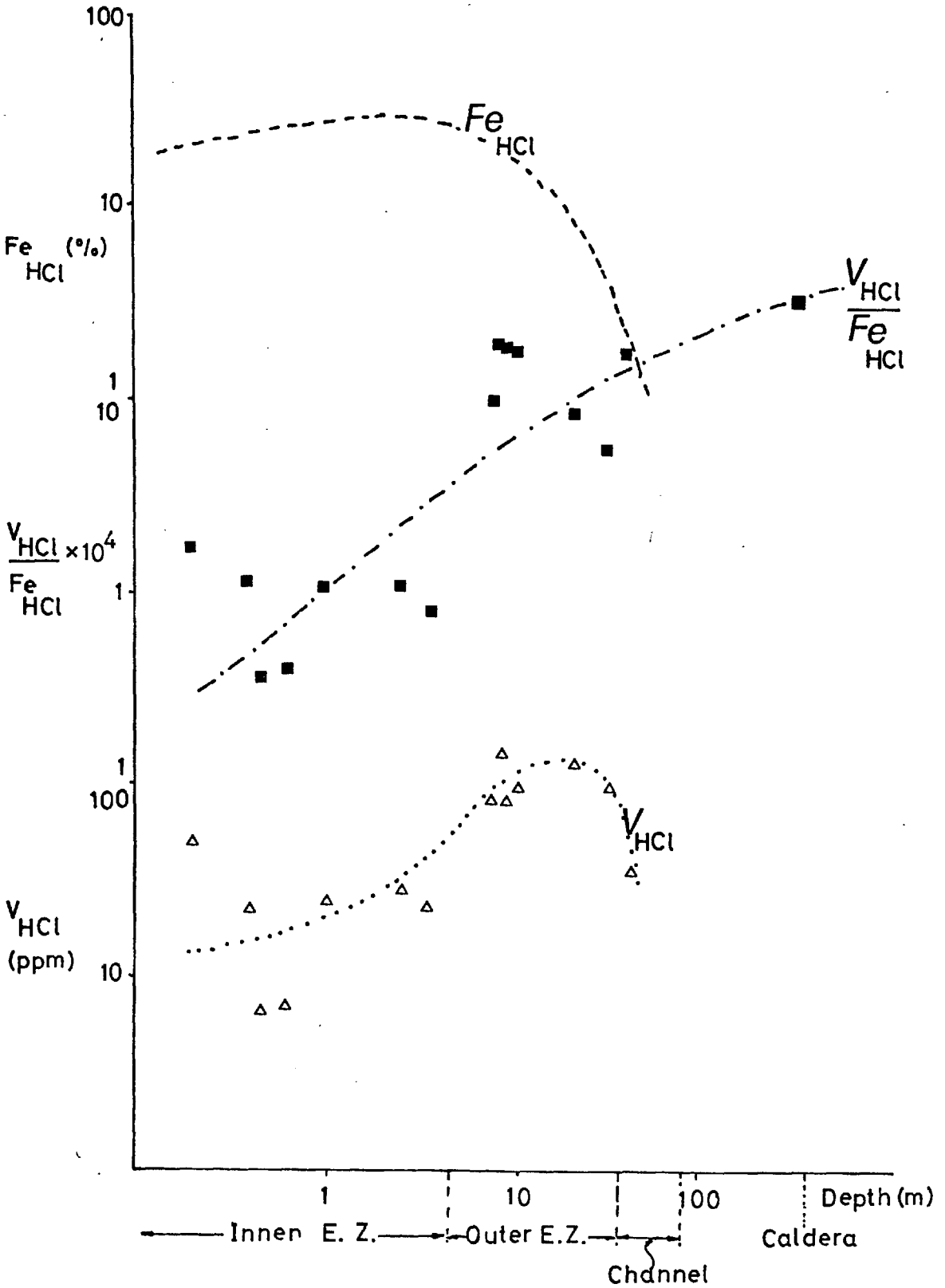


Figure 7.31 Profiles of HCl-soluble Fe(see figure 7.27),V, and the V/Fe ratio with depth.

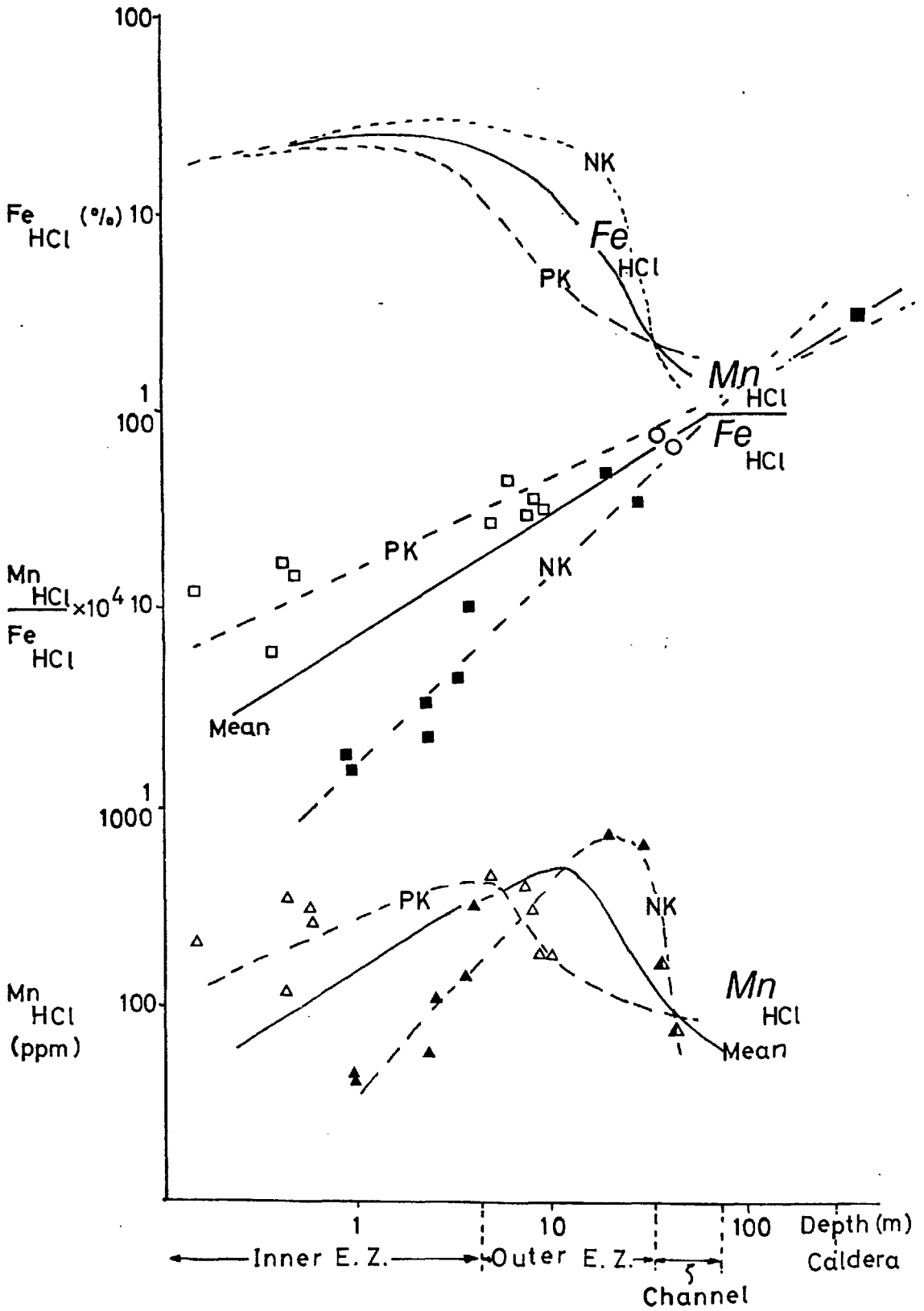


Figure 7.32 Profiles of HCl-soluble Mn,Fe(see figure 7.27), and the Mn/Fe ratio with depth.The broken lines show the profiles for individual embayments(NK - Nea Kameni,PK - Palaea Kameni).

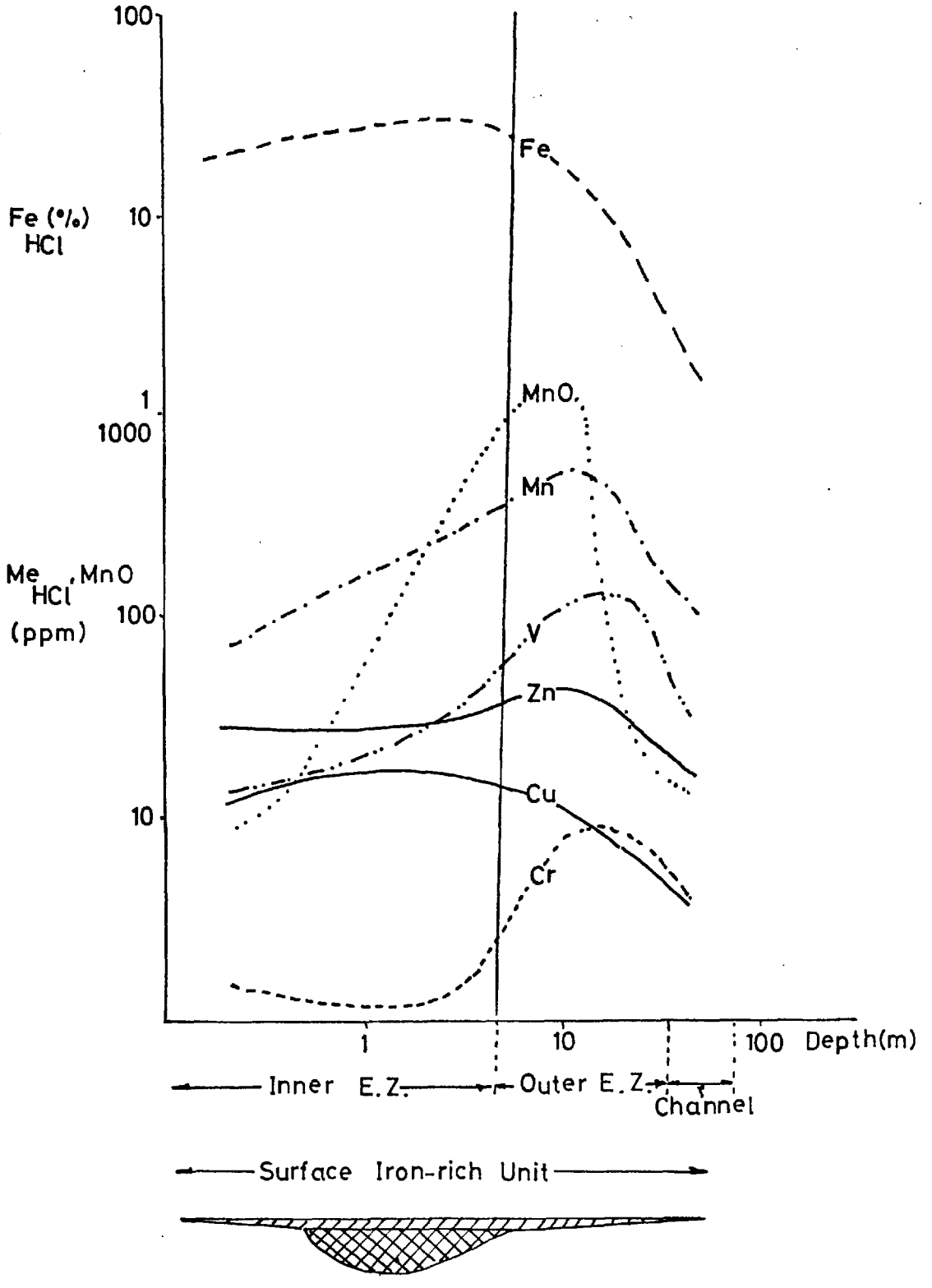


Figure 7.33 Element zoning within the surficial iron-rich unit.(MnO refers to the hydroxylamine-soluble Mn.)

and (3) a moderate hydrothermal influence and a moderate mobility results in a gradual increase in the ratio and enrichment in the outer exhalative zone (Mn, Zn, V).

7.6.7c The Dispersion of Fe, Mn and the Heavy Metals

Dispersion of Fe, Mn and the heavy metals begins at three major sources:-

(1) basement metamorphic and sedimentary rocks (Ni and Cr);

(2) the solid products of volcanic activity (Fe, Mn, Zn, V, Cu, Ti);

and (3) hydrothermal fumarolic activity (Fe, Mn, Zn, V and Cu).

In (1) and (2) the elements occur mainly as lattice held constituents of solid phases. Dispersion is, therefore, controlled by the physical forces involved in volcanic eruption, erosion, transport and sedimentation. For the pyroclastic products of volcanic activity the dispersion can be extensive. Ninkovich and Heezen (1965) have suggested that products from the major eruptions of Santorini can be found in many parts of the Aegean and eastern Mediterranean. Of more local importance are the extensive pumice horizons of both the shelf and caldera zones, which may be derived from the direct sedimentation of pyroclastic fallout or from the slumping of similar material accumulating onshore or nearshore. "Pumice" facies from the shelf zone, and possibly lower horizons of the caldera zone, are derived from the 1400 B.C. eruption. Later eruptions have been of less magnitude and apparently limited dispersion, only affecting the caldera zone to a limited extent. In fact, much of the pumice from the Kolomvos eruption may well have floated into the caldera - a fairly unusual mechanism of dispersion.

Pumice strata cover much of the Santorini Archipelago and so erosion of these deposits also contributes substantial pumice to the shelf and caldera sediments. Material derived from this source is thought to be the major component of the "normal" sediments of the caldera and shelf zones, apart from the carbonate. Extent of dispersion in this case is limited by the size and specific gravity of the erosion products. Critical is that much of the material has to pass through the zone of wave action at the beach. Heavy minerals, in particular, are trapped in the nearshore zone (see Raab and Stoffers, 1975), thereby enriching the sediments in

associated heavy metals. Only fine-grained materials are able to pass through this zone and disperse to the deeper parts of the shelf to form "normal" sediments.

A similar fate awaits material eroded from the exposures of basement metamorphic and sedimentary rocks on Santorini. However, fine-grained minerals, especially micas, may escape the nearshore zone to contribute to the 'terrigenous' fraction of the shelf zone "normal" sediments. The abundances of Ni and Cr, in particular, are thought to be controlled by this fraction but more extensive dispersion of clay minerals from more distant Aegean sources may also be possible.

The steep gradients of the shoreline of the caldera do not permit the extensive development of beaches. Much eroded coarse material is able to reach deeper water, particularly by slumping. This is most evident in the south-eastern basin whefe pumice horizons are thickest. Deeper parts of the northern basin are distant from sources of slumped material and fine-grained sediment predominates.

In summary, substantial pumice is dispersed to most submarine areas by one means or another and this is reflected in moderate contributions of detrital Fe, Mn, V, Zn, Ti and Cu to the sediments. Erosion of metamorphic and sedimentary rocks may supply sufficient fine-grained material to account for the relatively higher abundance of Ni and Cr in the shelf zone "normal" sediments.

Possibly one of the most significant aspects of the present investigation is the examination of the disperal mechanisms of hydrothermally derived heavy metals. It is thought that hydrothermal solutions contribute elements to the following degree:- Fe > Mn > Zn > V > Mo > Cu > Sc, Pb > Cr The mobility of these elements illustrate the interplay between the three factors thought to control the concentration of minor elements in Fe-Mn deposits, namely (a) the amount of each particular element introduced in the bottom water by the hydrothermal sources; (b) its solubility in seawater; (c) the "scavenging" of minor elements from seawater by the Fe and Mn hydroxides (Bonatti et al., 1972b).

Critical to hydrothermal dispersion is the behaviour of iron. As it enters the inner exhalative zone it rapidly precipitates to form colloidal hydrated iron oxides. Iron escaping from the inner exhalative zone is almost entirely particulate. Dispersion of iron from hydrothermal sources, consequently, is best described by

dispersion of particulate iron phases and figure 7.3 4 illustrates the extent of particulate iron dispersion. Two phases control most of the abundance of iron within the sediments - pumice and iron oxides. Shelf zone samples illustrate the pumice control by the strong direct relationship between Fe and Al, whereas the exhalative zone samples reflect the antipathetic nature of the oxide and detrital phases. The caldera zone normal sediments include 1% to 2% excess iron (section 7.6.4) and, therefore, particulate iron appears to disperse to all zones except the shelf.

The remaining elements studied are generally soluble in the inner exhalative zone and mobility is governed by the scavenging action of the hydrated iron oxides. Elements such as Cu and Pb are dominantly scavenged in the inner exhalative zone, resulting in a limited mobility. Contribution of these elements to outer zones is in association with the particulate iron phases. Scavenging in the inner exhalative zone is apparently not sufficient to remove all the soluble Mn, V, and Zn and so these elements have a greater mobility and are able to pass into the outer exhalative zone in solution.

At this point, the mobile trace elements and some of the Mn are scavenged by the particulate iron oxides. "Soluble" Mn may also oxidise in this zone resulting in the formation of particulate manganese oxides which either accumulate in a narrow zone at the landward ends of the outer exhalative zone or disperse seawards.

The hydrothermal contribution to the caldera is, therefore, in the form of particulate iron and, possibly, manganese oxides. Heavy metals and manganese, however, are also carried into the caldera as part of the Fe phase, the actual amount being a function of the amount scavenged in the exhalative zones.

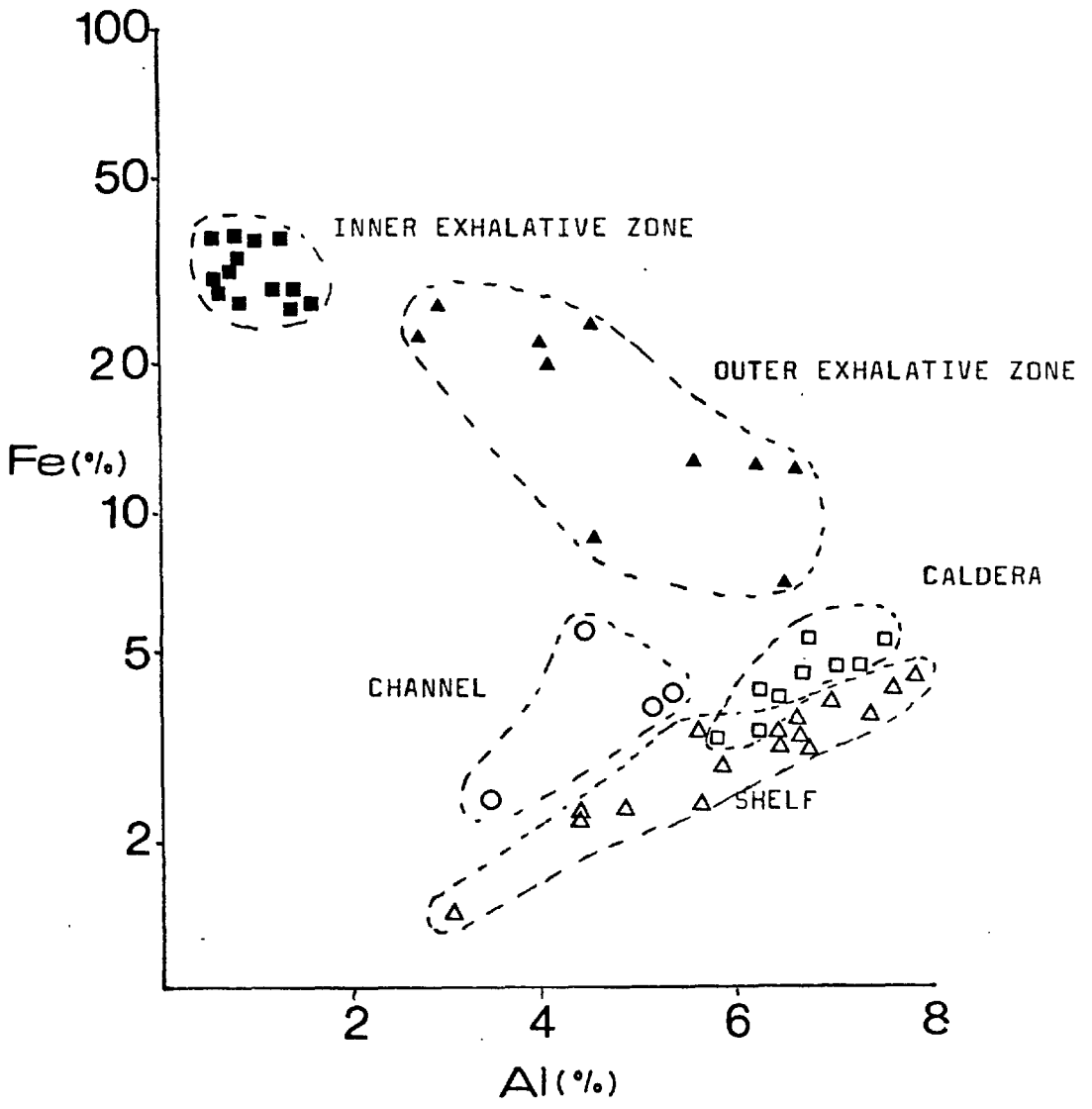


Figure 7.34 Scatter plot of iron against aluminium for all zones in and around Santorini.

CHAPTER 8 MARINE GEOCHEMICAL EXPLORATION

8.1 INTRODUCTION

Applied geochemical surveys are well-established in mineral exploration programmes on land (Hawkes and Webb, 1962; Levinson, 1974) and research over the last decade by the Applied Geochemistry Research Group and others has shown that such techniques are also applicable to offshore exploration (Tooms, 1969; Cronan, 1976b; Smith and Cronan, 1975b; Bignell et al., 1976). One of the objectives of the present investigation was, therefore, to assess the problems likely to be encountered in using geochemical techniques to explore the continental shelf of the Aegean Sea, and to examine hydrothermal deposits presently forming at Santorini in the context of exploration for similar deposits in ocean basins and older geological formations.

8.2 GEOCHEMICAL EXPLORATION ON THE CONTINENTAL SHELF

8.2.1 Introduction

Placer deposits are unlikely to occur on the continental shelf of the central Aegean Sea because although ultrabasic rocks with showings of chromite crop out in the area (e.g. on Andros) they are small and other appropriate source rocks are absent as far as is known. Consequently, bedrock mineralisation is the most likely target but dispersion haloes around outcropping lodes probably do not extend much beyond the immediate vicinity because solid particles liberated by submarine weathering are probably rapidly diluted on mixing with other components, particularly bioclastic material. Therefore, to have discovered anomalous samples related to submarine mineralisation with sample spacings typical of the reconnaissance survey (about one sample per km^2) would have been entirely fortuitous. Instead, the reconnaissance survey was designed to establish the background levels and natural variance of element concentrations, and to identify the normal factors governing the compositional variance. Such information is a prerequisite if significant anomalies (i.e. those related to mineralisation) are to be identified and distinguished from high concentrations resulting from other causes.

As anticipated, significant anomalies have not been found but background concentrations for each area have been established and these are given in table 3. Factors governing compositional variance are discussed in chapters 2 to 7 and reviewed in chapter 9. In addition, results of the reconnaissance survey reveal certain constraints to geochemical exploration on the continental shelf of the Aegean. They are discussed under two headings, based on the main aims of any geochemical exploration programme, namely 'significant anomaly recognition' and 'delineation of dispersion pathways'.

8.2.2 Significant Anomaly Recognition

Once found, it is necessary to distinguish between 'significant' (i.e. related to mineralisation) and false anomalies. False anomalies derive from a wide range of sources (see Levinson, 1974) but the most important on the Aegean shelf appear to be caused by scavenging of trace metals by manganese oxides and contamination. Anomalously high concentrations of trace metals due to scavenging by manganese oxides is a well-known problem in land-based exploration (see e.g. Chao and Theobald, 1976) and the marine environment is no exception. Off Andros, for example, high concentrations of Ni in some samples relates to scavenging rather than an ultrabasic provenance as initially suspected. Cu and, to a lesser extent, Zn may be similarly affected. To cope with the problem it is probably sufficient to simply be aware of the influence of manganese scavenging but it requires that Mn be measured if Ni, Cu or Zn are used as tracer elements.

Contamination is the bane of exploration geochemists working in areas of past or present mining activity. Anomalies related to new mineralisation and those from past mining are very difficult to distinguish. Ironically, shelves with the greatest mineral potential by virtue of the close proximity onshore of extensive deposits with a favourable geological structure (e.g. Sounion) are also those most likely to have surface sediments contaminated by the associated mining operations. Obviously, geochemical exploration is seriously hampered. Sounion is a good example but the problem may be common to many shelves with a similar mineral potential (e.g. Cornwall).

8.2.3 Delineating Dispersion Pathways

Establishing the significance of an anomaly is not particularly helpful if it is not then possible to delineate dispersion pathways and to pinpoint the potential source area. In stream sediment surveys, for example, a unidirectional flow regime simplifies the procedure considerably, but offshore the problem is much more complex. Reworking of sediments by wave and current action, for example, may modify or obscure dispersion pathways. Anomalies related to relict components would be particularly difficult to decipher because they could derive from a wide variety of sources including subaerial or shoreline erosion at a lower stand of the sea-level or relict alluvial deposits. In addition, much of the relict material may have been redistributed during or since the passage of the Holocene transgressing shoreline. Only terrigenous material derived since the last transgression appears to leave a detectable dispersion pathway. Off Kithnos, for example, lobes of very fine sand and silt trend approximately perpendicular to the shoreline and follow valleys in the shelf topography. Because Pb and Zn are held within a known modern component - mine waste - the distribution of these elements off Sounion also illustrate the dispersion pathways of modern terrigenous material (see figures 6.15 and 6.16) particularly well.

A final problem has already been mentioned - any dispersion haloes would be rapidly masked by dilution on mixing with other components of the sediment, particularly the calcareous fragments. One way to amplify the dispersion halo might be to leach the sample with acetic acid and thereby remove much of the diluting material. Unfortunately, anomalous metals in the dispersed particles may occur as secondary carbonates (e.g. cerussite) and would be soluble, therefore, in acetic acid and any trace of an anomaly removed.

8.2.4 Conclusions

In conclusion, it is evident that geochemical exploration for bedrock mineralisation on the continental shelf has severe limitations unless samples are collected at close-spacing near the possible outcrop of any mineralisation. Consequently, comprehensive geophysical survey is essential to establish areas of outcrop or thin sediment cover. Therefore, an appropriate basis on which to plan

an effective geochemical exploration programme on the continental shelf is a geophysical survey combined with an orientation survey of the type used in the present investigation.

8.3 HYDROTHERMAL DEPOSITS AT SANTORINI

8.3.1 Introduction

Despite the iron rich deposits of Santorini being of limited extent and low in base metal sulphides and manganese, a common genesis with other hydrothermal metalliferous deposits presently forming on the ocean floor (see Bonatti et al., 1972b; Bonatti 1975; Bignell et al., 1976a) and ancient stratiform massive sulphide, manganese and iron deposits (see Stanton, 1972b; Sillitoe, 1972) now present on land, suggest the deposits have a wider relevance than their extent and composition might imply. The lateral development of manganese and heavy metal zoning is a particularly significant feature. In this section the characteristics of the zoning of significance to mineral exploration are reviewed.

8.3.2 The Sulphide - Iron Oxide Association

Earlier investigations (Harder, 1964; Butuzova, 1966, 1969; Puchelt, 1972; Puchelt, et al., 1973) have considered the Santorini sediments rich in iron as a modern equivalent of the Lahn-Dill type of deposits (exhalative - sedimentary iron formation with a volcanic association - James, 1966). The influence of the physico - chemical environment on the development of iron facies is certainly well illustrated by the classic vertical sequence of oxide-carbonate-sulphide facies evident in the deposits. However, this investigation is mainly concerned with the upper section of this sequence (the oxide facies) and which may have greater application to exploration for massive sulphides.

Ferruginous horizons, enriched in silica and manganese, are often observed in association with stratiform base metal sulphide deposits (e.g. Kinkel, 1966; Stanton, 1972a and b; Sillitoe, 1972; Hutchinson, 1973; Stanton, 1976a; Halls et al., 1977). Specific examples recently described include the umbers of Cyprus (Elderfield et al., 1972; Constantinou and Govett, 1972; Robertson, 1975); the iron and manganese-rich units of the Hanesavo

beds overlying the sulphide mineralization on the islands of the Florida Group, B.S.I.P. (Taylor, 1974); the sedimentary iron formation associated with the Tynagh base metal sulphide deposit in Ireland (Russell, 1975); and the iron rich unit associated with the Broken Hill deposit in Australia (Stanton, 1976a and c). The only major base metal sulphide deposits so far discovered on the present ocean floor, i.e. the Red Sea deposits,are also associated with extensive iron rich horizons (Backer, 1973; Bignell et al., 1976b). In many ways the structure of the Santorini deposits are analogous in that an extensive iron rich unit overlies a carbonate/ sulphide deposit of limited extent. As at Santorini, the ferruginous horizons in the above deposits are often more extensive than the associated sulphides and consequently are of potential importance in the exploration for massive sulphides (Stanton, 1972b; Stanton, 1976a; Halls et al., 1977).

The genesis of the surficial ferruginous horizon at Santorini is described in this and previous (e.g. Harder, 1964; Butuzova, 1966; Puchelt, 1972; Puchelt, et al., 1973) investigations. Knowledge of the constraints governing the development of the iron-rich unit at Santorini may help to unravel the origins of similar units elsewhere, both in ancient deposits and modern deep-sea environments. The latter are not as easily monitored as these shallow deposits at Santorini.

A complex web of interactions govern the development and extent of the iron - rich unit. The composition of the hydrothermal fluids reaching the seafloor and the intensity of the hydrothermal activity (i.e. the flowrate of the hydrothermal fluids onto the seafloor) govern the amount of iron reaching the exhalative zone through hydrothermal activity. At Santorini, the composition of the waters immediately above the fumaroles seem to be typical of environments where the hydrothermal fluids consist of recirculating seawater containing abundant CO_2 and where the country rocks are mainly volcanic (see section 7.6.5). Elsewhere (e.g. the Red Sea) much larger amounts of iron may reach the seafloor because of more intense hydrothermal activity or the different nature of the hydrothermal fluids (see section 7.6.5), and this could lead to thicker and/or more extensive deposits.

Mildly acid and oxidising conditions within the inner exhalative zone cause the bulk of the iron to precipitate almost immediately and so the extent of the iron-rich unit depends upon the dispersion of the

particulate phases. Different physico-chemical environments, however, may increase the dispersion in the soluble form (e.g. strongly acid environments) or limit the development of oxides (e.g. reducing environments with available sulphide). Nevertheless, it is unlikely that such environments would extend far beyond the vicinity of the hydrothermal activity and so iron probably disperses over a wider area as particulates in most volcanogenic sedimentary-exhalative environments.

Mechanical dispersion of the particulate iron oxides is a response to the hydrodynamic regime and the local topography. The small areal extent and shallow depths of the embayments restricts the dispersion at Santorini but in deeper deposits a greater body of water will allow a more extensive dispersion if the particulate material can escape the confines of the exhalative area. In this context, the work of Sato (1972) on the change in density of ore-forming solutions on mixing with seawater is relevant. Mixed hydrothermal fluid/seawater solutions which are denser than seawater sink and tend to be confined in any local topographic depression. Dispersion of any particulate phases formed at this stage would be more difficult than for those derived from mixed solutions which are lighter than seawater (type III - Sato, op.cit.). The latter will rise, escape any confining topography and disperse over a wider area.

Finally, the development of distinct iron-rich units will also depend on the accumulation rates of other components of the sediment. In the outer exhalative zone at Santorini the accumulation of detrital material dilutes the iron abundance. In depositional environments which are deeper, but remain above the calcite compensation depth (e.g. the Mid-Atlantic ridge), carbonate accumulation may swamp other phases to such an extent that iron-rich units may only be found close to the hydrothermal source.

To summarise, extensive iron-rich units associated with massive sulphides may develop when and where:-

(1) sufficient iron is able to escape the sulphide zone when direct precipitation of sulphides (rather than the post-depositional development of sulphide horizons) is important;

(2) the topography, depth and hydrodynamic conditions allow the particulate iron oxides to escape the zone of sulphide accumulation and disperse over a wider area;

and (3) the accumulation of other components does not mask the accumulation of the iron minerals.

It also follows from the above discussion that massive sulphides may be present but without the extensive iron unit or, conversely, the iron unit may be extensive but the massive sulphides absent. Unfortunately, these features may reduce the potential of the iron-rich unit as an exploration tool (see Kinkel, 1966; Stanton, 1972*b* and 1976a).

8.3.3 Manganese in Sediments from Santorini

Certain features of the occurrence of manganese are of significance to mineral exploration. Before considering the exploration aspects, these features are reviewed by reference to the major zones. Vertical profiles of Mn with depth into the sediment are illustrated in figure 8.1, and, as Fe/Mn ratios are often used to characterize geochemical environments, they are shown in figure 8.2.

Inner exhalative zone : The iron-rich surficial unit is typically low in Mn with Fe/Mn in excess of 1100 (figure 8.2). Manganese is thought to be co-precipitated with hydrated iron oxides (section 7.6.6). Furthermore, data from Puchelt et al., (1973) suggest that two distinct layers occur in sediments of the inner exhalative zone (figure 8.1). An upper layer, low in Mn, includes the surficial layer examined as part of this investigation. Indeed, values of Fe and Mn presented by Puchelt et al., agree well with those of this investigation (figure 8.2). Apart from the upper oxide horizon, this low Mn layer also includes the more reducing lower horizons characterised by the predominance of ferrous iron.

In contrast to the upper layer, a highly oxidising lower layer is present in some cores (thought by this writer to be a pumice layer deposited just after the formation of the embayment but before extensive hydrothermal activity) and is characterised by a much greater Mn abundance of the order of ½% (figures 8.1, 8.2). It seems that hydrothermal solutions entering the deposits from below precipitate both iron and manganese in the highly oxidising lower layer. Unlike the upper layer (inverse relationship between Fe and Mn), a direct relationship between the Fe and Mn is apparent (figure 8.2) and no effective separation of iron and manganese is observed. A similar feature (i.e. lack of separation) was noted in other highly oxidising environments (e.g. Ferguson and Lambert, 1972).

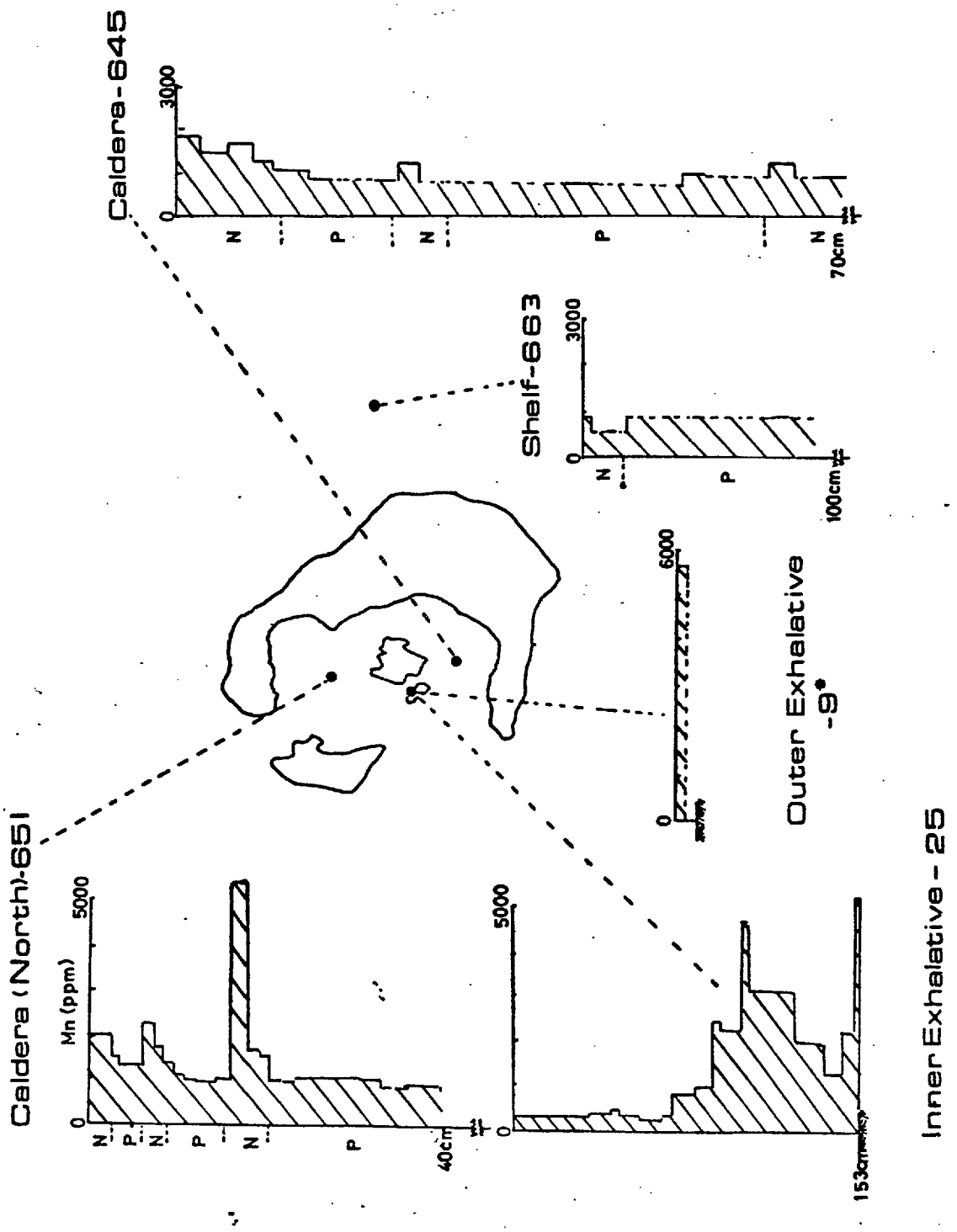


Figure 8.1 Profiles of manganese with depth into the sediment from each zone in and around Santorini. (N.B.core lengths not to scale)
Core 25 from Puchely et al.(1973).

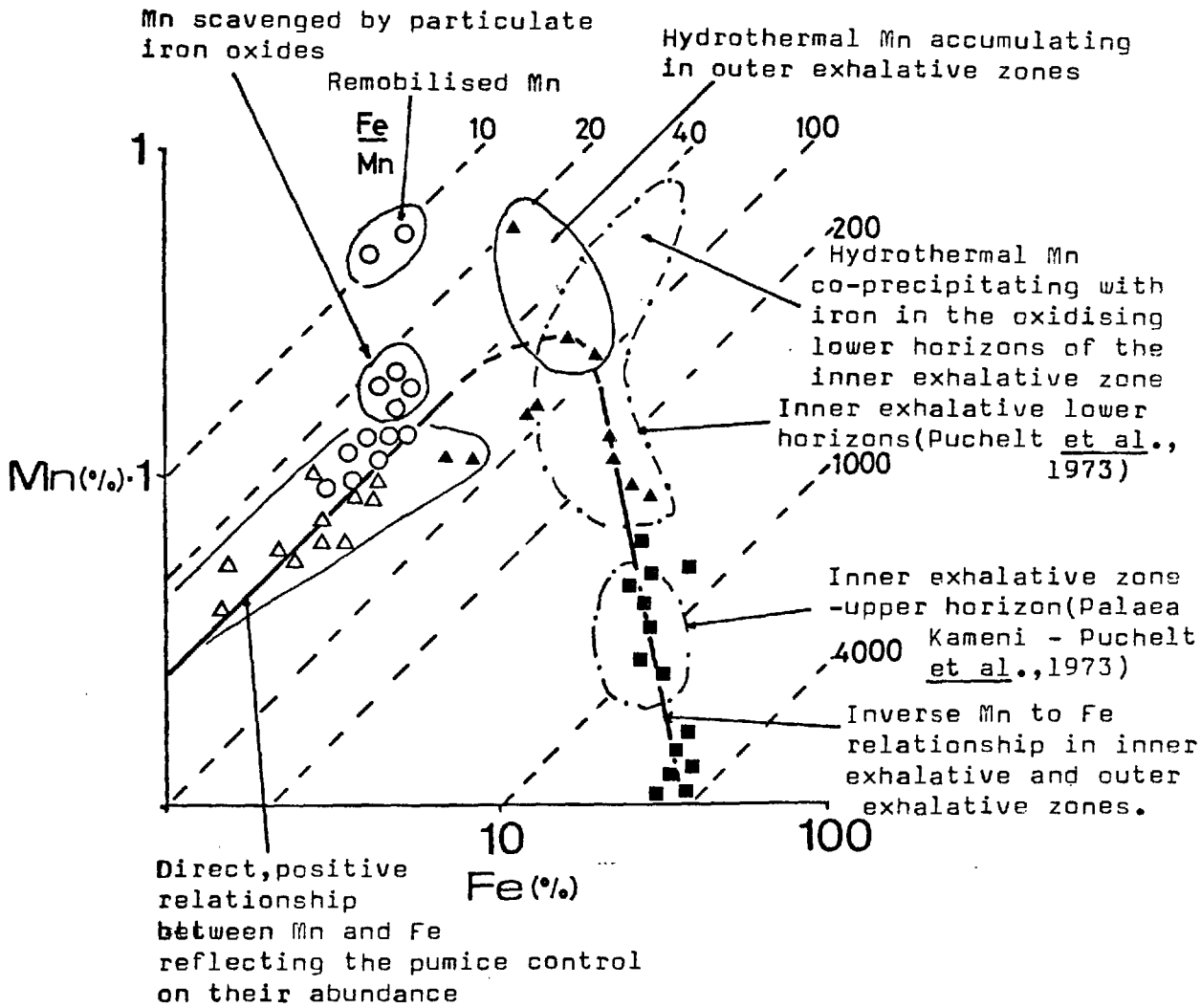


Figure 8.2 Scatter plot of manganese against iron for samples from all zones (■ inner exhalative, ▲ outer exhalative, O caldera, △ shelf).

Therefore, it seems that manganese derived from the hydrothermal solutions has a variable fate, depending on the sediment cover above the source conduit. Where the cover is thin or non-existent, as around the edges of the deposit, the Mn in solution enters almost directly into the water column where the prevailing physico-chemical environment allows the Mn to remain in solution unless co-precipitated by the hydrated iron oxides. Two possibilities exist when a thick sediment cover is present. Either (as already considered) the Mn enters a highly oxidising environment and precipitates with the hydrated iron oxides or, where a lower layer of pumice does not exist, manganese may enter directly into the reducing to mildly oxidising conditions of the lower horizons of the upper layer (the ferrous hydroxide/carbonate/sulphide horizons). In this case it remains in solution and passes into the water column. It's fate is then similar to Mn entering under the thin cover of sediment.

In the deposits of the inner exhalative zone, therefore, the manganese profile is either similar to that of core 25 (figure 8.1) in which a low Mn overlies a high Mn horizon, or simply a continuous low Mn profile. Naturally, further variations on this theme would be evident if highly oxidising layers occured at other locations within the sediment column.

Outer Exhalative Zone : Certain samples from the outer exhalative zone contain a distinct manganese oxide phase (see section 7.6.6b) and Fe/Mn is as low as 20 (figure 8.2). Soluble Mn is thought to be dispersed from the inner exhalative zone to subsequently precipitate as a distinct hydrothermal manganese oxide in the more oxidising environment of the outer exhalative zone.

Caldera Zone : Normal sediments from the caldera include samples with the lowest Fe/Mn (approx. 10). Core 651 (figure 8.1) exhibits a Mn profile considered to reflect precipitation at an oxidising interface following diagenetic remobilisation of the Mn (section 7.6.4). In general, Fe/Mn increases from 10 in the uppermost part of the "normal" horizons, through 20 in the lower parts, to 40 in the "pumice" sediments in which detrital Mn is the dominant phase (figure 8.2).

Shelf Zone : Under normal conditions, very little manganese from hydrothermal sources is thought to escape onto the shelf. Detrital pumice is the dominant control on Mn abundance but remobilization may be occurring to a minor extent in the "normal" sediments of the shelf (figure 8.1, see section 7.6.3).

From the point of view of ore genesis and mineral exploration, there are several points about the behaviour of manganese in these hydrothermal deposits that are worthy of note:

(1) Santorini deposits are a significant modern example of the separation of iron and manganese,derived from hydrothermal solutions, on the seafloor. This phenomenon is explained by a model formulated by Krauskopf (1957) and since invoked by many investigators of both modern and ancient environments. Pushkina suggested as much in 1966 (Pushkina, 1967) and has since been supported by the published work of Butuzova (1966, 1969) and Bonatti et al., (1972a). In fact the model example is better than these workers suggested. Perhaps their interest in the iron deposits caused them to overlook the sediments on the floor of the outer exhalative zone. High Mn from the caldera zone was thought to reflect selective dispersion but this investigation indicates that diagenesis is a more likely cause of the high Mn. The true area of accumulation of hydrothermal manganese precipitates selectively dispersed from the iron is the outer exhalative zone.

(2) An important feature of the iron rich units found in association with massive sulphide deposits is the development of distinct metal zoning (Fryer and Hutchinson, 1976). Typically, the zoning features a lateral sequence away from the sulphide deposits of Fe rich, Mn poor→Fe rich, Mn rich→Hostrock Fe, anomolous Mn→ Hostrock Fe, background Mn (i.e. distal enrichments of manganese in the iron-rich unit, and an extensive manganese halo). Taylor (1974) reports such a sequence in the Hanesavo beds overlying the massive sulphides found on islands of the Florida Group, B.S.I.P, and so also do Derry et al., (1965) and Russell (1975) for the iron formation associated with the Tynagh massive sulphide deposit. At Meggan the iron rich unit is limited in extent but there is an extensive Mn halo (Gwosdz and Krebs, 1977). In the modern Red Sea deposits Bignell et al. (1976b) describe a similar dispersion of manganese resulting in an halo extending upto 10km from the deposit. At Santorini, manganese is also distally enriched in the iron-rich unit. This suggests that:-

(a) the model derived to describe the observed distribution of iron and manganese may be applicable to other deposits exhibiting similar zoning;

and (b) such Mn zoning may be a common feature of the volcanogenic exhalative - sedimentary (submarine hydrothermal)

ore-forming process and consequently important in exploration for such deposits (Cronan, 1976b).

(3) Equally impressive is the range of manganese deposits occurring within the limited geographical area of the caldera. These include hydrothermal deposits of both iron-rich and iron-poor varieties (i.e. without and with separation from iron) and diagenetic deposits. Given manganese in similar abundance to the ore-forming solutions of the Red Sea and Matupi Harbor (see section 7.6.5 and table 13) it is not impossible to envisage a range of manganese ore deposits forming within the caldera - perhaps varying from hydrothermal deposits close to the source to diagenetic deposits in deeper water.

(4) This same variability in the type of manganese deposit also indicates that a certain amount of care should be taken in interpreting dispersion haloes. They may be invaluable in the exploration for both modern and ancient deposits but checks should be made to ensure that the anomalies are due to hydrothermal dispersion and not to secondary enrichments through diagenetic processes. This problem may be further compounded by high background detrital manganese or hydrogenous manganese in areas of low sediment accumulation rates.

8.3.4 Heavy Metal Zoning

Like manganese the selective dispersion and consequent zoning of heavy metals within the iron-rich unit may also be a useful exploration guide. Russell (1975), for example, describes zones of Pb and Zn enrichment in the distal manganiferous layers associated with the Tynagh massive sulphide deposit. Distal enrichment of Cu, Zn and Hg in the iron-rich unit is also a feature of the Red Sea deposits (Bignell et al., 1976b). Although the abundances are, generally, much lower, a similar zoning of heavy metals related to hydrothermal activity occurs at Santorini.

A detailed discussion of the dispersion and consequent zoning of elements at Santorini is presented in section 7.6.7 and only the main points are reviewed here. Figure 7.33 illustrates the element zoning using the HCl-soluble element against depth profiles, and figure 8.3 summarises, schematically, the element zones within the surficial iron-rich unit.

Heavy metal zoning related to hydrothermal activity develops because of the scavenging action of the scavenging phases present.

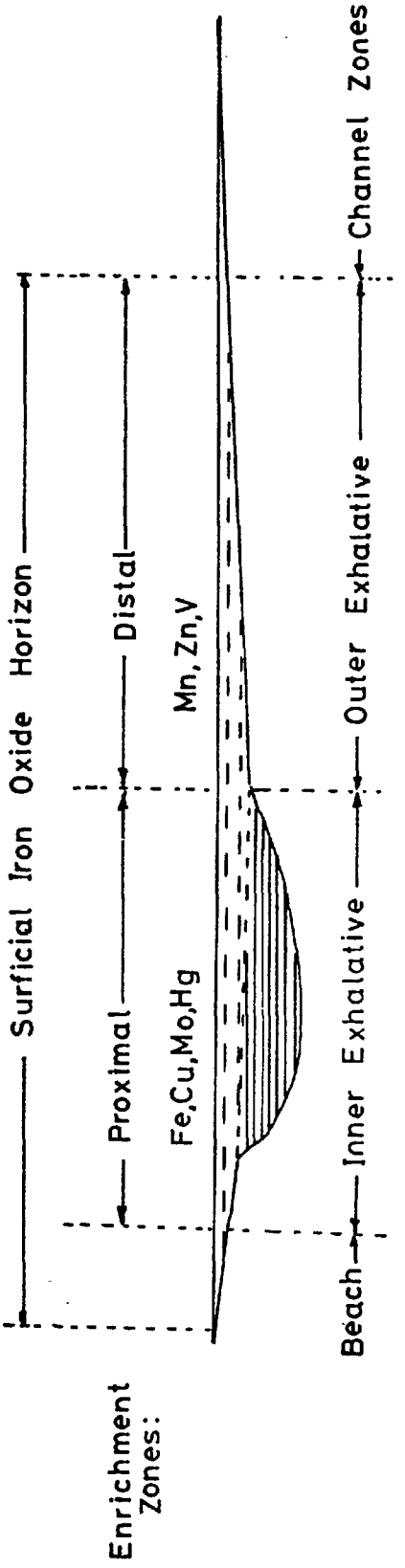
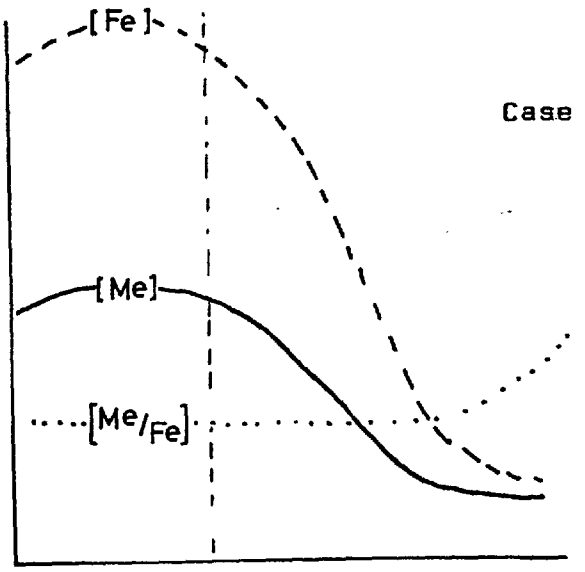


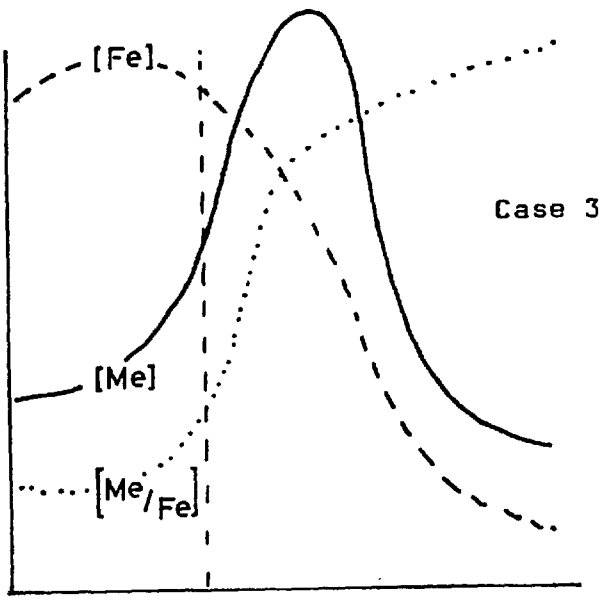
Figure 8.3 Schematic zoning of elements in the surficial iron-rich horizon.

At Santorini the iron oxides are the major scavenging phase but elsewhere manganese oxides could be equally or more important. The concentration of the scavenged elements and, therefore, the consequent element zoning is a function of the amount of the scavenging phase accumulating in the sediments and the scavenging ratio (see section 7.6.7b) of the accumulating scavenging phase (see figure 8.4). The scavenging phase abundance decreases with distance away from the fumaroles (Fe profile in figure 8.4) and, in these circumstances,'proximal enrichment' occurs when the hydrothermal influence is (1) small and element mobility is limited (case 2 - figure 8.4) (e.g. Cu, Mo, Pb, Sc and Hg); or (2) large, in which case solubility rather than scavenging is the main constraint on mobility (e.g. Fe). 'Distal enrichment' occurs when there is (1) no hydrothermal influence and enrichment results simply from scavenging from normal seawater (case 1 - figure 8.4) (e.g. Cr) - this feature may be particularly significant for deeper volcanogenic sedimentary - exhalative environments (e.g. the Red Sea and mid-oceanic ridge or rise systems) where the dispersion of the particulate scavenging phase may be widespread; (2) a moderate hydrothermal influence and moderate mobility (case 3 - figure 8.4) (e.g. Zn and V); and (3) a substantial hydrothermal influence where, once again, solubility is more important than scavenging but the gradual change in the physico-chemical environment allows the element to pass to the outer zones before precipitation (e.g. Mn).

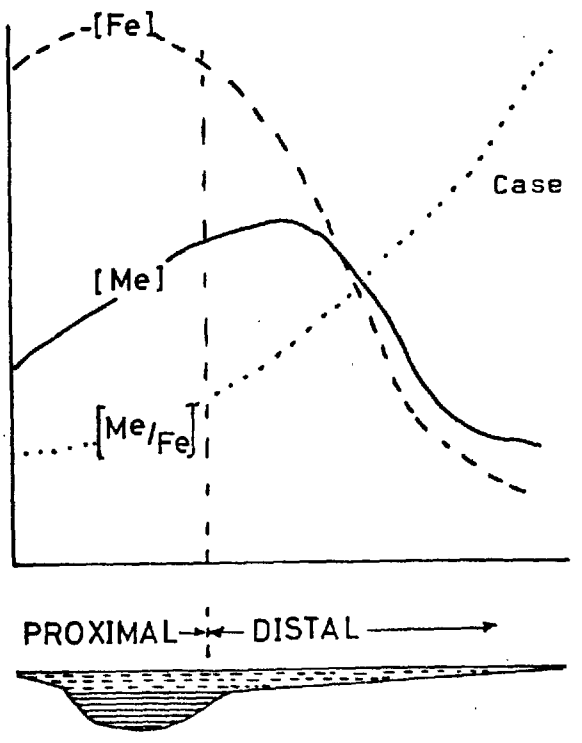
In terms of exploration for other modern deposits, these observations may have great potential value (Cronan, 1976b). In the Red Sea, for example, dispersion haloes are many times the extent of the deposits (Bignell, et al., 1976b). Therefore regional geochemical surveys may be a useful way of exploring for volcanogenic sedimentary-exhalative deposits on the ocean floor. Several cautionary points should be borne in mind, however. Firstly, extensive iron or manganese horizons are not necessarily associated with massive sulphides (Kinkel, 1966; Stanton, 1972a and 1976a; section 8.3.2). Dispersion haloes may well pinpoint the source of the hydrothermal activity but sulphides may not be present. Conversely, sulphides may be forming but not the extensive haloes. Secondly, care is required when interpreting manganese haloes because of the variety in the forms of manganese accumulating (section 7.7.3).



Case 2 - Elements with limited mobility(e.g. Cu)and a fairly constant metal to scavenging phase ratio - proximal enrichment



Case 3 - Elements with a mobility greater than iron(e.g. Zn)have an increasing metal scavenging ratio - distal enrichment



Case 1 - Normal seawater supply of scavengeable elements and the scavenging ratio increases away from the fumaroles through increased contact time - small distal enrichment(e.g.Cr).

Figure 8.4 Schematic models for the development of element zoning through the scavenging action of iron oxides derived from hydrothermal solutions.

CHAPTER 9

GEOCHEMICAL INVESTIGATIONS OF RECENT SEDIMENTS FROM THE AEGEAN SEA: A REVIEW OF THE RESULTS AND MAIN CONCLUSIONS

9.1 INTRODUCTION

Sediments from the Aegean Sea have been investigated by a variety of geochemical and sedimentological techniques and the results and main conclusions are reviewed in this final chapter of the thesis. At the outset, the main objectives were to establish the general levels of heavy metals, to identify the main controls on the chemical composition, and to delimit areas of anomalous composition. The areas studied fall into two broad categories: continental margin sediments from off the southern tip of the Attica peninsula (Sounion), and the islands of Kithnos, Serifos, Andros and Naxos, including an additional survey off Sounion to investigate the impact of onshore mining on the chemical composition of the adjacent marine sediments; and sediments from in and around the caldera of Santorini to assess the influence of hydrothermal activity on the geochemistry of the sediments, including the implications for mineral exploration. Each category is reviewed separately, beginning with the continental margin sediments.

9.2 CONTINENTAL MARGIN SEDIMENTS

In each area, the first task was to assess the nature of the seafloor topography using bathymetric profiles recorded during the sampling programme. The open shelves (i.e. Kithnos, Serifos, Andros and Sounion) are narrow, and range in width (based on the average distance from the shoreline to the 170m isobath) from 2km off Andros to 7km off Sounion. Naxos, in contrast, is part of a much wider continental shelf (see figure 1.1). Sediments were sampled at depths ranging from 30m to greater than 300m but in no single area was the complete depth range covered because of consideration for navigational safety which restricted sampling to beyond ½km from the shoreline. Off Kithnos, for example, the seafloor plunges steeply so that even at ½km from the shoreline

depths exceed 90m. In contrast, the inner shelf off Sounion is much wider and it was possible, therefore, to sample shallower sediments. Despite differences in seafloor morphology, there appear to be common topographic zones:

less than 60m	- a gently sloping inner shelf. (Off Kithnos, Andros and Serifos this zone is very narrow and has not been sampled.)
60m to 100m	- mid-shelf slope, characterised by steeper slopes and an irregular topography. (Off Naxos this is the deepest part and forms a basin).
100m to 120m	- outer shelf terrace, with gentler slopes and valleys and ridges trending approximately perpendicular to the present shoreline.
120m to 170m	- shelf edge, with steep slopes (especially off Andros where this zone extends beyond 300m), and a complex relict morphology resembling the present shoreline.
greater than 170m	- flat - lying offshore zone off Kithnos and Serifos. In other areas the shelf edge extends beyond 170m.

A sedimentological framework within which to discuss the geochemistry of the deposits was created using textural analyses, combined with the qualitative examination of the main components of the samples. As on continental margins worldwide, the deposits are mixtures of relict, reworked, and more recent components, and may be described in terms of the relative proportions of five textural sub-populations, which appear to be common to all areas:

(1) Mud, with a mode ranging from coarse silt on the continental shelf to fine silt offshore, suggesting progressive sorting during transport across the continental margin. It comprises modern, terrigenous material and is equivalent to the 'modern mud blanket' found on other margins (Curray, 1965). Mud accumulation mainly occurs in three zones: on the inner shelf, close to the source of terrigenous sediment; on the outer shelf terrace, below about 100m (slightly shallower off Naxos); and offshore, deeper than approximately 170m. However, the amount

of terrigenous material supplied to an area, the prevailing energy regime, and the morphology of the shelf (particularly the width of the various depth zones), modifies the overall pattern. Although mainly terrigenous, the mud sub-population offshore also contains an approximately equal amount of biogenic sediment.

(2) Very fine sand, with a mode of about 3phi, is also thought to represent terrigenous material deposited at some time during the Holocene. It is most abundant in two areas, coincident with the coarse silt zones: on the inner shelf, close to the source of terrigenous material; and on the outer shelf terrace. When the outer shelf very fine sands accumulated is difficult to estimate - they could represent either modern, terrigenous sediment which has by-passed the narrow inner shelf, or similar sediment deposited at a lower stand of the Holocene sea level. Detrital minerals (i.e. the chlorite-mica group, quartz, and feldspar) are the main components of the very fine sand off Kithnos, Serifos and Andros, and so deposits from these areas containing a large proportion of this sub-population are classified as detrital sands (i.e. less than 50% $CaCO_3$). At Naxos and Sounion, however, marbles and other calcareous rocks form a large part of the local geological terrain and so the terrigenous very fine sands also contain detrital carbonate minerals. Therefore, although texturally similar to the detrital sands, deposits with a large proportion of this sub-population off Sounion and Naxos classify as bioclastic sands.

(3) Fine sand, with a mode around 2phi, is a significant fraction of most shelf samples. At depths greater than 90m, the constituents are thought to be either relict or reworked to form a transgressive sand sheet (Curray, 1965) with which more recent sediments are mixed. The same sub-population at depths of less than 60m probably comprises a much larger proportion of modern sediment.

(4) Medium to coarse sand, with a mode coarser than 1.5phi, is mainly bioclastic material. Above 120m, it probably contains a large proportion of more recent bioclastic material (particularly coralline algae fragments), and it is most abundant close to the coralline algal communities which develop on the steeper slopes (e.g. the mid-shelf slope), topographic highs, and other elevated parts of the shelf, and which act as a source of more recent

bioclastic material. Deeper than 120m, the medium-to-coarse sand probably contains a greater proportion of relict sediment.

(5) Gravel, is a fifth sub-population but which was removed before the textural analyses. Nevertheless, it is an important fraction of some samples and mainly consists of branching, encrusting, or nodular coralline algae and is most abundant on elevated or current-swept (e.g. Sounion, eastern sector) parts of the shelf.

The distribution of sedimentary facies reflects the mixing of the five sub-populations and reveals a broad depth zonation, despite a considerable lateral range in sediment facies within each depth zone. The zones are as follows:

less than 60m	- fine bioclastic sands, terrigenous very fine sands and coarse silts mixed with fine bioclastic sands, and calcareous muds (coarse silt) in areas where there is a large terrigenous input and/or a more sheltered environment. In elevated or current-swept areas - algal nodules, 'maerl' sands and gravels, rock outcrops occur.
60m to 100m	- bioclastic (often 'maerls') sands and gravels, algal reefs.
100m to 120m	- medium/coarse bioclastic sands around elevated areas, transgressive fine bioclastic sands, lobes of terrigenous very fine sand and coarse silt mixed with the transgressive sands, calcareous muds (coarse silt - Naxos), and algal nodules in current-swept areas (Sounion, eastern sector).
120m to 170m	- fine and medium/coarse bioclastic sands, both dominantly relict and with a range in the proportion of mud (gradually increases with depth).
greater than 170m	- calcareous muds (fine silt dominant) with a range in the proportion of relict medium/coarse bioclastic sand.

Equivalent sedimentary facies have been found at similar depths in other parts of the Mediterranean (see e.g. Blanc, 1968; Caulet, 1972).

Geochemical studies reveal that the following six factors govern the overall chemical composition of the continental margin deposits from the Aegean Sea, and are common to most areas:

(1) Dilution of elements held within the terrigenous component by $CaCO_3$ poor in all elements except Ca, Mg and possibly small amounts of 'non-detrital' trace elements. The $CaCO_3$ mainly derives from the biogenic compoent of the sediments but provenance may also play a small part because terrigenous $CaCO_3$ may be a significant component in areas where the local geological terrain includes marbles and other calcareous rocks (e.g. Naxos and Sounion).

(2) The range in mineralogical composition of the terrigenous component, particularly the relative proportions of quartz (depleted in all the elements studied), feldspar (depleted in all elements except Al and Ti), the chlorite-mica group (containing Fe, Mg, Al, Ti, Cu, Zn, Ni and Cr), and dolomite (containing Ca and Mg). The relative proportion of these minerals depends partly on:

(a) differences in the sedimentological environments and, hence, texture - quartz and feldspar are concentrated in the sandy samples whereas the chlorite-mica group are preferentially concentrated in the muds;

and (b) differences in provenance - at Kithnos, Serifos, and Andros mica-schists dominate the local geological terrain and the terrigenous mineral assemblage comprises quartz, feldspar, and the chlorite-mica group, whereas in areas where marbles dominate (e.g. Naxos) the mineral assemblage comprises quartz, feldspar, and dolomite, with only traces of the chlorite - mica group.

(3) Hydrogenous manganese 'oxide' accumulation and the associated scavenging of trace elements. Lower sediment accumulation rates appear to equate with more hydrogenous Mn 'oxides' and, accordingly, the calcareous muds from the deeper waters offshore contain the highest concentrations of Mn. Nevertheless, it has not been possible to assess the significance of other factors which could also affect the accumulation of Mn 'oxide', such as the availability of appropriate nucleii

for precipitation or the oxidation potential of the depositional environment - these might be interesting areas for further research. Cu, Ni and Zn are often associated with the Mn 'oxide' (e.g. the calcareous muds off Andros) and are probably scavenged from the water column.

(4) Authigenic iron mineral formation in the relict component of the sediments. Certain bioclastic sands from deeper than about 80m (especially those from deeper than 120m) contain an 'excess Fe' attributed to the formation of authigenic iron minerals in the relict component of the deposits, particularly foraminiferal tests.

(5) Mineralogical composition of the biogenic component. The amount of Mg found in the deposits depends partly on the mineralogical composition of the biogenic component, particularly the relative proportions of magnesian calcite, calcite and aragonite. The deposits off Kithnos, for example, contain a larger proportion of coralline algae (magnesian calcite) and are richer, therefore, in Mg than the equivalent deposits off Sounion which contain a larger proportion of shelly material (calcite/aragonite).

(6) An unidentified 'non-detrital' contribution to the abundance of the trace elements, particularly Cu, Zn and Pb. The origins of the 'non-detrital' contribution to the abundance of the trace elements is a seldom clear. Often it appears to be associated with 'non-detrital' Mn but may also derive from adsorption on fine-grained material (including organic matter) or as lattice-held trace elements within the biogenic components.

Differences in the chemical composition of samples from both within and between areas are mainly a function of the different sedimentological environments sampled - calcareous muds, for example, contain a larger proportion of fine-grained chlorite-mica minerals and hydrogenous Mn 'oxides' and so tend to be enhanced in many of the elements studied. In contrast, Naxos deposits lack both authigenic iron minerals and hydrogenous Mn 'oxides' because these shallower deposits contain a smaller relict component and have greater sediment accumulation rates. Nevertheless, provenance accounts for certain differences in the chemical composition, particularly the paucity of the chlorite-mica group in Naxos samples because of the absence of the appropriate source rocks nearby.

Provenance is most significant, however, off the southern tip of the Attica peninsula (Sounion) where markedly enhanced levels

of Pb and Zn derive from the adjacent onshore mining district of Laurium. Concentrations are highest in the beach and near-shore deposits and gradually decrease offshore. Nevertheless, mine waste pervades most of the continental shelf in the area and the dominant dispersion pathways appear to follow valleys in the shelf topography. Selective leaching indicates that much of the Pb (but less Zn) may be in a form available for uptake by the marine biota which, in turn, suggests that the dispersal of mine waste into the adjacent marine environment represents a potential pollution hazard. Only direct analysis of the appropriate marine biota is able to establish the degree of contamination.

Finally, in the context of marine mineral exploration, the use of applied geochemical techniques to explore for bedrock mineralisation on the continental margin of the Aegean Sea has several limitations. Dispersion pathways are complicated and dispersion haloes around lodes are likely to be limited in extent. Consequently, geochemical surveys should centre on areas of outcrop or sub-outcrop. An effective geochemical survey should be preceded, therefore, by geophysical surveys to establish appropriate target areas. In addition, non-significant anomalies arise from a variety of causes including the scavenging of trace elements by manganese 'oxides' in zones of lower sediment accumulation rates, and contamination from previous mining activity. The latter problem is, of course, most evident off Sounion.

9.3 SEDIMENTS FROM IN AND AROUND THE CALDERA OF SANTORINI

Five bathymetric zones form the framework for the discussion of the geochemistry of deposits from Santorini. Each has distinctive sedimentological and geochemical characteristics and these are reviewed below:

Inner Exhalative Zone sediments are the major iron deposits and show a classical vertical sequence of facies characteristic of decreasing oxidation potentials - an 'oxide' surface layer overlies siderite and ferrous hydroxide horizons, with local patches of sulphide in the presence of sulphate reducing bacteria or volcanic H_2S. Other components include rock and pyroclasts, vivianite, and opaline silica. The geochemistry of the surficial deposits is dominated by the accumulation and scavenging action

of hydrothermal iron 'oxides' which contribute Fe, Mn, Cu, Zn, Pb, Mo, V, Sc and Ba. Al and Ti derive from small amounts of pumice and the concentrations of Si reflect the combined influence of pumice and hydrothermal activity.

Outer Exhalative Zone sediments reflect the decreasing influence of hydrothermal activity and the increasing proportions of detrital, volcanic material. The deposits are mixtures of iron 'oxides', volcanic sands and pumice, with only small amounts of biogenic carbonates and organic matter. The chemical composition of the deposits depends upon the relative proportions of these main components: iron 'oxides' supply Fe, Mn, Zn, Mo and V; detrital components - Al, Ti, Si, K, Ca, Mg, Mn, Zn and Ba; and bioclastic material - Ca, Mg and Sr. In addition, this is also the zone in which Mn derived from hydrothermal solutions precipitates.

Channel Zone sediments comprise bioclastic material, organic debris, volcanic sands and lapilli pumice. The pumice and volcanic sands supply Al, Ti, Si, K, Mn, Zn, Mo, Ga and Ba; the carbonates Ca, Mg and Sr; and an unidentified hydrogenous component Mn, Pb, Ga, Ba and Li.

Caldera Zone sediments comprise two main facies: pumice muds deposited rapidly at times of volcanic disturbance, and pre- and post-volcanic 'normal' deposits. 'Normal' sediments are a mixture of pumice derived from the erosion of the 'upper pumice' strata, biogenic carbonates, organic matter, and iron oxides. At the surface brown muds are typical of 'normal' sediments, whereas at depth they are modified by the post-depositional development of mildly reducing conditions. Iron and manganese derive from the dispersion of particulate phases from the exhalative zones. Subsequent remobilisation of Mn produces enriched layers at the tops of 'normal' horizons in the sediments from the northern basin. The combined influence of pumice and the scavenging by iron 'oxides' govern the abundance of V, Cu, Pb, Ni, Cr, Ba and Zn, whereas biogenic carbonates contribute most of the Ca, Mg and Sr.

Shelf Zone sediments exhibit a lateral sequence of facies from volcanic sands nearshore, through coralline algal deposits, to beige muds in deeper water. Underlying these deposits are extensive pumice horizons derived directly or indirectly (e.g. slumping) from the 1400 B.C. eruption. The geochemistry of the deposits is governed by the relative proportions of three end members: pumice (Al, Fe, Ti, Cu, Mg, V, Zn, Cu, Sc and Ga); biogenic carbonates (Ca, Mg, Sr);

and an unidentified terrigenous component within the 'normal' sediments (Ni, Cr, Ba). Pumice also supplies Mn but remobilisation may occur to enrich the surface layers of the 'normal' sediments.

Analysis of filtered water samples from the exhalative and channel zones confirms that the hydrothermal solutions contribute Fe, Mn, Zn and small amounts of Cu and Pb, to waters of the inner exhalative zones. In addition, Mn and Zn appear to be more mobile than Fe and Cu. Any iron escaping from the inner exhalative zone is in the form of particulate 'oxides', whereas Mn may also be in a soluble form. Any Mn leaving the outer exhalative zone, however, is also more likely to be in the form of particulate 'oxides'.

A significant geochemical characteristic of the exhalative zone deposits is the enrichment of Fe, Mn and the heavy metals in distinct zones, stemming from the selective dispersion of elements derived from the hydrothermal solutions. Solubility constraints govern the separation and zonation of Fe and Mn: under the prevailing physico-chemical conditions Fe precipitates rapidly in the inner exhalative zone, whereas some of the Mn passes into the more oxidising conditions of the outer exhalative zones before precipitation. In contrast, heavy metal zoning is a function of the increasing capacity of iron oxides to scavenge the heavy metals with distance away from the fumaroles, and the amount of heavy metal available for scavenging in any zone. Enrichment in the inner exhalative zone results where there is a small hydrothermal contribution but limited mobility (Cu, Mo, Pb, Sc, Hg). In the outer exhalative zone, enrichment occurs under two sets of circumstances: no hydrothermal contribution and simple scavenging from seawater (Cr); or a moderate hydrothermal contribution and moderate element mobility (Mn, Zn and V).

A common genesis with volcanic-exhalative massive sulphide, manganese and iron deposits suggests that the present study can help clarify the processes involved in their formation and the formation of features useful in exploration, particularly the extensive iron-rich horizons, primary dispersion, and the associated metal zoning. Extensive iron-rich units, rich in silica and manganese, are often associated with both ancient and modern massive sulphide deposits. Because they extend beyond the limits of the orebody itself, they are a useful exploration tool. They develop where sufficient iron is able to escape during sulphide formation; the topography, depth, and hydrodynamic conditions permit the particulate iron oxides to escape the immediate vicinity of the

hydrothermal activity and disperse over a wider area; and the accumulation of other components does not mask the accumulation of the iron. It follows that the massive sulphide may exist but not, necessarily, the extensive iron-rich unit. Conversely, sulphides may be absent despite the existence of an extensive iron-rich unit. Both features limit the potential of the iron-rich unit as an exploration tool.

Iron, manganese, and heavy metal zoning within the iron-rich unit is also a common feature of both modern and ancient volcanic-exhalative deposits and may be useful for exploration. The mechanisms involved in the development of zoning are reviewed above. There are two main zones:

'proximal' enrichment - Fe, Cu, Mo, Pb, Sc, Hg

'distal' enrichment - Mn, Zn, V

Because these dispersion haloes seem to be a common feature of deposits presently forming on the ocean floor, regional geochemical surveys may be an effective technique for exploring for associated massive sulphides. When interpreting Mn haloes, however, it is necessary to distinguish between anomalies related to primary dispersion and non-significant anomalies related to diagenetic or hydrogenous processes.

Finally, apart from Santorini being a significant example of the separation of Fe and Mn, the range of possible Mn deposits within the environment of a volcanically active, submerged caldera is impressive. Iron-rich and iron-poor varieties of hydrothermal Mn deposits occur close to the hydrothermal activity, and diagenetic deposits in deeper waters.

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APPENDIX A SAMPLE COLLECTION AND PREPARATION

The sediment and water samples used in this investigation were collected during three cruises to the Aegean Sea:aboard the R.R.S.SHACKLETON in 1972 and 1974,and aboard the Hellenic Ship PLIAS in 1973.Sample locations were fixed by a combination of radar and gyro-compass,supplemented by sextant angles close to the Sounion shoreline(1973 cruise).Precision depth recorder (P.D.R.)profiles recorded during the sampling programme aboard SHACKLETON were used to produce bathymetric charts for each area with depths corrected according to Mathews'tables(Mathews,1937).

Bulk surface samples were recovered with a Shipek grab and stored onboard in sealed plastic bags with small amounts of sea-water.Beach samples from Sounion were collected by hand and a hand-held snapper grab was used to collect samples from the shallow zones between the Kameni Islands,Santorini.Before storage any stratification within the often almost undisturbed sample was noted,plus a brief description of the sample.

In the laboratory samples were oven-($40^{o}C$) or air-dried, mixed,coned and quartered,and sub-sampled using a non-contaminating splitter.Subsamples for chemical analysis were ground to a fine powder in an agate-tema mill and stored in plastic vials.For reference and textural analysis subsamples were stored in paper bags.

Cores were obtained with a U.M.E.L.gravity corer containing a plastic liner.Once on deck the liner was removed from the core barrel,capped,and sealed.On the 1972 cruise cores were then frozen and stored but this was not possible on other cruises and so the cores were not frozen until reaching the laboratory.In the laboratory the frozen cores were split by cutting the liner with a circular saw and splitting the core with a pallette knife. After thawing the cores were described and colour coded according to the Munsell system.One half of the core was kept for reference and the other half sampled.Subsequently samples were oven-dried, ground to a fine powder in an agate-tema mill,and stored in plastic vials awaiting analysis.

Seawater from the shallow zones between the Kameni Islands was sampled with N.I.O.reversing water bottles.After collection the samples were filtered through a .45 micron filter,acidified (pH 1) with redistilled concentrated HNO_3,and stored in polythene bottles.

APPENDIX B ANALYTICAL TECHNIQUES

BULK CHEMICAL ANALYSES

Ca,Mg,Fe,Al,Ti,Pb,Zn,Cu,Ni,and Cr were analysed by atomic absorption spectroscopy (A.A.S.) following a combined HF-$HClO_4$-HNO_3 digestion involving a double fuming with $HClO_4$.Either 100 mg or 200 mg of finely ground powder was attacked by 10ml HF, 3ml HNO_3,and 3ml $HClO_4$.The P.T.F.E. beakers were then warmed on a hot-plate for approximately 12 hours and until fuming stopped.A further 2ml of $HClO_4$ was added and the beakers returned to the hot-plate until fuming once again ceased.Once cool,the residues were taken up in 6M HCl , made upto volume to give a final solution of approximately 1M HCl,and aspirated through a Perkin-Elmer 403 atomic absorption spectrograph.Normally,about 100 samples were analysed in each batch but approximately 20% were blanks,standards or duplicates.

Unfortunately,the continental margin samples contain large amounts of Ca which can interfere with the analysis of some trace elements.To estimate the Ca interference in each batch,known solutions of Ca were aspirated along with the other samples and the absorption on the Cu,Pb,Zn,Ni,and Cr wavelengths recorded. For Cu,Zn,and Cr this interference was not significant but for Pb and Ni it caused considerable enhancement.Consequently,it was necessary to correct the observed readings for Pb and Ni and this was achieved through correction curves derived from the aspiration of known solutions of Ca and measuring the equivalent absorption on the Pb and Ni wavelengths.For each sample,therefore, the apparent concentration due to Ca interference was subtracted from the observed concentration to give the accepted value.

To check the effectiveness of this procedure,five samples from Sounion were treated in the same way but the Pb and Ni recovered by solvent extraction using APDC-chloroform.This approach is more accurate than the routine analysis and should give a good estimate of the 'true' concentrations of Pb and Ni.The results shown in table B.1 are the means of duplicate analyses.Blanks and known solutions were included in each batch to check for contamination and to ensure complete extraction.Cu and Zn were also determined out of interest.From the data given in table B.1 it is evident

TABLE B.1 Comparison between the concentration of elements determined by solvent extraction and routine analysis.

Sample Number	Ni		Pb		Zn		Cu	
	1	2*	1	2*	1	2	1	2
p-11	45	50	85	80	73	77	13	12
p-24	62.5	60	153	145	160	134	18	20
p-33	50	45	320	305	326	345	19	20
p-46	75	80	198	185	209	173	18	17
p-52	50	45	375	395	302	285	17.5	17.5

1 - concentration using solvent extraction

2 - routine analysis

2*- routine analysis with Ca correction

TABLE 8.2 Accuracy of chemical analysis by A.A.S.

		Standards				
		W1	BCR-1	992001	992002	992003
Ca	a.	6.85	4.90	29.03	19.80	19.05
	b.	6.00-7.70	4.00-5.30	27.0-32.0	17.8-22.0	17.0-20.8
	c.	7.83	4.95	-/25.6	-/18.4	-/16.8
Mg	a.	4.06	2.21	2.04	2.52	2.57
	b.	3.60-4.60	2.00-2.50	1.80-2.30	2.30-2.80	2.40-2.80
	c.	3.99	2.09	-/-	-/-	-/-
Fe	a.	7.98	9.81	1.60	2.89	3.02
	b.	7.70-8.30	9.00-10.4	1.40-1.70	2.50-3.10	2.68-3.40
	c.	7.76	9.37	1.50/1.63	2.58/2.93	2.80/2.93
Al_2O_3	a.	14.40	13.57	3.77	7.68	7.85
	b.	13.1-15.3	12.9-14.0	3.30-4.00	7.15-8.50	7.00-8.80
	c.	15.00	13.61	3.70/3.40	7.60/7.05	8.20/7.10
TiO_2	a.	1.25	2.60	0.33	0.49	0.49
	b.	1.16-1.33	1.80-3.17	.25-.40	.33-.60	.37-.58
	c.	1.07	2.20	.30/-	.52/-	.47/-
Mn	a.	1165	1300	1200	3200	392
	b.	1120-1200	1170-1600	1000-1400	2800-3600	360-460
	c.	1278	1406	1200/1300	3400/3600	400/400
Cu	a.	118	21	33	41	28
	b.	114-125	18-24	28-36	38-45	25-31
	c.	110	18.4	30/30	40/40	30/30
Zn	a.	90.5	140	117	132	73
	b.	80-101	121-160	98-131	117-145	62-83
	c.	86	120	130/200	140/200	90/100
Pb	a.	bd	bd	18	22.5	36
	b.	-	-	10-35	10-40	20-50
	c.	7.8	17.6	62/-	75/-	62/-
Cr	a.	115	17	30	59	62
	b.	105-125	5-25	15-45	40-78	50-80
	c.	114	17.6	30/40	60/70	65/75
Ni	a.	86	10	29	58	44
	b.	77-100	5-30	15-40	50-80	35-50
	c.	76	15.8	32/20	55/20	40/20
		(4)	(11)	(15)	(13)	(13)

- not determined
bd below detection

Number of analyses in parentheses

a. average value found
b. range in values found
c. the accepted value for W1 and BCR - 1 (from FLANAGAN,F.J.,1972: 1972 values for international geochemical reference samples. Geochim.Cosmochim. Acta,37,p1189-1200.).Analyses of the in-group standards 992001,etc.,by the Rosenstiel School of Marine and Atmosperic Sciences,University of Miami,U.S.A.,and by the Preussag Laboratories at Berkehopen,W.Germany.

TABLE B.3 Graphical estimates of the overall precision(%) at at the 95% confidence level of the analyses by A.A.S.

	Continental margin samples	Santorini samples
Ca	9	12
Mg	10	11
Fe	20	5
Al	10	11
Ti	27	20
Mn	8	15
Cu	20	13
Zn	25(8)	10
Pb	40(25)	-
Cr	40(20)	-
Ni	40	-

- at Santorini not analysed by A.A.S.

N.B. Figures in parentheses are the precisions for concentrations greater than 60ppm.

that there is good agreement between routine and solvent extraction analyses which suggests that routine analysis combined with Ca correction achieves reasonably accurate estimates of the concentration of Pb and Ni in the presence of large amounts of Ca.

Estimates of accuracy and precision for the routine analysis are given in tables B.2 and B.3 and are based on replicate analyses of five standards (U.S.G.S.-BCR 1,U.S.G.S.-W 1,and the in-group marine sediment standards 992001,992002, and 992003)and graphical techniques for estimating both within-batch and overall analytical precision(Thompson and Howarth,1973). For all elements the accuracy seems to be reasonable but the analytical precision for Cr,Pb,and Ni is low,particularly at the lower concentrations found in continental margin sediments with large amounts of $CaCO_3$.In table B.3,the figures in parentheses are estimates of the precision for concentrations greater than 60ppm,and they show a considerable improvement.Because of the poor precision of some elements ,individual sample dataare treated with considerable caution.In addition,the data used are often the mean of duplicate analyses and more emphasis is placed on the average composition of the main sediment types and on consistent trends in element abundance.

In addition to A.A.S.,Santorini samples were also by direct-reading emission spectrography using an ARL 29008 Quantometer with a sodium flouride and carbon powder buffer for the elements Si,K,Sr,Mo,V,Co,Ni,Cr,Ga,Ba,Li,and Sc.Full details of the technique are given elsewhere (A.G.R.G.,1973).On the basis of duplicate measurements and replicate analyses of internal standards, the accuracy and precision of the technique is better than $\pm$ 40% at the 95% confidence level.The final data are the means of either triplicate or duplicate analyses.

Because some samples contain large amounts of iron,it was necessary to check the influence of this atypical matrix on the analysis.Accordingly,artificial standards cotaining known amounts of iron(0-30%) and trace elements (0-1000ppm)were analysed by D.R. Determined values were then compared with the known values to assess the influence of the iron.For most elements this influence was not significant.For Mo,however,the greater amount of iron appears to depress the concentration.No attempt was made to correct for this which means that the values given for Mo in the inner

exhalative zones are probably slightly low.Nevertheless,the highest concentrations of Mo still occur in the iron-rich samples and so the depressing effect of iron reduces the contrast in abundance between the outer and inner exhalative zones but does not mask the overall trend.

Mercury analyses were carried out by flameless atomic absorption spectrophotometry after digestion of air-dried samples in concentrated nitric acid,and reduction to elemental mercury by stannous chloride.

PARTITION STUDIES

To investigate the major,minor,and trace element partition in sediments from the exhalative and channel zones at Santorini, a modification of the methods proposed by Chester and Hughes (1967) and Cronan and Garrett(1973) was employed.Separate sample aliquots of either .5 g or 1.0g were leached by:(a) 25% v/v acetic acid;(b) 25% v/v combined acetic acid - hydroxylamine hydrochloride;and (c) hot 50% HCl.However,the residues were analysed rather than the solutions because concentrations of some elements were low and would have required some form of preconcentration prior to analysis,some leach solutions would have contained large amounts of the interfering element Ca, and the range of elements would have been restricted to those determinable by A.A.S.After leaching the residues were suction-filtered onto pre-weighed membrane filters.Filter paper and residue were then placed in a dessicator and allowed to dry overnight.After weighing again to determine the weight loss on leaching,the residues were stored in plastic vials.Each sample was analysed in duplicate or triplicate by the techniques outlined above.

To relate the residue analyses to the original bulk composition they are multiplied by the relative weight of the residue.Concentrations converted to the bulk sample equivalent are subtracted from the bulk concentration and each other to give the amounts of each element attributable to a particular leach.To clarify the procedure,a sample calculation for the partition of Zn in sample SAN 2 is given below.

	Acetic Acid	Hydrox.	HCl
Weight of sample(g)	1.000	1.000	1.000
Weight of residue(g)	.726	.715	.333
Relative weight	.726	.715	.333
Concentration of Zn in residues (ppm)	72	71	37
Concentration of Zn converted to bulk sample equivalent(ppm)	52.3 (i.e. 72x.726)	50.8	12.3

Therefore,we have:

	Bulk equivalent Zn (ppm)	Amount of Zn attributable to each leach (ppm)	
Bulk	79.5		
		27.2	Acetic acid
Acetic acid	52.3		
		1.5	Hydrox.
Hydrox.	50.8		
		37.5	HCl
HCl	12.3		
		12.3	Detrital

A similar procedure was used for continental margin studies except that partition studies were restricted to acetic acid leaches of selected samples.

To determine the easily leachable Cu,Pb and Zn in selected samples from Sounion,0.5g of sample was shaken for 5 minutes in a centrifuge tube containing 10ml of 0.05M E.D.T.A. (ethylenediaminetetracetic acid),and centrifuged.The supernatant liquid was transferred to a test tube and directly analysed for Cu,Pband Zn by A.A.S. Standards were made up in 0.05M E.D.T.A. and a series of blanks and duplicates were included in each batch.The reproducibility of the results was excellent.

WATER ANALYSES

Seawater samples from the exhalative and channel zones at Santorini were analysed for Fe,Mn,Cu,Pb,and Zn by A.A.S. following preconcentration through a double extraction by sodium diethyldithiocarbamate in chloroform.Sets of blanks,duplicates,and solutions

with known concentrations of the elements in question, were included to assess contamination, reproducibility, and the efficiency of the solvent extraction respectively.

MINERALOGICAL TECHNIQUE

The mineralogical composition of selected acetic-acid residues from continental margin deposits was qualitatively determined by X-ray powder diffraction using a Phillips PW 1010/80 diffractometer and CoKα radiation. Ground samples were backloaded onto aluminium cavity mounts and scanned at 1° per minute over a 2θ range of 4° to 74°.

APPENDIX C GRAIN SIZE ANALYSIS

Bulk samples were initially sieved through an 8 mesh B.S. sieve to remove any gravel present.This coarse material was mainly coralline algae and,even though the weight was determined, gravel was not included in the textural analysis except as part of a preliminary sediment classification scheme.

For the grain size analysis,subsamples of about 100g were weighed,disaggregated in de-ionised water,and thoroughly wet-sieved through a 240 mesh B.S. sieve to separate sand from mud. The sand fraction was dried,weighed,and stored prior to sand size analysis by settling techniques(see later).For selected samples the mud fraction was retained after wet-sieving and dispersed,using Calgon,in 1 litre of de-ionised water.Pipette analysis was then carried out using the standard techniques described by Folk(1968).

Representative subsamples (approximately 5 grams)of the sand fraction were analysed in duplicate using a Woods Hole type rapid sediment analyser(see Zeigler et al.,1960 and Schlee, 1966)installed at the Sedimentary Petrology Laboratory, Institute of Geological Sciences,South Kensington,London.The fall distance was 150 cm and the grain size curve for each sample were determined by reference to the fall velocities of quartz spheres(Zeigler and Gill,1959).The same technique was used by Cronan(1969) to investigate sediments from the north-eastern Irish Sea.

Stastical parameters of grain size were calculated using a simple computer program and the formulae given in Folk(1954), namely:

$$\text{Median},M_d = \phi_{50}$$

$$\text{Graphic Mean},M_z = \frac{(\phi_{16}+ \phi_{50}+ \phi_{84})}{3}$$

$$\text{and Graphic Standard Deviation (Sorting)},\sigma_G = \frac{\phi_{84}- \phi_{16}}{2}$$

where ϕ_{16},ϕ_{50},and ϕ_{84} are the phi sizes at the 16th.,50th,and 84th. percentiles respectively on the cumulative grain size curves.

It should also be noted that the computer program to calculate the textural parameters assumes that for those samples with

with more than 15% mud 95% of the sample is coarser than 8 phi. This is generally consistent with the pipette analyses but it means that the calculation of textural parameters is not sensitive to the proportions of coarse and fine silt.