The sedimentology, diagenesis and palaeo-oceanogeaphy of diatomites from the miocene of Sicily

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ABSTRACT

There were two bouts of diatomaceous sedimentation in Sicily during the Miocene: the first in the Aquitanian/ Burdigalian and the second during the Messinian.

The Lower Miocene deposits are found in only a few widely distributed outcrops and their stratigraphic context is uncertain. They occur as thinly bedded cherts and porcelanites which consist of either opal CT or quartz. Although diagenesis has destroyed much of their original texture, a diatomaceous origin for the silica can be inferred from the presence of many corroded diatom frustules. Mineralogical diagenetic changes appear to be related to burial associated with early to middle Miocene tectonism while textural variations probably reflect compositional differences in the original sediment.

The Messinian diatomites are moderately well exposed in central and southwestern Sicily and underlie the Mediterranean Evaporites. They belong to the Tripoli Formation which consists of alternating diatomite and claystone horizons with each of the latter comprising a grey dolomitic marl overlain by a brown terrigenous shale. Diatomite deposition took place under normal marine conditions in response to the upwelling of deep nutrient-rich waters while isotopic evidence suggests that the claystones, usually devoid of biogenic remains, were deposited in stagnant, highly evaporated waters. The cyclic nature of Tripoli sedimentation is thought to be due to a combination of sea level fluctuations controlled by Antartic glacial activity and the existence of a shallow sill separating the Mediterranean from the Atlantic. Restricted conditions developed during low sea-level stands while the diatomites were deposited as sea levels were rising. The waters of the Mediterranean became increasingly saline and restricted during the Messinian until diatomaceous sedimentation ceased. Eventually communication between the Atlantic and the Mediterranean was severed and the Messinian Salinity Crisis followed.

THE SEDIMENTOLOGY,

DIAGENESIS AND PALAEO-OCEANOGRAPHY

OF DIATOMITES FROM THE

MIOCENE OF SICILY.

A Thesis
submitted in accordance with
the requirements of the University
of Durham for the degree of
Doctor of Philosophy
by

GRAEME BENNET

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DEPARTMENT OF
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FRONTISPIECE

A pelagic fish of the Scombrid family from the diatomites of the Tripoli Fm., Capodarso, Sicily.

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INTRODUCTION

The occurrence of diatomaceous sediments of both early and late Miocene age in Sicily is remarkable in itself, since because such sediments are only rarely preserved in the geological record. However, the late Miocene (Messinian) diatomaceous deposits are of particular interest because they are found immediately underlying the Messinian evaporites not only in Sicily, but also in North Africa and other countries surrounding the Western and Central Mediterranean.

The discovery of these evaporites beneath the deep Mediterranean basins during Leg 13 of the Deep Sea Drilling Project and the controversial theory put forward by some members of the cruise to account for their origin (Hsü et al.1973) has provoked considerable interest not only in the evaporites, but also in the events which preceded and followed their deposition. As a result, this aspect of late Miocene geology which has become known as the Messinian Salinity Crisis, has been the subject of a great deal of detailed sedimentological, geochemical and biostratigraphical research over the last few years. (see Hsü et al. 1978 for a summary of recent work on this topic).

which one?

which one?

As regards the diatomaceous sediments it is unfortunate that Glomar Challenger is not equipped to drill in hydrocarbon-bearing formations and has therefore been unable to penetrate the pre-evaporitic sequence beneath the deep Mediterranean basins. Nevertheless these sediments are moderately well exposed on land and because of their important position with respect to the evaporites one would expect that they would have already been thoroughly investigated. In fact, little detailed information has appeared on the North African diatomites since Anderson's work on the Beida Stage of Algeria published in 1933. Similarly in Sicily where, apart from some interest shown by biostratigraphers (Bandy 1975, D'Onofrio et al. 1975, Catalano and Sprovieri 1971, Colalongo et al.1976, Wornardt 1973), the pre-evaporitic marls and diatomites have been almost totally ignored by geologists since Ogniben's study of the evaporites and associated sediments published in 1957. The neglect of the Sicilian deposits is perhaps the more surprising of the two in view of its easier access for European geologists. It is therefore the principal aim of this thesis to rectify this omission and thereby to further elucidate the causes and events which led up to the Messinian Salinity Crisis.

The Lower Miocene diatomites are less well exposed and have undergone considerably more diagenetic alteration than their Upper Miocene counterparts. However, by comparing the two deposits with each other and with the similar diatomaceous sediments of the Monterey Formation of California it is hoped that some conclusions may be drawn regarding the depositional environment and diagenetic history of these Lower Miocene diatomites.

Fieldwork has involved two visits to Sicily; one by way of a reconnaissance in September 1975 which was followed by a full field season during the summer of 1976. Comparisons between the Sicilian diatomites and those of the Monterey Formation also necessitated a short visit to California during July and August of 1977.

In Sicily, the Lower Miocene diatomaceous sediments occur more commonly in the north while late Miocene diatomites are confined to central and south-western parts of the island; an area characterised by low undulating hills in which most of the land is given over to agriculture. Exposure Outcrop is therefore largely restricted to road cuttings and quarries of which recent road and housing developments have fortunately ensured that there is a plentiful supply. The quality of exposure outcrop is variable, because since the friable fine grained sediments show little resistance to weathering and rapidly become overgrown with even recent exposures usually being covered by a weathered crust a few centimetres thick. The lack of continuous exposure outcrop, which is further disrupted by ubiquitous minor faulting, thus makes field mapping impossible and fieldwork is restricted to measuring and sampling the best exposures and taking 'spot' samples from the smaller exposures outcrops. Even in the best exposures weathering may obscure faulting and for this reason the true thicknesses of some sections may be regarded as suspect, especially where there are breaks in exposure.

The samples thus collected have been studied petrographically by means of thin sections and smear slides (where suitable). X-ray diffraction was widely used for the qualitative determination of the mineralogical composition of the sediments and quantitative methods were also attempted but not found to be very successful. The chemical composition of certain samples from the major sections has been determined by X-ray fluorescence analysis and limited use has also been made of scanning electron microscopy.

NOMENCLATURE.

Diatomaceous sediments of early Miocene age are commonly found in an advanced stage of diagenesis, not only in Sicily but in the rest of the Mediterranean region and California also. In many of these sediments no evidence of a diatomaceous origin for the silica remains ~~since~~ because the diagenesis invariably involves the dis solution and reprecipitation of the silica in the diatom frustules. The silica may therefore occur in a variety of polymorphic and textural forms depending on several factors which will be discussed later. In describing the mineralogy of these sediments the terminology proposed by Jones and Segnit (1971) will be used. The textural terminology followed is that of Bramlette (1946) who ~~defines~~ defined the three principal textural divisions of the siliceous sediments in the Monterey Formation as follows: Diatomite:- "The name Diatomite is used for the purer diatomaceous rocks though the term implies no very definite degree of purity and is often used loosely by geologists for any of the soft, "punky" rock in which diatoms are conspicuously present."

Porcelanite:- "silica cemented rocks that are less hard, dense and vitreous than chert. Such rock has minute pore spaces, which usually give it a dull or matte lustre resembling that of unglazed porcelain".

Chert:- "relatively pure silica rocks that consist mainly of opal or mainly of chalcedony and regardless of colour".

Bramlette's definition of porcelanite is based on that of Taliaferro (1934) who ~~defines~~ defined the term as meaning, "a rock with the general appearance and texture of unglazed porcelain". In neither Bramlette's nor Taliaferro's definition is there any mineralogical connotation; the term implies nothing other than texture. It is unfortunate therefore that recently the term has often been used to denote a rock composed of opal-CT (Calvert 1971, von Rad et al 1978 and others) ~~since~~ because in both California (Murata and Nakata 1974) and Sicily porcelanites exist which are not composed of opal-CT but of quartz.

In this ~~report~~ thesis therefore the terms 'porcelanite' and 'chert' are used referring only to the texture of the rock and not the mineralogy.

CHAPTER 1.

THE TECTONIC EVOLUTION OF THE WESTERN MEDITERRANEAN REGION DURING THE OLIGO - MIOCENE.

Today, the Mediterranean Sea consists of a series of connected basins of less than oceanic depth surrounded by more or less linear mountain ranges. The region as a whole has been the site of tectonic activity caused by the interaction of the African and Eurasian Plates throughout the Mesozoic, Caenozoic and it remains seismically and volcanically active today. To the north the area is dominated by the Alpine Fold Belt which, with its characteristic association of ophiolites and blueschists (Fig 1.1) can be traced from Turkey in the east as far west as the northern Apennines or even southern Spain (Bernoulli and Jenkyns 1974). This prominent feature is thought to have been the result of a sequence of compressional tectonic events which began in the late Cretaceous and were brought about by the opening of the North Atlantic causing a change in the relative motion of Africa and Europe (Hsü and Bernoulli 1978). These events culminated in a complete continent - continent collision at the end of the Eocene, resulting not only in the formation of the Alpine Fold Belt but also in the destruction of the Tethyan Ocean which had separated the two continents since the Jurassic (Dewey et al. 1973, Laubscher and Bernoulli 1978).

The Levantine and Ionian Basins of the Eastern Mediterranean are now believed to be relics of this former ocean while the basins of the Western Mediterranean (Fig 1.1) have been shown to be post-orogenic (Hsü 1978, Laubscher and Bernoulli 1978). However, the data collected during D.S.D.P. Legs 13 and 42A strongly ~~suggests~~ suggest that the Western Mediterranean Basins were in existence by the late Miocene in which case they must have formed during the Oligocene and/or early Miocene (Hsü et al.1973, 1978, Ryan 1976). The Oligo-Miocene of the Mediterranean therefore appears to have been a time of important tectonic activity, quite distinct from the events of the Alpine Orogeny.

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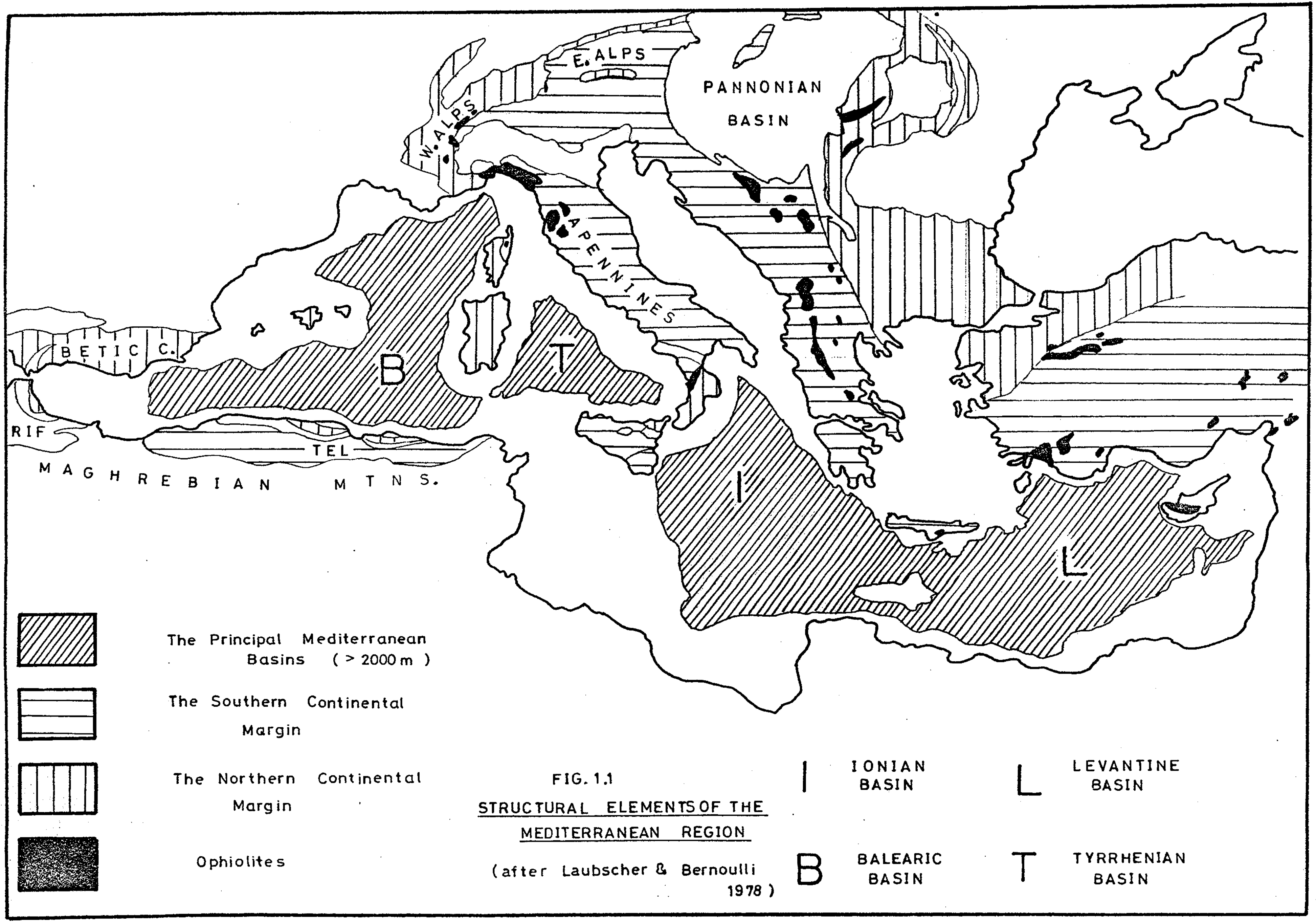


FIG. 1.1

STRUCTURAL ELEMENTS OF THE MEDITERRANEAN REGION

(after Laubscher & Bernoulli 1978)

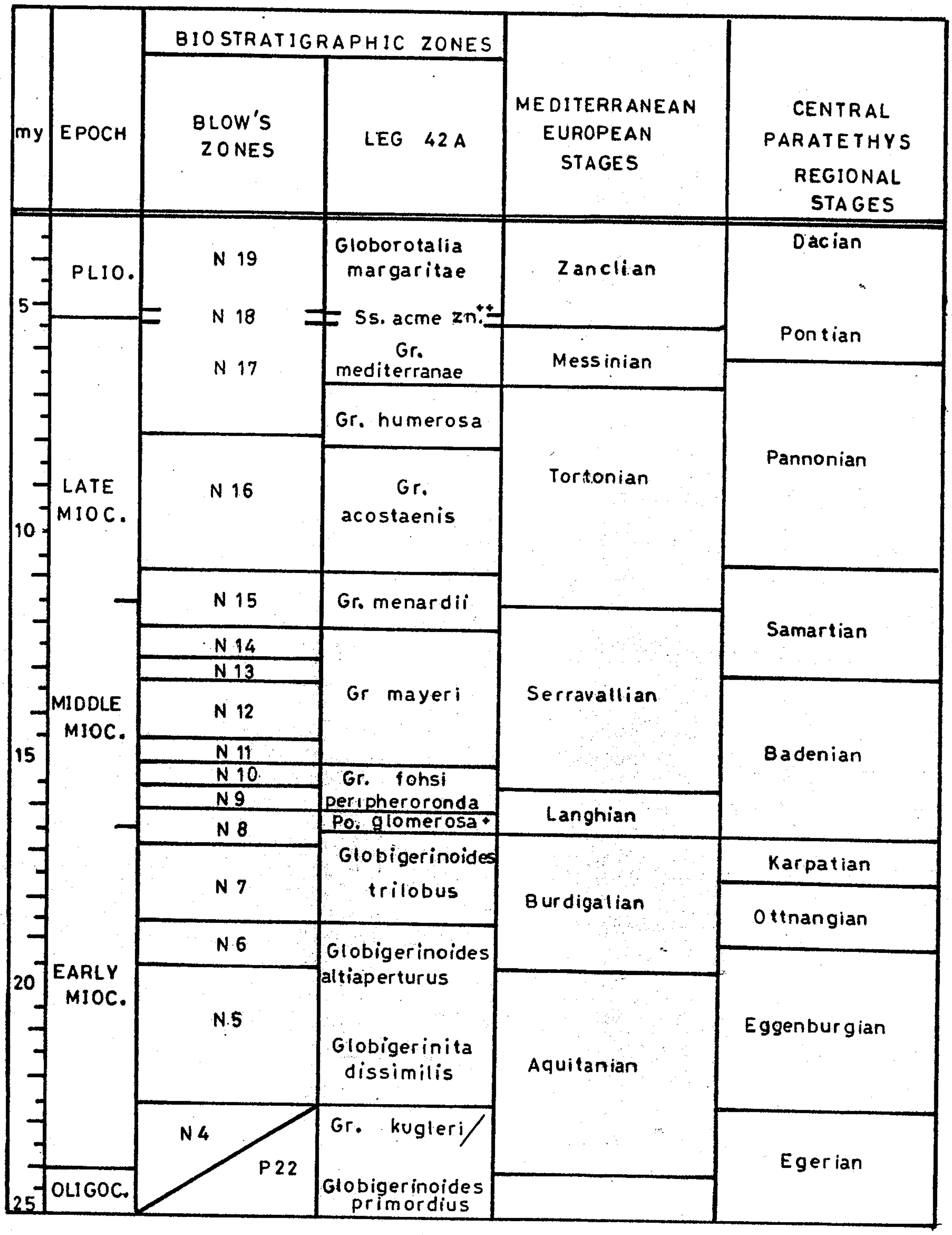
The Western Mediterranean is bordered to the east, south and west by the Maghrebian - Apennine Fold Belt which includes Calabria, Sicily, the Betics of Spain as well as the Rif-Atlas mountains of North Africa and the Apennines of Italy (Fig 1.1). The Maghrebian part of the fold belt appears to have been formed largely by the deformation of Oligo-Miocene flysch, emplaced by uplift and gravity rather than by deformation at a plate margin (Wezel 1975). The Apennines also contain allochthonous units of Oligo-Miocene flysch but unlike those of the Maghrebian Mountains, they also contain evidence to suggest that sub - or obduction has taken place (Alvarez 1973, Sestini 1974, Boccaletti and Manetti 1978).

Apart from the series of flysch nappes of late Jurassic - early Miocene age, there are two other characteristic units which make up this fold belt (Auzende et al. 1973). They are; 1) An 'external' zone belonging to the North African continental margin that has been subject to post - Alpine deformation. This deformation appears to be diachronous: having taken place in Algeria during the late Burdigalian but not until the early Langhian in Sicily (Wezel 1975). 2) An 'internal' zone of Palaeozoic and Mesozoic material that has undergone Eocene deformation. It exists in fragments which now make up the Western Betics, the Kabylies, northeastern Sicily and Calabria.

The internal zones have been interpreted as fragments of a continental area that existed in the Western Mediterranean prior to the formation of the deep basins (Auzende et al.1973). This has been referred to under a variety of names; the 'Sardinian Province' (Caire 1970), the 'Alboran Plate' (Andrieux et al. 1971) or, more recently, the 'Protoligurian Massif' (Alvarez 1976). The existence of such a continental area is proposed largely on the basis of evidence provided by several Lower Tertiary formations in the Maritime Alps (e.g. the Annôt Sandstone). Palaeocurrent directions as well as sediment and heavy mineral distributions indicate that the clastic material originated to the south of the present French coast in the site of the Ligurian Sea (Stanley and Mutti 1968). However, today the Ligurian Sea is the site of a basin over $2\frac{1}{2}$ kilometres deep which forms a northeastern extension of the Balearic Basin and, like the Balearic and parts of the Tyrrhenian Basins, is believed to be underlain by oceanic crust (Hsü 1978, Moullade 1978). The source area for the Lower Tertiary clastic formations in the Maritime Alps therefore appears to have either migrated laterally or to have undergone subsidence and 'oceanisation' at some time prior to the onset of the Messinian Salinity Crisis.

Caire (1970) proposed that the 'Sardinian Province' was an unstable continental area which supplied clastic material to its peripheral regions and which eventually collapsed to become the present Tyrrhenian Basin. This collapse was accompanied by the emplacement of flysch nappes around the margins of the basin, a process which the author likened to an 'orogenic wave' spreading radially outwards. Van Bemmelen (1972) supported and expanded this hypothesis to encompass other Western Mediterranean Basins. He postulated three 'focal centres of orogeny' in the Alboran, Balearic Ligurian and Tyrrhenian Basins; these were all unstable crustal domes which foundered during the late Caenozoic, accompanied by intense volcanism, and became the deep Western Mediterranean basins of today. Stanley and Mutti (1968) on the other hand, accounted for the disappearance of the source for the Lower Tertiary clastics by suggesting that it had rotated anticlockwise and now formed Corsica and Sardinia. Many subsequent geological and geophysical studies have supported this interpretation and have shown that Sardinia has probably rotated somewhat further than Corsica (Nairn and Westphal 1968, Zidjerwald et al. 1970, Alvarez 1972 and others). More recently, palaeomagnetic evidence has suggested that parts of Peninsular Italy have also undergone anticlockwise rotation since the Eocene (Vandenberg et al. 1978) and Bayer et al.(1973) even claim to have recognised 'Vine and Matthews type' sea-floor spreading lineations in the Ligurian Sea. Alvarez (1973) has pointed out however, that with the exception of the Corso-Sardinian rotation, many of the features normally associated with plate tectonic processes are absent in the Western Mediterranean: There are no mid-ocean ridges, no linear seamount chains, no trenches and no obvious pre-drift reconstructions. Nevertheless there is considerable evidence to suggest that the evolution of the Western Mediterranean Basins may be interpreted in terms of the rifting and rotation of sialic blocks, the 'microplates' of Dewey et al. (1973), such as Corso-Sardinia and the 'internal' zones of the Maghrebian-Apennine Fold Belt.

The age of rifting in the Ligurian Sea would appear to be Aquitanian (Fig 1.2) although late Oligocene andesitic volcanism in Sardinia suggests that movement actually began somewhat earlier (Alvarez et al. 1974). Other ages have been suggested and these range from Eocene (Ryan et al.1971, Stanley and Mutti 1968) to Burdigalian/Langhian (De Jong et al. 1973). The Alboran Basin (which is shallower than the other basins) and the surrounding areas now occupied by the Betic and Rif Mountains also appear to have been subjected to an extensional regional stress during the Oligo-Miocene (Loomis 1975). Gravity studies have led Bonini et al. (1973) to suggest that this was due to an episode of crustal extension and thinning along a central zone in the Alboran Sea caused by the injection of mantle material. The age of the onset of this crustal spreading has been estimated as early Miocene both from radiometric dating of the Ronda and Beni Bouchera ultramafic massifs and from the onset of andesitic volcanism in the region (Loomis 1975). Other basins in the Western Mediterranean are thought to have opened at approximately the same time; the Valencia Basin in either the Aquitanian (Alvarez et al. 1974) or Burdigalian (Hsü and Ryan 1973) and the Balearic Basin in the latest Oligocene or Aquitanian (Hsü et al. 1977, Alvarez et al. 1974). The exception however, is the Tyrrhenian Basin which is thought not to have been initiated until the Middle Miocene (late Langhian/ Tortonian) (Alvarez et al. 1974, Hsü 1978). The similarity in the timing of these events together with the recognition of



* Praeorbulina glomerosa

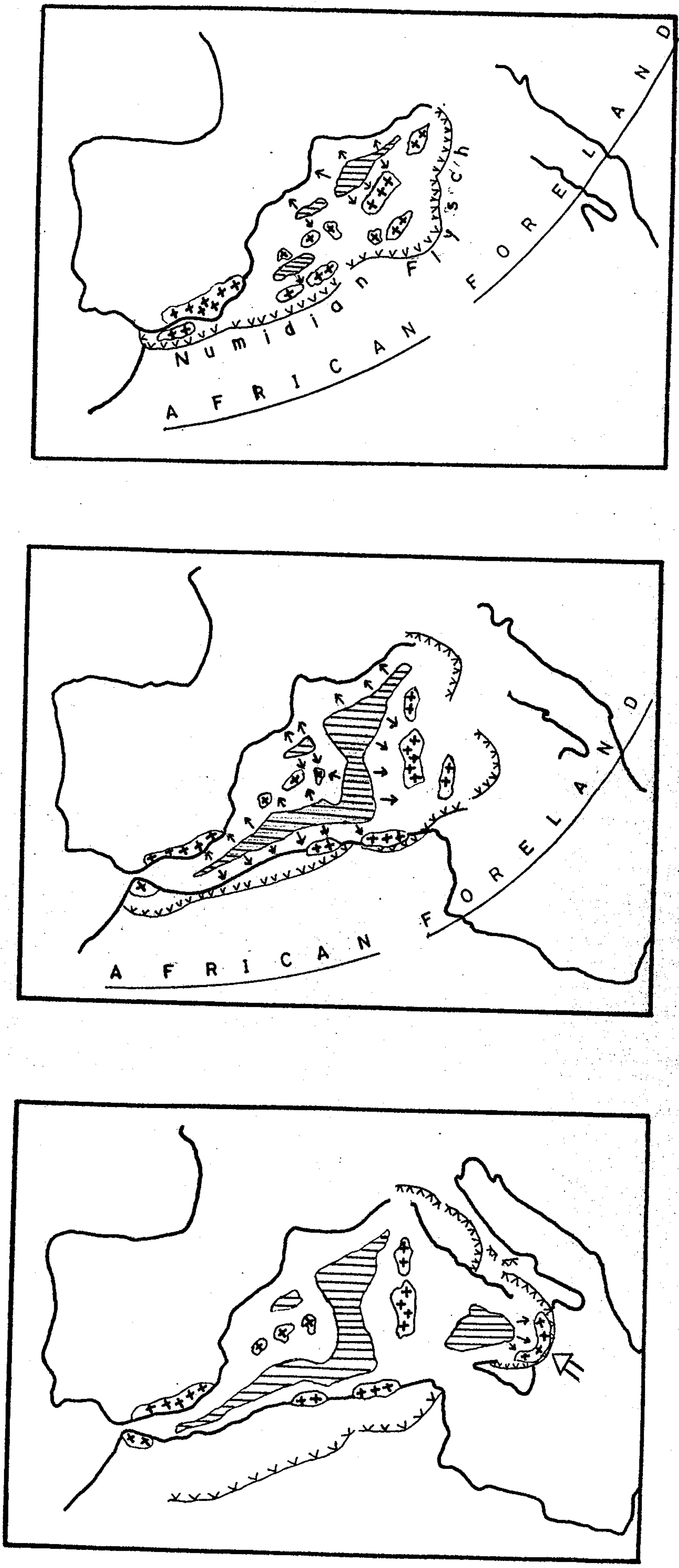
** Sphaeroidinellopsis acme zone

FIG. 1.2 MIOCENE BIOSTRATIGRAPHY

(after Rögl et al. 1978)

easterly extension, into the Balearic Basin, of the gravity high that marks the Alboran spreading axis (Loomis 1975), suggests that the Western Mediterranean may be largely the result of Oligo-Miocene rifting along an axis extending from the Alboran to the Ligurian Seas. (Fig 1.3 a-c)

Bayer et al. (1973) have attempted a pre-drift reconstruction of the Balearic and Ligurian Basins based on magnetic anomalies. They suggest that the 'internal zones' were at one time joined together, then split up and drifted apart causing the basins to open in their wakes. This hypothesis is supported in principle by Boccaletti and Guazzone (1974) who regard the Balearic and Ligurian Basins as back-arc marginal basins that opened behind the advancing Rif-Tellian and Apennine arcs during the Miocene. A similar interpretation is also put forward by Alvarez et al. (1974) and Alvarez (1976). They suggest that the 'internal zones' were once the westward continuation of the Alpine Fold Belt and have attempted to document the sequence of events by which it broke up and was dispersed throughout the Western Mediterranean. They propose that the process began in the Aquitanian with the opening of the Valencia Trough and the rotation of Corsica-Sardinia-Calabria away from France to form the Ligurian Sea (Fig 1.3a). Sardinia-Calabria separated from Corsica in the early Burdigalian after the latter had collided with the sialic crust of the Northern Apennines at the end of the Aquitanian (Fig 1.3b). During the Langhian the Kabylia 'microplates' collided with the North African continental margin and at the end of the Langhian Sardinia-Calabria collided with the Tunisian margin causing the Sicilian part of the Calabrian massif to override the Numidian flysch on the North African continental slope (Fig 1.3b). As a result of the collision with Tunisia, Calabria separated from Sardinia at some time in the Middle Miocene and continued to migrate south-eastwards forming the Tyrrhenian Basin in its wake (Fig 1.3c). This southeasterly motion is believed to be continuing today as the Calabrian Arc overrides the Ionian Sea (Ritsema 1969 , Boccaletti and Manetti 1978) and only the Western part of the



A)
LOWER MIOCENE

B)
BURDIGALIAN -
TORTONIAN

C)
RECENT

present day Calabrian Arc
Fragments of the Alpine Mountain Belt
Mediterranean Basins
Folded Arcs
Direction of spreading

FIG. 1.3 THE EVOLUTION OF THE WESTERN MEDITERRANEAN BASINS.
(After Boccaletti & Guazzone 1974 and Boccaletti & Manetti 1978)

Tyrrhenian Basin, where the Messinian evaporites can be recognised on seismic traces, is therefore believed to be of pre-Messinian age (Alvarez et al. 1974).

The Oligo-Miocene evolution of the Mediterranean Region however, remains highly controversial despite the considerable amount of research devoted to this complex topic over the past decade (see Biju-Duval et al.1978, Hsü 1978). In particular, there is a significant body of opinion which, like Caire (1970) and Van Bemmelen (1972), regards 'vertical' tectonics such as crustal foundering as being far more important in the development of the Western Mediterranean basins than is suggested above (Wezel 1977 , Laubscher and Bernoulli 1978). It must therefore be emphasized that the above outline of the Oligo-Miocene development of the Western Mediterranean is merely one possible interpretation and as Laubscher and Bernoulli (1978) comment, "there is still no single model that would not be seriously questioned by one part or another of the earth science community".

However, irrespective of the mechanism by which these basins were initially formed, they appear to have undergone continued and rapid subsidence throughout the early and middle Miocene. Data collected during D.S.D.P. Leg 42A suggest~~s~~ that the Balearic Basin, for example, was at least 900 metres deep in the Burdigalian, 1200 metres in the late Burdigalian, 1500 metres by the end of the Middle Miocene and at least 2500 metres prior to the onset of the Messinian Salinity Crisis (Ryan 1976, Wright 1978). Other Mediterranean basins, with the possible exception of the Alboran Basin, also appear to have subsided and all are believed to have been deep open seas throughout the early and middle Miocene (Wright 1978).

Outside the Mediterranean Region however, tectonic events during the Miocene saw the progressive isolation of both the Eastern Mediterranean and the newly formed Western Mediterranean basins. The closure of the marine connection between the Mediterranean and the Indian-Pacific Oceans began in the

Burdigalian and was completed in the Serravallian (Hsü et al. 1977, Rögl et al. 1978). The connection with Paratethys through the perialpine depression was terminated by the middle-early Miocene events in the Helvetic Alps and the Mediterranean was probably totally cut off from Paratethys in the Serravallian when the link through northern Italy and northwestern Yugoslavia closed (Hsü et al. 1978, Rögl et al. 1978). The one remaining link with the world ocean was via the Betic and Rif Straits but these too became increasingly restricted after the end of the Middle Miocene (Hsü et al. 1977, Benson 1976, 1978, Hsü et al. 1978). By the beginning of the Messinian the deep Mediterranean Basins had thus become virtually isolated and their subsequent desiccation inevitably led to the onset of the Messinian Salinity Crisis.

CHAPTER 2.

LOWER MIOCENE DIATOMITES FROM SICILY.

2.1 Geological Setting of the Lower Miocene Diatomites.

Fine grained siliceous sediments of Lower Miocene age have been reported from several localities in Sicily (Fig 2.1), they are often in an advanced stage of diagenesis and occur most commonly in the northern part of the island associated with the Numidian Flysch. The Numidian and Nebrodian Flysch are of Oligo-Miocene age and are largely composed of quartz-arenites derived from the African Craton (Wezel 1970). They are the youngest of a series of successive flysch sequences spanning the Lower Cretaceous-Middle Miocene which young to the southwest and form an imbricate zone underlying the crystalline massif of the Peloritani Mountains (Fig 2.2)(Wezel 1974).

The siliceous sediments associated with the flysch are invariably quartzitic and have been described from Finale (Broquet 1973) and the region between Gangi and Sperlinga (Campisi 1962, Andreieff et al. 1974). However, in Central Sicily, siliceous sediments of comparable age have been found composed of opal-CT and in the vicinity of Agrigento diatomaceous sediments, closely resembling those of the Tripoli Formation (see Chapter 3) but of Lower Miocene age, have been reported (Decima and Sprovieri 1973). It therefore appears (Fig 2.1) as if there may be a 'diagenetic gradient' extending across Sicily with the least altered diatomites in the southwest and the most altered quartzitic sediments in the northeast.

2.2 Quartzitic Sediments.

At Finale on the north coast of Sicily the siliceous sediments are associated with the Numidian sandstones and occur approximately 1.6 kms to the east southeast of the village. The section is about 10 metres thick and reveals slumps with east-west axes indicating displacement towards the south. They overlie Oligocene shales but are separated from them by a single horizon of Numidian Flysch (Broquet 1973).

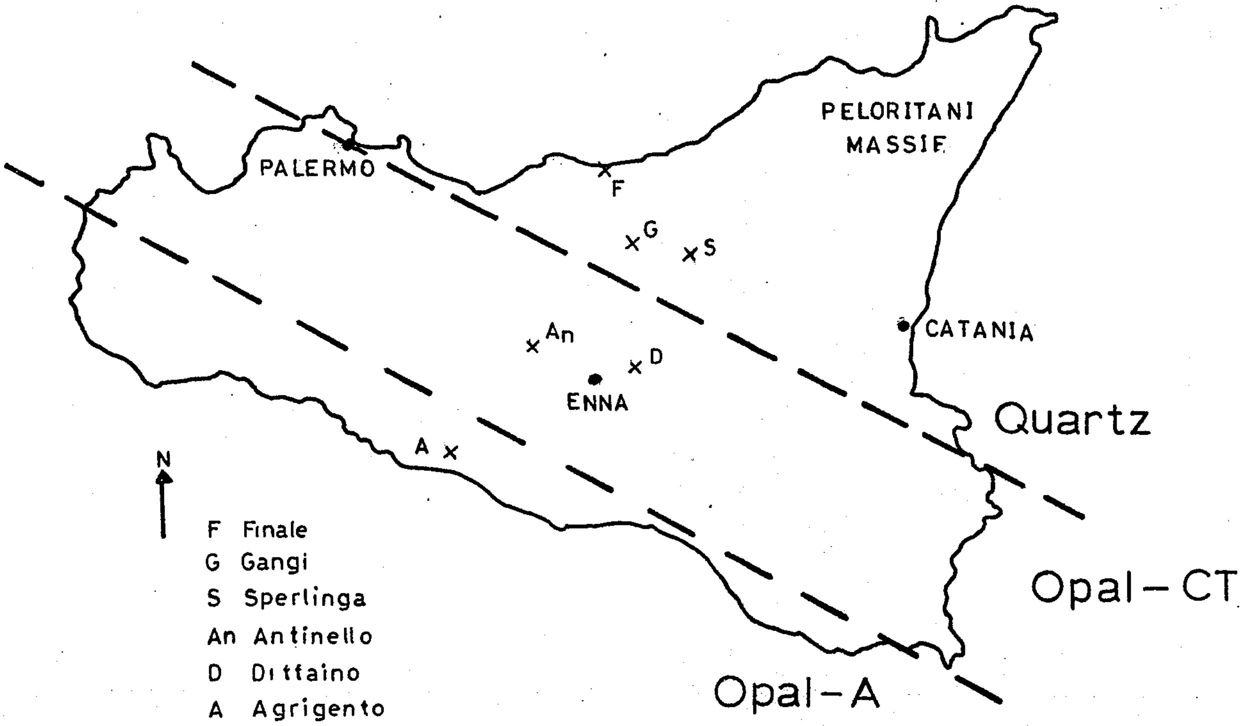


Fig. 2.1 SICILY: LOCATION MAP & DIAGENETIC ZONATION OF THE LOWER MIOCENE SILICEOUS SEDIMENTS.

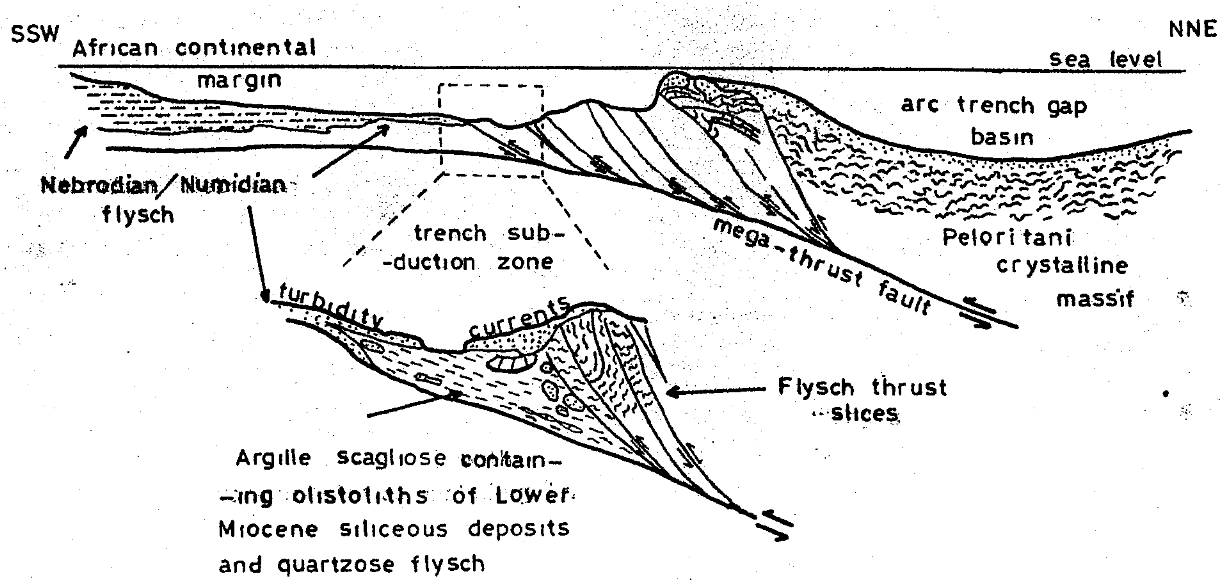


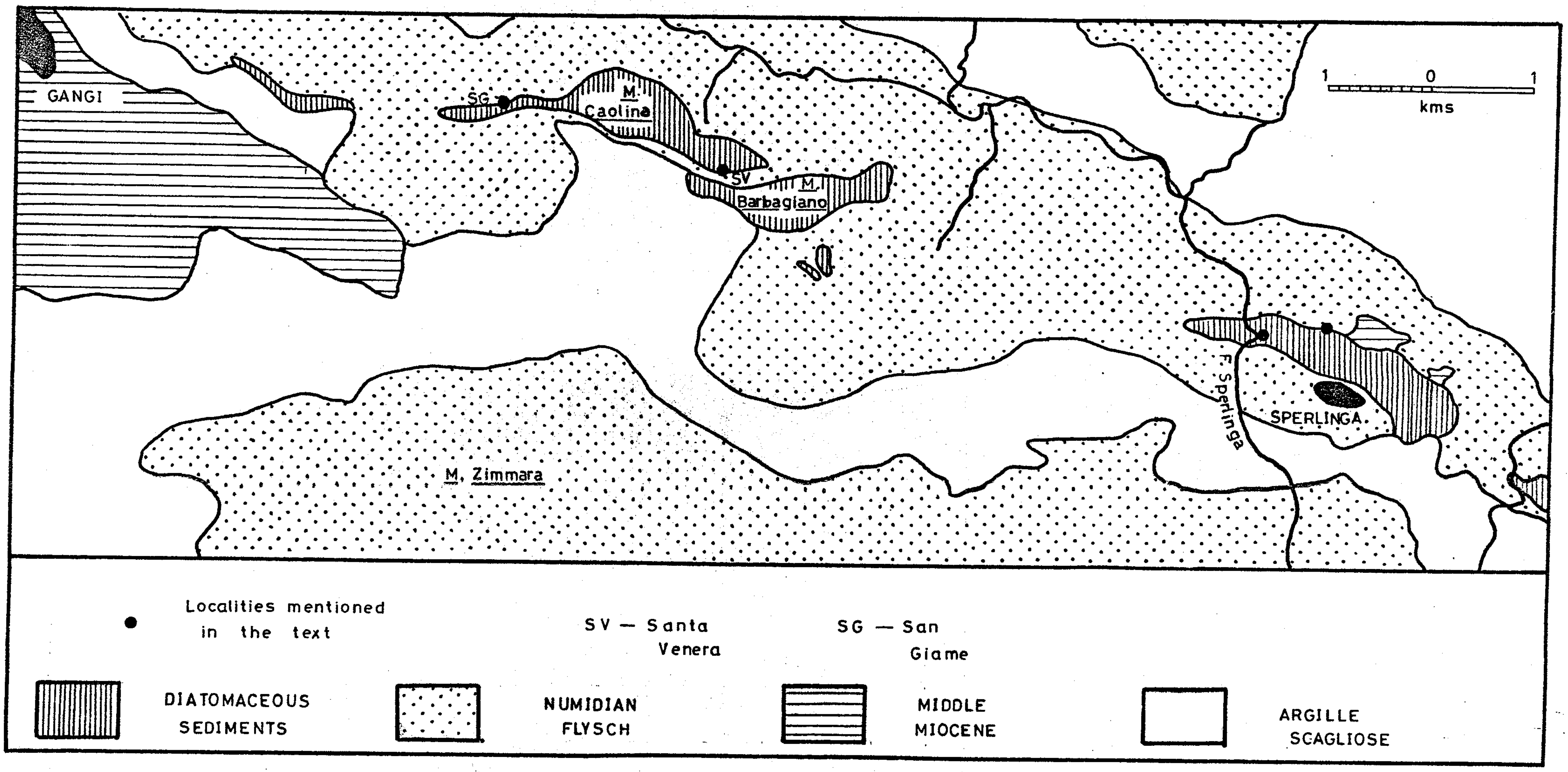
Fig. 2.2 A HYPOTHETICAL SECTION ACROSS SICILY IN EARLY BURDIGALIAN TIME.
(after Wezel 1974)

The best known occurrences of these siliceous sediments and those first described from Sicily occur some 30 kms. southeast of Finale in the area between the villages of Gangi and Sperlinga (Campisi 1962). The best exposures are in the Santa Venera Valley between Monte Caolina and Monte Barbagiano and on the flank of Monte Caolina overlooking the valley (Plate 2.1,Fig 2.3). They are both 10-15 metres thick and the section in the valley is apparently overturned (Andreieff et al. 1974). Both sections are apparently under and overlain by Numidian Flysch and although the contacts are never actually seen, they would appear to be very sharp since there is no evidence of clastic material within the siliceous horizons.

Small outcrops of siliceous sediments occur to the west along the crest of Monte Caolina and a further section has been described from near the farm of San Giame near Gangi. This exposure is 8 to 10 metres thick and its structural position is obscure: Andreieff et al. (1974) have described it as representing the core of an anticline within an envelope of Numidian Flysch, while Campisi (1962) considers that there is no overall relationship between bedding in the occasionally contorted siliceous horizons and the flysch. On Monte Barbagiano the relationship between sandstones and siliceous sediments appears to be different again since Campisi (1962) reports that the siliceous sediments are seen regularly intercalated with the quartzarenites of the Numidian Flysch. The most easterly outcrops of the siliceous sediments are near the village of Sperlinga where there are two outcrops: one adjacent to a quarry in the Numidian Flysch, 1 km to the north of the village and the other at the bend in the Fiume Sperlinga 1 km to the west. Again the stratigraphic context of the siliceous horizons is obscure but the uncertain bedding relationships and abrupt lithology changes suggest that their contact with the Numidian Flysch might not be conformable.

It is impossible to be certain about the stratigraphical relationship between the siliceous sediments and the Numidian Flysch and while the two lithologies have a normal stratigraphic contact at Finale and Monte Barbagiano, this is apparently not always the case. It is possible that the outcrops at Santa Venera, San Giame, Monte Caolina and Sperlinga are olistoliths or 'pods' of siliceous

FIG. 2.3 GEOLOGICAL MAP OF THE GANGI PLATEAU (after Campisi 1962)



sediment that have become detached from their original stratigraphic setting. If so, this would most likely have occurred during the tectonic upheavals of the Middle Miocene which led to the emplacement of the nappes in northern Sicily.

2.2.1 Appearance.

These siliceous sediments have a similar appearance wherever they occur; they consist of thinly bedded sediments, light brown to grey in colour (Plate2.2)that are resistant to erosion and as a result usually form topographic highs when set in the less resistant quartzarenites of the Numidian Flysch.

The individual beds may be up to 10 cms thick, generally hard and well indurated with a porcelanitic texture although some of the thinner horizons may be rather friable. Bedding is regular except where the growth of nodules of brown chert causes it to pinch and swell (Plate 2.3) In the Santa Venera Valley the brown cherts are more common in the thicker beds near the top of the section which, since the section is apparently overturned and youngs to the north, must be the oldest beds. The younger beds are thinner, and more argillaceous; closely resembling the outcrops along the crest of Monte Caolina. The cherts are not confined to the thicker beds elsewhere however, and a roadcutting near the Sperlinga Quarry reveals thin alternations of fractured brown cherts and thin argillaceous interbeds (Plate 2.4).

The interbeds in these siliceous sequences are hard, thin, dark grey-green horizons rarely more than 1cm thick, which often show faint colour banding and contain many planktonic foraminiferal tests. The boundary between the siliceous and argillaceous beds is usually sharp and regular although rarely the argillaceous horizons can be seen diffusing into the siliceous sediment. Very fine laminations are present in the siliceous beds and extend into the cherts (Plate 2.5), however, they are occasionally so intensely crenulated that the sediment commonly appears to be virtually homogenous. Because Since the bedding surfaces between siliceous and argillaceous beds reveal no similar crenulations it would appear that they are the result of diagenetic processes within the sediment rather than folding or slumping.

2.2.2 Petrography.

X-ray fluorescence analysis has shown that the silica content of these sediments is over 60% in all the argillaceous horizons, over 70% in all the porcelanitic horizons, over 80% in the porcelanitic sediment adjacent to chert nodules and over 90% in all the cherts (Fig 2.4). X-ray diffraction has further shown that all the silica is present in the form of quartz.

The sediments are very fine grained and consist of tests of planktonic foraminifera and other detrital grains set in a very fine groundmass in which finely disseminated calcite is abundant and can be identified by its high birefringence (Plate 2.6). Opaque material is fairly common and is probably limonitic since it is apparently amorphous to X-rays.

As might be expected the detrital components are more common in the argillaceous horizons where planktonic foraminiferal tests are common and may be either broken or whole and are often infilled with microcrystalline calcite. When they are broken the fragments tend to remain close together suggesting that there has been little or no reworking of the sediment. Silt-sized angular or subangular grains of quartz and feldspar are evenly distributed throughout the sediment and since they are less than 50mm in diameter are probably at least partially wind transported (Rex and Goldberg 1962). The feldspar appears to be andesine/oligoclase from its optical properties but it is not present in sufficient quantities for this to be confirmed by X-ray diffraction. Small laths of muscovite are present and there is a strong optical orientation of mica/clays parallel to bedding, as shown by the sensitive tint , indicating the presence of many grains too fine to be resolved optically. X-ray diffraction however, shows that the clay minerals present include montmorillonite and probably illite.

The contacts between the argillaceous and siliceous beds appear very sharp in hand specimen but in fact are gradational over about a millimetre with pods of siliceous sediment separated by wisps and lenses of argillaceous material (Plate 2.7). The groundmass of the more siliceous beds is lighter in colour and

GROUP	SiO_2 %	PETROGRAPHY
CHERTS	95.7* 93.2 92.5	Replacement of groundmass by microcrystalline quartz. This becomes more pervasive towards the centre of the chert and the original laminae are destroyed. Banding appears due to alternating horizons being replaced by microqtz. and others retaining the original texture. Characteristic cracks appear to be confined to the cores of the more extensive cherts. (Plate 2.16)
PORCELANITES (within 10 cms of chert horizon)	90.6 89.2 82.1	The denser groundmass is possibly due to the precipitation of cryptocrystalline quartz in the interstices of the existing sediment structure. Crenulated laminae are still visible. No replacement of groundmass by microqtz. Occasional infill of forams. by chalcedony.
PORCELANITES	81.5 81.3 80.2 78.5 78.3 78.0 76.9	These are the most porous and friable quartzitic sediments. Some corroded diatom fragments still visible suggesting that the structure of the sediment has not been greatly altered during diagenesis. No infilling of voids by chalcedony. No replacing of groundmass by microcrystalline quartz. Planktonic foram tests infilled by calcite. (Plate 2.6)
ARGILLACEOUS INTERBEDS	73.3 69.8 68.9 67.2	Broken and whole planktonic foram tests set in a fine groundmass of detrital quartz, feldspars (andesine/oligoclase) and clay minerals(illite & montmorillonite) which are strongly aligned parallel to bedding. (Plate 2.7)

(*sample from Sperlinga Quarry, all others from Monte Caolina)

Fig. 2.4 PETROGRAPHIC AND DIAGENETIC FEATURES OF THE QUARTZITIC SILICEOUS SEDIMENTS apart from the finely disseminated calcarous material most of the sediment seems to consist of reprecipitated silica and corroded diatom fragments. The remnants of a fine millimetre lamination is visible in places although the laminae have been so intensely distorted and broken up by diagenesis that the sediment now has an irregular blotchy appearance. The original laminated texture is often discernible only because the outlines of the darker laminae are preserved by iron staining or because of their greater argillaceous and detrital content (Plate 2.6).

Other detrital particles found in the siliceous beds include rare phosphatic material probably due to skeletal fish remains and pieces of lignite found in the sections on Monte Caolina overlooking the Santa Venera Valley and by the Fiume Sperlinga.

2.2.3 Age.

Campisi (1962) when first drawing attention to the Gangi-Sperlinga siliceous deposits ascribed their age to the Upper Oligocene on the basis of a rather poor microfauna recovered from one of the clayey horizons. Broquet (1973) also suggests an Upper Oligocene age for the Finale deposits since they are closely associated with shales of that age. However Andreieff et al. (1974) consider them somewhat younger, being Upper Aquitanian or Lower Burdigalian which is the same age that Didon et al. (1969) have proposed for similar deposits in Spain and Northern Italy.

2.3 Opal-CT Sediments

Siliceous sediments composed of opal-CT have not previously been described from Sicily, however, two localities have been found in the centre of the island. The first is at Dittaino 20kms east of Enna along the Enna-Catania road and the other is at Antinello roughly half way between San Cataldo and Marianapoli. Ogniben (1957) has described cherts within the Tripoli Formation from this locality but, although Messinian dolomitic and aragonitic sediments were found (see Chapter 3), the only siliceous sediments were of early Miocene age. At neither locality could anything be seen of their stratigraphic setting, in fact at Antinello the siliceous material was not even found in situ but only as fragments in a ploughed field. However, the general appearance of the landscape at both localities suggests that the siliceous rocks are probably associated with shales and clays of the Argille Scagliose. Although several small sandstone outcrops near to Antinello suggest that the ridge upon which the siliceous sediments were found may be a pod of Numidian Flysch within the Argille Scagliose.

2.3.1 Appearance.

The appearance of the two sediments is quite different; the Antinello samples are dark brown/grey finely laminated cherts with a slightly resinous lustre. At Dittaino, on the other hand, the rock is light brown or light grey in colour with a light, homogenous porous, porcelanous texture (Plate 2.8). The light grey sediment is denser, less porous and more fractured than the light brown (Fig 2.5) and occurs as diffuse patches which bear no apparent relationship to any primary sedimentary features. Bedding is usually difficult to see because of the homogenous nature of the sediment however thin laminae are sometimes visible and are often distorted, possibly as a result of slumping.

2.3.2 Petrography.

The silica concentration of these rocks is more variable that the quartzitic siliceous sediments to the north (Fig 2.6): the Antinello sample is 89.2% SiO_2, the light grey porcelanite from Dittaino contains 75-85% while the light brown porcelanite is only 50% SiO_2 and has a much higher CaO content. The principal silica mineral in all these sediments is opal-CT with lesser amounts of quartz.

The opal-CT chert from Antinello contains many planktonic foraminiferal tests usually infilled with chalcedony or microcrystalline quartz set in a very fine matrix. This matrix contains fine millimetre laminations, often distorted and interupted by patches of sediment in which the opal-CT groundmass is being replaced by microcrystalline quartz. Despite this , much of the original texture of the groundmass remains unaltered and can

FIG.2.5 PHYSICAL AND MINERALOGICAL PROPERTIES AND DIAGENETIC CHARACTERISTICS OF OPAL-CT SEDIMENTS.

Sample :-	1	2	3	4	5
% SiO_2	89.20	84.90	74.80	53.70	46.10
% Qtz	17.58	20.95	1.50	3.31	1.76
% Calcite(XRD)	8.55	16.57	27.52	66.32**	67.26**
% " (XRF)	8.95	15.59	26.94	43.91	49.32
d(101) spacing Å of Opal CT over two runs :-	4.105 4.099	4.092 4.092	4.082 4.094	4.077 4.075	4.080 4.073
Dry bulk density gms/cc*:	2.28	2.11	-	-	1.75
Texture :	chert	dense porcelanite		porous porcelanite	
Lepispheres :	no	no	no	yes	yes
Diatom preservation :	good	poor	poor	poor	poor
Groundmass replacement :	Qtz	Qtz?	None	None	None
Infill of foram tests. :	Qtz	Qtz/cte	Qtz/cte	cte/none	cte/none

Sample numbers are the same as in Figure 2.6

* Dry bulk densities for the quartz rocks range from 2.09 gms/cc for porcelanites to 2.88 gms/cc for the quartzitic cherts.

** The large discrepancy between the XRD and XRF values is probably due to errors in the XRD method when calculating relatively large percentages of any one mineral. The XRF values are therefore thought to be the more accurate in this case.

FIG. 2.6 XRF MAJOR ELEMENT ANALYSIS OF OPAL-CT SEDIMENTS.

Sample:-	1	2	3	4	5
	%	%	%	%	%
SiO_2	89.20	84.90	74.80	53.70	46.10
Al_2O_3	1.30	1.49	2.36	3.58	3.63
Fe_2O_3	0.67	0.69	0.90	1.38	1.34
MgO	0.40	0.33	0.48	0.87	0.94
CaO	5.57	9.19	15.76	25.81	28.92
Na_2O	0.13	0.03	0.13	0.31	0.31
K_2O	0.57	0.20	0.31	0.65	0.63
TiO_2	0.10	0.11	0.13	0.16	0.15
S	-	-	-	-	-
P_2O_5	0.10	0.12	-	0.04	0.08
CO_2*	4.40	7.26	12.45	20.39	22.85
Total:-	102.44	104.89	107.32	106.89	104.94

Sample 1 : Opal CT chert from Antinello.
" 2 : Dense opal CT porcelanite from Dittaino.
" 3 : Dense grey opal CT porcelanite from Dittaino located adjacent to sample 4.
" 4 : Porous light brown opal CT porcelanite from Dittaino located adjacent to sample 3.
" 5 : Porous light brown opal CT porcelanite from Dittaino.

* Calculated from MgO and CaO values assuming all MgO present as dolomite and all remaining CaO present as calcite.

be seen to consist largely of fragments of both pennate and centric diatoms and a few coccoliths set amid what is probably reprecipitated silica (Plate 2.9).

The millimetre laminations are present in places at Dittaino and again have a crenulated appearance (Plate 2.10). Although it is not so intense as to destroy the continuity of the laminae as occurs in the quartzitic sediments near Gangi and Sperlinga. The groundmass is very fine grained but as well as silica contains a considerable amount of $CaCO_3$ evenly distributed throughout the sediment, much of it as coccoliths and discoasters (Plate 2.11). The silica appears to be mainly reprecipitated but corroded diatoms and opal-CT lepispheres are fairly common (Plates 2.12 & 2.13). Complete planktonic foraminiferal tests are common and occur in varying sizes scattered randomly throughout the sediment. These are either unfilled or are filled with sparry calcite in the light brown porcelanite but in the denser grey porcelanite, those that haven't already been infilled by calcite contain microcrystalline quartz and chalcedony. There is no perceptible boundary between the two types of porcelanite, the contact is marked only by the denser appearance of the groundmass and the siliceous infilling of foraminiferal tests in the light grey patches of sediment.

Other grains scattered throughout the sediment include phosphatic material (skeletal remains of fish) and the ubiquitous silt-sized detrital quartz grains and opaques. In at least one case these form a thin graded horizon indicating the redeposition of sediment. The detrital component is perhaps less common than in the quartzitic sediments to the north and although minor amounts of illite may be present there is no marked mica/clay orientation.

2.3.3 Age.

Samples of these sediments have been sent to Dr. M. Hart of Plymouth Polytechnic and Dr. G. Jenkins of the Open University for possible dating. Their conclusions may be summarised as follows:- The siliceous sediments contain only a poor calcareous microfauna making accurate dating impossible, although they can be dated within certain limits. Dittaino is Lower Middle Miocene (or possibly slightly older) to Upper Miocene but probably Middle Miocene (Hart 1977 p.c.) while Antinello is Lower Miocene (Jenkins 1978 p.c.) (Fig 1.2). The two localities are therefore of similar, though not identical, ages. The Gangi-Sperlinga deposits are possibly the same age as the opal-CT chert from Antinello.

2.4 Opal-A Sediments.

Diagenetically unaltered diatomaceous sediments of Aquitanian-Lower Burdigalian age and identical to the diatomites of the Messinian Tripoli Formation (Chapter 3) have been reported from several localities in the vicinity of Agrigento in southwest Sicily (Decima and Sprovieri 1973). It appears that all of these outcrops occur as Lower Miocene olistoliths set within the Middle Miocene shales of the Argille Scagliose (Decima 1972).

2.5 Diagenesis.

As mentioned above, there are a number of textural and mineralological variations to be found within the Lower Miocene siliceous sediments in Sicily due to their often extensive diagenesis. The diagenesis of siliceous sediments has been the topic of considerable recent research based largely on the Monterey Formation in California and on core material collected by the Deep Sea Drilling Project (Fig 2.7); as a result the literature on the subject is extensive but recent reviews are provided by Murata and Larson (1975), Kastner et al. (1977) and Hein et al. (1978).

Unfortunately work on the diagenesis of these Sicilian sediments is greatly hampered by their lack of exposure so that any conclusions are of necessity based on very little and possibly non-representative data. Nevertheless despite the lack of outcrop a wide variety of mineralogical and textural 'types' have been found; making it possible at least to speculate on the diagenetic history of of these sediments.

2.5.1. Regional Variations in Mineralogy

The transition of diatomaceous sediments into opaline (cristobalitic) cherts and porcelanites and then into quartzitic cherts

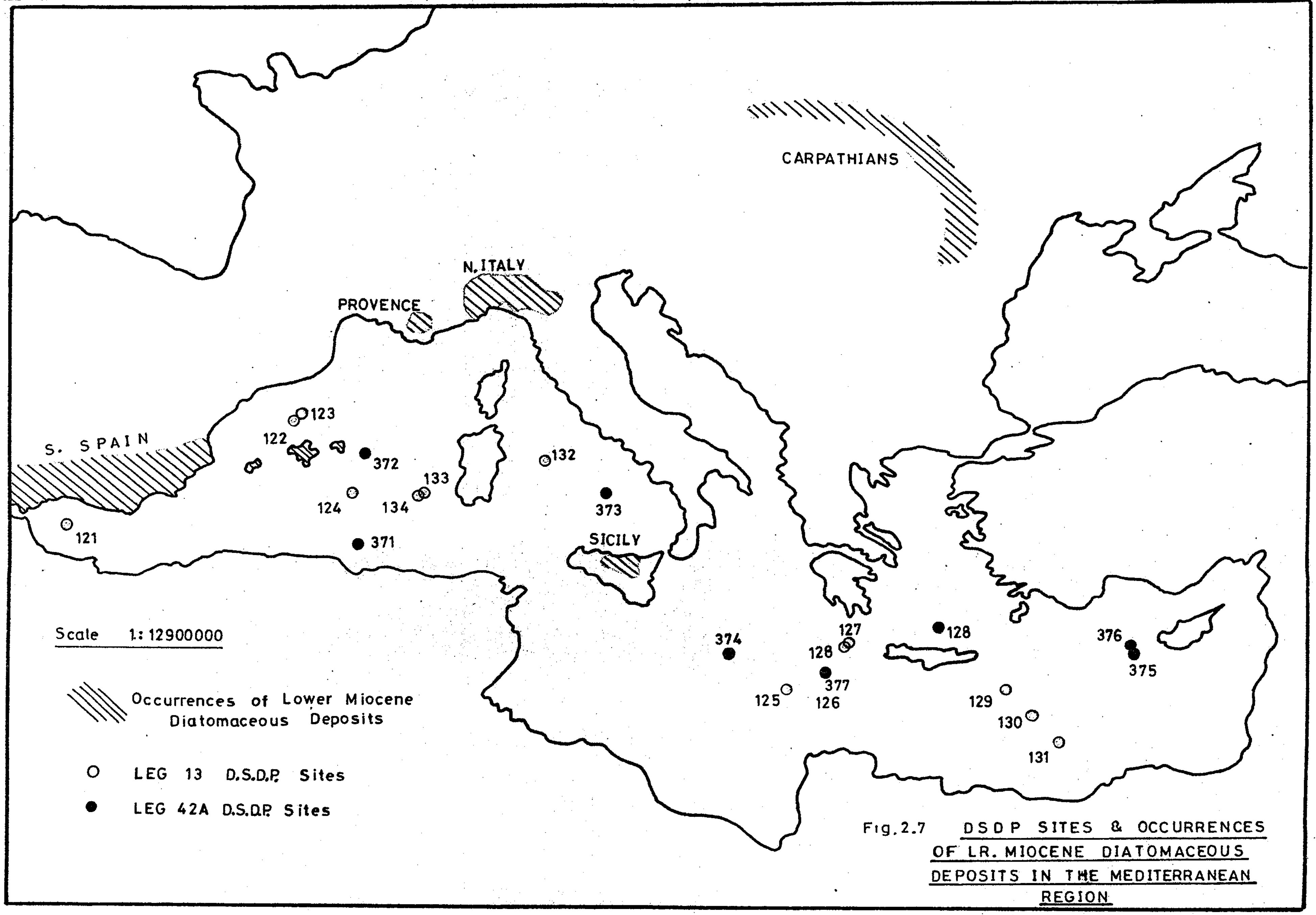


Fig. 2.7 DSDP SITES & OCCURRENCES OF LR. MIOCENE DIATOMACEOUS DEPOSITS IN THE MEDITERRANEAN REGION

and porcelanites has been described by Bramlette (1946) from the Monterey Formation in California. The controlling factors in these diagenetic transformations were thought to be time and temperature with the latter being dependant on depth of burial and/or geothermal gradient (Bramlette 1946, Heath and Moberly 1971). More recently Von Rad et al.(1978) reached the same conclusions from studying siliceous sediments recovered from the Eastern Atlantic in DSDP Leg 41. It therefore seems likely that the transition from diatomites in the southwest to opal-CT sediments and then to quartzitic sediments in the northeast of Sicily may be related to increasing depth of burial because since all the sediments are of approximately the same age (Fig 2.1). Whereas in California the depth was attained by the rapid accumulation of sediment in subsiding basins (Ingle 1973), in Sicily it was most probably brought about by burial under the pile of nappes of Lower Cretaceous-Middle Miocene flysch, which were emplaced during the tectonic events of the Middle Miocene and are now found in the northern part of Sicily.

2.5.2 Diagenesis within the opal-CT Sediments.

As well as time and depth of burial controlling silica diagenesis it has recently been shown that the original composition of the sediment and the silica concentrations in the interstitial waters have an equally important effect (Lancelot 1973, Keene 1975, Kastner et al.1977) although Von Rad et al.(1978) suggest that this is only because they control the rate at which the diagenetic changes occur. However, whatever caused the textural variations in the opal-CT sediments at Dittaino it can have been neither time nor depth of burial since the samples come from the same outcrop and must therefore be of the same age and have had identical thermal histories. The diagenetic variations in the sediments at Dittaino and probably Antinello are therefore thought to have been primarily due to differences in the original sediment.

A summary of the properties and diagenetic characteristics of the opal-CT sediments is given in Figure 2.5. The five samples consist of a chert from Antinello (Sample 1) and four porcelanites from Dittaino; representing a transition from the dense grey porcelanites (Sample 2) to the light brown, porous porcelanites (Sample 5) with two intermediate samples (3 and 4), one of either texture, adjacent to the boundary. On appearance and texture alone the five sediments would seem to represent a sequence of increasing diagenesis from the light, porous porcelanite to the hard, dense chert. This assumption is indeed born out by some of the other properties mentioned in Figure 2.5; namely the amount of silica and quartz in the sediment, the increase in density and evidence of replacement of the groundmass and infilling of foraminiferal tests by quartz. On the basis of these observations it is possible to propose a diagenetic sequence by which the porous porcelanite might be transformed into a chert.

The transition from porous to dense porcelanite (Sample 4 to sample 3) is sharp and well defined texturally (Plate 2.8) but is obviously gradual in other respects as shown by the gradual increase in silica content from the porous porcelanite through to the chert. The increase in silica and density across the textural boundary is not reflected by an increase in quartz despite some foraminiferal tests becoming infilled with chalcedony; they must therefore be due to the increased precipitation of opal-CT in the pore space of the sediment. Away from the porous porcelanites the silica content continues to increase but the amount of quartz shows an even more marked increase (Sample 2). Since there is no apparent increase in the amount of chalcedony in foraminiferal tests this can only be due to the development of cryptocrystalline quartz within the groundmass of the sediment. The nature of the transition of opal-CT into quartz is generally thought to involve dis solution and then reprecipitation of the silica (Carr and Fyfe 1958 Murata and Larson 1975, Stein and Kirkpatrick 1976) although a solid state inversion has also been suggested (Ernst and Calvert 1969, Heath and Moberly 1971). The final stage of the diagenetic sequence (Sample 1) is when the cryptocrystalline quartz in the groundmass develops into microcrystalline quartz. Since there is no overall increase in the silica content this must imply the widespread replacement of opal-CT by quartz.

However while this final stage outlines what is likely to happen to the Dittaino sediments in the future, the Antinello chert clearly was never comparable with the Dittaino porcelanites. Etching the chert with HF revealed diatom fragments that had obviously undergone very little dissolution (Plate 2.9) contrasting with the highly corroded appearance of the rare diatom remains in the Dittaino porcelanites. Kastner et al. (1977) has suggested that the preservation of diatom remains in diagenetically advanced sediments may be achieved by the rapid precipitation of opal-CT in the early stages of diagenesis coating and protecting the siliceous fragments from further dissolution. This necessitates the initial sediment at Antinello being very rich in opaline silica since the preservation of the fine laminae suggests that the sediment was fine grained as well as rather impermeable and would thus prevent the influx of silica-rich waters. The association of opal-CT chert development with the very purest diatomite horizons in the Monterey Formation in California (Murata and Larson 1975) also suggests that the Antinello chert was originally a very pure siliceous sediment.

The calcium carbonate content of the Dittaino porcelanites shows that these sediments can have been nothing like as pure and the advanced diagenetic state of some of the sediment is probably due to the known ability of $CaCO_3$ to increase the rate at which silica diagenesis occurs (Lancelot 1973, Keene 1975, Kastner et al. 1977). Von Rad et al. (1978) suggest that the first stage in the diagenesis of a porous calcite-rich siliceous sediment is the formation of lepispheres in voids and the patchy replacement of calcite matrix by opal-CT. This is certainly consistent with the occurrence of lepispheres in the pore space of the lighter porcelanites (Plates 2.12 & 2.13) and, by increased or prolonged precipitation of opal-CT, could account for the patchy appearance and lower porosity of the grey porcelanite as well as its lack of lepispheres.

Murata and Larson (1975) and Von Rad et al. (1978) have both emphasized that the progressive ordering of opal-CT is a necessary precursor to its conversion into quartz. In California, this is shown by the increasing sharpness of the peaks on the X-ray diffraction trace as depth and extent of diagenesis both increase (Murata and Larson 1975). A similar trend may be recognised in Sicily and is also related to the degree of diagenetic alteration (Fig 2.8). However, the Sicilian porcelanites do not support the proposed relation between decreasing opal-CT d-spacing and depth recognised in California by Murata and Nakata (1974). In fact, the Sicilian porcelanites reveal precisely the opposite trend (Fig 2.5) and support Von Rad et al's assertion that further investigations are necessary before the numerical value of the d-spacing can be used as an index of the structural state and diagenetic 'maturity' of opal-CT.

Von Rad et al.(1978) have identified several diagenetic 'pathways' by which a sediment rich in opaline silica may be transformed into a quartzitic chert. The evidence from the opal-CT sediments of Sicily is consistent with their conclusions and suggests that the chert from Antinello and the porcelanites from Dittaino belong to different 'pathways' primarily because of the differences in their initial composition. The Antinello chert was a relatively pure sediment , rich in opaline silica that has undergone diagenesis mainly by in situ replacement. The Dittaino porcelanites, on the other hand, were rich in calcium carbonate and their diagenesis has been dependent on the passage of interstitial fluids causing the solution and reprecipitation of the various silica phases.

2.5.3. Diagenesis within the Quartzitic Sediments.

The quartzitic sediments comprise both nodular and bedded cherts as well as light brown porcelanites which, although harder and denser, have a similar appearance to the porous opal-CT porcelanites at Dittaino.

The nodular cherts are found growing within porcelanitic horizons and are particularly well developed in the thicker, older porcelanite beds in the Santa Venera valley and on Monte Caolina (Plate 2.14). They start as small nodules in the centres of the beds and gradually expand outwards until further growth is prevented by an argillaceous horizon whereupon growth continues laterally until separate chert nodules join up and a bedded chert horizon is produced. Thin argillaceous wisps and laminae within the

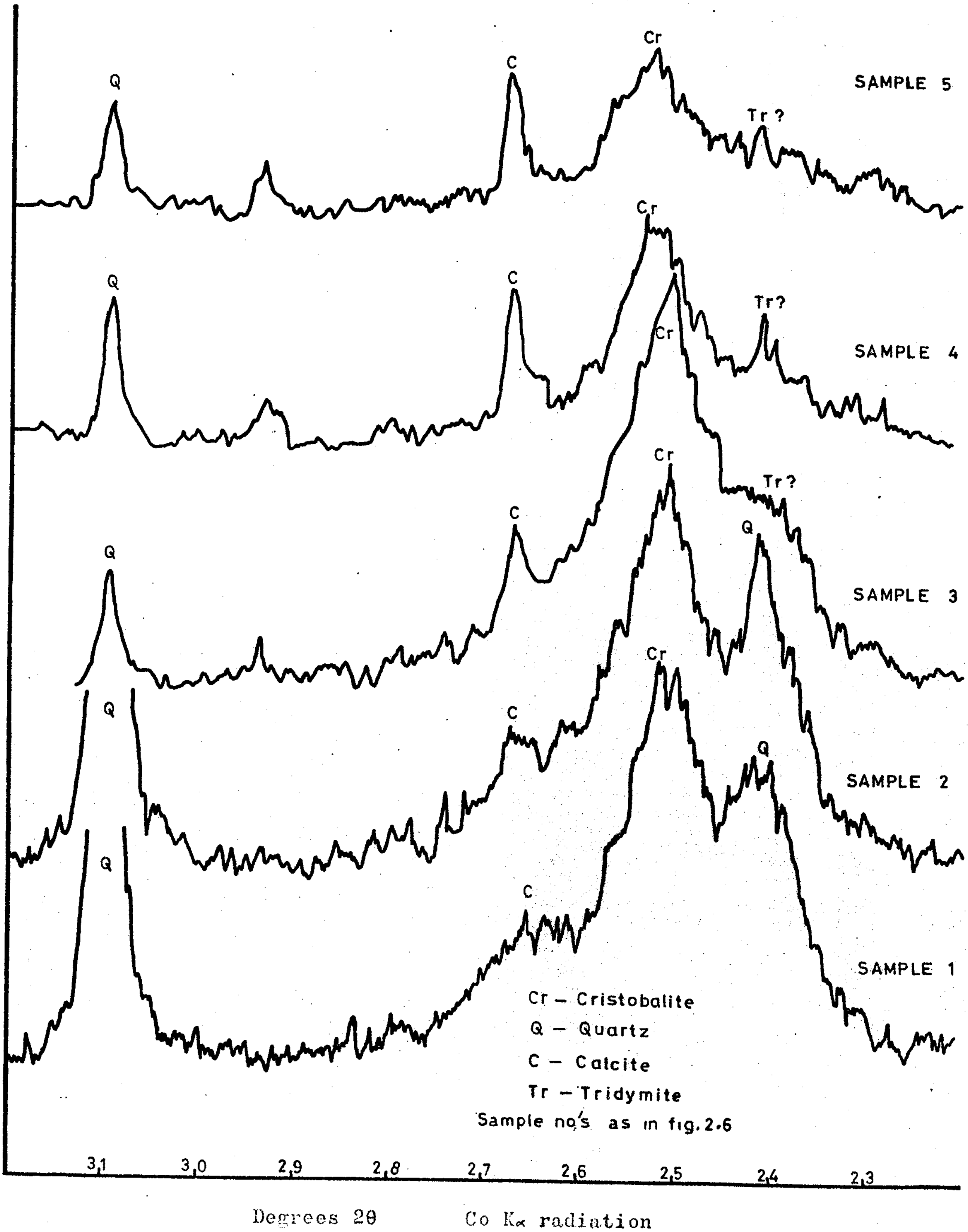


Fig. 2.8 X-RAY DIFFRACTION TRACES OF OPAL–CT SEDIMENTS.

porcelanite appear to hinder the expansion of chert nodules perpendicular to bedding and promote the development of nodules elongate parallel to bedding (Plate 2.15).

The millimetre laminations seen in the porcelanites are continuous into the chert although they frequently fade out into the very cores of the cherts which also have a tendency to be grey rather than brown. Where the laminae are visible they show little or no deviation suggesting that the process of chertification involves little or no volume change (Plate 2.5). Thus, since the chert is denser than the porcelanite (Fig 2.5) and has a markedly higher silica content (Fig 2.4), the development of the chert nodules must involve a net influx of silica.

The contact between chert and porcelanite may be sharp in which case it is probably defined by an argillaceous stringer but more normally the boundary is gradual and it is often difficult to define where the vitreous chert changes into the rougher, slightly porous texture of the porcelanite (Plate 2.5).

The existence of a silica 'gradient' around each chert nodule extending into the surrounding porcelanite, which might be expected from the gradual transition between chert and porcelanite, is clearly shown in Fig 2.4. When the various sediments from Santa Venera and Monte Cablina in Figure 2.4 are listed in decreasing silica content they clearly fall into four zones: the vitreous cherts, the porcelanites within 10 cms of a chert, other porcelanites and argillaceous horizons. A summary of the petrographic and diagenetic features of each group is provided in Figure 2.4. The development of the cherts appears to be largely controlled by the availability of silica since there is a marked silica gradient around the nodules. Furthermore their tendency to develop in the centres of the thicker porcelanite beds is probably due to this being the optimum position to receive a good supply of silica from all sides. The argillaceous horizons therefore must act as barriers to chert development because they restrict the supply of silica probably both by acting as a permeability barrier and because they themselves are relatively poor in silica. The source of the silica is hard to establish.

It is possible that the silica was supplied from outside; or, more likely perhaps, is that since the bedding often has an irregular undulating appearance where chert nodules are developed, silica is being supplied to the chert nodules by the solution of siliceous material in the less indurated porcelanites and argillaceous horizons.

There is no trace of opal-CT in any of these sediments although, as mentioned above, the appearance of the least siliceous porcelanites is not unlike that of the porous porcelanites at Dittaino. It is therefore impossible to do more than speculate on their possible diagenetic history. However, certain observations may be made: If these sediments were deposited in the Aquitanian - Lower Burdigalian then their burial as the nappes advanced must have been both rapid and have occurred soon after deposition. Furthermore the argillaceous material associated with these siliceous sediments is known to retard silica diagenesis just as calcium carbonate is known to promote it (Lancelot 1973, Keene 1975, Kastner et al. 1977). The association of rapid burial and slow rates of diagenetic change may therefore be responsible for sediments in a mineralogically advanced stage of diagenesis retaining early diagenetic textures.

2.6. Lower Miocene Siliceous Sediments elsewhere in the Mediterranean Region.

Siliceous sediments, similar to those described above from Sicily and termed "silexites" by French authors, have been reported from Spain, the Balearic Islands, Northern Italy, Poland Czechoslovakia and Romania (Fig 2.7).

In Eastern Europe they occur throughout the Carpathian Mountains usually as diatomaceous intercalations associated with Oligo-Miocene flysch derived from the Russian Platform, just as the Sicilian examples are associated with flysch derived from the African Craton (Contescu et al. 1966). The sediments are often in an advanced stage of diagenesis and appear as bands or lenses of quartzitic chert usually centimetres or millimetres thick but occasionally up to several metres thick (Kotlarczyk 1966, Mahel et al. 1968). These diatomites are usually brown-grey in colour with a fractured tabular or platy appearance; fine crenulated laminae composed of alternating opaline and argillaceous horizons commonly occur and the diatom frustules themselves are found set in the opaline -argillaceous matrix. Siliceous sediments with a porcelanitic texture do occur but are fairly rare (Kotlarczyk 1966).

Diatomites apparently unaffected by diagenesis have been described from Rumania (Filipesco 1930); these have been termed 'diatom earth' by the author presumably due to their very friable texture. They are very rich in diatom frustules, are of late Oligocene or early Miocene age and are immediately overlain by Oligo-Miocene Flysch, here represented by the Kliwa Sandstone.

Similar diatomaceous sediments of approximately the same age are known in southern Spain where they are termed 'moronitas'. These characteristic deposits occur in the Guadalquivir Basin and the Prebetic zone of the Betic Cordillera (Fig 2.9); they extend into the Balearic Islands and even into southern France. They are white-blue/grey diatomaceous marls which also contain an abundant calcareous planktonic fauna and are associated with globigerinal marls and marly sandstones(Colom 1952). Despite having a remarkably uniform lithology all the deposits are not thought to be of the same age Colom (1952) but they are all thought to lie within the period Oligocene to Middle Miocene (Chauve 1968).

Further south in the Subbetic and Internal zones of the Betic Cordillera other siliceous deposits are known (Fig 2.9). In the external (Subbetic) zone there are only a few white siliceous sediments which are associated with marls and detrital limestones. The silica here occurs both in the form of quartz and opal-CT with the ratio of opal-CT/Quartz being directly proportional to the amount of silica deposited (Riviere and Courtois 1976). In the Median and Internal zones the siliceous sediments are fairly widespread and, although their stratigraphic relations are often obscure, they would appear to be associated with conglomerates, sandstones and marls in the Median zone and and with flysch in the Internal zones (Didon et al. 1969). The

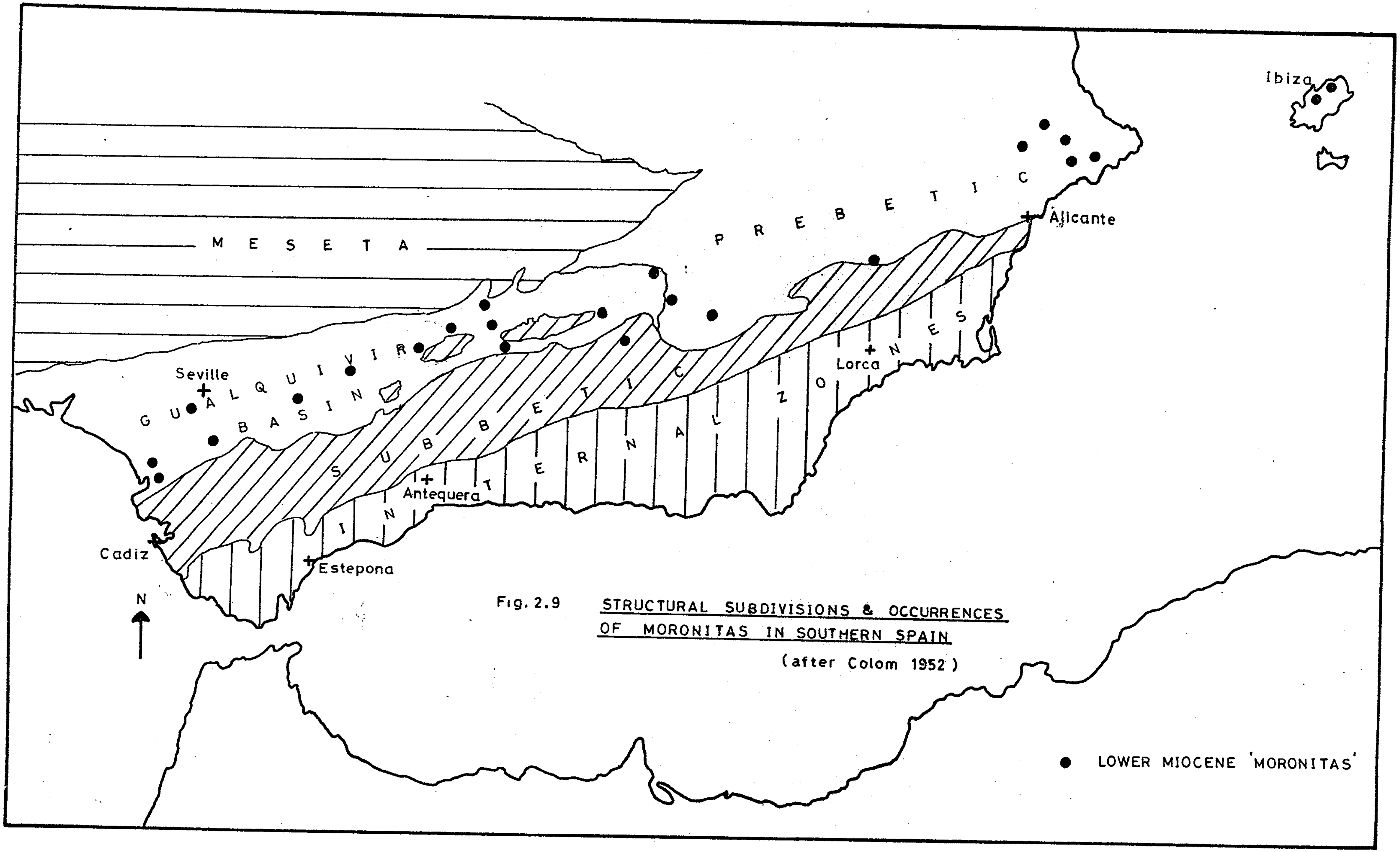


Fig. 2.9 STRUCTURAL SUBDIVISIONS & OCCURRENCES OF MORONITAS IN SOUTHERN SPAIN (after Colom 1952)

siliceous sediments themselves occur as brown siliceous marls with many chert beds. The dominant mineral in these beds is silica in the form of quartz; calcite becomes more important towards the external zones and there are minor amounts of dolomite with illite being the most important clay mineral (Riviere and Courtois 1976). The age of these siliceous deposits is thought to be late Aquitanian which corresponds with the age of the oldest moronitas (Didon et al.1969).

In northern Italy similar sediments are known on the southern edge of the Liguro-Piedmont Basin. They consist of thin, brown-grey beds of siliceous material set in marls and marly sandstones of an age corresponding to the Aquitanian-Burdigalian boundary. They are very similar to the Spanish deposits but are associated with more abundant and more varied terrestrial detritus (Didon et al.1969).

2.7. Sources of Silica.

These silica-rich deposits (up to 95% in the quartzitic chert in Sicily) are all of a similar age, often of similar appearance and have similar sedimentary associations. Therefore it seems probable that in each case, the principal source of silica must also have been the same.

Near Agrigento (Decima and Sprovieri 1973) and at Antinello the source of the Silica is clearly the skeletal debris of diatoms and to a lesser extent radiolarians. At Dittaino there are sufficient corroded remnants of diatom fragments to suggest that the source of the silica is the same but that the frustules have undergone dissolution in the course of diagenesis. Evidence of diatom frustules is much rarer in the quartzitic deposits; however, corroded fragments have been found and large whole diatom frustules have been reported from the Gangi-Sperlinga outcrops (Campisi 1962). Diatom frustules have also been shown to be the main source of silica for the siliceous deposits of Poland and, as mentioned above, both the 'moronitas' of Spain and the 'diatom earth' of Rumania are composed largely of diatomaceous debris (Filipesco 1930, Colom 1952, Kotlarczyk 1966). It is therefore thought likely that all these siliceous sediments were originally deposited as diatomites and that present variations in their mineralogy and texture are principally due to the effects of diagenesis.

The association of diatomaceous sediments and volcanism has been recognised for some time; Taliaferro (1933) documented many examples from all over the world and proposed that there was a direct genetic relationship between the two. This hypothesis was generally accepted until work on the recent diatomaceous deposits of the Gulf of California (Calvert 1964, 1966a, 1966b) showed that there was sufficient dissolved silica in ocean water to sustain the necessary high phytoplankton productivity provided that a mechanism such as the upwelling of deeper waters could continually supply sufficient nutrients and silica to the euphotic zone. The influx of terrigenous material is very low so that fairly pure siliceous sediments are able to accumulate without volcanism playing any significant role. The upwelling itself is dependent on coastal and seafloor topography so that the association of diatomites and volcanism is due to the tectonic processes which create the suitable topography and with which volcanism is associated (Orr 1972).

Volcanic material is present in the Sicilian siliceous deposits and occurs more commonly in the argillaceous horizons. Recent authors have therefore followed Taliaferro's example in favouring a direct link between these siliceous deposits and volcanism (Didon et al.1969, Broquet 1973, Riviere and Courtois 1976, Wezel 1977). The presence of small laths of andesine/oligoclase is consistent with the dominantly andesitic volcanism which characterised the region at this time (Wezel 1977) and the presence of montmorillonite in the argillaceous horizons may also be regarded as indicating volcanic activity (Griffin et al. 1968). However, these components make up a very small part of the total sediment. Furthermore, TiO_2/Al_2O_3 ratios which have been used in Spain to distinguish between detrital clastic and pyroclastic sediments (Riviere and Courtois 1976) are not consistent even with a predominantly pyroclastic origin for the argillaceous horizons associated with the Sicilian siliceous sediments (Fig 2.10) (see also Fig 2.4).

SPAIN (Riviere & Courtois 1976)		SICILY	
Acid pyroclastic	0.012 - 0.016	Argillaceous interbeds	0.042 - 0.047
Normal clastic	0.050 - 0.080	Siliceous sediments	0.052 - 0.109

Fig. 2.10 TiO_2/Al_2O_3 RATIOS OF SILICEOUS SEDIMENTS IN SICILY AND SPAIN.

The volcanic contribution to the siliceous horizons would therefore appear to be far too small to be regarded as a significant source for silica. The concentration of planktonic foraminiferal tests as well as the lack of any obvious increase in grain size suggests that the argillaceous horizons are caused by a decrease in diatomaceous sedimentation rather than a sudden influx of terrigenous or volcanic material.

2.8. Geological History of the Lower Miocene Siliceous Sediments.

It has been suggested above that many of the outcrops of siliceous sediments may be olistoliths set within the Numidian Flysch or Argille Scagliose. Nevertheless, even if this is the case, the outcrops at Finale and Monte Barbagiano clearly show that the siliceous material and the sandstones must have been laid down in very similar depositional environments. It was this association with clastics that led Filipesco (1930) and Colom (1952) to propose that the siliceous sediments had accumulated in shallow coastal waters. However, their faunal content and characteristic appearance indicate that this is highly unlikely. Planktonic foraminifera, radiolarians, diatoms, skeletal fish debris, together with their finely laminated appearance and absence of clastic material other than that small enough to have been wind transported, all suggest a pelagic origin. Furthermore, they closely resemble sediments reported from the Californian Continental Borderland (Emery 1960) and Gulf of California (Calvert 1964), suggesting that present day conditions there may be analogous to those prevailing during the early Miocene in Sicily.

The lithological similarity between the Sicilian and other siliceous deposits suggests that they were all deposited in similar environments. In southern Spain the moronitas are strongly associated with the North Betic Strait within which they occur extensively and although all the deposits are not coeval, they are all confined to the Aquitanian/Burdigalian (Colom 1952). This Strait provided a marine connection between the Atlantic and the 'proto' Western Mediterranean and was possibly further connected with the Carpathian diatomaceous deposits via the Peri-Alpine depression which maintained a marine connection between the two areas until the beginning of the Tortonian (Gignoux 1955). Sicily must also have had a marine connection with the open ocean although it was not necessarily in marine communication with the Spanish diatomites since it is possible that the Sicilian connection with the ocean was via the Rif rather than Betic Straits.

The flysch and Argille Scagliose were accumulating in the deep and narrow seaways which probably characterised the Western Mediterranean at this time. Within these troughs some small basins must have existed that were shielded from terrigenous input and in which diatomaceous sediments were able to accumulate. As the Calabrian Massif moved against the North African continental margin during the early-middle Miocene (Fig 2.2), some of these deposits would have become detached from their immediate stratigraphic surroundings while the most northerly would have been buried beneath the pile of nappes accumulating along the Calabrian Arc (Alvarez et al.1974, Biju-Duval et al.1978). The siliceous deposits thus often appear as olistoliths and would have undergone progressively deeper burial to the north, thereby explaining the increasingly advanced diagenesis seen from southwest to northeast across Sicily (Fig 2.1).

It is interesting to note that in the Betic Cordillera it appears that the transition from the Internal zones through the Subbetic into the Prebetic zone is also matched by a transition in the mineralogical composition of the siliceous sediments from quartz, through opal-CT to unaltered opal-A. This is identical to the diagenetic zonation seen in Sicily and may well be due to a similar cause. Published data on the Carpathian examples is more limited but their similar sedimentological and tectonic history suggests that they too may be diagenetically zoned.

CHAPTER 3.

UPPER MIOCENE (MESSINIAN) DIATOMITES FROM SICILY.

3.1. Geological Setting.

3.1.1. Messinian Salinity Crisis.

Upper Miocene diatomaceous sediments occur as a thin sequence of diatomites and marls known as the Tripoli Formation. This is found not only in Sicily but in many countries surrounding the Western Mediterranean and is overlain by the thick sequence of evaporites known as the "Mediterranean Evaporite" or the "Formazione Gessoso - Solfifera". These evaporites, together with the Tripoli Formation, form a distinctive lithostratigraphic unit deposited during the interval between the end of the Tortonian Stage and the beginning of the Pliocene (Figs 1.2 and 3.1) Selli (1964) has defined this interval as the Messinian Stage and as a result, the evaporitic 'event' that dominates Mediterranean geology during the late Miocene has become known as the 'Messinian Salinity Crisis' (Hsü et al. 1973).

The Mediterranean Evaporite is remarkable firstly, for its size (only the Tarim Basin in China contains an evaporite body of comparable proportions - Nesteroff 1973) and secondly, because its existence was not proven until as recently as 1970 when Glomar Challenger completed Leg 13 of the Deep Sea Drilling Project (D.S.D.P).

Diapiric structures seen on seismic profiles had previously suggested the presence of evaporites beneath the present Mediterranean Sea and small evaporite deposits of late Miocene age had been known for some time from regions surrounding the Mediterranean (Hersey 1965, Kozary et al. 1968, Ryan et al. 1971). However, Leg 13 not only confirmed the presence of the evaporites, it also showed that they extended under much of the present Mediterranean Sea and were up to 4000 metres thick in places (Fig 3.2) (Montadert et al. 1978).

It has been shown that at least some of these evaporites were deposited under shallow water or supratidal conditions (Schreiber and Friedman 1976, Schreiber et al. 1976). Yet, both the Tortonian deposits below and the Pliocene deposits above, are represented

Age m.y.	EPOCH	STAGE		SICILIAN SUCCESSION
	Pliocene	Zanclian		Trubi Fm.
5	Upper Miocene	Messinian	Upper	upper and lower evaporites
$5\frac{1}{2}$				C. di Base
			Lower (Sahelian)	clastics
6				Tripoli Fm.
				"Whitish Marls"
$6\frac{1}{2}$		Tortonian		blue marls

FIG. 3.1 UPPER MIOCENE STRATIGRAPHY IN SICILY

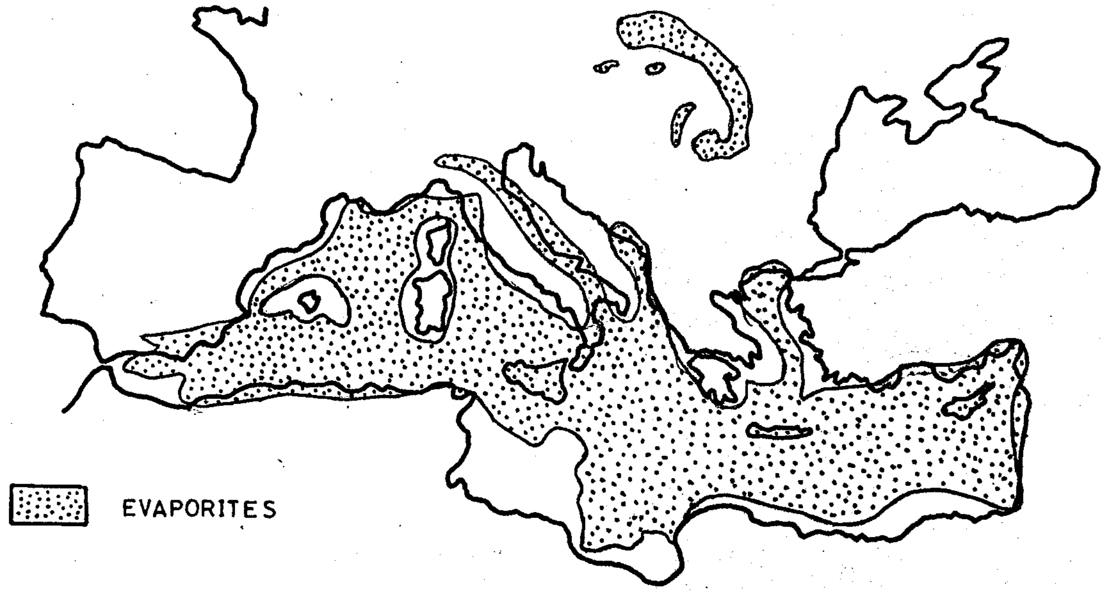


Fig. 3.2 The distribution of the Mediterranean Evaporites.
(after Biju-Duval et al. 1978)

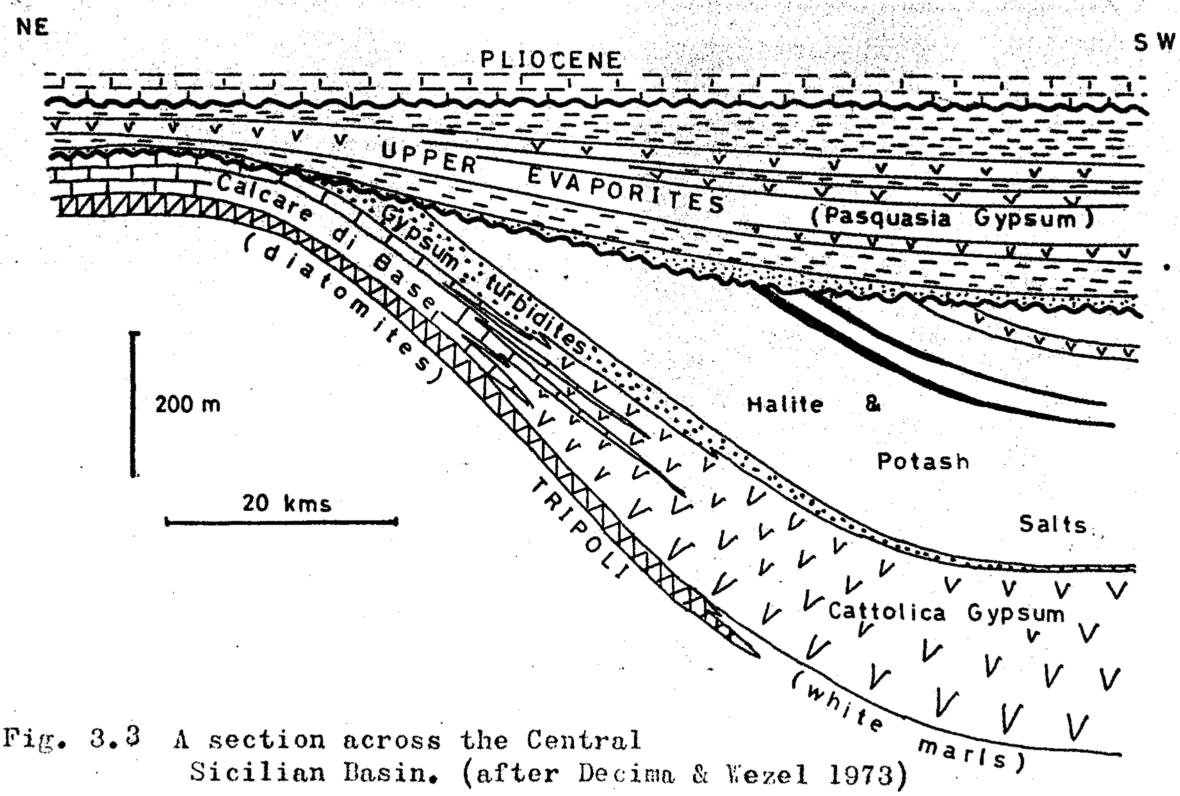


Fig. 3.3 A section across the Central
Sicilian Basin. (after Decima & Wezel 1973)

by open marine,pelagic sediments generally thought to have been deposited in deep water! (Nesteroff 1973., Cita et al. 1978). This apparent contradiction naturally prompted considerable controversy regarding the origin of the evaporite and the nature of the basin in which it was deposited.

Reviews of the conflicting theories put forward to account for the deposition of this evaporite body are provided by Hsü et al. (1973), Drooger (1973) and Sonnenfeld (1975). The model initially proposed by Hsu et al. in 1973 and developed by Hsü et al. (1978) is known as the "Deep Desiccated Basin Model" and has been summarised by Hsü et al. (1973) as the, "Desiccation of a deep Mediterranean basin isolated from the Atlantic; evaporites were precipitated from playas or salt lakes whose water levels were dropped down to thousands of metres below the Atlantic sea level." It is this model, initially greeted with considerable scepticism, that has subsequently gained widespread although still not universal acceptance (see Fabricius et al. 1978).

3.1.2. The Central Basin of Sicily.

a) Physiography.

Some of the best exposures of both the evaporites and the diatomites are to be found in the Central Sicilian Basin, or Caltanissetta Basin as it is also known (Decima and Wezel 1973, Schreiber et al. 1976). This is a fault-bounded trough, some 140 kms long by 80 kms wide that contains a Middle Miocene - Quaternary succession up to several kilometres thick in places (Caire 1970). It is confined to the north by the Sicani, Madonie and Nebrodian Mountains; to the southeast by the Ragusa Platform (Fig 3.4) and may extend across the Sicilian Channel into eastern Tunisia (Caire 1970, Decima and Wezel 1973, Selli 1973).

A section across the basin (Fig 3.3) shows it to contain a large volume of halite and potash salts which, in accordance with the Deep Desiccated Basin Model, are confined to the deepest parts of the basin (Decima and Wezel 1973). The presence of such large quantities of these salts, which must have been the last

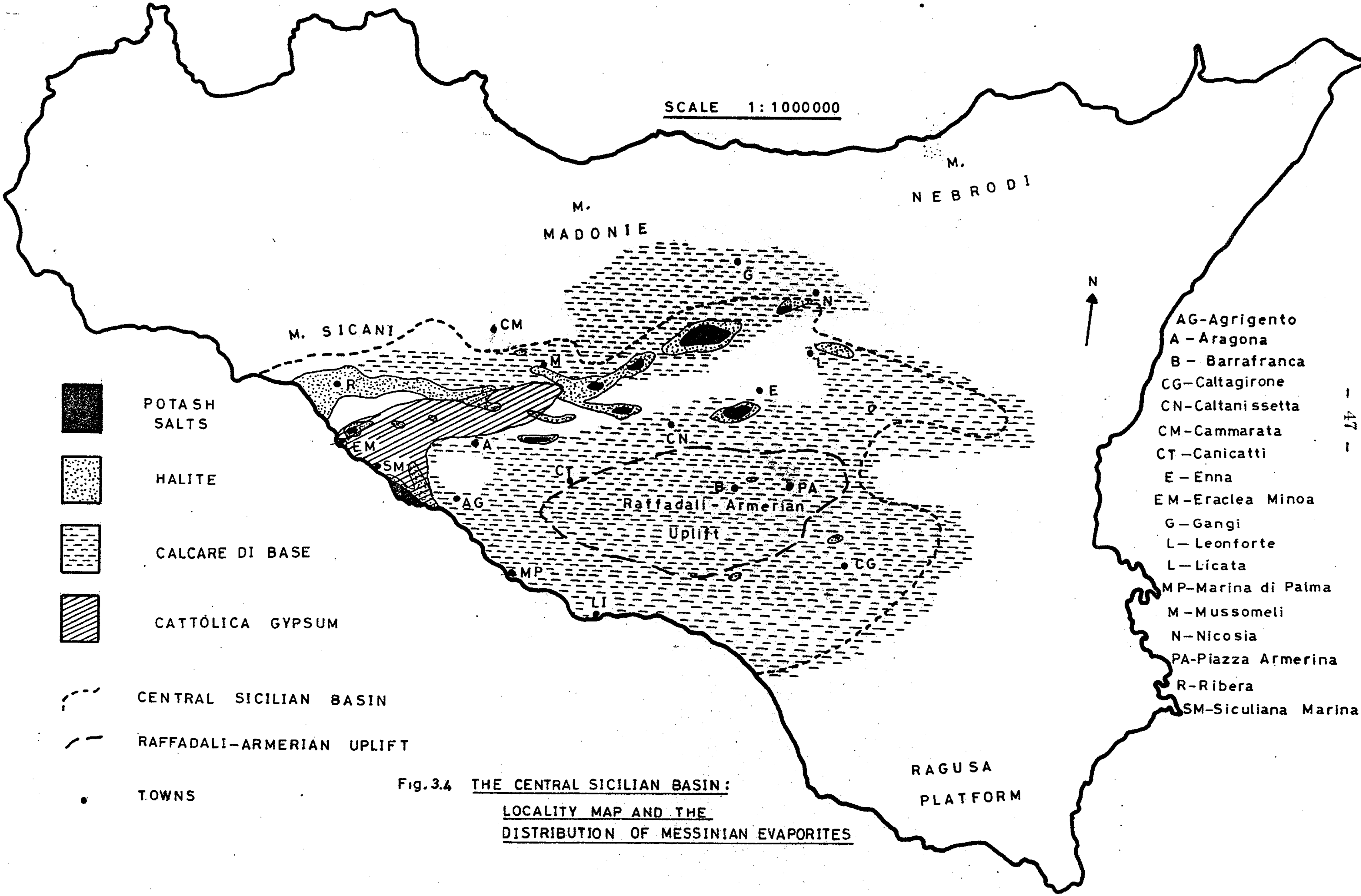


Fig. 3.4 THE CENTRAL SICILIAN BASIN: LOCALITY MAP AND THE DISTRIBUTION OF MESSINIAN EVAPORITES

evaporite minerals to precipitate, shows that these parts of the basin had no communication with still deeper basins. The Central Sicilian Basin must therefore have been one of the deepest of the Mediterranean Basins during the Messinian (Hsü et al. 1978).

The areal distribution of the halite and potash salts (Figs 3.4 and 3.5) shows that the deepest part of the basin was a narrow trough located close to its northern margin and known as the "Platani Trough" (Richter Bernburg 1973) or the "Cattolica Basin" (Decima and Wezel 1973). This deep trough is flanked to the southeast by the "Raffadali - Amerian Uplift"; an area, conspicuous in the Central Basin for its lack of evaporite cover, where the Messinian is represented solely by carbonate sediments (Richter Bernburg 1973).

b) Pre-Messinian Deposits.

Sediments of Middle Miocene - Tortonian age, collectively known as the "Argille Scagliose", are found throughout the Central Sicilian Basin and are well exposed along the coast northwest of Marina di Palma (Fig 3.4). They consist of grey/brown terrigenous shales composed of silt sized quartz and feldspar grains set in a fine, iron stained, kaolinitic groundmass. The shales contain nodules, many localised slumps and an abundance of exotic material, in which blocks of a grey foraminiferal marl are particularly common. The amount of resedimented material in these shales gives them a chaotic appearance that is common to many of the pre-Messinian deposits of the Central Sicilian Basin (Decima 1972, Cita 1973a).

In contrast to these chaotic shales, a few kilomatres to the north, at Camastra, there are blue Tortonian marls exposed only a few metres below the diatomites of the Tripoli Formation. These are soft, massive, blue/grey mudstones (Plate 3.1) that have a mottled appearance suggesting extensive bioturbation, although the only possible evidence of burrowing organisms are occasional molluscan shell fragments. Planktonic foraminifera tests are very common and occur in a murky groundmass containing abundant

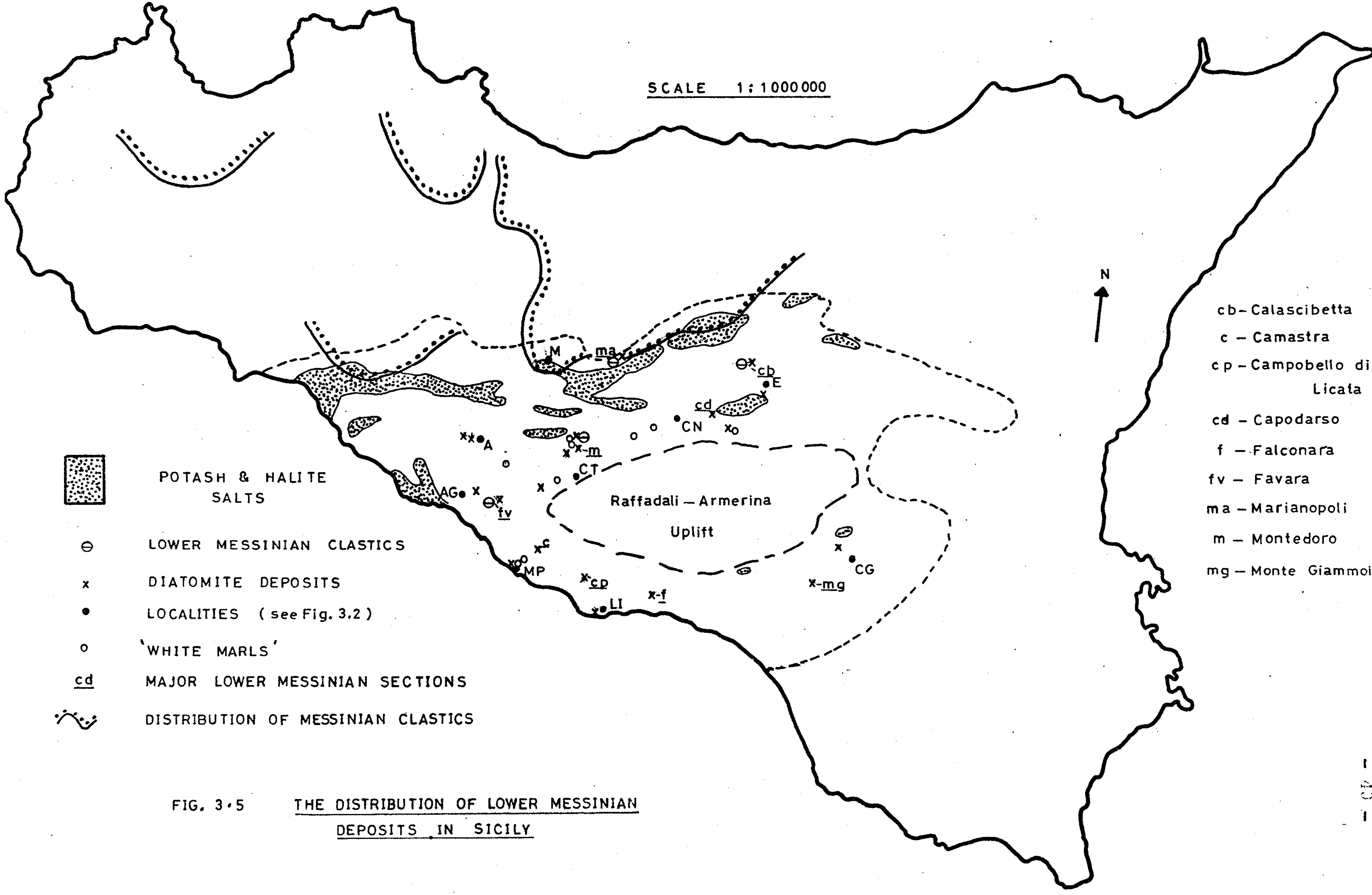


FIG. 3.5 THE DISTRIBUTION OF LOWER MESSINIAN DEPOSITS IN SICILY

coccoliths, discoasters, fine terrigenous material and finely disseminated opaques. Non-stoichimetric dolomite (mole % excess Ca of 5.3%) is present but represents only a small proportion of the total sediment (See Section 3.10.3 and Appendices 1 - 2). It occurs as small euhedral rhombs, 20-30 μ in diameter, scattered randomly throughout the sediment.

Blue/grey sandy marls and clays similar to the Tortonian deposits at Camastra are also found beneath the diatomites at Capodarso, Falconara and Monte Giammoia (Catalano and Sprovieri 1971, D'Onofrio et al. 1975).

Middle Miocene and Tortonian sediments are also known in many areas around the Mediterranean and have been reported from several D.S.D.P. holes. In the Western Mediterranean they are generally similar to the Sicilian deposits and have been interpreted as hemipelagic sediments characteristic of normal marine conditions (Hsu et al. 1977, Cita 1973a). The abundance of resedimented material, marine organisms and the presence of large olistoliths within the Sicilian deposits shows that these must also have been deposited in a deep basin and under normal marine conditions (Decima 1972, Cita 1973a). Faunal evidence from Capodarso confirms this and suggests a water depth in excess of 2000 metres (Bandy 1975) .

3.1.3. The Tortonian/Messinian Boundary.

According to Selli's (1960) original lithostratigraphic definition of the Messinian Stage the Tortonian/Messinian boundary can be placed at the contact of the blue marls and the diatomites of the Tripoli Formation. However, such a definition is of limited value where these particular lithologies happen not to be developed and of no value outside the Mediterranean Region (D'Onofrio et al. 1975). In order to rectify this situation, attempts have been made to try and define both the upper and lower limits of the Messinian Stage in terms of its planktonic foraminiferal assemblage.

In the case of the lower boundary, Selli's choice of the Capodarso-Pasquasia sections in Sicily as the neostratotype has been shown to be particularly inauspicious, since subsequent slumping has obscured the Tortonian/Messinian contact as he defined it (D'Onofrio et al. 1975). Nevertheless, a faunal change has been recognised some time prior to the Salinity Crisis and D'Onofrio et al. (1975) have proposed that the Tortonian/Messinian boundary should be taken as the first appearance of Globorotalia conomoizea. At Falconara and Monte Giammoia sections in Sicily this faunal boundary closely correlates with the appearance of the diatomites of the Tripoli Formation (Colalongo et al. 1976, D'Onofrio et al. 1975). Catalano and Sprovieri (1971) recognise the same faunal change but choose a slightly different horizon and relate it to the disappearance of the Tortonian blue marls. In contrast to most other sections, the same faunal change at Capodarso is recognised some distance below the Tripoli and within the blue marls (Wornardt 1973, Bandy 1975, D'Onofrio et al. 1975).

The work is still in progress (Colalongo et al. 1976) but, however the Tortonian/Messinian boundary is defined, there seems to be general agreement that in Sicily it corresponds roughly to the first appearance of the diatomites of the Tripoli Formation.

In the field, the contact can be seen to be both gradual and conformable. At Camastra (Fig 3.6) and Falconara (Fig 3.7) the first appearance of diatomaceous material is marked by the replacement of the homogenous blue marls by friable grey shales. Within these shales the diatomites initially appear as thin white partings but gradually they become thicker and more frequent until some horizons take on a laminated appearance (Plate 3.1).

This basal shale unit is just over two metres thick at Camastra and the sediment is composed largely of foraminifera tests and terrigenous material similar to that found in the underlying Tortonian. The foraminifera are often concentrated in particular horizons or lenses and may be so abundant in some places that the sediment takes on a sandy appearance. Some

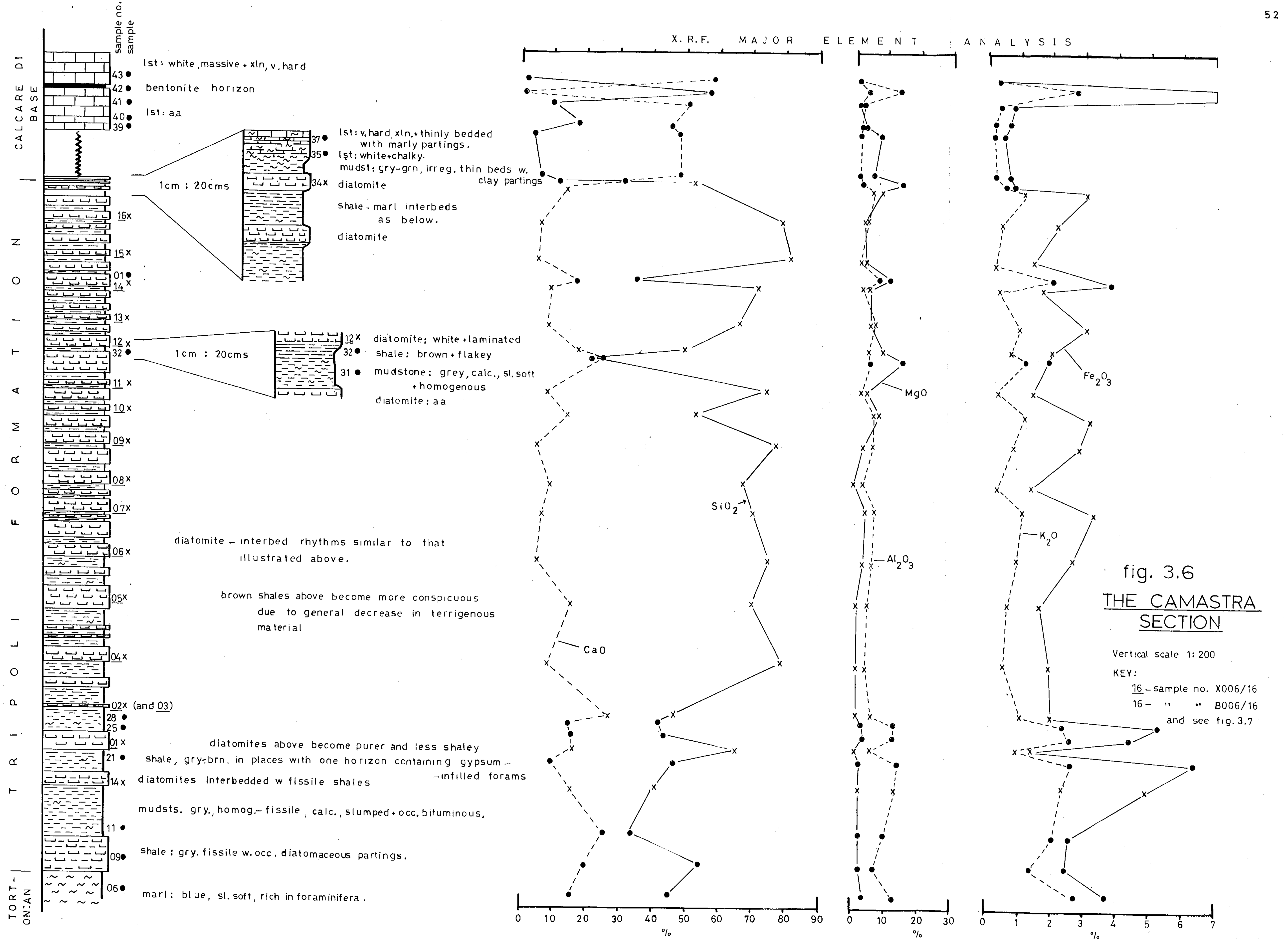


fig. 3.6
THE CAMASTRA SECTION

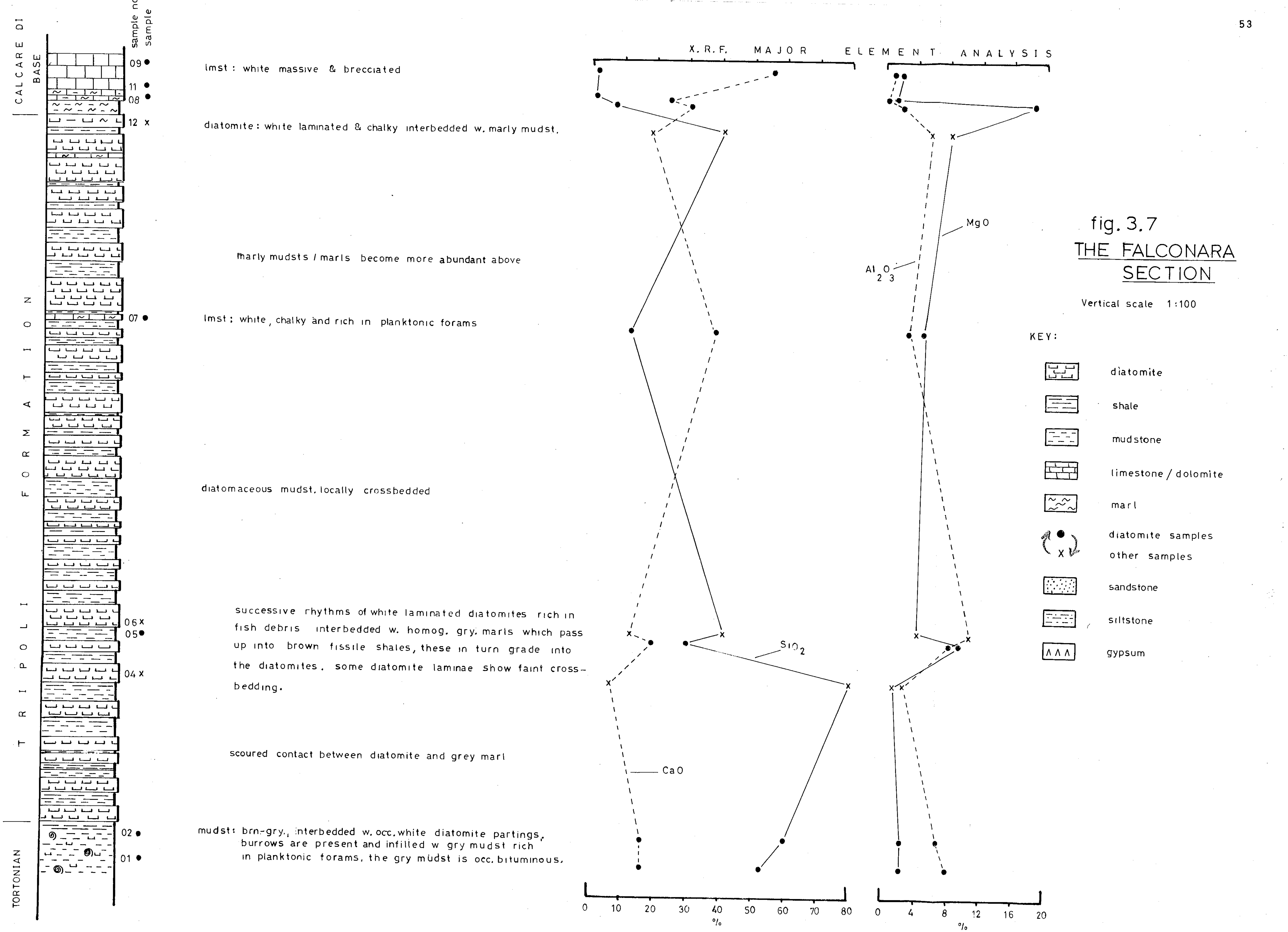


fig. 3.7
THE FALCONARA SECTION

of these horizons are regularly spaced about 1 cm apart and are clearly graded, indicating that much of the sediment has probably been redeposited (Plate 3.2). Diatom frustules are locally abundant, while silicoflagellates, discoasters, radiolaria and coccoliths are also fairly common. The terrigenous material includes clay minerals (mainly kaolinite), micas, finely disseminated opaques and fine, angular to subangular grains of quartz and feldspar. These never exceed a size of 50 μ and may therefore have been wind transported (Rex and Goldberg (1962). Small dolomite rhombs are also present and are randomly distributed throughout the sediment.

Above the basal shale are three metres of less friable mudstone. Unlike the shales, these appear to have been extensively bioturbated and in the equivalent interval at Falconara, one diatomaceous shale horizon contains several burrows infilled with the overlying grey muds. Bituminous mudstones are found at both Camastra and Falconara and are similar to those described from the Tortonian/Tripoli boundary by Selli (1973). However, at Camastra they occur only within an intensely disturbed horizon some 20 cms thick which is thought to have been caused by synsedimentary slumping.

The exposures of the contact between the Tortonian marls and the Tripoli diatomites at Monte Giammoia and Capodarso appear to be similar to those at Falconara and Camastra. However, the thin and much faulted section at Marina di Palma reveals a much sharper contact: the diatomites are here interbedded with brown shales identical to those of the underlying Tortonian. This may be due to the paucity of resedimented and calcareous material compared to Falconara and Camastra, although it is also possible that part of the section has been 'faulted out'.

3.2 The Tripoli Formation.

3.2.1. Distribution and Thickness.

The Tripoli Formation is characterised by diatomaceous sediments and it is these that distinguish it from adjacent formations. It is of early Messinian age, a period also known as the Sahelian (Catalano and Sprovieri 1971), which extended from the end of the Tortonian until the beginning of evaporite deposition (Fig 1.2 and 3.1). Other early Messinian sediments in the Central Sicilian Basin include the "Whitish Marls", thought to be the Tripoli's deep water equivalent by Decima and Wezel (1973) and the clastic deposits found adjacent to the northern margin of the basin. The Calcare di Base, from which the Tripoli is separated by an erosion surface at Monte Giammoia, is thought to be more closely related to the evaporites and to belong to the Upper Messinian (Colalongo et al. 1976, Cita et al. 1978).

The distribution of the Tripoli is shown in Figure 3.5. It is confined to three particular zones:

1) From Enna west-southwest to just north of Agrigento, broadly following the line of halite and potash deposits but apparently avoiding what would have been the deepest parts of the basin.

2) From Agrigento east-southeast along the southern margin of the Raffadali - Amerian Uplift.

3) There are also some outcrops of Tripoli near Caltagirone which belong to neither of the above trends.

The thickness of the Tripoli is highly variable, being absent over much of the basin but attaining a thickness of 60 metres near Barrafranca (Ogniben 1957). A thickness of 75 metres is to be found a few kilometres northwest of Calascibetta but this section contains large amounts of fine grained calcareous and argillaceous material due to it being situated close to the northern margin of the basin. Near Agrigento the Tripoli is much purer and thinner with the 40 metres at Camastra being the maximum observed thickness, although Ogniben (1957) records a thickness of 50 metres near Favara.

3.2.2. The Diatomite-Marl Couplets.

Above the shaley base of the Tripoli Formation the argillaceous content of the sediment rapidly decreases and it takes on a much 'cleaner' appearance. This is clearly illustrated by comparing the chemical composition of the sediments represented in columns 1 - 5 in Figure 3.8: The silica content shows a progressive increase from the Tortonian (sample 1), through the basal diatomaceous shale (sample 2), to the normal diatomites (samples 3,4 and 5) indicating an increase in the diatom content. However, the Al_2O_3, Fe_2O_3, K_2O and TiO_2 contents, which are mostly due to the sediment's argillaceous component, all show a consistent decrease.

As the sediment becomes cleaner, it is seen to consist of successive couplets of alternating diatom-rich and diatom-poor horizons. These couplets are one of the characteristic features of the Tripoli and are always well developed, except when masked by argillaceous material in the bottom few metres of the formation.

On closer inspection each couplet, or rhythm, is seen to consist of three components: a diatomite bed and a non-diatomaceous interbed which is made up of a grey marl overlain by a brown shale (Plate 3.3). The contact between the diatomite and the overlying grey marl is usually sharp and may even be scoured (Plate 3.4) while other contacts are generally gradational. This brief hiatus indicates that each rhythm probably commenced with the deposition of a grey marl, followed by a brown shale and terminated with a diatomite.

Alterations to the rhythm are rare and usually only occur when one of the components is absent. Alternatively, the grey marl and brown shale sometimes merge into each other to form a single brown marly interbed. Occasional clastic or limestone horizons are also found, particularly near the top of the formation, but these will be discussed below.

3.2.3. The Diatomites.

The diatomites are the characteristic lithology of the Tripoli Formation as well as the most conspicuous despite representing only a little over half of the total sediment thickness. The average thickness of the individual diatomite

SAMPLES

	1	2	3	4	5	6	7	8	9	10	11	12
	%	%	%	%	%	%	%	%	%	%	%	%
SiO_2	44.90	56.70	81.00	75.20	80.20	44.40	24.40	40.20	67.20	17.10	56.70	89.90
Al_2O_3	13.23	7.29	1.80	1.69	2.72	12.62	6.13	11.48	6.27	4.99	16.83	1.12
Fe_2O_3	3.73	2.48	1.12	0.98	1.70	6.45	2.50	5.99	3.05	1.38	9.49	0.52
MgO	3.44	2.52	0.60	1.23	1.02	3.11	8.25	7.67	5.59	15.31	3.62	0.34
CaO	14.01	18.40	8.27	11.68	7.00	11.45	25.70	11.10	6.95	23.72	1.34	0.87
Na_2O	0.29	0.22	0.17	0.30	0.52	0.52	0.25	0.21	0.46	0.42	0.54	0.23
K_2O	2.76	1.38	0.26	0.29	0.44	2.45	1.34	2.10	0.93	1.16	2.83	0.17
TiO_2	0.57	0.32	0.10	0.08	0.16	0.62	0.27	0.69	0.35	0.27	0.93	0.09
S	0.21	0.55	-	0.01	-	0.55	-	0.13	-	-	-	-
P_2O_5	-	-	0.09	0.08	0.09	0.11	0.17	0.15	0.15	0.03	0.11	0.06
CO_2 *	14.79	17.23	7.16	10.53	6.62	12.42	29.27	17.16	11.61	35.48	5.03	1.05
TOTAL :	97.93	107.09	100.57	102.07	100.47	94.70	98.28	96.88	102.56	100.36	97.42	94.35

1. Tortonian Blue Marl from Camastra, Sicily.
2. Shaley Diatomite from near the base of the Tripoli at Camastra.
3. Diatomite from Montedoro, Sicily.
4. " " Monte Giammoia, Sicily.
5. " " Falconara "
6. Brown shale / grey marl interbed from Favara, Sicily.
7. Grey marl interbed from near Campobello, Sicily.
8. Brown shale interbed from Capodarso, Sicily.
9. Dolomitic diatomite from Camastra, Sicily.
10. Dolomitic grey marl interbed from Camastra, Sicily.
11. Brown shale interbed from Camastra, Sicily.
12. Commercially extracted diatomite, Lompoc Quarry, California.

FIG. 3.8. X.R.F. MAJOR ELEMENT ANALYSIS OF SEDIMENTS FROM THE TRIPOLI FORMATION.

horizons is about 60 cms with a maximum thickness approaching two metres (Fig 3.9).

They quickly become less argillaceous away from the base of the formation and eventually emerge as light coloured, laminated diatomites (Plate 3.5) although the base of each bed often has a brown colouration due to the influence of the underlying brown shales. They vary in colour from light brown and grey to white depending on the amount of argillaceous material in the sediment, but are invariably dark grey or black when recovered from boreholes due to their high organic content (Ogniben 1957, Roda 1967).

They are conspicuously light in weight, very friable, porous and usually highly fissile with a strong tendancy to break along laminae parallel to bedding. The very fine laminae are characteristic of diatomites (Pl.3.6 & 3.7) and consist of alternating white and light grey or brown horizons. Each lamina is a fraction of a millimetre thick and is due to variations in the argillaceous content of the sediment with the laminae being more conspicuous when the argillaceous content is high and virtually indiscernable when it is low. These laminae have been interpreted as seasonal varves with each couplet (ie one dark plus one light lamina) representing one years sedimentation (Ogniben 1957).

The sediment is almost entirely composed of whole and fragmented diatom frustules, with both pennate and centric forms being present (Plates 3.8 and 3.9). Silicoflagellates, coccoliths and discoasters are almost invariably present (Pl 3.10 and 3.11), although the calcareous nannoplankton are absent in the upper part of the Tripoli section at Camastra where micritic dolomite is the only carbonate mineral present in the sediment (see below). Planktonic foraminifera and radiolaria are locally common (Plates 3.12 and 3.13) with the latter largely confined to the lower parts of the formation. Benthonic foraminifera however, are apparently absent as are all macrofossils with one notable exception. These are fish remains, which are particularly well preserved and are one of the characteristic features of the Tripoli Formation (see Arambourg 1925).

Section	Total Thickness	Total Diatomite Thickness	Total Interbed Thickness	Number of Rhythms	Average Diatomite Thickness	Average Interbed Thickness	Diatomite/ Interbed Ratio
Falconara	21.73	12.50	9.23	28	0.45	0.33	1.36
Calascibetta*	92.70	24.35	68.35	15	1.62	4.56	0.36
Montedoro*	17.30	11.35	5.95	12	0.95	0.50	1.90
Campobello di Licata*	8.79	5.75	3.04	10	0.57	0.30	1.90
Monte Giammoia**	6.59	4.44	2.15	12	0.37	0.18	2.06
Favara*	8.85	5.71	3.14	8	0.71	0.39	1.82
Capodarso**	5.83	3.13	2.70	7	0.45	0.39	1.16
Camastra	39.95	24.25	15.70	34	0.71	0.46	1.55
All Sections	-	-	-	-	0.60	0.36	1.67

* Incomplete sections
** Sections complete but unreliable due to slumping
All thicknesses are in metres

Fig. 3.9 THE DEVELOPMENT OF DIATOMITES AND INTERBEDS AT MAJOR SECTIONS IN SICILY.

They include everything from individual fish scales to complete skeletons (Frontispiece), while in thin section they are seen as irregularly shaped phosphatic fragments aligned parallel to bedding.

The argillaceous component of the sediment is identical to, though far less abundant than, that found in the basal diatomaceous shales. It consists of fine quartz grains, laths of mica, clay minerals, finely disseminated opaques and occasional exotic grains such as fragments of wood.

The laminae are usually flat and regularly spaced although disturbed horizons may sometimes be found. These are particularly common at the section near Campobello di Licata where they tend to occur near the tops of diatomite beds (Plate 3.14). The inspection of polished sections through diatomite reveals that completely unlaminated horizons are also fairly common (Plates 3.6 and 3.7). These are up to a few centimetres thick and often reveal convolute and distorted laminae at their base, suggesting that their homogenous appearance is due to the reworking of the sediment as a result of slumping or intermittant current action. Elsewhere, disturbances within the laminated intervals are rarely seen due to the weathered nature of the outcrops.

3.2.4. The Interbedded Marls.

As mentioned above, the interbeds which separate the beds of diatomite consist of two units; a homogenous grey marl and overlying friable brown shale.

Grey Marls:- In the basal 10 metres of the Tripoli section at Camastra the grey marls have a very similar appearance to the blue Tortonian marls. They have a uniform medium grey colour but are darker and softer except where exposed to the surface. The tests of planktonic foraminifera are common and there are even occasional thin walled mollusc shells. Calcareous nannoplankton are also common and are found, together with small dolomite rhombs, in a predominantly calcareous groundmass. However, apart from at the very base of the formation siliceous organisms are conspicuously absent, in sharp contrast to diatomite beds. The relative abundance of $CaCO_3$ and lack of SiO_2 can be seen by comparing the composition of the grey marls with that of other Tripoli and Tortonian sediments in Figure 3.8. The amount of dolomite increases higher in the formation as the amount of calcite and particularly the calcareous nannoplankton decrease. In the sections at Camastra, Falconara and Calascibetta there are several horizons in which the sediment is totally devoid of calcite, leaving dolomite as the only carbonate mineral (Figs 3.10-3.12). Elsewhere, varying amounts of calcite in the form of nannoplankton and micrite are usually present.

The dolomitic grey marls are very fine grained, have a homogenous appearance and a uniform medium grey colour. They are composed almost entirely of anhedral grains up to 10μ across giving the sediment a fine sucrosic texture. Large euhedral rhombs of dolomite up to 100μ across occur within the micrite and can rarely be seen to be enclosing smaller grains (Plate 3.15).

Small grains of glauconite and occasional fish remains are also found in these marls, together with the ubiquitous fine detrital quartz grains, mica laths and opaque minerals. The last of these occasionally reveal a square outline and are often found infilling the tests of foraminifera.

Brown Shales:- The brown shales form a thin friable horizon separating the grey marls from the overlying diatomites (Plate 3.3) and are usually, but not always, the thinner of the two 'interbed' lithologies. They are not well developed in the lower part of the formation but elsewhere , they appear as well defined brown shaley mudstone beds which occasionally have a silty appearance due to the presence of abundant foraminiferal tests (Plate 3.16). The brown colouration is caused by the oxidation of iron-rich opaque minerals which, as in the dolomitic marls, are often found infilling foraminiferal tests. Also found infilling foraminiferal tests in one horizon at Camastra (see Fig. 3.6) are crystals of gypsum (Plate 3.17).

The groundmass is laminated and a murky green-brown colour.

Fig. 3.10 Dolomite distribution at Camastra.
(see also fig. 3.6)

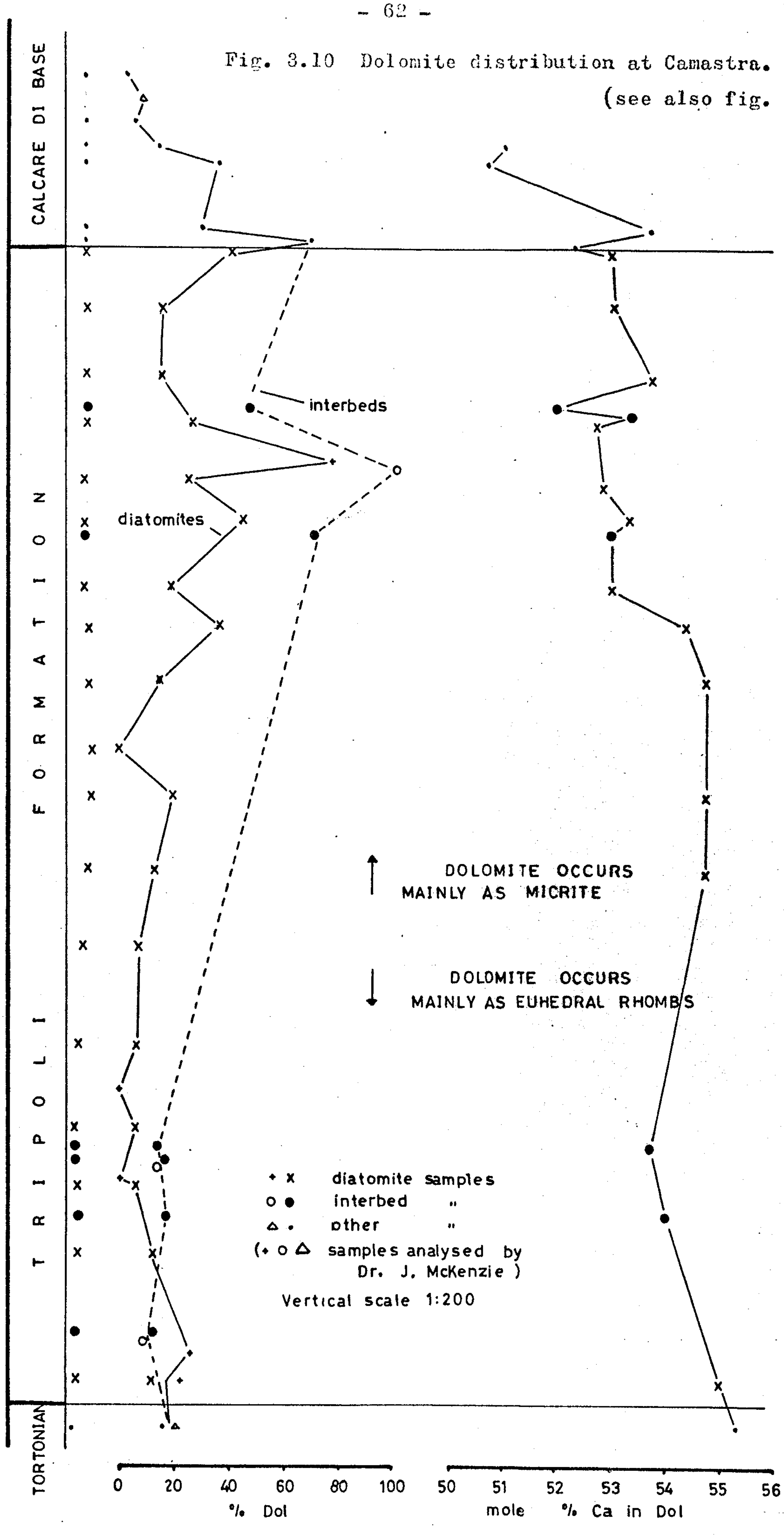


Fig. 3.11 Dolomite distribution at Falconara.
(see also fig. 3.7)

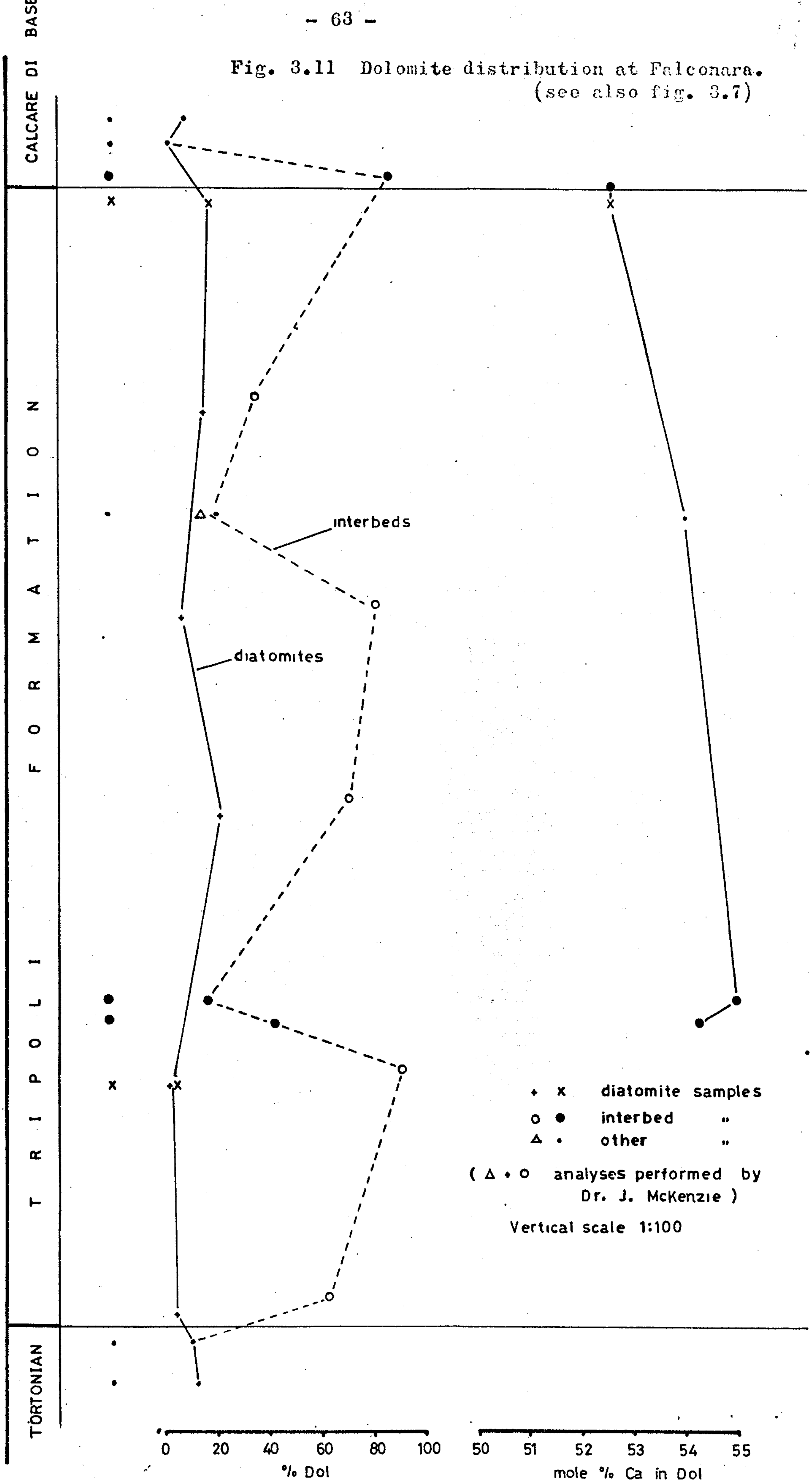
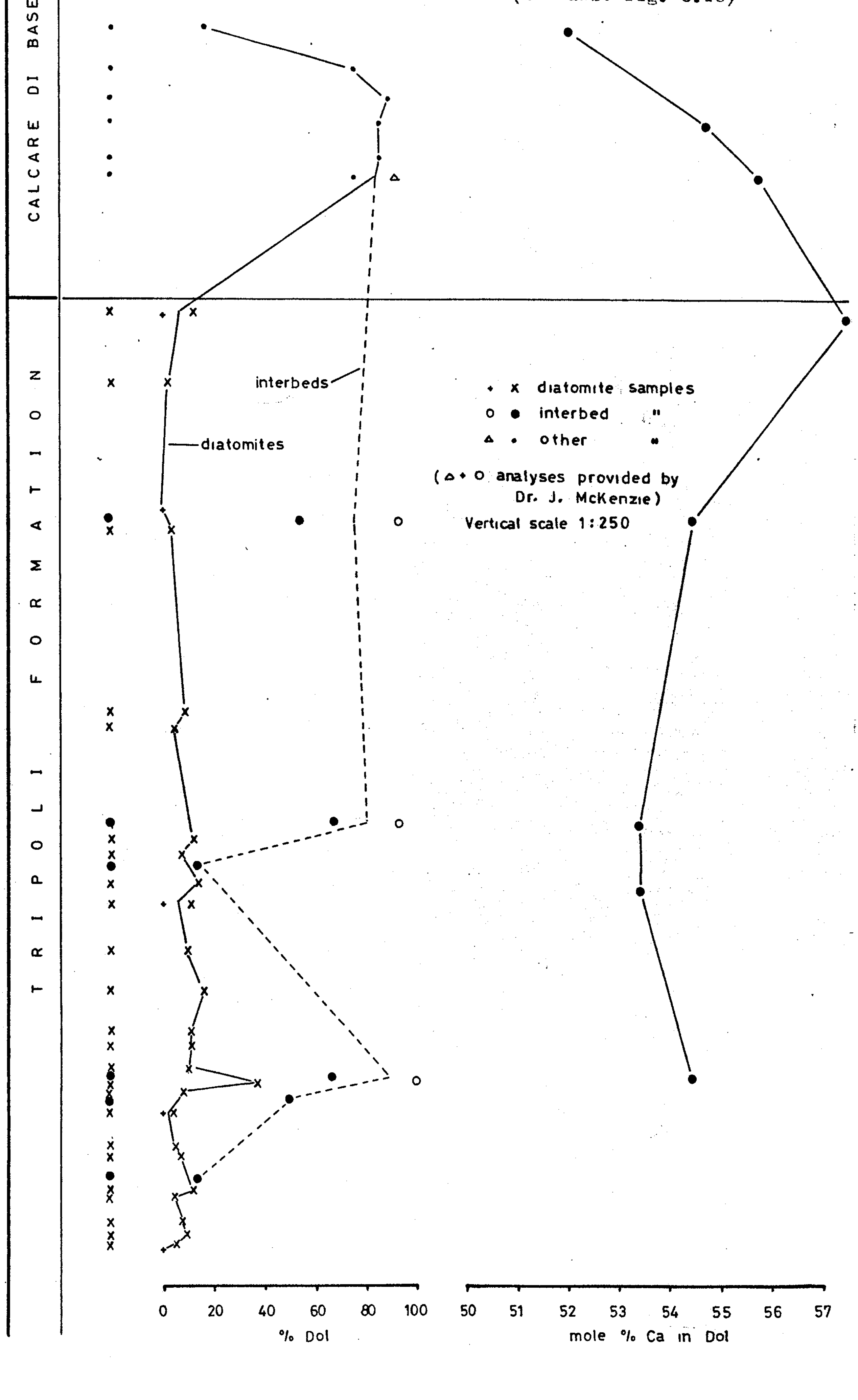


Fig. 3.12 Dolomite distribution at Calascibetta.
(see also fig. 3.18)



Clay minerals (mainly kaolinite) make up a large part of the sediments and, together with small laths of mica, are strongly aligned parallel to bedding giving the sediment an overall length slow orientation as seen with a sensitive tint plate. Fine detrital grains of quartz and feldspar are liberally distributed throughout the sediment as are fish scales, small dolomite rhombs, calcareous nannoplankton and occasional grains of glauconite (see columns 6 & 8 Figure 3.8). Diatoms and radiolaria are rare except near the base of the formation.

The sections at Camastra and Calascibetta contain several brown shale horizons which are almost entirely made up of terrigenous debris with little carbonate material. The only carbonate material present is usually either as whole foraminifera tests (Plate 3.16) or as small dolomite rhombs. Rarely, even this may be absent and the shale is totally devoid of any carbonate or biogenic matter.

The transition between the grey marls and brown shales is nearly always gradual although it takes place within a centimetre. Occasionally there is no discernable boundary and the two lithologies appear to be mixed together forming a single interbed. The contact with the overlying diatomites also shows a gradual change beginning with the brown shales taking on a laminated appearance due to the development of white diatomaceous partings. These gradually become better developed until no shale material remains. The transition occurs over a few centimetres and is clearly defined by the colour change as brown terrigenous sedimentation gives way to the white diatomaceous deposits.

3.2.5. Limestones in the Tripoli Formation.

The dolomite grey marls are not the only carbonate horizons that occur within the Tripoli Formation since beds of limestone are also to be found in several sections. These are confined to the upper part of the formation and are similar in appearance to both the diatomites and grey marls. However, they are easily distinguishable from the former by their greater density and lack of laminae and from the latter by being lighter in colour, harder and more resistant to weathering.

The Tripoli sections at Montedoro (Fig 3.13) and Campobello di Licata (Fig 3.14) are generally richer in $CaCO_3$ than other sections and both contain limestone horizons. At Montedoro they are highly fractured and although they appear to be slumped, it is impossible to be certain because of the poor exposure. The Campobello di Licata section however, includes at least one graded limestone bed which is notable for its abundance of planktonic foraminiferal tests (seen above the laminated diatomites in Plate 3.5). The tests are well sorted, about 0.5mm in diameter and set in a non-dolomitic, micritic matrix which also contains many coccoliths and discoasters. This limestone has a sharp contact with the underlying brown foraminiferal marl, while the contact with the overlying bed, also a brown marl, is more gradual. Both of these brown marls are laminated and rich in planktonic foraminifera although in the overlying bed they soon die out and the sediment grades into the usual friable brown shale.

The Campobello di Licata section contains several other calcareous horizons rich in foraminiferal tests but there are also at least two limestone beds in which foraminifera are not so common. Similar horizons are also to be found in sections at Falconara, Favara (Fig 3.15) and Monte Giammoia (Fig 3.16). In all cases they are underlain by diatomites and overlain by brown shales, suggesting that they have taken the place of the dolomitic grey marl in the sedimentary rhythm. They are a light grey-fawn colour, hard with homogenous chalky textures and at Falconara and Favara they merge into soft and marly, but otherwise identical horizons beneath. Dolomite, in the form of small rhombs, is present at Falconara (Fig 3.11) and Campobello Di Licata (Fig 3.17) but represents less than 20% of the sediment. Elsewhere, calcite is the only carbonate mineral present. Although much less abundant than in the graded limestones, planktonic foraminifera are again the only large particles to be found in these horizons and are again set in a very fine grained micritic matrix rich in calcareous nannoplankton. The tests are usually whole although some fragments

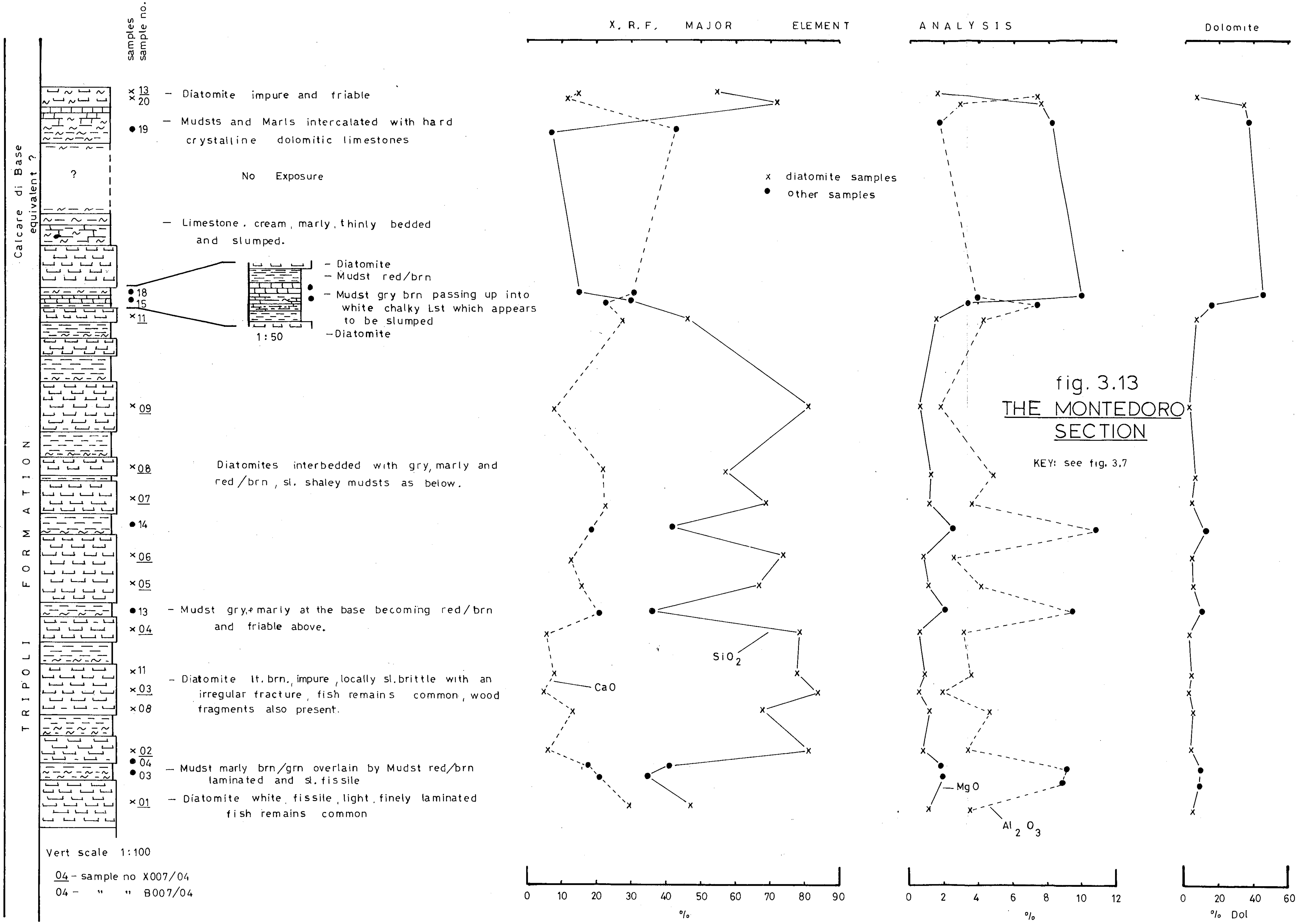


fig. 3.13
THE MONTEDORO SECTION

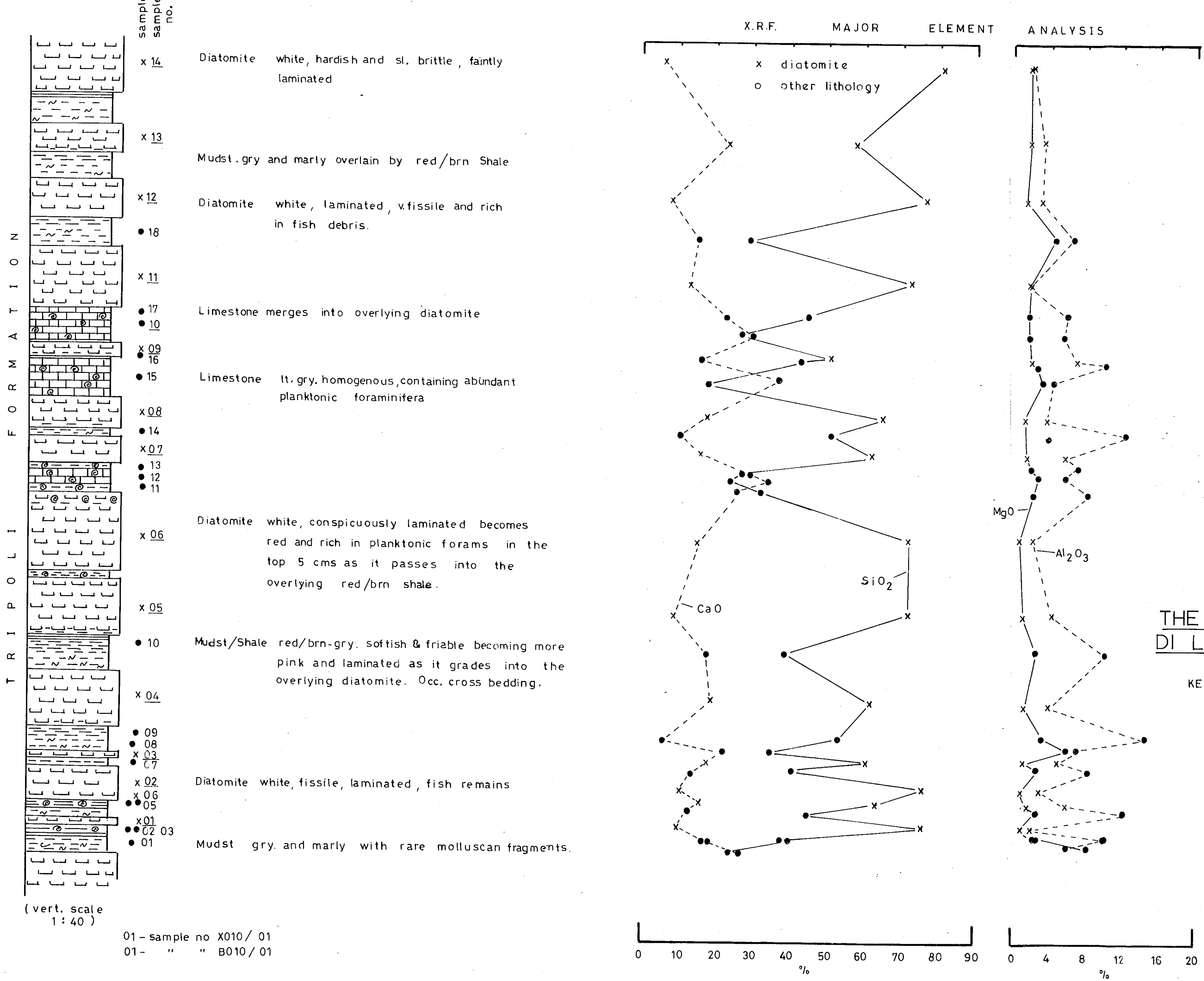


fig. 3.14
THE CAMPOBELLO DI LICATA SECTION

KEY: see fig. 3.7

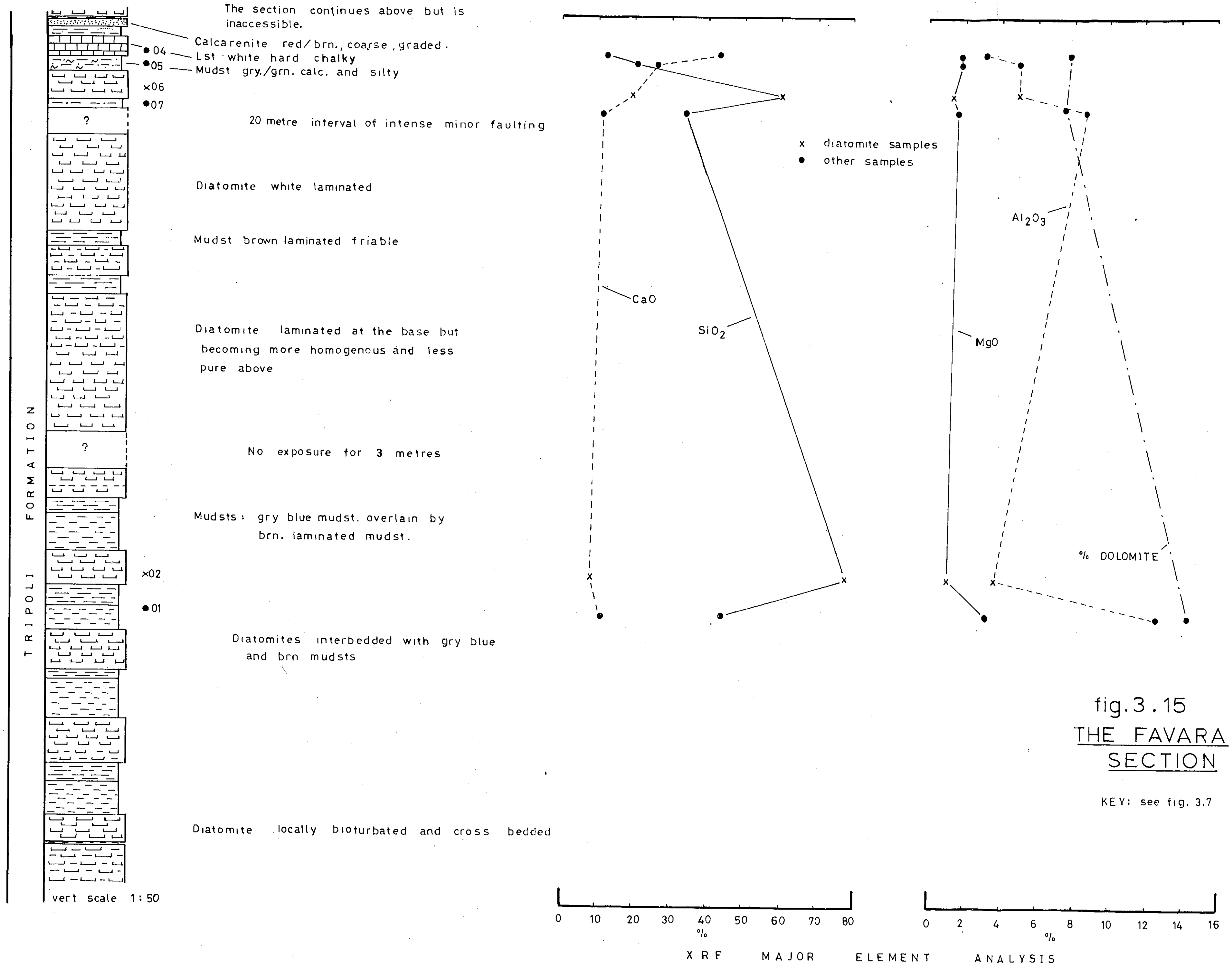


fig.3.15
THE FAVARA SECTION

KEY: see fig. 3.7

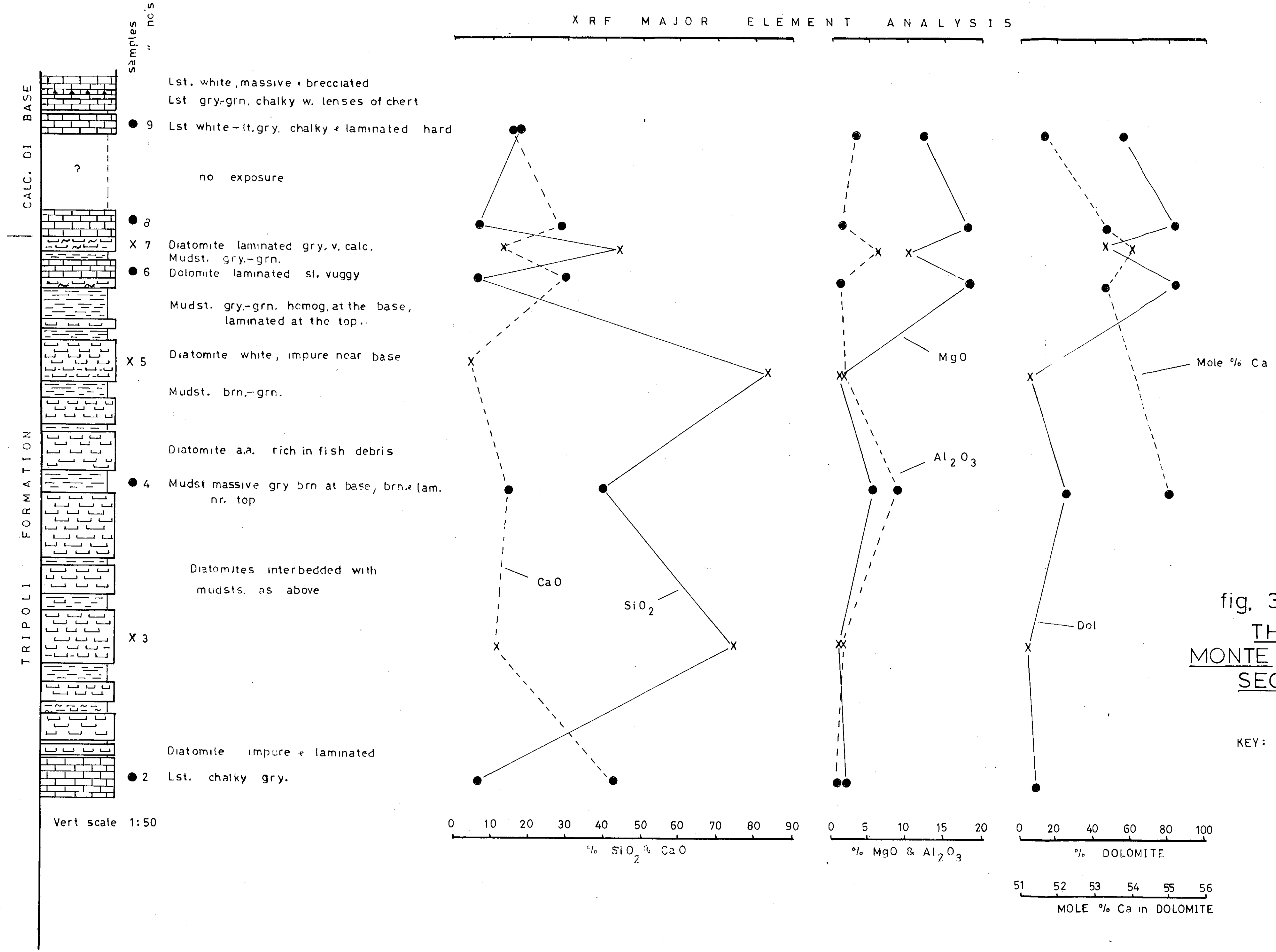


fig. 3.16
THE MONTE GIAMMOIA SECTION

KEY: see fig. 3·7

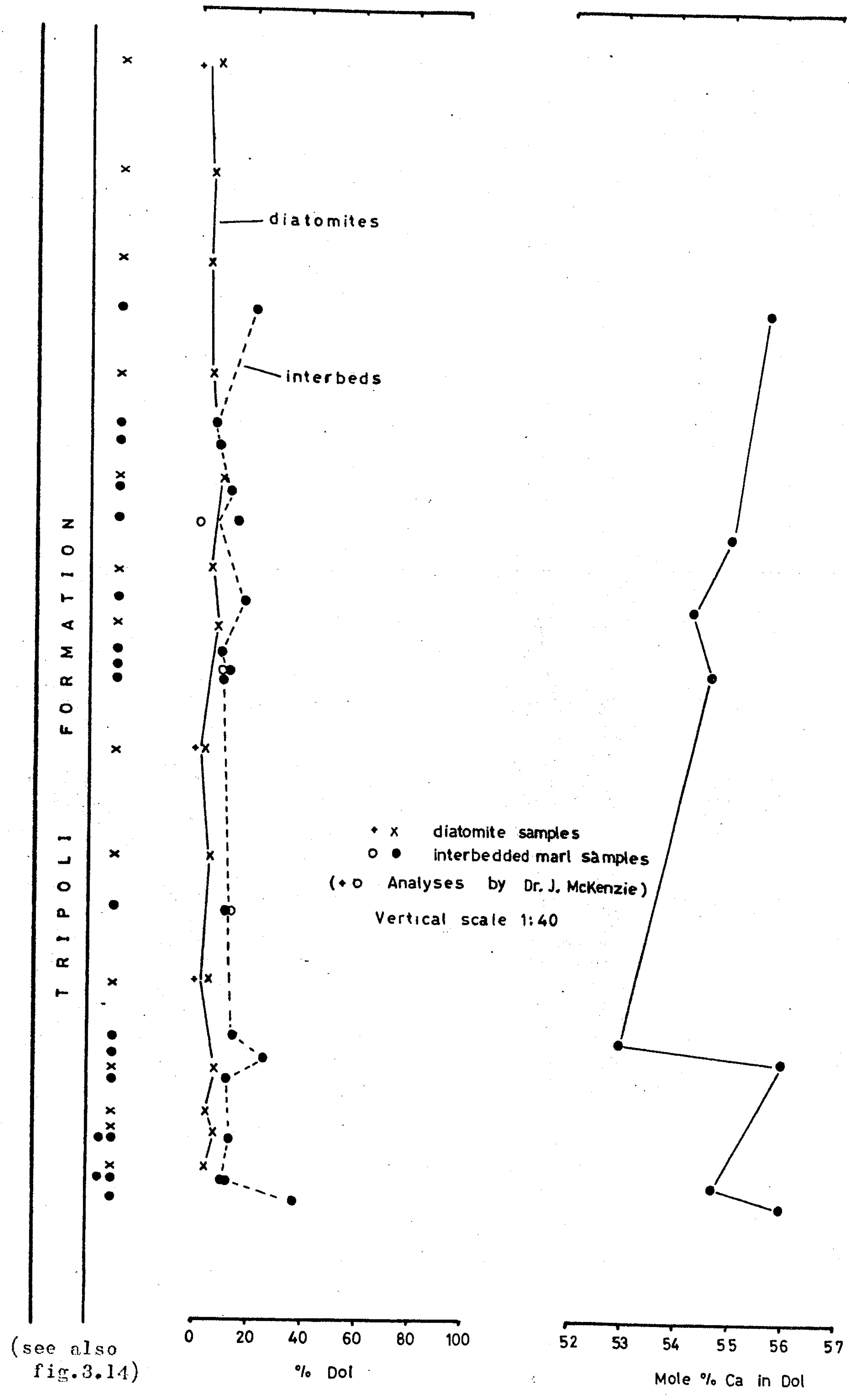


Fig. 3.17 Dolomite distribution at Campobello di Licata.

may be found in the groundmass which shows no sign of lamination but often has a mottled appearance (plate 3.23). This 'mottling' has the appearance of a mass of rather diffuse pellets and has been recognised by Ogniben (1957), who refers to it as "struttura grumosa" and attributes it to bioturbation. The same structure has been recognised elsewhere, but more recent opinion considers it more likely to be due to the effects of diagenesis (Bathurst 1975 p511).

3.2.6. The Tripoli Formation - Calcare di Base Boundary.

Wherever the top of the Tripoli Formation is exposed it is found to be overlain by the carbonate deposits of the Calcare di Base (see below) and the sediments actually in contact with the diatomites invariably prove to be dolomitic. Even where the Calcare di Base has been described as being absent (Decima and Wezel 1973, Richter Bernburg 1973), the diatomites are never found in direct contact with the evaporites but are always separated by a dolomitic interval (e.g. the exposures at Calascibetta (Fig 3.18), Enna, Montedoro, Capodarso (Fig 3.19) and Sutera).

The contact between the Tripoli and the Calcare di Base is apparently conformable although a brief hiatus has been recognised at the Monte Giammoia in the eastern part of the basin (Colalongo et al. 1976). It represents the transition from predominantly siliceous to carbonate sedimentation and is most clearly defined by the sharp decrease in the silica content of the sediment (Figs 3.6 and 3.18). In contrast, the build up of carbonate in the Tripoli sediments is much more gradual and is caused by the increasing abundance of micritic dolomite. This is noticeable only in the top few rhythms at Capodarso and Monte Giammoia but at Camastra and Falconara almost the entire upper half of the formation is dolomitic. The diatomaceous horizons, as well as the interbeds, are affected and near the top of the Tripoli the micritic dolomite often occurs to the total exclusion of all micritic calcite and calcareous nannoplankton. However, there is no significant corresponding decrease in the silica content of these Tripoli sediments (Fig 3.8) and at Camastra, Falconara and Calascibetta the uppermost diatomite

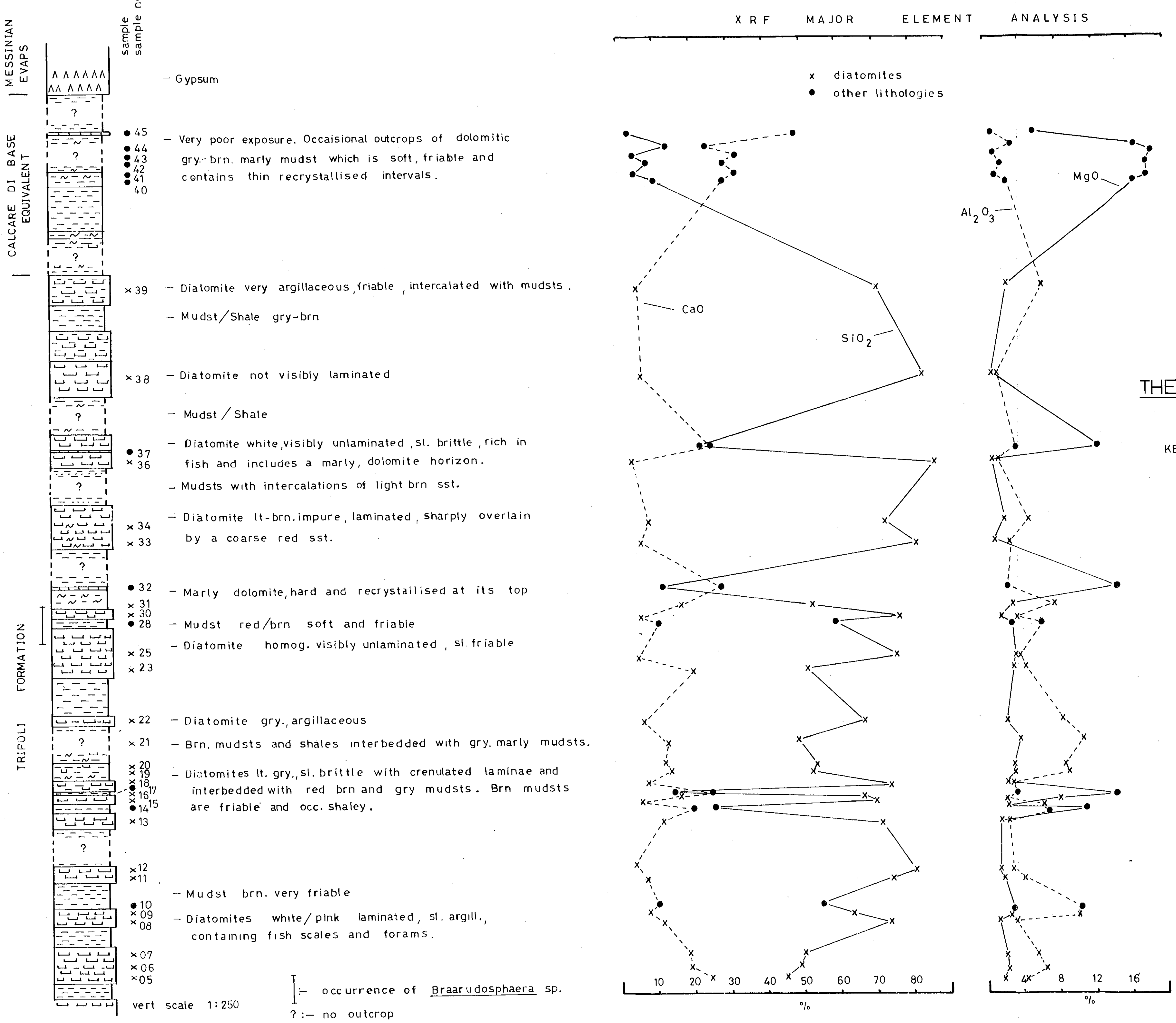


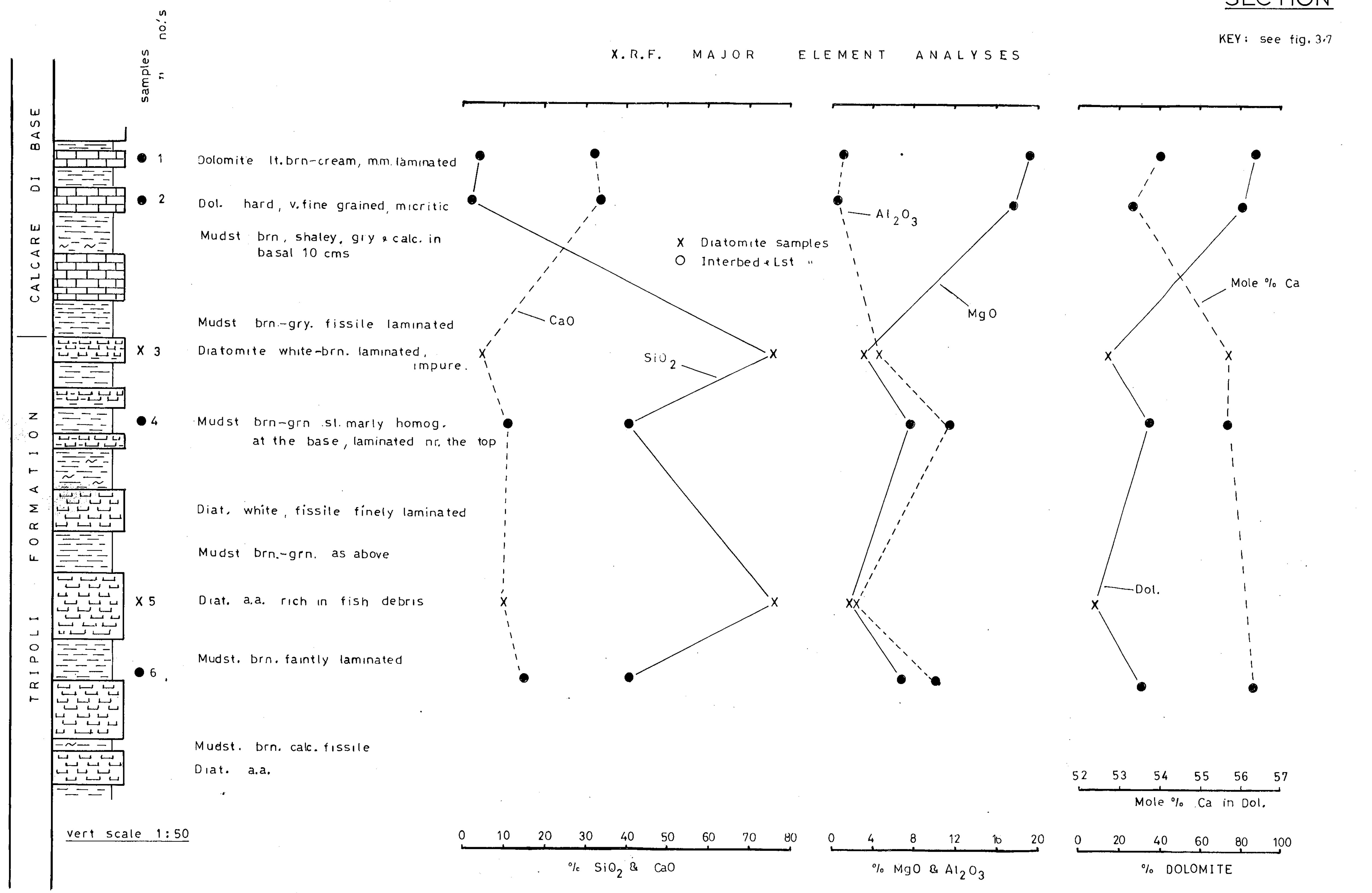
fig. 3.18
THE CALASCIBETTA SECTION

KEY: see fig. 3.7

fig. 3.19

THE CAPODARSO SECTION

KEY: see fig. 3.7



consists solely of diatoms and silicoflagellates in a micritic dolomite matrix. These dolomitic diatomites are laminated, fissile, contain fish debris and, apart from their slightly brownish colour, are indistinguishable from the underlying diatomites.

The sudden disappearance of the siliceous phytoplankton leaves a sediment composed entirely of micritic dolomite. Usually this also marks the end of the rhythmic nature of the sedimentation but in some places (Capodarso and Castrofilippo) the micritic dolomites merely replace the diatomaceous horizons and a rhythmic pattern is recognisable for some distance into the Calcare di Base.

3.3. Other Lower Messinian Sediments.

3.3.1. The "Whitish Marls",

White chalky foraminiferal marls occur quite commonly within the Central Sicilian Basin and include those belonging to the Lower Pliocene Trubi Formation as well as the chalky limestone horizons of the Tripoli Formation. There are also some foraminiferal marls which clearly belong to neither of the above formations but are found throughout the basin (Fig 3.5). These are lithologically distinct from the Trubi marls and although they are occasionally associated with diatomites, they can be distinguished from the chalky limestones of the Tripoli since they are never part of a sedimentary rhythm. They consist of whole and fragmented planktonic foraminifera tests set in a fine, off-white to fawn chalky matrix and are lithologically almost indistinguishable from the Tripoli marls. Bedding is extremely variable; at Palma di Montechiaro beds up to 20 cms thick are separated by thin muddly intervals (Plate 3.18), while at Grotte some 20 metres of massively bedded marls are exposed without any interbeds at all. The marls themselves are usually unlaminated and their homogenous appearance, together with the absence of any preferred crystallographic orientation in the clay minerals, suggests the former presence of a burrowing infauna. However, fossil evidence of these benthonic organisms is rare in contrast to the relative abundance of planktonic foraminifera.

The latter occur in various sizes and are occasionally replaced or infilled by concentrations of opaque material. Other opaque matter occurs as disseminated grains which occasionally reveal a square outline indicating a cubic symmetry (Plate 3.19). This suggests that much of this opaque matter has probably been derived from the oxidation of pyrite in the sediment. Detrital material is ubiquitous but never very common and consists of silt-sized grains of quartz together with small laths of mica. Phosphatic material in the form of fish scales and rounded grains of glauconite is also to be found.

The stratigraphic position of these foraminiferal marls is difficult to ascertain since they are not usually exposed in association with other lithologies. Their appearance suggests that they may be identical to the "Whitish Marls" described by Decima and Wezel (1973) as the deep water equivalent of the Tripoli Formation. However, Decima and Wezel's description of benthonic and planktonic foraminifera occurring in roughly equal amounts is difficult to reconcile with the paucity of benthonic organisms in the sediments described above. Nevertheless, marly and diatomaceous sediments are found together in outcrops at Marcato Bianco (approx. 15 kms southwest of Enna (Fig 3.4) and near Bompensiere (4 kms northwest of Montedoro (Fig 3.4)), suggesting that some sort of relationship may well exist between them.

At Marcato Bianco the nature of any relationship between the marls and diatomites is obscured by the poor exposure, faulting and the similar appearance of the two lithologies. However, in at least one place they can be seen to grade into each other with apparent sedimentary continuity. The diatomites at this locality are similar to those of the Tripoli but are neither visibly laminated nor are they part of any recognisable sedimentary rhythm. The marls also differ slightly from those found elsewhere by being less extensively bioturbated so that the original lamination and some small burrows are still preserved.

The other outcrop, a small roadcutting roughly half way between Montedoro and Bompensiere, shows the marls to be overlain by diatomites but separated from them by a brown sandstone bed about one metre thick. The sandstone is clearly graded as well as being generally friable and poorly sorted, particularly near its base. Its contact with the underlying marls is scoured and irregular with occasional isolated pods of sandstone occurring in the top few centimetres of marl. Ripped up clasts of the marl are also to be found near the base of the sandstone and clearly show that the deposition of this horizon caused considerable disturbance in the underlying sediments. A wide variety of other clastic material is also present and includes; quartz grains (often strained), feldspars (usually albite/andesine and often cloudy), glauconite, tourmaline, fish debris, planktonic foraminifera tests including occasional nummulitids and sponge fragments. Lithic fragments are fairly common and include diatomite, quartzite, a micritic limestone and a fine grained basic igneous rock. The groundmass consists of micritic carbonate, mica flakes, chlorite and opaque material which give many grains a dark iron (?) rich coating and infills some foraminiferal tests.

As the sandstone becomes finer, sorting improves and it becomes less friable in places due to the development of a sparry calcite cement. The variety of clastic material also decreases and is generally limited to rounded-subangular quartz feldspars and foraminiferal tests which often reveal syntaxial overgrowths of calcite. Occasionally the foraminifera tests have been completely replaced by secondary calcite leaving only the iron stained rim as a ghost within the sparry cement (Plate 3.20).

Eventually this sandstone grades up into a soft grey green mudstone in which abundant diatoms, radiolaria and silicoflagellates occur together with fine detrital material. A sharp colour change then marks the contact with the overlying diatomites which are otherwise very similar to the mudstone and probably represent a continuous sedimentary succession. The diatomites are similar to those at Marcato Bianco but are harder and, in contrast to all Tripoli diatomites, they tend to fracture across rather than parallel to bedding (see Section 3.7 below).

From the amount and variety of exotic material contained in this sandstone it clearly could not have been generated locally but must have been transported over a considerable distance. As it also has a scoured base and consists of a single graded unit, it is thought that this clastic horizon must have been the result of some kind of sediment flow (possibly a turbidity current) that originated in a peripheral part of the basin. The grey-green muds and rather unusual diatomites above the sandstone must therefore represent the fine sediment which settled out of suspension after the flow subsided. The presence of large amounts of diatomaceous material in suspension, together with the clasts of diatomite in the flow itself, clearly suggest that the flow passed over a diatomaceous substrate en route to its final position. These marls must therefore have been accumulating at the same time as diatomites and in a deeper part of the basin. This strongly suggests that despite the conflicting evidence of the benthonic foraminifera, these marls are the same as those described as the deep water equivalents of the Tripoli Formation by Decima and Wezel (1973).

3.3.2 Clastic Sediments.

The outcrop near Bompensiere, described above, is not the only place where sandstones are found to be associated with sediments of the Tripoli Formation. They also occur at Favara, Calascibetta and at Marianopoli, where several clastic horizons are found in a dolomitic sequence immediately overlying the Tripoli diatomites. Marianopoli is undoubtedly the most sandstone-rich of the Tripoli sections and since it is located in the north of the basin, suggests that the clastic material was derived from the north.

All of these horizons are similar in composition to the sandstone bed near Bompensiere (see above) and consist primarily of quartz grains, feldspars and foraminifera tests. The feldspars have often undergone extensive alteration but occasionally albite twinning can be recognised and where an identification is possible they are generally found to be either albite or andesine. Quartz grains are the most abundant clastic component in these deposits and normally have a subangular outline except at Calascibetta where the majority of the grains are subrounded to rounded. The sandstone at Calascibetta also contains relatively few planktonic foraminifera tests compared with Bompensiere and Favara possibly due to them lying further to the south and closer to the centre of the basin. Grains of glauconite, opaque minerals, fish remains and rock fragments are also present but, with the exception of the opaques, they are never very common. The groundmass is very fine grained and consists largely of micritic carbonate mixed with fine terrigenous material, some of which have altered to chlorite. Coccoliths are commonly visible in the micrite and it is probably the recrystallisation of this micritic carbonate that is responsible for the development of a sparry calcite cement in many places.

These clastic intervals are predominantly sandstones although both finer and coarser material is also present, particularly at Marianopoli. The individual beds may be up to a metre thick and are often conspicuously graded with a sharply defined base. A variety of bed-forms can be recognised including; convolute, flaser, parallel and crossbedding. These are most conspicuous in the finer grained, upper parts of the graded units and strongly suggest that these sediments have been redeposited as a result of current action. At Marianopoli the sandstone horizons are separated by thicker intervals consisting of fine grained, light brown carbonate sediments and darker friable mudstones. These intervals are usually homogenous but sometimes the mudstones contain partings of the lighter marl giving the sediment a laminated appearance. These carbonate rich intervals contain a variety of carbonate minerals including dolomite, aragonite and calcite. Similar sediments are found elsewhere in the northern part of the basin, so it appears that at

Marianopoli they represent the 'background' sedimentation upon which the clastic deposition is superimposed.

Conglomerates and other coarse clastic sediments of Messinian age have also been reported from the area lying to the north of a line joining Trapani and Enna (Fig 3.5). Several delta fans have been identified within these deposits and not only confirm that the sediment came from the north but also show that the northern shoreline of the basin was parallel to the present north coast of Sicily (Richter Bernburg 1973). The most likely source of the sandstone horizons associated with the Tripoli sediments is therefore thought to be periodic southerly incursions made by this clastic material into the basin. For reasons outlined above (see section 3.3.1) sediment flows may have been responsible for transporting the sediment into the basin. However, the presence of so many graded units containing a variety of bed forms suggests that many of these clastic intervals could be turbidites.

3.4. The Calcare di Base.

The Calcare di Base always overlies the diatomites of the Tripoli Formation and forms the lowest member of the Evaporitic Series, hence its name meaning "basal limestone". The thickness of the Calcare di Base varies considerably within the basin, being particularly well developed over the Raffadali - Armerian Uplift and reaching a maximum thickness of 80 metres near Licata (Ogniben 1957, Richter Bernburg 1973). It is not well developed in the whole of the basin, however, and is either reduced to a few thin dolomite beds or is absent altogether in parts of the Platani Trough (Fig 3.4) (Ogniben 1957, Richter Bernburg 1973).

Wherever it attains any great thickness it is conspicuous for its massive, white brecciated limestone horizons which can be up to several metres thick. These are well cemented, very hard and form many conspicuous outcrops throughout the Central Basin. The breccias and their marly interbeds are predominantly calcareous and appear to be confined to the upper part of the Calcare di Base. Beneath them is sequence of chalky marls which overlie the Tripoli

Formation and are identical to the breccia interbeds except that they are dolomitic. This dolomitic lower part of the Calcare di Base has been commented upon by Ogniben (1957) but it rarely attains any great thickness where the brecciated horizons are present. However, in the northern part of the basin, adjacent to the Platani Trough where the brecciated beds interfinger with and pass laterally into the Cattolica Gypsum (Decima and Wezel 1973), the dolomitic marls may be several tens of metres thick. The Calcare di Base may therefore be considered in two parts; a non-dolomitic, brecciated upper unit and a marly dolomitic lower unit.

3.4.1. The Dolomitic Marls.

The lower part of the Calcare di Base consists of light coloured chalky marls interbedded with thinner, more fissile horizons (Pl.3.21). The chalky marls occur in beds which can be anything from a few centimetres up to a metre thick and, although they appear unlaminated, a closer inspection often reveals a faint lamination parallel to bedding. This lamination is usually better developed in the more fissile intervals which also occasionally reveal small synsedimentary slumps and thin cross-bedded horizons. The laminae themselves have been caused by periodic fluctuations in the supply of fine terrigenous sediment. This is clearly illustrated at Antinello where the laminae in a thin fissile horizon can be seen to consist of successive graded units, each a couple of millimetres thick (Plate 3.22).

The sediment is very fine grained and apart from the fine terrigenous material, it is composed solely of micritic carbonate. This consists of an equigranular mass of anhedral grains each a few microns across and may be laminated, homogenous or even have a mottled appearance (the "struttura grumosa" of Ogniben (1957)) (Plate 3.23). Unfortunately it is impossible to determine its mineralogy by optical means except at Enna, Castrofilippo and Marianopoli where coccoliths may occasionally be found. The outward appearance of these sediments is similarly unaffected by their mineral content so that the only reliable means of identifying the minerals present is by X-ray diffraction. This shows that the micrite may be composed of aragonite,dolomite, calcite or any combination of these minerals (Fig 3.20).

Aragonite has been found in sediments at Antinello, Aragona, Enna and Sutera. Usually it occurs in association with other carbonate minerals, but at Sutera it is found by itself and forms beds up to 80 cms thick. Electron microscopy shows that the aragonite occurs as needle-like crystals which commonly form rosettes about 10 microns across (pl. 3.24). Otherwise the sediments are micritic, homogenous or laminated, devoid of any biogenic material and indistinguishable from other micritic carbonates.

Dolomite is the most abundant mineral in the lower part of the Calcara di Base and commonly occurs in beds as the sole carbonate mineral (Fig 3.20). The pore space in these micritic dolomites is occasionally found to have been filled by either gypsum or celestine. The gypsum also occurs in veins which commonly have a fresh appearance suggesting that they may be recently formed by gypsum rich ground-waters percolating down from the overlying evaporites. The celestine is less widespread than the gypsum and is only found near Enna and San Cataldo. It does not form veins and is more pervasive than the gypsum suggesting that it formed during or soon after deposition (Pl. 3.25).

Thinly bedded dolomitic sediments that are coarser grained than the micrites occur at Marina di Palma (plate 3.26). They are very friable and consist of alternating dense and porous horizons which are rarely more than 1 cm thick. The denser horizons commonly contain vertical fractures which sometimes extend into the more porous intervals and appear to be due to differential contraction between the alternating layers. However, the infilling of some fractures with sediment shows that at least some of the contraction must have occurred prior to lithification. Apart from the fractures, the denser horizons consist of successive, slightly undulating horizontal lamellae while the porous intervals are composed largely of circular or elongate micritic grains which have a pelletal appearance. The overlying horizon in the Marina di Palma

Section	Dolomite	Dolomite & Calcite	Calcite	Calcite & Aragonite	Aragonite	Aragonite & Dolomite	Aragonite Calcite & Dolomite
Marianopoli	–	x (1)	x (1)*	–	–	–	x (2)
Antinello	–	x (1)	–	x (2)	–	–	–
Calascibetta	x (5)	x (1)	–	–	–	–	–
Aragona	–	x (1)	–	x (1)	–	–	–
Enna	x (3)	x (3)	–	x (1)	–	–	x (1)
Sutera	x (1)	–	–	–	x (3)	–	–
Camastra	–	x (5)	x (1)	–	–	–	–
San Cataldo	–	x (2)	x (1)	–	–	–	–
Grotte	–	–	x (2)	–	–	–	–
Castrofilippo	x (1)	x (1)	x (1)	–	–	–	–
Marina di Palma	x (4)	–	–	–	–	–	–

* Detrital sediment

Figures in brackets inicate the number of samples in which the particular combination has been found.

Fig. 3.20 THE COMBINATIONS OF CARBONATE MINERALS FOUND IN THE LOWER CALCARE DI BASE SEDIMENTS.

section has a disturbed appearance and contains disorientated angular fragments of a similar laminated dolomite (Pl. 3.27). It has little obvious porosity and is remarkably similar to certain horizons found in the overlying brecciated Calcare di Base.

Low magnesian calcite is quite common in the lower part of the Calcare di Base, but it is usually found only in small amounts and is rarely the most abundant carbonate mineral in a bed. However, at Castrofilippo and Grotte such beds do exist and comprise hard, laminated micritic limestones in which there is little or no biogenic material. The source of the calcite is often problematical but is clearly of secondary origin since, in some horizons, it occurs as a cement and in others as microspar (Bathurst 1975 p.566) growing within the dolomitic host sediment (Plate 3.28). In one horizon at Sutera the microspar proved to be dolomite but elsewhere, the calcite is identifiable by the lack of rhombic crystals, X-ray diffraction and the reduction of intergranular porosity caused by its growth (Friedman and Sanders 1967 p. 295). The continued development of either this microspar or a calcite cement eventually results in the original dolomitic sediment being totally replaced by sparry calcite. Limestones which appear to have formed in both of these ways are found in the upper part of the Calcare di Base. Those which developed from microspar consist of a mosaic of equigranular anhedral calcite crystals in which the only remaining signs of the original texture are occasional iron stained or argillaceous partings. However, in limestones which developed from a calcite cement the texture of the original sediment is still discernible . The calcite cement therefore appears to have grown within veins and the pore space of the micritic dolomite to form an anhedral mosaic which has been superimposed upon the original texture (Plate 3.29).

3.4.2 The Breccias.

The upper part of the Calcare di Base consists of massive brecciated limestones interbedded with thinner, less deformed horizons. The breccias may be up to 3 or 4 metres thick or even more in places (Plate 3.30) while the thickness of the intervening beds rarely exeed 30 to 40 centimetres.

The sediments between the brecciated units comprise white to grey, laminated or homogenous, chalky marls and limestones. These include some horizons with a hard crystalline saccharoidal texture but otherwise they resemble the dolomitic marls of the lower Calcare Di Base. There are also some darker, green to brown, laminated clays which are composed largely of smectites suggesting that they are of volcanic origin. All of these beds have a wavy, irregular appearance in outcrop and are often highly contorted or sheared (pl. 3.30).

The breccias are composed of rounded and angular clasts of both laminated and homogenous limestones, almost all of which resemble sediments found elsewhere in the Calcare di Base. They are set in a fine grained, often recrystallised calcium carbonate matrix which, although occasionally rather sugary and friable, is usually very hard and well cemented. There has been extensive solution and reprecipitation of calcite in these sediments; a pelletal limestone clast found at Camastra contained several solution horizons (pl.3.31) while some horizons at Falconara resemble vadose crusts. Vugs and cavities are also very common and often have angular outlines due to the angular nature of many of the clasts. Some vugs have a rectangular shape and, together with calcite pseudomorphs of a cubic mineral (Plate 3.32), are thought to indicate the former presence of halite (Ogniben 1957). Other evaporite minerals are rare; gypsum is found at Montallegro where the brecciated Calcare Di Base passes laterally into the "Cattolica Gypsum" and celestine has been found in an undeformed horizon near San Cataldo. Native sulphur is fairly common in small amounts and occurs throughout the basin in this interval.

3.5. The Age and Rates of Deposition of the Tripoli Sediments.

Most recent estimates agree that the Messinian Stage lasted from 6.5 or 6.7 Ma until 5.0 or 5.2 Ma and that the Tripoli Formation represents between 0.5 and 1.0 my. of this period (Van Couvering et al. 1976, Adams et al. 1977, Smith 1977, Burckle 1978). However, Ogniben (1957) calculated that the Tripoli lasted for only

120,000 years and in doing so he assumed that the interbeds of grey marl and brown shale were deposited at the same rate as the diatomites. The considerable discrepancy between this and currently accepted values obviously throws considerable doubt on Ogniben's assumption that the whole of the Tripoli Formation was deposited at a constant rate.

If, as seems likely, the fine laminae can be regarded as seasonal varves, then the time taken to deposit the diatomites relative to the interbeds can be estimated as follows:

The average thickness of each seasonal varve = 0.2 mm

$\therefore$ 1 mm of diatomite would be deposited every 2.5 years.

The average thickness of the diatomite horizons = 0.60 m (Fig 3.9)

$\therefore$ the duration of each diatomite horizon $\simeq$ 600 x 2.5 years
= 1500 years.

The maximum number of rhythms in the Tripoli Formation is 34 at Camastra.

$\therefore$ Assuming that the Tripoli lasted for at least 0.5 my each rhythm must have lasted for at least 500,000/34 years
$\simeq$ 15,000 years.

Thus, although the diatomites are the dominant lithology of the Tripoli Formation and represent 63% of the sediment thickness, they were being deposited for no more than 10% of its total duration.

Another, independent method of estimating the relative duration of the diatomites and interbeds is provided by the data in Figure 3.8: It can be seen that the ratio of diatomite thickness to interbed thickness is fairly constant except at Calascibetta. This is thought to be due to the added influx of fine grained detrital material to the formation as a result of Calascibetta's location near the northern margin of the basin.

Therefore, if the diatomite horizons lasted for T years and the interbeds for T' years:

Since the basinwide average diatomite thickness = 60cms,
" " " interbed " = 36cms,
and; the average diatomite thickness at Calascibetta = 162cms
" " interbed " " = 456cms

Then the rate of deposition of the additional detrital material at Calascibetta would be $(162-60)/T$ cms/year and in the interbeds it would be $(456-36)/T'$ cms/year.

Assuming that the rate of deposition of this extra detrital material is constant during both the interbeds and the diatomites then:

$$\frac{162-60}{T} = \frac{456-36}{T'}$$

$$\therefore \quad T'/T = 420/102 \simeq 4$$

By this method, the time taken to deposit the interbeds is four times that taken for the diatomites and is somewhat smaller than, but of the same order as, the ratio of 10:1 calculated above

The diatomaceous horizons have therefore clearly accumulated at a substantially higher rate than the interbeds and this probably accounts for Ogniben's underestimating the duration of the Tripoli Formation. Furthermore, although the two ratios calculated above are of the same order, the higher of them is probably the more reliable. This suggests that the rate of deposition of the additional detrital material at Calascibetta has not been constant but was greater during the times of diatomaceous sedimentation.

3.6. Fauna and Flora.

Although no attempt has been made to study the fauna and flora of the Tripoli Formation in any detailed or systematic way, it has nevertheless been possible to make certain relevant observations.

One of the most remarkable features of the Tripoli sediments is the contrast between the diatomaceous beds, composed almost entirely of biogenic material and the marly interbeds which contain only rare coccoliths or discoasters. The diatomaceous beds have a distinctly pelagic fauna which includes diatoms, silicoflagellates, radiolarians, planktonic foraminifera, coccoliths, discoasters and fish remains.

The diatom assemblage shows that they were laid down under marine conditions and since variations in the assemblage are recognisable basin-wide, there must have been good surface communication between all parts of the basin (Gersonde 1977 pers.com). Gersonde has further shown that a three part division of each diatomite horizon can be recognised and consists of:

upper part:- only strongly silicified and poorly preserved diatoms i.e. dissolution

main part:- weakly and strongly silicified frustules with abundant cold water species

basal part:- only weakly silicified diatoms.

Silicoflagellate remains are to be found in all diatomaceous horizons even though they represent only a minor part of the sediment.

Calcareous nannoplankton are present in most of the diatomaceous horizons except at the very top of the formation where the diatomites become increasingly dolomitic as part of the transition into the Calcare di Base. This is particularly noticeable at Camastra (Fig 3.10) where of twelve samples taken from the uppermost 22 metres of the Tripoli, only one was found to contain any calcareous nannofossils. It was also the only sample <u>not</u> to contain dolomite, which strongly suggests that calcareous nannoplankton and dolomite are mutually exclusive within the diatomaceous horizons.

The coccolith <u>Braarudosphaera</u> sp. (Bigelowi ?) was found to be very common in a 2-metre thick interval at Calascibetta (Fig 3.18). It usually occurs in coastal and other marine waters of less than normal salinity (Bukry 1974), which may indicate that this northern part of the basin was adjacent to a shoreline and subject to periodic influxes of fresh water.

Radiolarians are commonly encountered with the diatomaceous sediments near the base of the Tripoli but become less abundant towards the top of the formation. Planktonic foraminifera show a similar tendency but are only completely absent where the sediments are dolomitic. Benthonic foraminifera on the other hand, have not been found in any of the Tripoli sediments (Decima and Wezel 1973).

Fish remains are common throughout the diatomaceous beds and are even occasionally found in the grey marl and brown shale interbeds. Some bedding surfaces have been found to contain especially abundant or well preserved skeletons but the fish debris as a whole is scattered throughout the sediment rather than confined to particular horizons. This suggests that the unusually abundant fish material is unlikely to be due to mass extinctions of fish in response to dinoflagellate blooms or "red tides" as they are also known. These have been observed to cause the widespread mortality of fish off Walvis Bay in South West Africa and have been suggested as a possible cause of the fish remains found in Kupferschiefer (Copenhagen 1953, Brongersma-Sanders 1969). A more satisfactory explanation is thought to be that these fish remains are simply due to the existence of unusually favourable conditions for their preservation. Furthermore, these conditions must have been particularly widespread since identical fish faunas composed largely of mesopelagic forms, have also been reported from the Tripoli of Piedmont and Algeria (Sturani and Sampo 1973).

No macrofossils other than fish are found within the Tripoli Formation, although thin-shelled molluscs occur in the underlying blue Tortonian marls, there are burrows at Falconara and pellets have been found in the Calcare di Base at Camastra. The only other evidence of macrofossils is from outside the Central Basin where molluscs and sponges have been reported from near Calatafimi (Richter Bernburg 1973).

3.7. Diagenesis.

In marked contrast to diatomaceous sediments found in the Miocene of California and the Lower Miocene of Sicily (Chapter II), there is little evidence of diagenesis in the diatomites of the Tripoli Formation. The first sign of the diagenetic alteration of diatomaceous sediments is usually the development of a porcelanitic texture which is accompanied by solution of the diatom frustules and reprecipitation of the silica as opal-CT (Bramlette 1946, Carr and Fyfe 1958). It is therefore surprising that some diatomites in the Tripoli Formation have assumed a slightly porcelanitic texture and yet are devoid of opal CT. These sediments are better indurated than other diatomites, their parallel laminae have become finely crenulated and they have developed a tendency to fracture across, rather than along the bedding. The most plausible explanation of these textural changes is thought to be that some of the silica has been dissolved and then reprecipitated as an amorphous silica cement. Corroded diatom frustules observed in the "porcelanitic" diatomite above the sandstone horizon near Bompensiere appear to confirm this, even though the microscopic character of the sediment is identical to that of normal diatomites.

The solution of diatom frustules and reprecipitation of the silica as an inorganic opal-A cement has been reported in cores recovered from the Bering Sea, where it occurs as one of the earliest signs of diagenesis at depths of about 600 metres (Hein et al.1978). However, even though such burial depths for the Tripoli diatomites are quite plausible in view of the thickness of the overlying evaporites, there is nevertheless no evidence of their having undergone any widespread diagenetic alteration. It therefore appears that depth of burial has not been a controlling factor in the development of the porcelanitic diatomites. In the case of these diatomites near Bompensiere it is thought that the textural changes are due to the diatoms having been returned to suspension and then resedimented. This would have the effect of causing further solution of the diatom frustules, thereby increasing the amount of silica in solution and accelerating the precipitation of a silica cement (Calvert 1974, Johnson 1976).

Small, nodular quartz cherts have been found in one thin horizon at the base of the Calcare di Base at Monte Giammoia (Fig 3.16). The presence of such a diagenetically advanced siliceous horizon in sediments that overlie and are therefore younger than totally unaltered diatomites is curious. As neither age nor depth of burial can have been the controlling factor in its diagenesis, it seems that the lithology of its host sediment must be largely responsible (Heath and Moberly 1971, Kastner et al. 1977). The rate of the diagenetic reactions which lead to the formation of the quartzitic chert are known to be increased by the presence of $CaCO_3$ (Lancelot 1973, Kastner and Keene 1975, Kastner et al. 1977). The occurrence of this cherty horizon is therefore probably the result of the $CaCO_3$ - rich environment in which the silica was originally deposited.

3.8. Stable Isotopes.

The Tripoli and Calcare di Base sections at Capodarso, Camastra, Campobello di Licata, Calascibetta and Falconara have been sampled so that the carbon and oxygen isotope compositions of the carbonate in the sediment could be determined. The analyses were carried out by Dr. J. McKenzie of the Geological Institute in Zurich and her results are presented in Figures 3.21 - 3.25.

As the analyses were performed on bulk samples, the results represent the net isotopic composition of the carbonate in the sediment and no differentiation is made between the various carbonate minerals. Nevertheless, by plotting ΔO^{18}_{PDB} against ΔC^{13}_{PDB} for all the samples, three distinct groups can be distinguished (Fig 3.26) These are:

Group A ΔC^{13}_{PDB} 0.0 to - 6.0 ‰

ΔO^{18}_{PDB} 0.0 to + 2.5 ‰

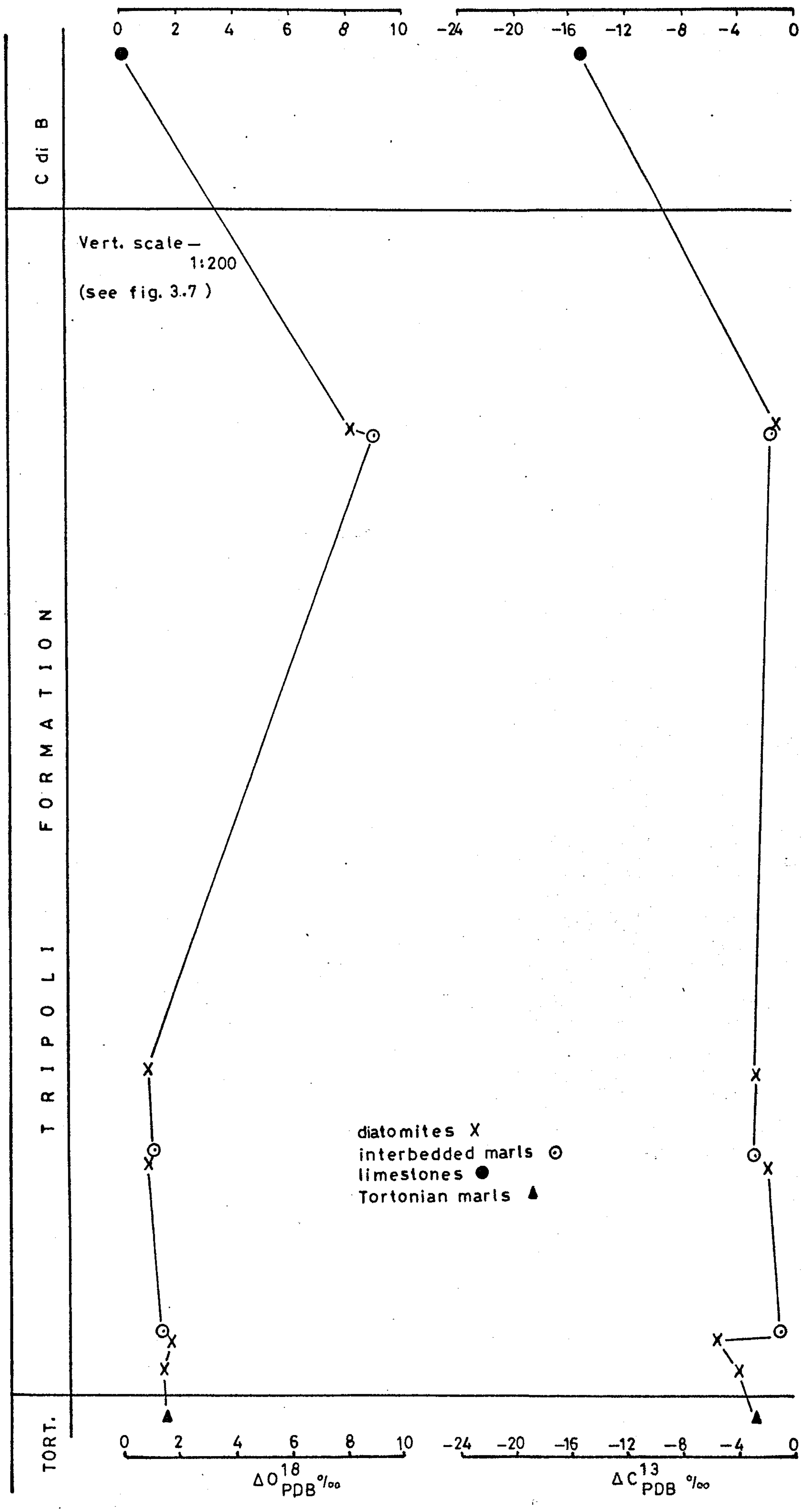


Fig. 3.21 Stable isotope distribution at Camastra.

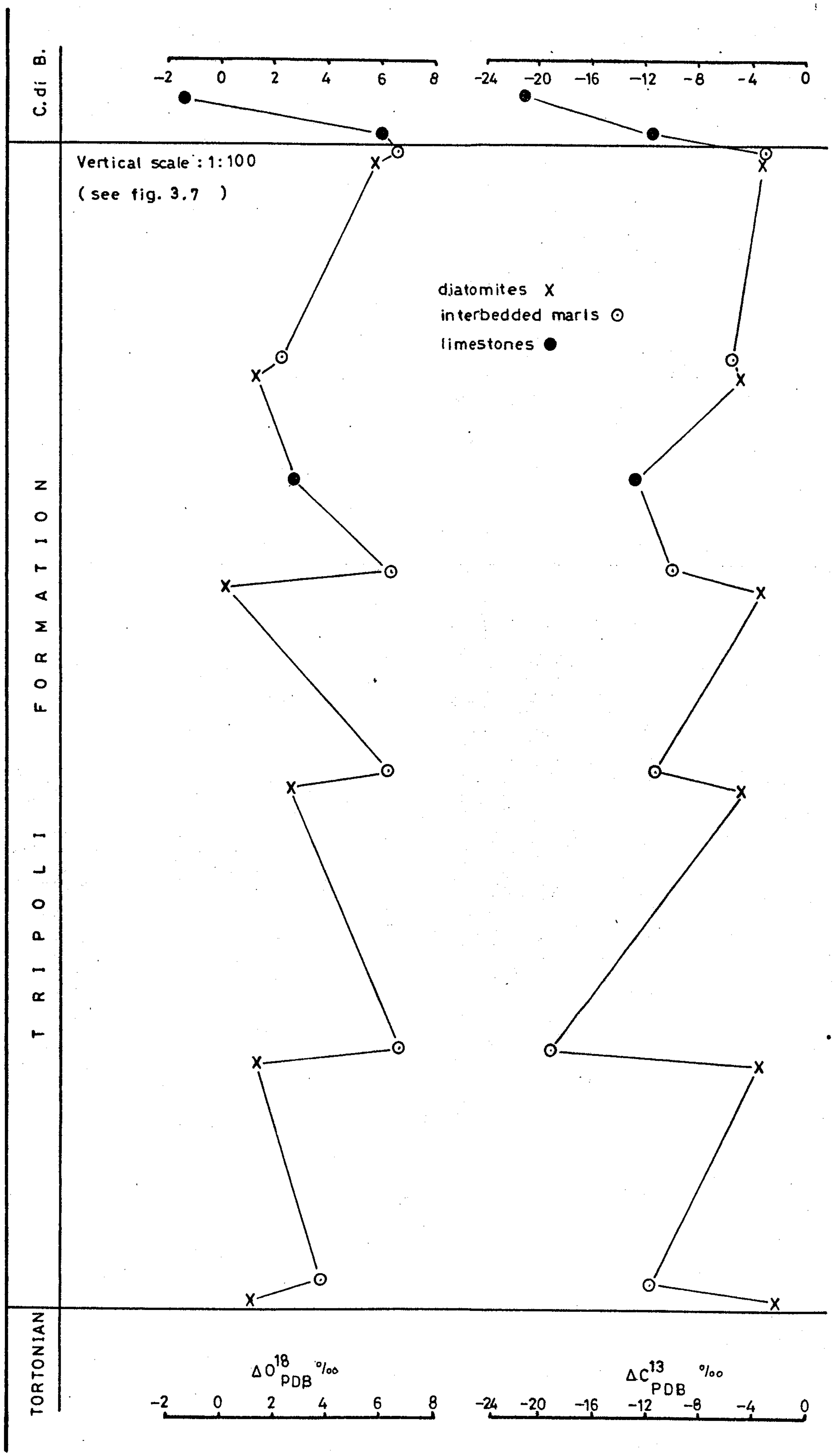


Fig. 3.22 Stable isotope distribution at Falconara.

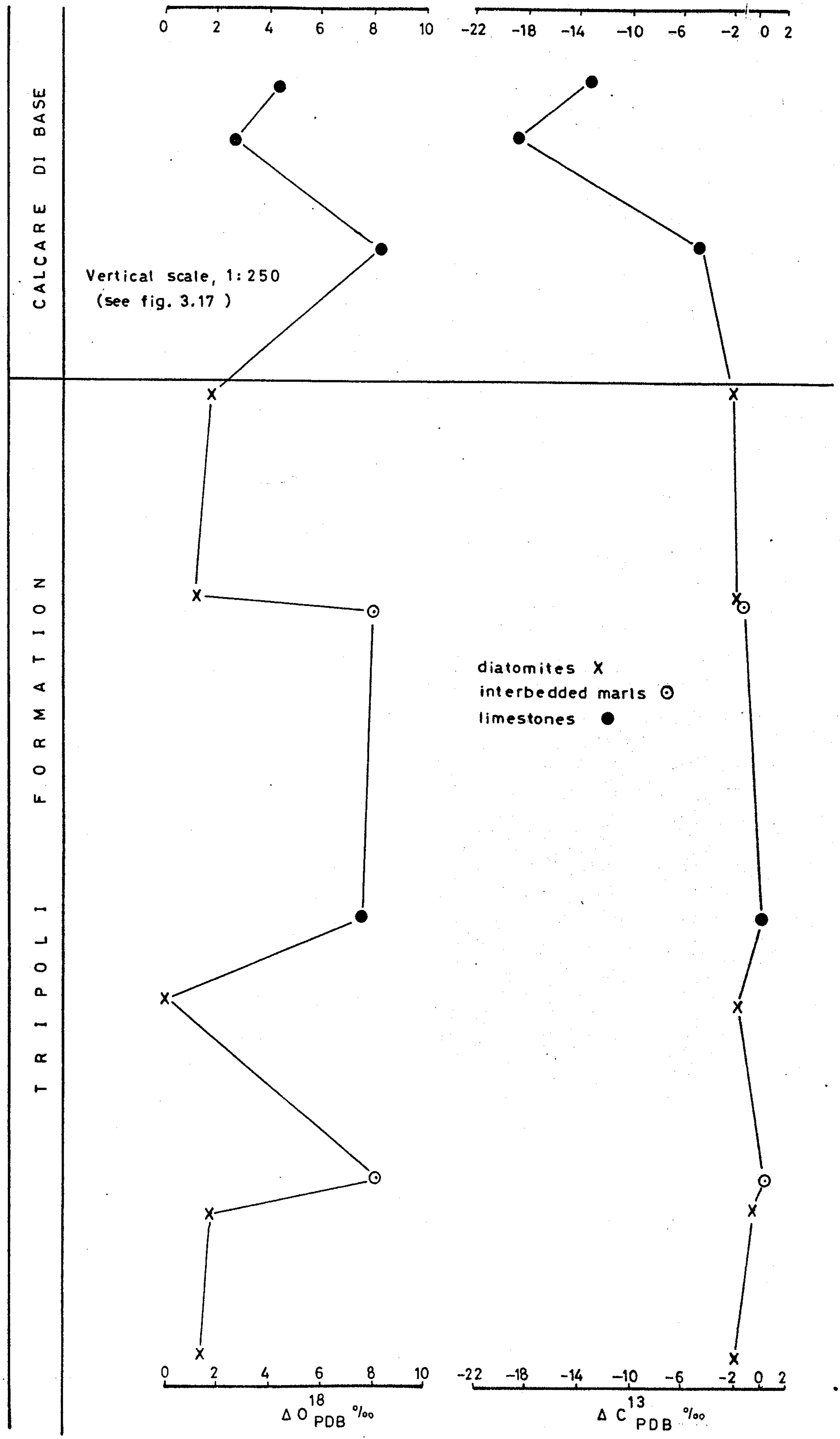


Fig. 3.23 Stable isotope distribution at Calascibetta

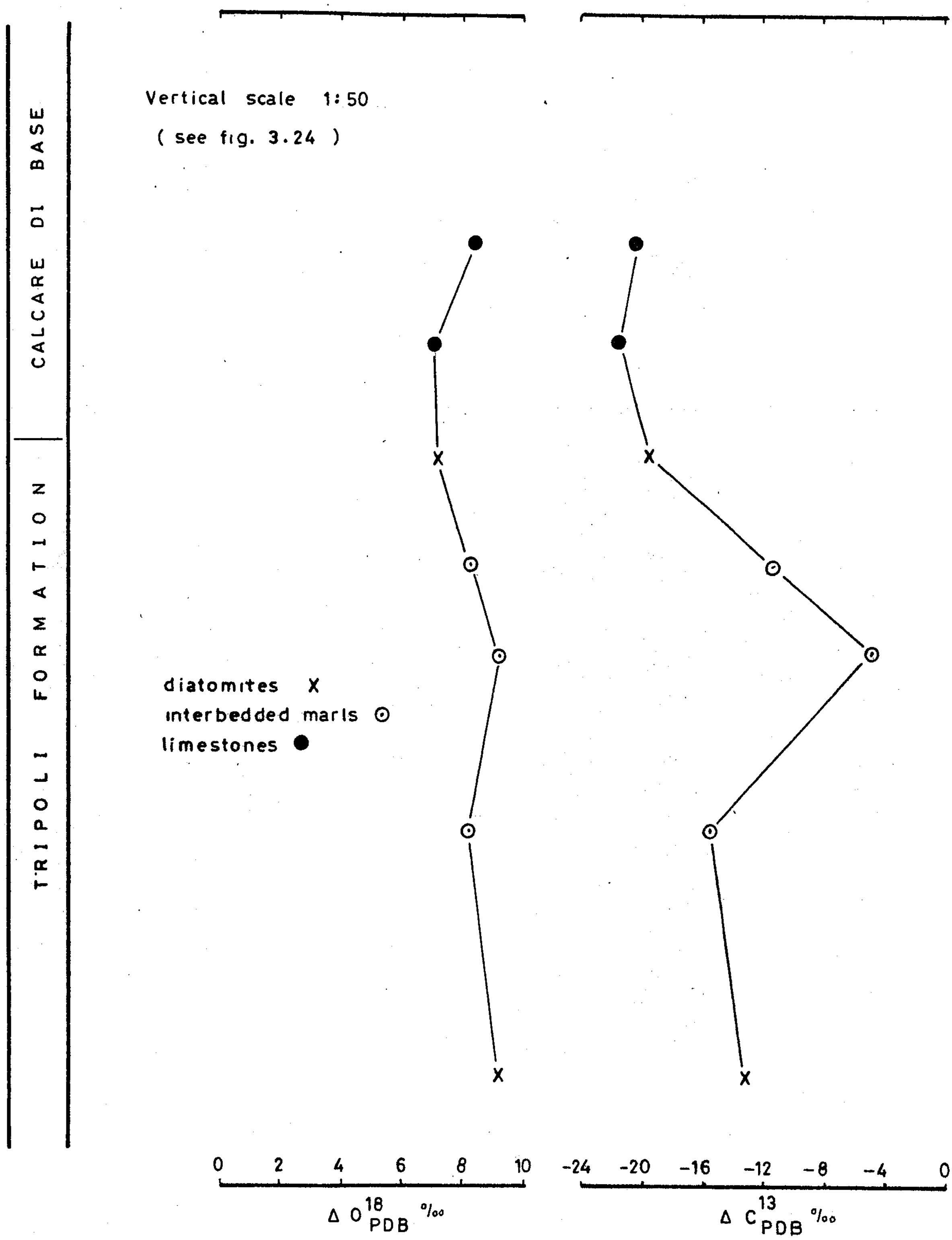


Fig. 3.24 Stable isotope distribution at Capodarso.

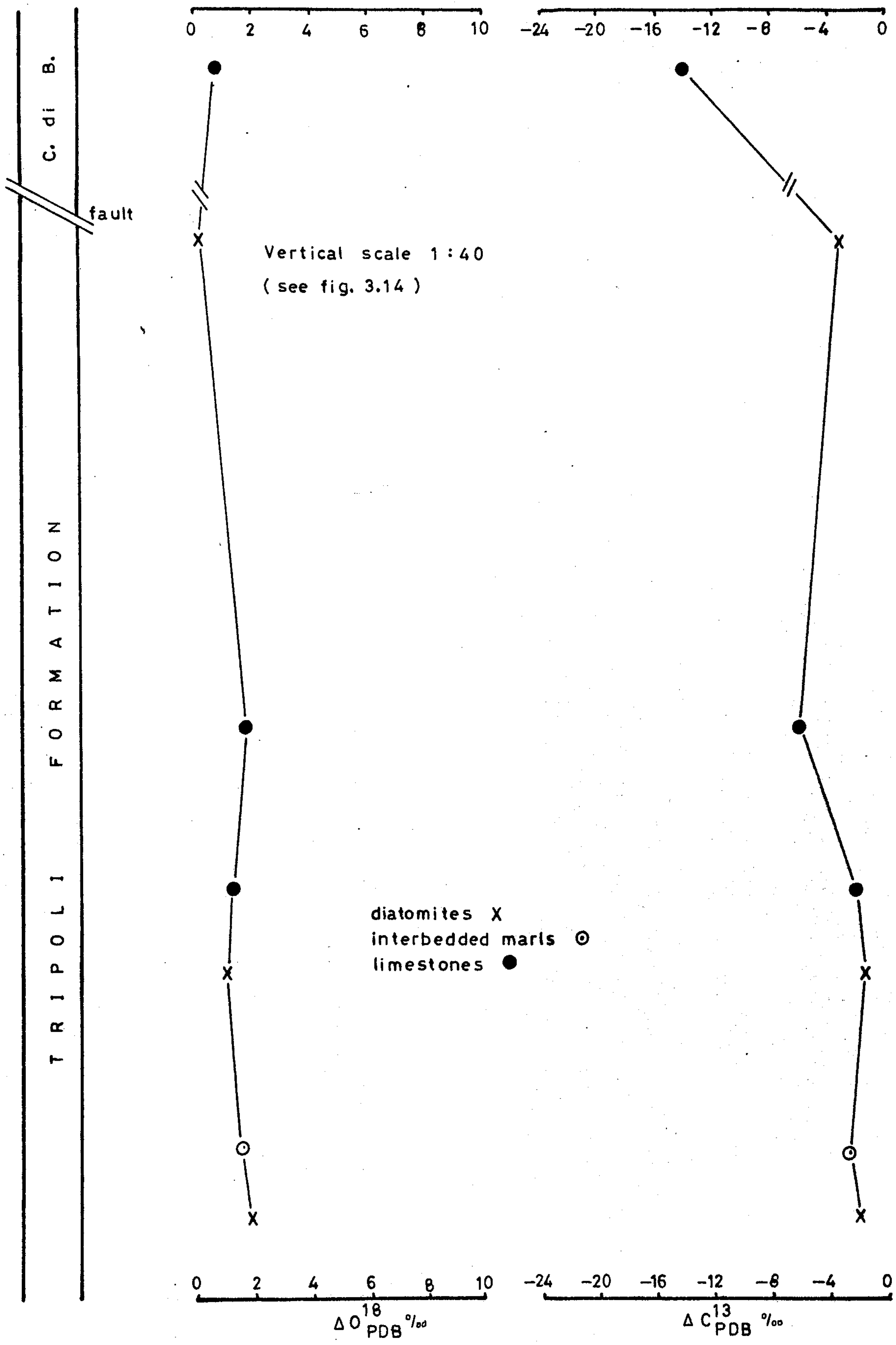


Fig. 3.25 Stable isotope distribution at Campobello di Licata

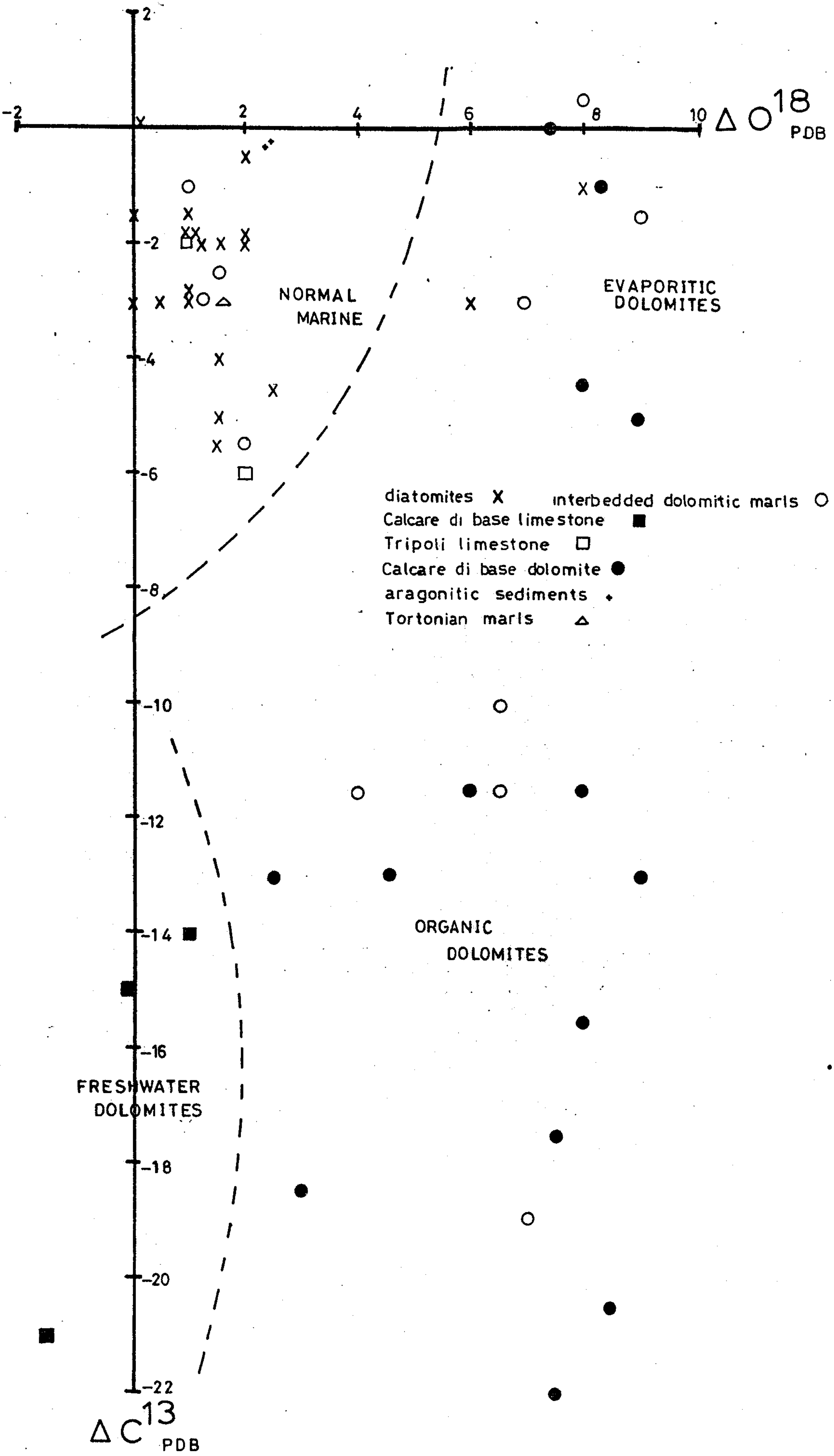


Fig. 3.26 ΔC^{13}_{PDB} vs. ΔO^{18}_{PDB} for Lower Messinian sediments

This group comprises most of the diatomites, the blue Tortonian marl from Camastra, the aragonites from Sutera and the Campobello limestone horizons. Four of the grey marl horizons also plot within this group but none are more than slightly dolomitic.

<u>Group B</u> ΔC^{13}_{PDB} + 0.5‰ to - 5.0‰

ΔO^{18}_{PDB} + 6.0‰ to + 9.0‰

All the samples in this group are dolomitic and among them are the dolomitic diatomites from Camastra and Calascibetta.

<u>Group C</u> ΔC^{13}_{PDB} - 10‰ to - 22‰

ΔO^{18}_{PDB} - 1.5‰ to + 9‰

This group is found to contain dolomitic sediments and calcareous Calcare di Base, both of which may be regarded as a distinct and separate group. Thus:

Group C_1 (Dolomites) ΔC^{13}_{PDB} - 10‰ to - 22‰

ΔO^{18}_{PDB} + 2.5‰ to + 9‰

Group C_2 (Calcare di Base limestones) ΔC^{13}_{PDB} - 14‰ to - 21‰

ΔO^{18}_{PDB} - 1.5‰ to + 1‰

The oxygen isotope values in Group A are characteristic of normal marine conditions and although the associated carbon is slightly too negative, it is thought that the carbonate in these sediments was deposited from normal marine waters (McKenzie p.c.). This is to be expected for the diatomites and blue Tortonian marls where planktonic foraminifera and calcareous nannoplankton can be seen to make up virtually all of the carbonate in the sediment. Neither is it surprising for the aragonites since recent aragonitic sediments in the Bahamas are known to be associated with waters that differ only slightly from normal marine conditions (Lowenstam and Epstein 1957). However, the inclusion within this group of the limestones at Campobello and some calcareous grey marls suggests that the carbonate in these sediments had a similar origin to that in the diatomites and Tortonian marls. In which case, almost all of the carbonate in the Tripoli Formation, including the dolomites, may have originally been deposited as the remains of calcareous planktonic organisms.

All dolomitic sediments lie within groups B and C1; they are characterised by highly variable negative carbon values ranging from + 0.5‰ to - 22‰ while the associated oxygen compositions are fairly constant, varying only between + 2.5‰ and + 9‰. These oxygen compositions are indicative of deposition in either highly evaporated or cold water (McKenzie p.c.) and in view of the many evaporitic associations of the Tripoli Formation, the former explanation seems the more likely. The dolomites of Group B would actually lie within the isotopic composition limits for evaporitic dolomites as defined by Milliman (1974 p.33) but for their slightly too negative carbon values. The dolomites in Group C1 however, have extremely negative carbon isotope compositions indicating that the carbon has probably been derived from CO_2 generated by the oxidation of organic material (McKenzie p.c., Spotts and Silverman 1966). Since subsurface cores of the Tripoli sediments are commonly bituminous (Ogniben 1957), it is almost certain that these anomalously negative carbon values are due to the former presence of organic matter in the sediment and probably indicate deposition under reducing conditions.

This combination of anoxic and evaporitic conditions has led McKenzie et al. (1979) to suggest that the Tripoli dolomites were deposited in an environment comparable to that of the present day Dead Sea. Both gypsum and aragonite precipitate from the Dead Sea but very little gypsum is found in the bottom sediments (Neev and Emery 1967). This is thought to be due to the action of sulphate-reducing bacteria which extract the oxygen required for their metabolism from the gypsum, utilising the organic matter in the sediment as an energy source. This reaction is summarised by the equation

$$4C_6H_6 + 15CaSO_4 + 3H_2O \longrightarrow 15CaCO_3 + 15H_2S + 9CO_2$$

The gypsum is thus reduced to hydrogen sulphide and the oxidation of the organic matter releases C^{13}- depleted carbon dioxide. This depletion of C^{13} is also reflected in the calcite precipitate and accounts for the extremely negative carbon isotope compositions observed in the sediments (Neev and Emery 1967, McKenzie et al.1979).

The dolomites of Group B and Ci cannot be differentiated in any way other than isotopic composition; they are lithologically similar and are not confined to any particular locality or to any particular stratigraphic horizon within the formation. However, the lack of any strong relation between dolomite content and carbon isotope composition (Fig 3.27) indicates that these highly variable carbon values cannot be simply due to the relative amounts of dolomite and calcite in the sediment. The most likely cause of the observed distribution of carbon isotope compositions is therefore thought to be local variations in depositional environment which resulted in the Group B dolomites being deposited in better oxygenated conditions than those of Group C_1.

The final group (C_2) contains only limestones from the Calcare di Base and highly negative carbon isotope values again suggest an organic source for the carbon. The oxygen compositions on the other hand are generally lower than those found in other groups and suggest deposition from non-marine waters (Milliman 1974 p.33). Similar oxygen and carbon isotope compositions have been shown to be consistent with deposition from meteoric waters in which the negative carbon was due to carbon dioxide

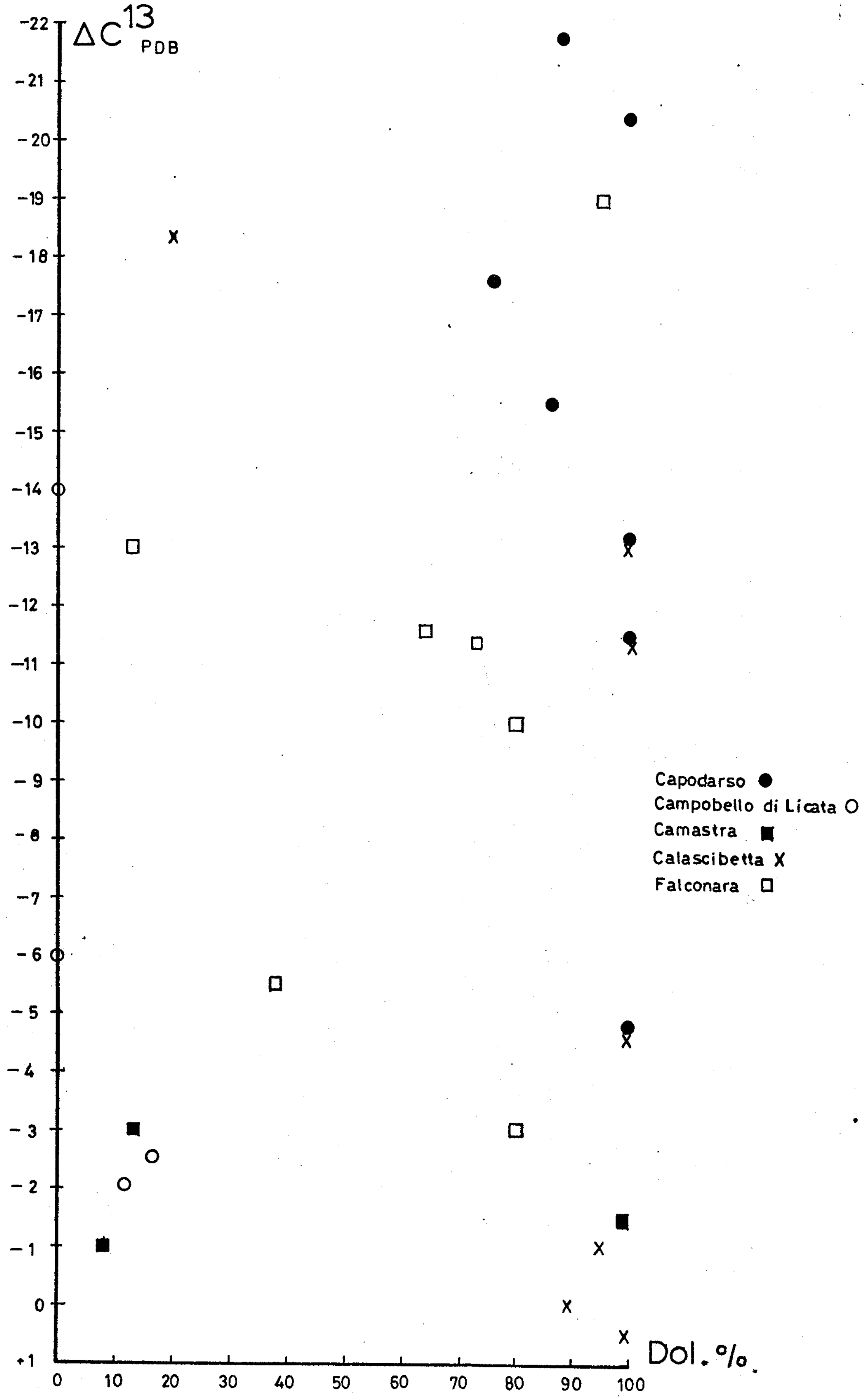


Fig. 3.27 % Dolomite vs. ΔC^{13}_{PDB} for Lower Messinian sediments.

derived from decaying organic soil material (Murata et al. 1969). It therefore appears that the Calcare di Base limestones may have been subject to vadose diagenesis.

3.9 Messinian Diatomites elsewhere in the Mediterranean.

The late Miocene appears to have been especially favourable for the deposition of diatomaceous sediments, not only in the Mediterranean (Fig 3.28) but throughout the world and particularly in the circum-Pacific regions (Bramlette 1946, Orr 1972, Wornardt 1969, Garrison 1976).

Mediterranean diatomites of Messinian age are found in most countries bordering on the Western Mediterranean and are always in the same stratigraphic position beneath the Messinian evaporites. They are commonly light in both colour and weight, fissile, finely laminated, associated with marly or pelitic sediments and also contain abundant well preserved fish remains. It is therefore not surprising that most authors have commented on their likeness to the diatomaceous sediments of the Sicilian Tripoli or Californian Monterey Formations.

The thickest and most extensive development of diatomaceous sediments appears to be in the Chelif Basin in Algeria where the outcrop extends for over 200 kms along strike on either flank of the basin and is up to 200 metres thick in places (Anderson 1933). These diatomites are commonly associated with continental deposits and are interbedded with gypsiferous horizons suggesting a shallow water origin. However, their fauna and flora reveal strong open marine associations so it is more likely that they were deposited in a marginal environment under both marine and continental influences (Anderson 1933, Tauecchio and Marks 1973, Baudrimont and Degiovanni 1974, Pierre 1974).

The poorest reported development of Messinian diatomites is in Greece where diatom-rich horizons occur within a predominantly marly sequence below the evaporites (Braune et al.1973). This suggests that there may be a general relationship between the development of diatomaceous sediments and proximity to the Atlantic

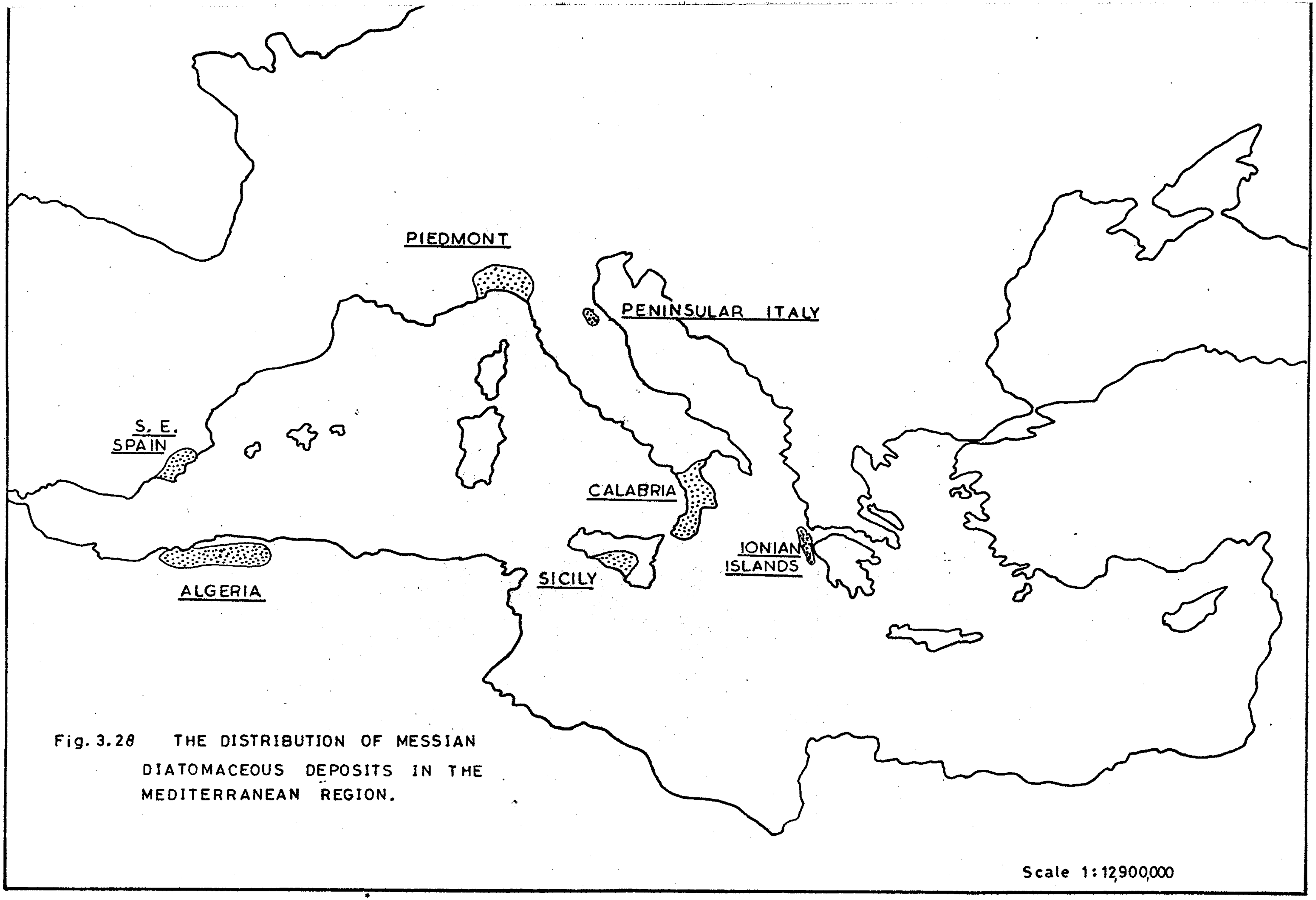


Fig. 3.28 THE DISTRIBUTION OF MESSIAN DIATOMACEOUS DEPOSITS IN THE MEDITERRANEAN REGION.

Ocean. However, if such a relationship exists then Spain would be expected to have thick accumulations of Messinian diatomites. Unfortunately it is impossible to say whether this is the case or not, since, in marked contrast to the Lower Miocene 'Moronitas', there is relatively little published data on Spanish Messinian diatomites. The available information suggests that they are marine and were deposited in either a near-shore or basinal environment (Montenat 1973, Geel 1976, Addicott et al. 1977, Burckle 1977). They may well be similar to the diatomaceous deposits of Piedmont which are better documented and are thought to have been deposited in deep, narrow, subsidiary basins along the edge of the Mediterranean (Sturani and Sampò 1973). These Piedmont diatomites contain an abundant mesopelagic fish fauna indicative of euxinic conditions and normal salinities. They are interbedded with pelitic sediments and fine sands which are bioturbated and occasionally contain a rich benthonic fauna indicating well ventilated bottom conditions. Water depths were thought to have been between 200 and 500 metres (Sturani 1973, 1978).

Messinian diatomites have also been described from Calabria (Di Nocera et al. 1974) and are known to exist further north in Peninsular Italy (Selli 1973). The Calabrian examples are only about 10 metres thick and contain occasional lamellibranchs suggesting somewhat better ventilated conditions than in Sicily. They are apparently not interbedded with argillaceous horizons as is normal elsewhere but do contain black or dark grey chert nodules. These are associated with the Calcare di Base at the top of the diatomaceous interval and may be analogous to the cherts found in a similar horizon at Monte Giammoia in Sicily.

All the diatomites have many characteristics in common and they are widely distributed around the Western Mediterranean. The conditions which led to their deposition are therefore thought to have been brought about by regional rather than local influences and it seems likely that access to the Atlantic was especially important. The Sicilian diatomites appear to have been deposited under less well oxygenated conditions than other diatomites which suggests that the Central Sicilian Basin was more restricted than other Mediterranean Basins.

3.10. Discussion.

Perhaps the two most notable features of the sediments which make up the Tripoli Formation are their pelagic character and the rhythmic nature of their deposition. Each rhythm has been shown to consist of a diatomaceous interval and an interval devoid of diatom remains which may be further divided into a lower grey marl and an upper brown shale. These sediments were deposited in the Central Sicilian Basin which was probably one of the deepest of the interconnected pre- 'Salinity - Crisis' Mediterranean basins that were linked to the Atlantic via the Betic and Rif Straits (Hsü et al. 1977, 1978).

Underlying the Tripoli Formation is a thick Tortonian sequence of hemiplegic sediments which are thought to have been deposited in deep, normal marine waters that may have been over 2,400 metres deep at Capodarso (Bandy 1975, Cita et al. 1978). However, the evaporites which overlie the Tripoli have been shown to be at least partially of shallow water origin (Schreiber et al. 1976). The pelagic sediments of the Tripoli Formation must therefore represent an overall regressive sequence joining the deep water Tortonian marls and the shallow water evaporites.

Any pelagic deposit which, like the Tripoli Formation consists largely of biogenic material will be a reflection of the chemical and biological activity in the overlying water column. In an enclosed sea like the Mediterranean, this activity will be controlled by water circulation patterns that are in turn dependent upon climate and basin topography of which the latter is particularly important, since it determines the nature of the connection to the open ocean (Lacombe and Tschernia 1972, Grasshoff 1975). Therefore, the sequence of events that led to the drastic marine regression between the end of the Tortonian and the deposition of the Messinian evaporites ought to be reflected in the sediments of the Tripoli Formation. Furthermore, the converse of this argument implies that the Tripoli's rhythmic sedimentation may be the result of some cyclic events which need not have been confined to the immediate environment of deposition but could have taken place anywhere.

In an attempt to clarify the evolution of the Mediterranean Region prior to the onset of the Salinity Crisis, it is therefore necessary to consider the depositional environments of the sediments that make up the Tripoli Formation, the oceanographic conditions that led to their deposition and the origin of the Tripoli rhythms.

3.10.1. The Diatomites.

Finely laminated diatomaceous sediments such as those found in the Tripoli Formation are today accumulating in waters with high surface productivity as a result of the upwelling of deep, cold, nutrient-rich waters. These conditions are generally confined to three parts of the world: a circum-Arctic latitudinal belt, a circum-Antarctic latitudinal belt and in regions of local upwelling along continental margins (Lisitzin 1972, Heath 1974), However, since the latitude of the Messinian Mediterranean was essentially the same as it is today, any modern analogue to the Tripoli Formation is most likely to be found on a continental margin rather that in circum-polar regions. Furthermore, in near shore areas the biogenic component of the sediment is often masked by clastic sediments, so that diatomaceous sediments only accumulate where the influx of clastic material is low or absent (Heath 1974). These areas include: the Gulf of California (Calvert 1964 1966a), Saanich Inlet, British Columbia (Gucluer and Gross 1964), the Southwest African continental shelf (Calvert and Price 1971) and the Californian continental borderland (Emery 1960). Sturani (1978) has already drawn an analogy between the diatomaceous sediments of the Santa Barbara Basin on the Californian continental borderland and those of the Messinian Piedmont Basin. However, in view of its location within a narrow gulf adjacent to the ocean, the Guaymas Basin in the Gulf of California may provide an even better analogue for the Central Sicilian Basin.

In both the Santa Barbara and Guaymas Basins the position of the laminated diatomites coincides with the minimum values of dissolved oxygen in the waters. The preservation of the laminae in these parts of the basins is therefore due to the lack of oxygen which results in the absence of bioturbating benthonic organisms and the subsequent development of H_2S in the sediment. Rhoads and Morse (1971) have shown that dissolved oxygen concentrations of less than 0.1 - 0.3 mls/l will prevent the establishment of a bioturbating benthonic fauna, although a small increase in the dissolved oxygen content may permit the introduction of soft bodied bioturbating organisms which can tolerate oxygen contents of 0.3 - 1.0 ml/l . The presence of thin bioturbated horizons in laminated diatomites recovered in cores from the Santa Barbara Basin (Emery and Hulsemann (1962) and of homogenous sediments in the Guaymas Basin (Calvert 1964) therefore show that these basins cannot be regarded as truly anoxic in the same sense as the Black Sea, Cariaco Trench and some Norwegian Fjords (Richards 1965). Poorly oxygenated conditions will develop whenever the rate of consumption of oxygen exceeds or approaches the maximum rate at which oxygen can be replenished by the circulation of the basin waters (Richards 1965). Although circulation within the Santa Barbara Basin is somewhat restricted, neither the Santa Barbara nor the Guaymas basins are stagnant and their low oxygen contents are due primarily to the influence of a well developed oxygen minimum zone in the sea off southern California and Mexico (Emery 1960, Emery and Hulsemann 1962, Calvert 1964). This is partially due to the metabolic uptake of oxygen in the upwelling fertile waters associated with the Californian Current, but is mainly due to the influence of the intense oxygen minimum zone which exists in the eastern tropical Pacific (Sverdrup et al.1942, Wyrtki 1962, Fischer and Arthur 1977). This layer of oxygen deficient water extends into the Gulf of California where local upwelling causes further depletion of oxygen. The good circulation of waters in the basins within the Gulf ensures that their deepest parts, beneath the oxygen minimum layer, are well ventilated and that laminated sediments are confined to where the oxygen minimum intersects the flanks of the basin (Fig 3.29) (Calvert 1964,1966, Brongersma - Sanders 1971). The Santa Barbara basin is somewhat different since the basin's sill lies within the oceanic oxygen minimum zone; thus the deeper parts of the basin can only be replenished with water that has already been depleted in dissolved oxygen (Fig 3.30) (Emery and Hulsemann 1962). As in the Gulf of California, upwelling occurs in the surface waters thereby causing the further consumption of oxygen both by metabolic uptake and by the oxidation of organic matter as it sinks through the water column. Periodically there may be insufficient oxygen available and organic-rich sediments will accumulate leading to the development of anoxic conditions (Emery and Hulsemann 1962, Berger and Soutar 1970, Emery 1960).

The diatomites themselves are the result of the high productivity of siliceous phytoplankton in the surface waters of these basins which is sustained by upwelling, deep nutrient rich waters (Hulsemann and Emery 1961 Calvert 1964, 1966a). In the Gulf of California upwelling occurs along the eastern side during winter and spring in response to strong northwesterly winds while during the summer and autumn less intense upwelling occurs on the western side due to southwesterly winds (van Andel 1964 p.263). Upwelling in the Santa Barbara Basin is not only due to surface winds but also to the entrainment of the basin's surface waters by the Californian Current as it passes Point Conception (Emery 1960 p.103). The presence of laminated diatomaceous sediments in some of the basins of the Californian continental borderland and the Gulf of California is therefore due to the combination of a well developed oxygen minimum zone, a lack of terrigenous sediment and the upwelling of nutrient rich waters which is itself dependent on favourable surface winds and suitable seafloor topography (Orr 1972).

The distribution of diatomaceous sediments within the Central Sicilian Basin (Fig 3.5) shows that they appear to be confined to the slopes of the basin, being absent in the deeper parts of the Platani Trough and in the shallow areas associated with the Raffadali-Armenian uplift. Decima and Wezel (1973) have

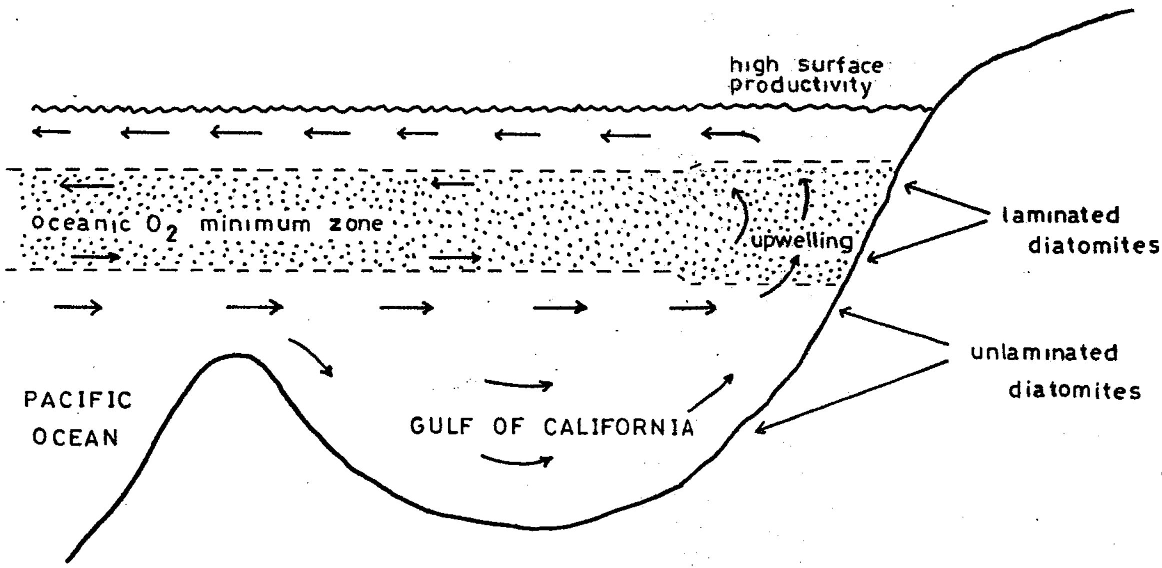


Fig. 3.29 Circulation patterns and dissolved oxygen distribution in the Guaymas Basin, Gulf of California.

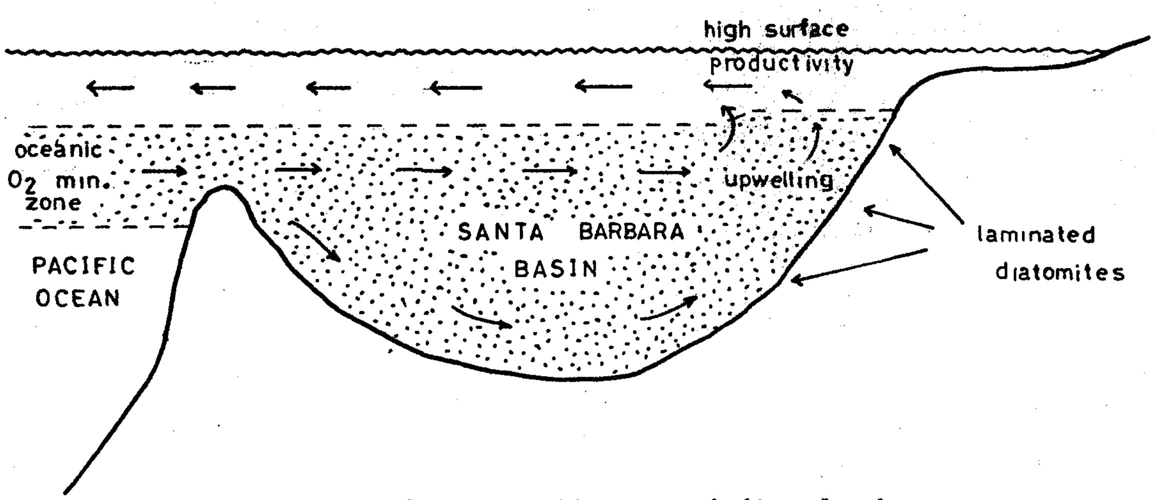


Fig. 3.30 Circulation patterns and dissolved oxygen distribution in the Santa Barbara Basin.

suggested that in the deepest parts of the basin the Tripoli is represented by 'whitish marls' while the diatomites are confined to the slopes. The presence of clasts of diatomite in a clastic horizon overlying white foraminiferal marls between Bompensiere and Montedoro shows that locally, marls must indeed have been deposited in deeper water than the diatomites. Furthermore, even though diatomites are pelagic sediments they are known to be accumulating in water depths of less than 100 metres on the Southwest African continental shelf (Calvert and Price 1971) and in the Gulf of California, they are first laid down in relatively shallow areas and then dispersed towards the deeper parts of the basin by water turbulence (van Andel 1964 p.267). Thus, as Burckle has suggested (1976 p.c. cited in Cita et al. 1978) diatomites are not necessarily indicative of deposition in deep water.

As well as the redeposition of diatoms in the Gulf of California mentioned above, the 'ponding' of diatomaceous sediment in surface hollows has been reported from the eastern Pacific (Johnson 1976) and it is thought likely that a similar redistribution of sediment would have occurred in the Central Sicilian Basin. Slumped carbonate material within Tripoli sections has been described above from Montedoro and Campobello di Licata and a massive resedimented diatomaceous interval overlies the clastic horizon between Bompensiere and Montedoro. Within the diatomites themselves; scoured horizons, ripped-up clasts and discordant laminae resembling cross beds suggest the existence of intermittent current activity. Thin horizons containing contorted laminae, slump structures which are overlain by homogenous intervals are also suggestive of current action and may be interpreted as distal turbidites. Thus, not all of the homogenous intervals found in the Tripoli diatomites should be interpreted as evidence of bioturbation. The reworking of sediment by bottom currents is also likely to be responsible for the much reduced, but apparently complete, Tripoli section at Marina di Palma, only eight kilometres from the much thicker section at Camastra. This, together with the variable dolomitisation of the Tripoli (see below) and the variable carbon and oxygen isotope compositions suggest that the basin topography was highly irregular. Several sub-basins may therefore have existed within the main Central Sicilian Basin and the distribution of diatomaceous sediments would almost certainly have been both irregular and discontinuous.

Despite the evidence that the Tripoli diatomites have been subjected to reworking and redistribution, they are nevertheless still confined to the basin slopes and are more extensively developed on the southeastern side of the Platani Trough than to the northwest. While this may be due to steeper gradients on the northwest side being less suitable for the accumulation of diatomaceous sediments, it is thought more likely that it is the result of upwelling occurring predominantly along the southeastern margin of the basin. On the Southwest African continental shelf upwelling produces diatomaceous sediments on the inner shelf which pass laterally into carbonate sediments on the outer shelf, where surface waters are less fertile (Calvert and Price 1971). Thus the distribution of diatomaceous and marly sediments in the Central Sicilian Basin is also thought to reflect the productivities of the overlying surface waters. The diatomaceous sediments are therefore situated on the margins of the basin where upwelling occurs and the marls confined to the deeper parts of the basin beneath less fertile waters. Whether the upwelling was in response to surface winds as in the Guaymas Basin or to a combination of winds and the entrainment of surface waters by currents as in the Santa Barbara Basin is impossible to say.

Ogniben's (1957) suggestion that the laminae seen in the Tripoli diatomites may be regarded as varves is supported by Calvert's (1966b) work on recent sediments in the Gulf of California where he has shown that the laminae are due to the seasonal influx of silt from rivers. The preservation of these laminae, in addition to fish remains, wood fragments and its organic-rich nature when recovered from boreholes, clearly indicates that the diatomites of the Tripoli Formation were deposited in poorly oxygenated conditions (Ogniben 1957, Rhoads and Morse 1971, Soutar 1971). However, like the Santa Barbara Basin, bottom conditions cannot have been permanently anaerobic as shown by the many thin homogenous horizons, the majority of which are thought to be due to the former presence of bioturbating organisms. The ubiquitous opaque material found not only in the Tripoli diatomites but also in the interbeds was almost certainly precipitated as pyrite since it occasionally reveals a cubic outline, has a tendency to infill foraminiferal tests and is associated with limonite (Deer, Howie and Zussman 1962, Berner 1969). Pyrite is a stable form of iron under reducing H_2S-rich conditions and is known to form in anoxic sedimentary environments (Berner 1970). Thus, while bottom conditions in the Central Sicilian Basin must have oscillated between being anaerobic and dysaerobic, conditions within the sediment were essentially anoxic. Similar diatomaceous sediments of the same age described from other parts of the Western Mediterranean (see Sect.3.9.) show that poorly oxygenated conditions must have been particularly widespread at this time, although the presence of thin shelled molluscs in the Algerian and Calabrian diatomites suggests that some parts must have been better ventilated than others. Dissolved oxygen concentrations also appear to have varied within the Central Sicilian Basin itself, since the marls found in the deepest parts of the basin are often unlaminated. Decima and Wezel (1973)describe these 'whitish marls' recovered from boreholes as containing a benthonic foraminiferal fauna of low diversity further suggesting that dissolved oxygen concentrations were sometimes higher in the bottom of the basin than on the flanks.The laminated diatomites are thus confined to the area where the oxygen minimum layer impinges on the sides of the basin in a manner analogous to the situation presently existing in the Guaymas Basin.

However, the existence of a well developed oxygen minimum zone cannot have been the only factor causing the widespread oxygen deficiency in the Western Mediterranean during the Messinian. Bottom conditions in the Guaymas Basin are well ventilated and have good communication with the open ocean (Calvert 1964). This is in marked contrast to the bottom conditions in the Central Sicilian Basin as shown by the organic-rich nature of the 'whitish marls', their low fauna diversity and the presence of pyrite, all of which suggest deposition in an oxygen depleted environment (Decima and Wezel 1973). Communication between the bottom waters of the Central Sicilian Basin and the open ocean must therefore have been restricted, suggesting that there was a physical barrier between the two water bodies. The existence of a sill separating the Mediterranean and the Atlantic has already been proposed to explain the absence of psychrospheric ostracodes from the Western Mediterranean during the Tortonian and Messinian (Adams et al.1977, Benson 1978). This sill could have caused oxygen depletion in the Mediterranean either by simply restricting circulation or, if it happened to intersect the oceanic oxygen minimum zone, by admitting only poorly oxygenated waters as happens in the Santa Barbara Basin.

Despite the presence of a sill, access to the Atlantic appears to have been an important factor in controlling the distribution of diatomites within the Mediterranean. This is probably because the deep Atlantic waters were the major source of the nutrients necessary to sustain the high diatom productivity. Sonnenfeld (1975) has suggested that any deep Atlantic waters flowing into the Mediterranean must have been deflected to the southwest by the Coriolis Effect, thus the nutrient-rich waters would have come along the Northwest African coast where upwelling is presently occurring in association with the Canary Current Sverdrup et al. 1942, Sonnenfeld 1974). These waters are today prevented from entering the Mediterranean by a 'tongue' of dense saline water flowing out at depth through the Straits of Gibraltar (Sonnenfeld 1974). This dense, saline water forms because the water lost by evaporation in the Mediterranean exceeds that gained by river discharge and precipitation. The water deficit therefore has to be made up by the influx of surface waters from the Atlantic through the Straits of Gibraltar; the Mediterranean thus gains nutrient-deficient surface water and loses denser saline waters (Lacombe and Tschernia 1972). This 'anti-estuarine' circulation pattern between the Atlantic and the Mediterranean explains why present productivity in the Mediterranean is so very low (Cita 1973b). For productivity to be increased, nutrient-rich deep Atlantic water would have to be admitted to the Mediterranean and this could probably only be achieved by reversing the present anti-estuarine circulation.

Since deep nutrient-rich waters exist today off the Northwest African coast it is reasonable to suppose that they did so during the Messinian, although there is little direct evidence of this. Some siliceous organisms have been reported in Upper Miocene sediments from DSDP site 369 off Northwest Africa (Lancelot et al.1977). However, the Upper Miocene in this area is otherwise represented almost exclusively by pelagic carbonate sediments (Hayes et al.1972, Lancelot et al.1977) and if upwelling occurred it must have been confined to inshore areas. The absence of evidence of upwelling at this time also suggests that it is unlikely that an oxygen deficiency could have developed in the eastern Atlantic comparable to that existing today in the eastern tropical Pacific. For this reason it seems likely that the distribution of dissolved oxygen concentrations within the Mediterranean during the Messinian was much less influenced by oceanic factors than is the Gulf of California or the Santa Barbara Basin today. More specifically it is thought unlikely that the well developed oxygen minimum zone within the Mediterranean could have been almost entirely due to the influence of an oceanic oxygen deficiency in the same way as in the Guaymas Basin. A further important contributing factor in the Mediterranean was probably the exaggerated effect that high surface productivities would have had on the distribution of dissolved oxygen in a basin already containing a poorly oxygenated body of water because of its geographical isolation.

3.10.2. The Inter-Diatomite Beds.

The intimate association of the diatomites and the grey marl and brown shale interbeds shows that they must have all been deposited in closely related sedimentary environments. The abundance of dolomite in the non-diatomaceous interbeds is therefore surprising in view of the pelagic origin of the diatomaceous horizons. At several localities (Falconara, Campobello di Licata, Monte Giammoia and Favara), the place of the dolomitic grey marl within the sedimentary rhythm is sometimes taken by undolomitised foraminiferal marls. These have stable isotope compositions which show that they could represent a pre-dolomitic sediment (Section 3.8). Furthermore, at Camastra, the presence of dolomite within the diatomaceous horizons has been shown to coincide with the disappearance of all the calcareous nannoplankton (Section 3.6). The dolomite in the Tripoli Formation is therefore not thought to be a primary deposit but to have formed by the replacement of calcium carbonate in the original sediment. It seems likely that this pre-dolomitic sediment could have resembled the foraminiferal marls mentioned above, which are themselves remarkably similar to the foraminiferal marls thought to be the "deep water" equivalents of the Tripoli Formation. If this is indeed so and the pre-dolomitic grey marls are identical to the deep water marls then, after each interval of diatomaceous sedimentation, foraminiferal marls must have been accumulating throughout the entire Central Sicilian Basin. It has been argued above that the lateral transition from diatomaceous sedimentation on the flanks of the basin to carbonate sedimentation in the depths is the reflection of a decrease in surface productivity of the overlying waters caused by the absence of upwelling in the centre of the basin. It is therefore likely that the vertical transition of diatomite overlain by grey marl is brought about in a similar way. In which case, the upwelling of nutrient-rich waters along the margins of the basin is the fundamental difference between the conditions which led to the deposition of diatomites and those which produced grey marls.

In contrast to the grey marls, the brown shales contain little carbonate material and sometimes none at all. In the absence of any evidence of the widespread dissolution of calcium carbonate, such as vugs or corroded foraminiferal tests, it is thought that this could be brought about in one, or a combination, of two possible ways. Firstly, there could have been a dramatic increase in the amount of fine terrigenous material being supplied to the basin or secondly, the fertility of the surface waters was further reduced so that they could only sustain a few calcareous organisms.

The presence of a strong clay mineral alignment in the brown shales and the commonly laminated appearance of the diatomite-brown shale transition shows that these sediments have never supported a bioturbating infauna. The grey marls, on the other hand, are never found to be laminated and even though the dolomitisation will have destroyed many sedimentary features, it is likely that they were deposited under sufficiently well oxygenated conditions to allow the colonisation of the sediment surface by a soft-bodied benthonic fauna. Indeed, pelitic sediments interbedded with diatomites in the Piedmont basin have been described as containing a rich benthonic fauna (Sturani 1973, 1978). The Central Sicilian Basin therefore appears to have been less well ventilated than other parts of the Mediterranean during the deposition of the grey marls, just as it was during the deposition of the diatomites.

Conditions on the sediment surface appear to have been better ventilated during the deposition of the grey marls than while the other Tripoli sediments were accumulating. However, the presence of oxidised pyrite in both the grey marls and the brown shales shows that conditions within the sediment must have remained permanently anaerobic, just as they had during the deposition of the diatomites. Under such conditions when all the available free oxygen has been used up, the oxidation of organic matter will usually continue by the reduction of sulphate ions (Goldhaber and Kaplan 1974). It is therefore surprising to find gypsum growing within foraminiferal tests in one brown shale horizon at Canastra. Gypsum is fairly common in Tripoli sediments, both as veins and void-fills, but at Camastra there are no immediately overlying evaporites. Neither are any foraminiferal tests found to be infilled by gypsum elsewherein the section, although gypsum has been detected in the sediment by X-ray diffraction. It therefore appears that this gypsum must be of either primary or early diagenetic origin.

The association of pyrite and authigenic gypsum has been described in late Miocene-early Pliocene sediments from the Southwest African continental shelf (Siesser and Rogers 1976). By analogy with similar present-day organic-rich sediments in the same region, the authors suggest that the gypsum was formed in the following way: The pH in the sediment was low enough to dissolve calcite so that all, or part of the calcareous matter reaching the sediment surface was dissolved, thereby providing the Ca^{2+} ions necessary for the gypsum. The sulphate ions were derived either from the incomplete reduction of pre-existing sulphate ions by sulphate-reducing bacteria or by diffusion from the overlying water; when its solubility product was exceeded then gypsum precipitated. The association of pyrite, calcareous foraminiferal tests and the organic nature of the Tripoli sediments suggests that such a mechanism could well account for the gypsum at Camastra, however, another possibility must also be considered. A parallel has already been drawn between the Tripoli sediments accumulating in the present-day Dead Sea (Section 3.8). In the Dead Sea, gypsum is precipitating from the surface waters but is then being consumed by sulphate-reducing bacteria before it can be preserved in the sediments. Therefore , if such a situation existed in the Central Sicilian Basin, as the isotope data suggests, the gypsum at Camastra must be due to the supply of gypsum briefly exceeding the rate at which it could be consumed by sulphate-reducing bacteria. This could be brought about either by increased evaporation or by a decrease in the supply of organic matter needed by the bacteria as an energy source. However, in view of the isolated occurrence of the gypsum, the most likely explanation is thought to be a localised and temporary increase in the dissolved oxygen content of the basin waters.

3.10.3. Dolomites in the Tripoli Formation and the Calcare di Base.

Dolomite occurs in nearly all of the Tripoli sediments even though it is often present only in very small amounts. Towards the top of the Tripoli Formation, however, the diatomites and especially the grey marls become increasingly dolomitic until they are eventually replaced by the dolomites of the lower, unbrecciated Calcare di Base. Although there is considerable variation in the extent of dolomitisation, both between localities and within individual sections, the increase in dolomite is recognisable in nearly all Tripoli sections. These dolomites assume a particular significance, since, the environmental changes responsible for their widespread development also appear to have been responsible for the eventual termination of diatomaceous sedimentation in the Central Sicilian Basin.

The Tortonian marls and diatomaceous shales at the base of the Tripoli Formation contain small amounts of dolomite but it represents no more than 10% and possibly as little as 1% of the total sediment (Fig 3.10 and see Appendices 1 & 2). The dolomite occurs as isolated, small euhedral rhombs which have apparently grown within the groundmass , while these may be detrital, dolomite rhombs have often been found in deep-sea calcareous oozes, particularly when they are associated with reducing conditions (Beall and Fischer 1969, Weser 1970, Davies and Supko 1973). An authigenic origin is therefore thought more likely for the dolomite rhombs in the Tripoli Formation and Calcare di Base. However, only a very small part of the total dolomite occurs as euhedral crystals and by far the most common form is micrite.

Recent dolomite has been reported from several places around the world; notably the Persian Gulf (Illing et al.1965), the Bahamas (Shinn et al.1965), the West Indies (Deffeyes et al. 1965) and the Coorong district of South Australia (Skinner 1963, Von der Borch 1965a, 1965b). All these, and other syngenetic dolomites, consist of micrite or fine grained crystals (Friedman and Sanders 1967), indeed, it has been suggested that micritic dolomite is indicative of either a primary or an early replacement origin (Folk 1974). However, the only reported occurrence of primary dolomite from the above localities comes from the Coorong (Skinner 1963) and even this has been considered doubtful (Bathurst 1975). The lack of a convincing recent model for the primary deposition of dolomite is therefore strong evidence in favour of the replacement origin for the Tripoli dolomites proposed above (Section 3.10.2). It seems equally unlikely that any of the Calcare di Base dolomites can be primary deposits, although the work of Folk and Land (1975) suggests that it cannot be entirely ruled out for those dolomites associated with aragonitic sediments.

The variations in the intensity of dolomitisation in the Tripoli Formation can be clearly illustrated by comparing the sections at Camastra, Falconara and Calascibetta. In the upper part of the Camastra section (Fig 3.10) dolomitisation has been especially intensive and no calcareous material is to be found in either the interbeds or the diatomites. This is not the case in the lower part of the section at Falconara (Fig 3.11) where a diatomite with many coccoliths and discoasters contains only 5% dolomite while the overlying interbed is 90% dolomite (McKenzie p.c.). A little higher in the same section a sample from an interbed contains 40% dolomite while the top of the same interbed is much richer in coccoliths and contains only 18% dolomite. Similar cases are to be found in other sections but at Calascibetta (Figs 3.12 and 3.18) some anomalously low dolomite contents were associated with the presence of the coccolith Braarudosphaera sp., suggesting that in this case the formation of dolomite may have been hindered by the influx of fresh water (Section 3.6). It is unlikely that such rapid fluctuations in the dolomite contents of these sediments could occur if dolomitisation had taken place after burial. While reactions with interstitial waters could possibly account for the development of the small euhedral rhombs, they could not produce the volume of micritic dolomite found in these sediments without some external source of Mg^{2+} ions (Manheim and Sayles 1974). However, if dolomitisation took place at or near the sediment surface then these local variations could be conveniently explained by differential rates of burial. This would also account for the concentration of dolomite in the interbeds since it has already been shown that their rate of sedimentation and hence their rate of burial is only one fortieth the rate for the diatomites (Section 3.5).

Despite the widespread occurrence of recent marine dolomites mentioned above, nowhere are substantial amounts of dolomite known to be accumulating in open marine waters of normal salinity. Small amounts of dolomite have been found in deep-sea sediments but with one apparent exception, they can be shown to be either detrital (Berger and Von Rad 1972), authigenic (see above) or to be associated with hydrothermal volcanic emanations (Bonatti 1966). The one exception is a lithified dolomite horizon described from the Equatorial Atlantic for which no satisfactory explanation has yet been forthcoming (Thompson et al. 1968, Chester and Aston 1976). Virtually all recent dolomites are associated with hypersaline conditions and some authors would even regard dolomite as an evaporitic mineral (Friedman and Sanders 1967, Berner 1971). While this is not necessarily true in all cases (Zenger 1972, Folk and Land 1975), it certainly applies to most recent marine dolomites (Supko et al. 1974) and suggests that an evaporitic origin is most likely for the dolomites of the Tripoli Formation and Calcare di Base.

Since most recent marine dolomites are formed in hypersaline environments, they are often associated with aragonite and evaporitic minerals of which the most common is gypsum (Illing et al. 1965, Deffeyes et al. 1965). In many cases, the most notable exception being the Coorong (Von der Borch 1965b), this gypsum plays a particularly important role in the dolomitisation process, even when it is not preserved in the sediment (Shinn et al. 1965). This is because the precipitation of both aragonite and gypsum has the effect of raising the Mg^{2+}/Ca^{2+} ratio of the surrounding water and it is this parameter that appears to be one of the most important single factors in controlling dolomitisation (Deffeyes et al. 1965, Bathurst 1975). The association of dolomite and aragonite is evident in the Calcare di Base (section 3.4.1) and the former presence of gypsum may also be inferred since, if pseudomorphs of halite are to be found in the Calcare di Base breccias (Ogniben 1957), then gypsum must surely have also been precipitated.

In the Coorong, dolomites with a stoichimetric composition have been found to originate in waters richer in Mg^{2+} ions than those associated with the non-stoichimetric dolomites (Von der Borch 1965a). Morrow (1978) has suggested that a direct relationship exists and that in general waters with higher Mg^{2+}/Ca^{2+} ratios will produce more magnesium rich dolomites. Marschner (1968) and Supko et al. (1974) have gone even further and suggested that the Mg^{2+}/Ca^{2+} ratio can also be related to salinity, however, it is doubtful whether waters with high Mg^{2+}/Ca^{2+} ratios are necessarily highly saline waters (Folk and Land 1975).

All of the dolomite in the Tripoli Formation is non-stoichimetric and reveals a fairly constant composition which varies between (Ca_{52} Mg_{48}) and (Ca_{57} Mg_{43}). However, in several sections (Calascibetta, Camastra, Monte Giammoia, Capodarso and Marina di Palma) there is a marked decrease in the mole % excess Ca^{2+} as the Tripoli Formation passes into the Calcare di Base (Figs. 3.10, 3.12;). Some 'event' must therefore have occurred at the end of the deposition of the Tripoli Formation which had the effect of increasing the amount of magnesium in the dolomite. According to Morrow (1978) this implies an increase in the Mg^{2+}/Ca^{2+} ratio of the waters in which the dolomite was being deposited. In view of the evaporitic associations of the Tripoli Formation and especially the Calcare di Base, the most likely way that this could be brought about is by the extraction of Ca^{2+} ions as a result of the widespread precipitation of gypsum. However, for this to have had a relatively sudden and basinwide influence on dolomite compositions, extremely large quantities of gypsum must have been precipitated. In the deeper parts of the basin only a thin dolomite horizon separates the Tripoli Formation, or its equivalent, from the 'Cattolica Gypsum' which passes laterally into the brecciated Calcare di Base (Ogniben 1957, Decima and Wezel 1973). It is therefore suggested that the change in dolomite composition at the end of the Tripoli Formation represents the beginning of the accumulation of the 'Cattolica Gypsum' in the deeper parts of the basin.

Gypsum precipitation probably commenced during the deposition of the Tripoli dolomites although, with the possible exception of the gypsum filled foraminifera tests at Camastra, none of it has been preserved in the sediments. The dolomites' stable isotope compositions, as well as the usual association of gypsum with evaporitic dolomite both suggest that this is likely. However, evaporitic minerals such as gypsum and dolomite are not usually found in association with pelagic deposits such as the Tripoli diatomites. A similar problem was encountered by Peterson and Edgar (1970) who discovered sepiolite and palygorskite in deep water sediments from the eastern Atlantic. They attributed them to the alteration of volcanic ash by magnesium-rich brines which were thought to have formed in a shallow, near-shore environment and then to have percolated downdip via older, porous sediments. This is similar to the "Seepage Reflux" model of dolomite formation proposed by Adams and Rhodes (1960) and could help explain the origin of the Tripoli's dolomitic sediments. The evaporitic character of the Tripoli dolomite suggests that in the Central Sicilian Basin the most likely place for magnesium-rich brines to form would have been in hypersaline environments around the margins of the basin. Eventually the brines must have spread into the basin itself and, being more highly evaporated and therefore denser, they would have sunk beneath the normal basin waters. A 'tongue' of magnesium-rich brine may therefore have developed which extended down towards the deeper parts of the basin and caused the dolimitisation of the Tripoli sediments accumulating on the basin flanks. However, if these dense descending brines were indeed the reason for the presence of dolomite in the Tripoli Formation, then one would expect the most dolomitic Tripoli sections to be those situated close to the basin margins. The evidence in most cases confirms this. The Tripoli sediments at Camastra and Falconara have certainly been more affected by dolomitisation than those at either Montedoro or Campobello di Licata (Figs 3.10, 3.11, 3.13, 3.17). They are also closer to the shallow-water area of the Raffadali- Armerian Uplift than Montedoro but the lack of dolomitisation in the Campobello section, located between Camastra and Falconara, is problematical. However, the paths taken by these dense brines as they sank into the basin would have been controlled by the local topography. Surface 'highs' or 'shielded' areas would therefore tend to escape dolomitisation while the brines would be trapped in surface depressions and it is in these depressions that dolomitisation would be most intensive. The low dolomite content of the section at Campobello is therefore probably due to it being either located on a 'high' or otherwise shielded from the dolomitising brines.

The proposed evaporitic origin for the dolomitising brines implies that as well as being denser and richer in magnesium than the normal basin waters, they must have also have been more saline. Their continued introduction into the Central Sicilian Basin during much of the deposition of the Tripoli Formation would therefore have tended to increase the salinity of the basin's bottom waters. A similar salinity build up during the Tortonian and Messinian has also been suggested for the Balearic Basin as a result of stable isotope studies carried out by Vergnaud-Grazzini (1978). However, the presence of diatoms and normal marine planktonic foraminifera in the Tripoli sediments (Van der Zwann 1978, personal communication quoted in McKenzie et al.1979) shows that normal salinities prevailed in the surface waters of the basin which were evidently in good communication with the open ocean. Since the only possible evidence of fresh water entering the basin is the occurrence of Braarudosphaera sp. at Calascibetta, any lowering of the basin's water level due to evaporation must have been counteracted by an inflow of marine rather than fresh waters. The absence of any significant influx of fresh water, together with the basin's restricted nature therefore means that there was nothing to prevent a continual build up of salinity in the basin waters during the deposition of the Tripoli dolomites. This would not necessarily be reflected in the sediments as long as there was a surface layer of normal marine waters in which the planktonic organisms, that make up most of the Tripoli sediments, could flourish. However, if the salinity of the surface waters began to increase then the siliceous flora, in particular, would soon become less diverse and disappear. This would undoubtedly be reflected in the sediments and it is likely that the almost monospecific diatom assemblages, comprising the euryhaline diatom Thalassionema nitzschoides, encountered near the top of the Tripoli Formation (Gersonde 1978) is evidence of just such an increase. Furthermore, it is unlikely that the precipitation of the Cattolica Gypsum could have taken place so soon after the end of the Tripoli sedimentation unless the basin contained an already highly evaporated, saline body of the water. The end of diatomaceous sedimentation at the top of the Tripoli Formation must therefore mark the end of open marine influence in the Central Sicilian Basin and probably also coincides with the final severing of communication with the open ocean.

In the Tripoli Formation the abundant remains of calcareous planktonic organisms would have provided all the calcium carbonate that was necessary for the Tripoli dolomite. However, the source of calcium carbonate for the Calcare di Base dolomite is uncertain since it is doubtful if sufficient biogenic sources could survive in a basin full of highly evaporated waters. The few undolomitised horizons contain little recognisable biogenic debris and although occasional coccoliths and planktonic foraminifera are to be found at Enna and Marianopoli, it is impossible to be sure whether they are detrital or represent a pre-dolomitic sediment.

Chemical precipitation of calcite is unlikely since high magnesian calcite would be expected to form in association with dolomite rather than the low magnesian variety (Folk and Land 1975). In the sabkhas of the Persian Gulf, dolomite is replacing aragonite that may be of either chemical or algal origin (Illing et al. 1965, Kendall and Skipwith 1969). The direct precipitation of aragonite and the formation of calcite by the bacterial reduction of gypsum have also both been reported from the Dead Sea (Neev and Emery 1967). However, the Calcare di Base dolomites deposited in the inferred deeper parts of the basin (ie. Sutera, Enna and Antinello) show no evidence of subaerial exposure. They are associated with aragonite at Sutera, Enna and Antinello and their negative carbon isotope values suggest an organic source of carbon (see Section 3.8). It therefore seems likely that they were formed under conditions similar to those existing in the present-day Dead Sea or its Pleistocene precursor Lake Lisan (Neev and Emery 1967, Begin et al. 1974). The Mg^{2+}/Ca^{2+} ratio in the waters of the Dead Sea is much lower than that normally associated with modern marine dolomite formation and probably accounts for the lack of dolomite in Dead Sea sediments (Friedman and Sanders 1967). Clearly no such constraint existed in the Central Sicilian Basin however, and a thick dolomite sequence was able to accumulate.

The vertical fractures infilled with sediment in the laminated dolomites at Marina di Palma are almost certainly due to desiccation and indicate that, unlike the dolomites mentioned above, these sediments must have undergone periods of subaerial exposure. The horizons in which the desiccation cracks occur have a finely laminated, undulating appearance resembling features described from stromatolites (Kendall and Skipworth 1968, Hofmann 1969, Davies 1970). The more porous, pelleted horizons at Marina di Palma are similar to sediments described from the Calcare di Base of the Messinian in the Northern Apennines (Vai and Ricci Lucchi 1977). A pelletal origin is discounted by these authors who interpret the grains as micrite coated algal filaments. Despite the association with possible stromatolites of algal origin it is unlikely that the dolomites at Marina di Palma can be interpreted in the same way since the grains are both shorter and thicker than those described by Vai and Ricci Lucchi (1977). Their morphology, as well as their association with desiccation features and stromatolites is consistent with a faecal origin, since faecal pellets are commonly preserved in low energy sub- and intertidal environments (Shinn et al. 1969, Evans et al. 1973, Vai and Ricci Lucchi 1977). These sedimentary features are clearly consistent with the generally accepted view that the Calcare di Base was deposited in the photic zone and underwent periodic emergence and desiccation (Decima and Wezel 1973, Schreiber and Friedman 1976, Cita et al. 1978)

3.10.4. The Calcare di Base Breccias.

The dolomitic marls found in the lower part of the Calcare di Base bear a strong resemblance both to the marly sediments which separate the brecciated horizons and to many of the clasts found within the breccias themselves. The highly vuggy appearance of the breccias, together with the presence of halite pseudomorphs (Ogniben 1957) suggests also that they once contained evaporite minerals. It therefore appears that the only fundamental difference between the dolomitic sediments of the Calcare di Base and the calcareous brecciated horizons is the change of mineralogy associated with the former presence of evaporites within the sediment. The breccias may therefore be interpreted as solution collapse breccias formed by the leaching out of the evaporite minerals and the subsequent collapse of the primary sedimentary structure (Cita et al. 1978). The presence of halite shows that the evaporitic horizons must have formed in the supratidal environment, therefore, since there are often several successive brecciated horizons separated by only slightly deformed interbeds there is clearly a cyclic pattern to the sedimentation. This appears to be due to the depositional environment oscillating between supratidal and inter- or subtidal conditions.

The leaching of the evaporites must have been performed by waters whose salinity was less than that of the waters from which the salts precipitated and the isotopic evidence suggests they were probably of meteoric origin. These same waters must also have been responsible for much of the solution and reprecipitation of calcite that has occurred in the Calcare di Base, the vadose crusts at Falconara, the solution horizons in the pelletal limestones at Camastra, the pseudomorphing of halite crystals by calcite and also for the calcareous nature of the sediments associated with the breccias.

The sediments in the lower part of the Calcare di Base are always predominantly dolomite whereas those associated with the breccias are predominantly calcite even though they are commonly physically identical. This dichotomy is so widespread that it cannot be due to recent diagenesis: the transition between the two units is a gradual one and involves the replacement of the micritic dolomite by the development of either microspar or a calcite cement. The original dolomitic sediment is therefore being dedolomitised. Dedolomitisation in the Calcare di Base is unfortunately not illustrated by the classical calcareous rhombic textures described by Shearman et al.(1961), Evamy (1967) and Scholle (1971) , nevertheless 'grumeleuse' textures (struttura grumosa) similar to those described by Evamy (1967) have been recognised, as has the replacement of dolomite by coarser calcite crystals described by Shearman et al. (1961). Dedolomitisation may be brought about by the reaction of waters rich in Ca^{2+} ions relative to Mg^{2+} ions with dolomite in a vadose environment (De Groot 1967, Evamy 1967, Braun and Friedman 1970). It is therefore likely that meteoric waters percolated down through the Calcare di Base, dissolving the evaporite minerals which were probably mainly gypsum, and thereby became enriched in Ca^{2+} ions. These fluids then reacted with the micritic dolomites dedolomitising them. The occurrence of celestine as a cement in some micritic dolomites provides further evidence in favour of dedolomitisation by meteoric waters since Shearman and Shirmohammadi (1969) have noticed a depletion in strontium accompanying dedolomitisation in some carbonates from the Jura. It therefore appears that strontium ions leached from the dolomites have combined with sulphate ions from gypsum to form the celestine found near Enna and San Cataldo.

$$\begin{tikzcd} \text{Solution of gypsum} \arrow[r, "Ca^{2+}", "SO_4^{2-}"'] & \underset{\text{dolomite}}{(Mg.Ca)\ CO_3} \arrow[r] \arrow[d, "Mg^{2+}\ Sr^{2+}"', "SO_4^{2-}"] & \underset{\text{dedolomite}}{CaCO_3} \\ & \underset{\text{celestine.}}{SrSO_4 \quad + \quad Mg^{2+}} & \end{tikzcd}$$

The same waters may also be responsible for the frequent development of calcite in aragonitic beds even though no evidence of the growth of calcite is visible. Nevertheless Figure 3.21 shows that the only locality to be completely devoid of evidence of dedolomitisation is also the only locality to contain pure aragonite beds. This suggests that the Sutera section was never exposed to the diagenetic effects of vadose waters, probably as a result of being deposited in the deeper part of the basin.

The solution of gypsum deposited in the Calcare di Base also accounts for the frequent occurrence of sulphur deposits in the Central Sicilian Basin. Sulphur deposits from the Gulf Coast of the U.S.A. are thought to have formed due to the reduction of dissolved sulphate by sulphur reducing bacteria to form H_2S which was then oxidised by more sulphate ions to form native sulphur (Feely and Kulp 1957). The frequent sulphurous odour described from the Calcare di Base (Ogniben 1957, Richter Bernburg 1973), together with the mutual association with cavernous limestones suggests that a similar origin for both deposits is likely.

3.10.5 Origin of the Tripoli Rhythms.

It has been argued above that the deposition of the Tripoli Formation's diatomaceous sediments can be related to periods of upwelling in the Central Sicilian Basin. Since the diatomites are characteristically interbedded with dolomitic marl horizons, the upwelling must have occurred at frequent intervals during the deposition of the Tripoli Formation. The regular occurrence of these bouts of upwelling strongly suggests that they were not simply a series of coincidental events but that they occurred in response to some external control. Lacombe and Tschernia (1972) have stated that the physical oceanography of the Mediterranean is controlled by the climatology of the region and Grasshoff (1975) has shown that local topography is also important in determining the circulation pattern of basin waters. The intermittent nature of the upwelling and the regular changes in circulation patterns that it implies may therefore be explained by regular changes in either climate or topography. However, the rythmic aspect of the changes, as reflected in the Tripoli sediments, strongly suggests that a climatic origin is the more likely.

Studies of Quaternary sedimentation in the Western Alboran Sea by Euang and Stanley (1972) have led them to suggest that a fundamental change took place in the circulation pattern of Mediterranean waters approximately 10,000 years ago, coinciding with the onset of warmer climates at the end of the Pleistocene. They propose that the present day anti-estuarine exchange of waters between the Mediterranean Sea and the Atlantic Ocean became established during the early Holocene but at the very end of the Pleistocene an estuarine circulation pattern existed. Other periods of reversed (estuarine) circulation have also been proposed for both the Pleistocene and the Pliocene (Vergnaud-Grazzini and Bartolini 1970, Huang and Stanley 1972, Sonnenfeld 1974). Therefore, in order to assess how climatic changes might have affected the circulation of Mediterranean waters during the Messinian, it is necessary to consider why estuarine circulation existed during the late Pleistocene and the effect that it had on sedimentation.

Huang and Stanley have suggested that the period of reversed circulation at the end of the Pleistocene coincided with the onset of more temporate climatic conditions following the last of the major glacial advances. This climatic amelioration would have resulted in not only the generation of considerable quantities of glacial meltwater but also an increase in precipitation and a lowering of evaporation rates (Ryan et al. 1966, Huang and Stanley 1972). The decrease in evaporation together with a large and relatively sudden influx of fresh water must inevitably have led to a reduction in the density of the Mediterranean's surface waters. Consequently, as these "fresh" Mediterranean waters entered the Atlantic through the Straits of Gibralter, they would have floated on top of the denser oceanic waters, thereby establishing an estuarine circulation pattern between the two water bodies (Huang and Stanley 1972). This episode of estuarine circulation terminated at the beginning of the Holocene when the supply of glacial meltwater had been much reduced and the influx of freshwater to the Mediterranean was no longer able to compensate for the loss by evaporation. As a result the Mediterranean developed a negative water balance which could only be counteracted by an inflow of surface water from the Atlantic. The flow of water between the Atlantic and Mediterranean was therefore reversed and an anti-estuarine circulation pattern established.

The late Pleistocene was also a time during which poorly oxygenated conditions existed throughout much of the Mediterranean and the occurrence of sapropels in cores recovered from the Tyrrhenian and Eastern Mediterranean Basins suggests that conditions may occasionally have been completely anoxic (Huang and Stanley 1972, Ryan 1972, Cita and Ryan 1973). The anoxic conditions in the Eastern Mediterranean have been attributed to the existence of a density stratified water body which was established as a result of an influx of glacial meltwater from the Black Sea (Olausson 1961). Ryan (1972) has also related the deposition of late Quaternary sapropels to warmer climatic conditions and suggests that they indicate times when the glacioeustatic rise in sea level resulted in communication being established between the Eastern Mediterranean and the Black Sea.

Although the Western Mediterranean is thought to have been better ventilated than the Eastern Basins during the late Pleistocene, the presence of sapropels in the Tyrrhenian Basin suggests that glacial meltwater from the Black Sea must have periodically spilled over into the Western Mediterranean and established a density stratified water body there also. In order to maintain this stratification and prevent vertical mixing, the less dense surface waters of the Western Mediterranean must have flowed into the Atlantic and been replaced by denser oceanic water at depth. The existence of anoxic conditions in the Western Mediterranean during the late Pleistocene is therefore fully in accordance with Huang and Stanley's proposal that at this time estuarine circulation existed between the Atlantic and the Mediterranean.

The findings of Legs 13 and 42A of the D.S.D.P., both of which encountered Pleistocene sapropels, have provided more evidence to support the association of anoxic conditions with warmer climatic conditions, glacial retreat and rising sea levels (Ciaranfi and Cita 1973, Marchetti and Accorsi 1978). Furthermore, sapropels are today associated with truly anoxic basins such as the

Black Sea and some Norwegian fjords, all of which are characterised by estuarine circulation (Calvert 1976). There is therefore considerable evidence to suggest that during the late Pleistocene a close relationship existed between the development of anoxic conditions and the existence of estuarine circulation and that both were the direct result of the post-glacial onset of warmer climatic conditions.

Unfortunately, no such simple relationship exists between climatic trends and productivity. Cold climates are generally thought to produce carbonate maxima by intensifying atmospheric processes and therefore intensifying oceanic circulation. This causes increased upwelling and hence increased carbonate productivity (Arrhenius 1952). However, while a correlation has been recognised between carbonate minima and inferred warm climates during most of the Pliocene the reverse appears to hold true for the early Pliocene and the late Quaternary (Cita and Ryan 1973). Cita (1973b) has also suggested that productivity will be higher when there is free exchange between the Atlantic and the Mediterranean and that it may also have been increased by the establishment of estuarine circulation. Huang and Stanley (1972) on the other hand have noticed an increase in pelagic carbonate sedimentation with the onset of anti-estuarine circulation at the beginning of the Holocene. The Pleistocene 'glacials' were characterised by lowered sea levels and the intensified atmospheric activity at this time is known to have resulted in an increase of wind transported terrigenous sediment (Fairbridge 1972, Huang and Stanley 1972). The apparently anomalous low carbonate productivity during the late Pleistocene is therefore thought to be due to a combination of two factors: Firstly, restricted circulation between the Atlantic and the Mediterranean as a result of lowered sea levels and secondly, the masking of carbonate sediments by an increase in the supply of clastic material (Cita and Ryan 1973).

Although the productivity of carbonate producing organisms appears to have increased during the late Pleistocene 'glacials', there was no comparable increase in silica productivity. The only occurrence of late Pleistocene diatomaceous sediments is in the Eastern Mediterranean. These thin diatomaceous horizons are associated with sapropels and are thought to be due to the influx of silica and nutrient-rich freshwater from the Black Sea during periods of deglaciation (Ryan et al. 1973).

Cita (1973b) has suggested also that the late Pliocene sapropels discovered by D.S.D.P. Leg 13 are the result of glacioeustatic sea level changes but that in this case they were caused by glacial fluctuations in regions other than the Mediterranean. The suggestion that sedimentation within the Mediterranean can be controlled by glacial activity elsewhere is of particular importance with respect to Messinian sediments, since a pronounced global cooling is known to have taken place during the late Miocene (Kennett and Vella 1975). This cooling event is thought to have been related to a major advance in the Antarctic Icecap which commenced in the early middle Miocene and was at its most extensive during the Kapitean (equivalent to the late Messinian) (Shackleton and Kennett 1975a 1975b). It resulted not only in a major increase in upwelling at the Antarctic convergence but must also have had a worldwide effect on ocean circulation and climates (Kennett et al. 1975). Therefore, since Mediterranean climates are known to have become progressively cooler and drier between the Tortonian and the Pliocene (Benda 1973, Marchetti and Accorsi 1978), it is inconceivable that Antarctic glacial activity did not have a profound influence on Mediterranean sedimentation during the late Miocene.

The coincidence of the Antarctic glaciation and the Messinian Salinity Crisis has been commented on by several authors including Adams et al. (1977) and Hsu et al. (1978). Nesteroff and Glacon (1975) have proposed a glacial origin for the sedimentary cycles seen in the Upper Evaporites in Sicily and a similar explanation seems likely for the cycles observed in the Calcare di Base. These have been described above (section 3.10.4) and shown to consist of alternating inter- or subtidal and supratidal deposits. The most plausible explanation for such alternations is clearly oscillations in sea level which, in view of the glacial activity in the Antarctic, are likely to be glacioeustatically controlled. Since the Calcare di Base cycles appear to be related to the rhythms in the underlying Tripoli Formation, it is likely that they too have a glacial origin. If cyclic fluctuations in Antarctic glacial activity are indeed responsible for the Tripoli rhythms, their periodicity must have been the same as the duration of each rhythm, that is between 15,000 and 30,000 years (section 3.5). This is remarkably similar to estimates of the period of Pleistocene glacial-interglacial cycles based on palaeontological and stable isotope studies of foraminifera from Quaternary sediments in the Red Sea (Berggren and Boersma 1969, Deuser and Degens 1969, Emery et al. 1969). Other estimates for the Pleistocene glacial cycles ~~in the Pliocene~~ are somewhat longer and may be as much as 100,000 years (Fairbridge 1972, Cita and Ryan 1973). This is nevertheless still of the same order and the similarity again argues strongly in favour of a glacial origin for the Tripoli rhythms. Although glacial activity in the Antarctic is obviously remote from the Mediterranean, it would certainly influence Tripoli sedimentation through its effect on climatic and oceanographic processes. It is therefore proposed that the rhythmic nature of Tripoli sedimentation is a reflection of climatic and oceanographic oscillations related to glacial activity in the Antarctic.

Since the Tripoli rhythms are believed to be related to climatic oscillations, their uniform appearance across the entire Central Sicilian Basin suggests that each of the constituent lithologies can be related to a particular part of the climatic cycle. The Tripoli sediments most characteristic of a particular set of depositional conditions are the diatomites. It has been shown above that these required a well developed oxygen minimum zone and a good supply of deep, nutrient rich waters to the Central Sicilian Basin. The availability of nutrient rich waters in the world ocean would have been at a maximum during or at the end of a 'glacial' period since this is when Antarctic bottom water activity and other oceanographic processes would have been at their most intense (Arrhenius 1952, Gordon 1971, Kennett et al. 1975). Increased upwelling and surface productivities at these times would also have tended to expand any oceanic oxygen minimum layer. However, this would have had little impact on the Central Sicilian Basin unless the existence of estuarine circulation allowed the deep nutrient-rich waters to be admitted to the Mediterranean. The evidence from the late Pleistocene suggests that estuarine circulation is most likely when the supply of fresh water to the Mediterranean is at a maximum. At Calascibetta an increase in the supply of detrital material has been shown to coincide with the deposition of diatomites and provides further evidence that this was the time of maximum freshwater discharge into the Central Sicilian Basin. Therefore, since there would probably have been a delay in oceanographic processes responding to climatic change, the post-glacial periods of climatic warming clearly provided the ideal conditions for diatomite deposition (Fig. 3.32 & 3.35).

A comparable situation may have existed in the Red Sea, where Goll (1969) has described a brief invasion of radiolaria which he tentatively dated as early Holocene. It is not known what brought about this invasion, but its timing with respect to glacial activity is interesting in that it corresponds to an

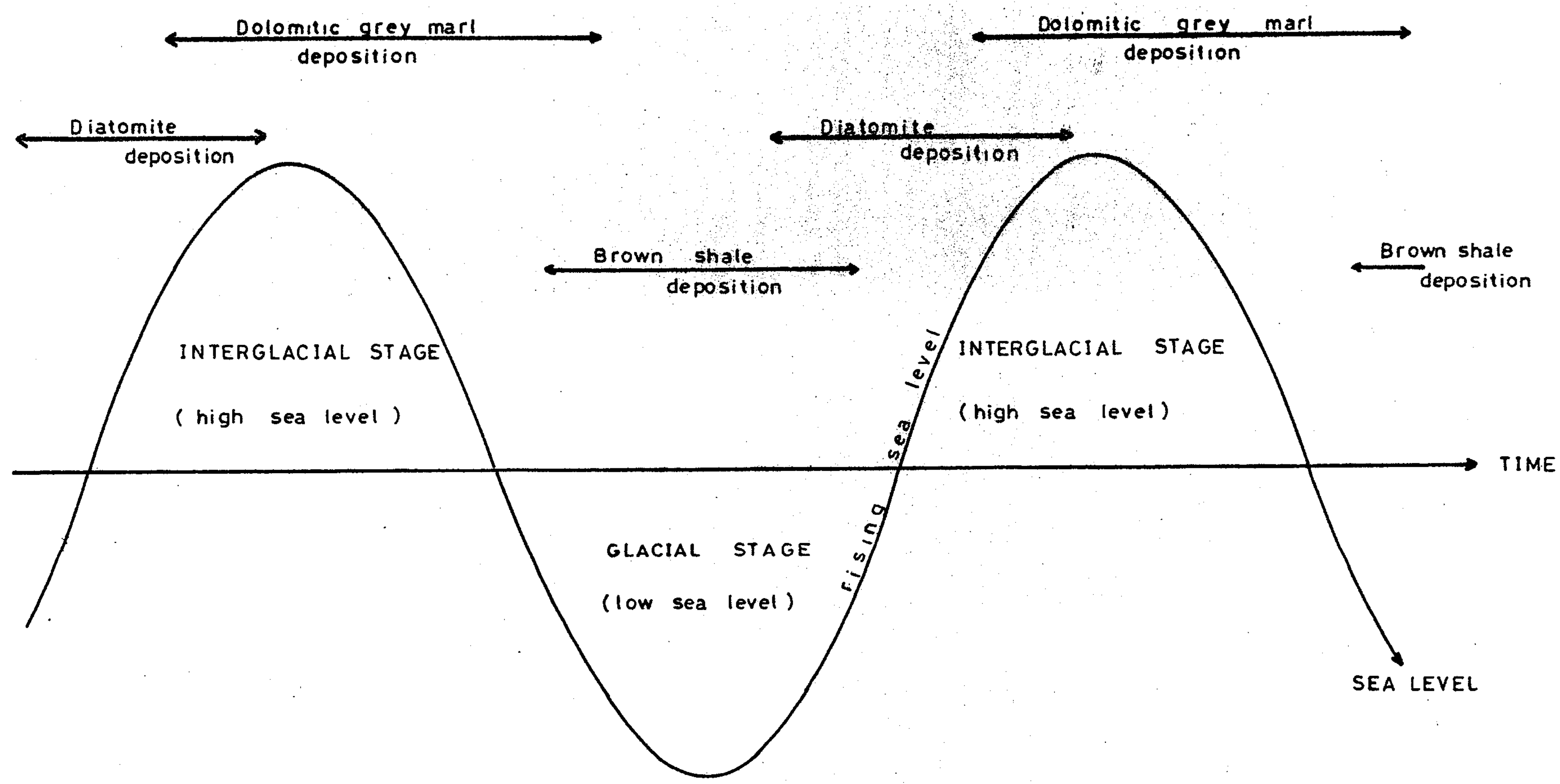
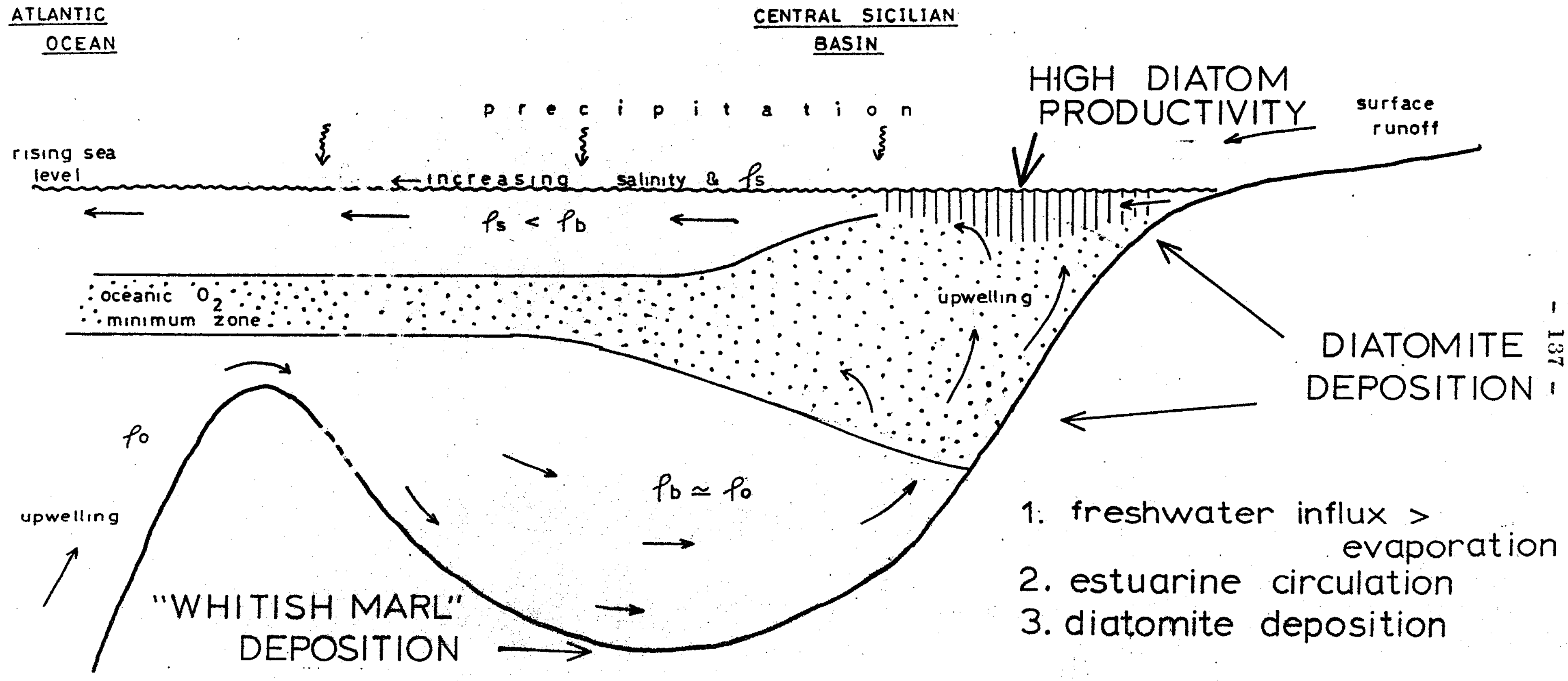
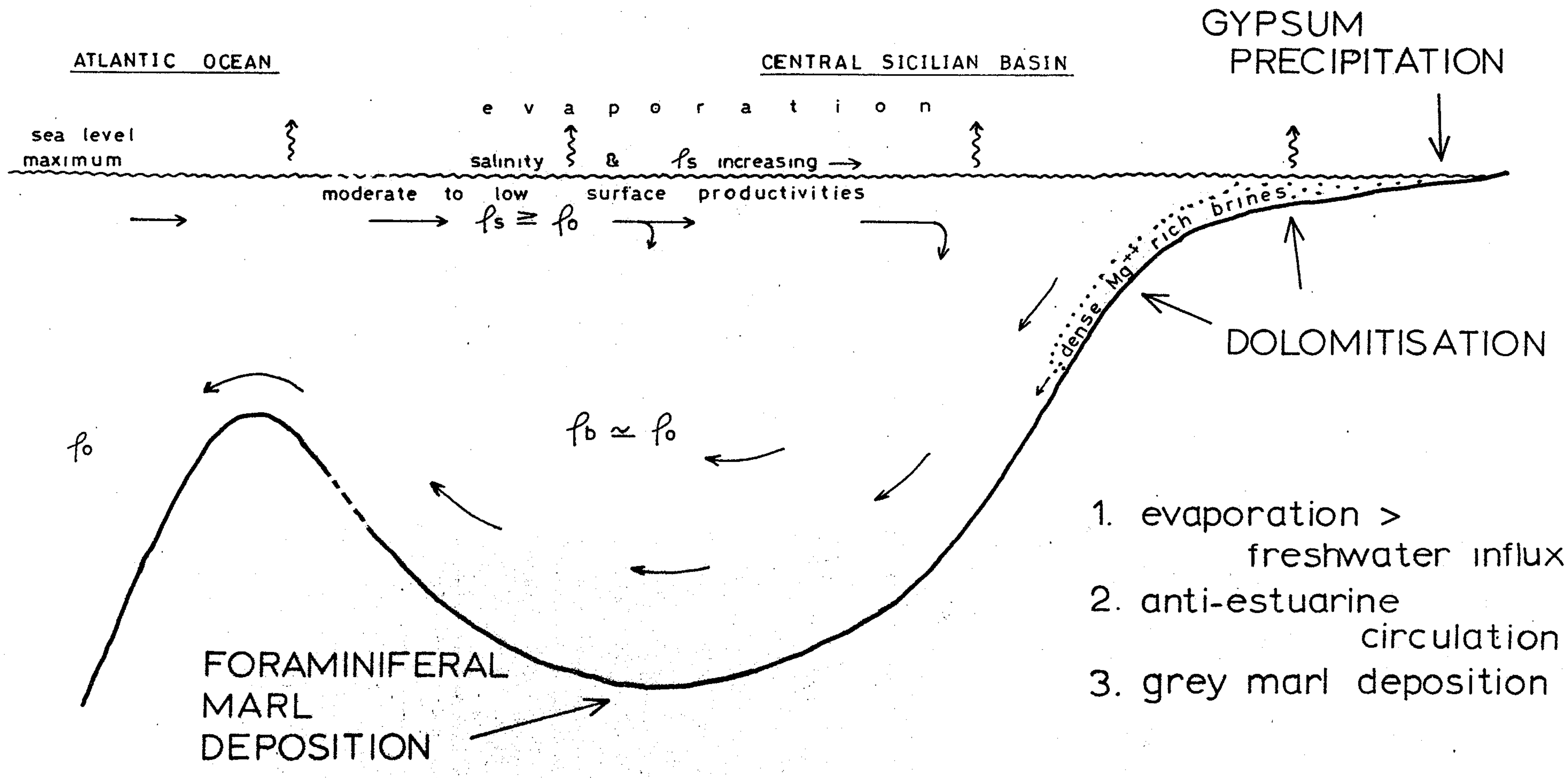


Fig. 3.31 THE RELATIONSHIP BETWEEN THE GLACIAL CYCLES AND TRIPOLI SEDIMENTATION.



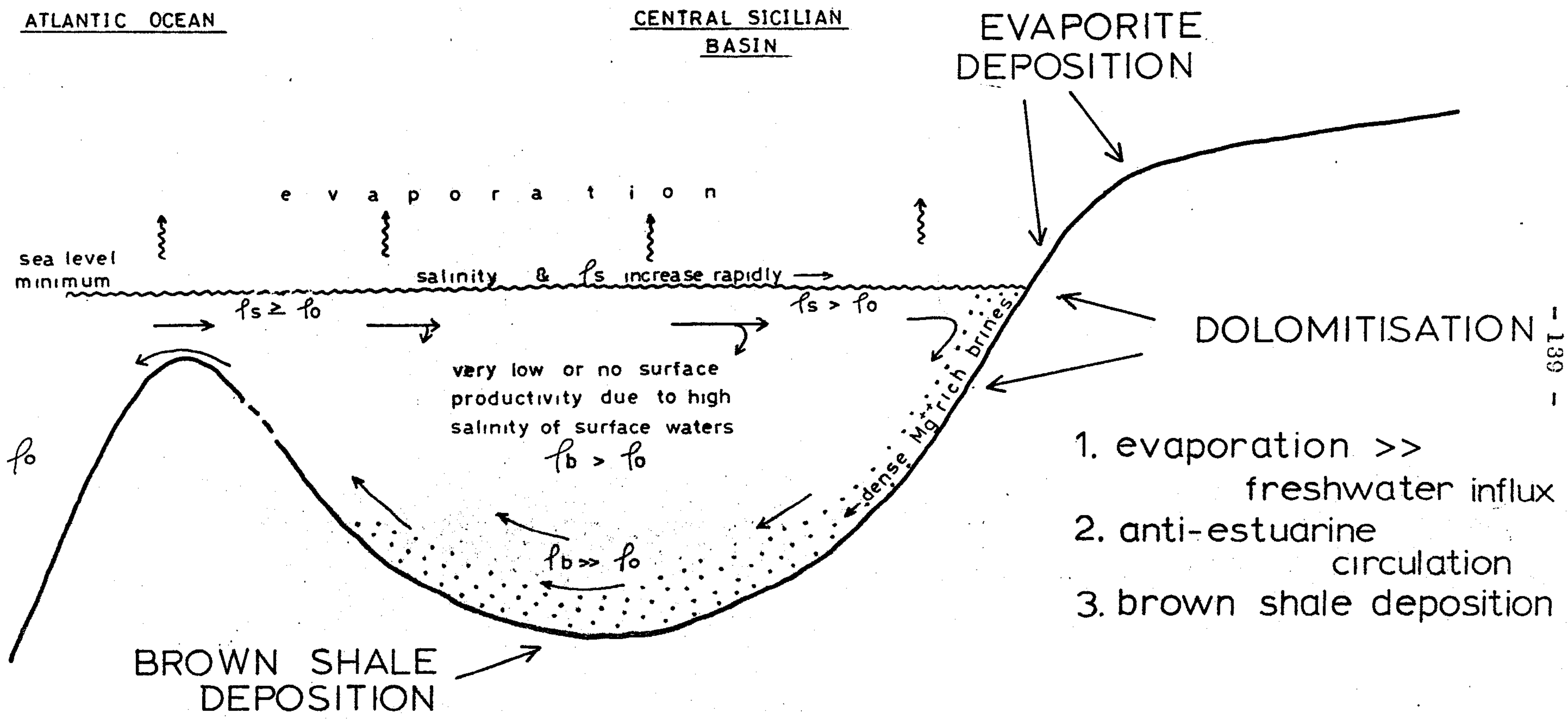
ρ_o density of oceanic waters
ρ_s density of surface waters
ρ_b density of basin waters
→ circulation pattern of basin waters

FIG. 3.32 THE PALAEO-OCEANOGRAPHY OF THE CENTRAL SICILIAN BASIN DURING PERIODS OF DEGLACIATION.



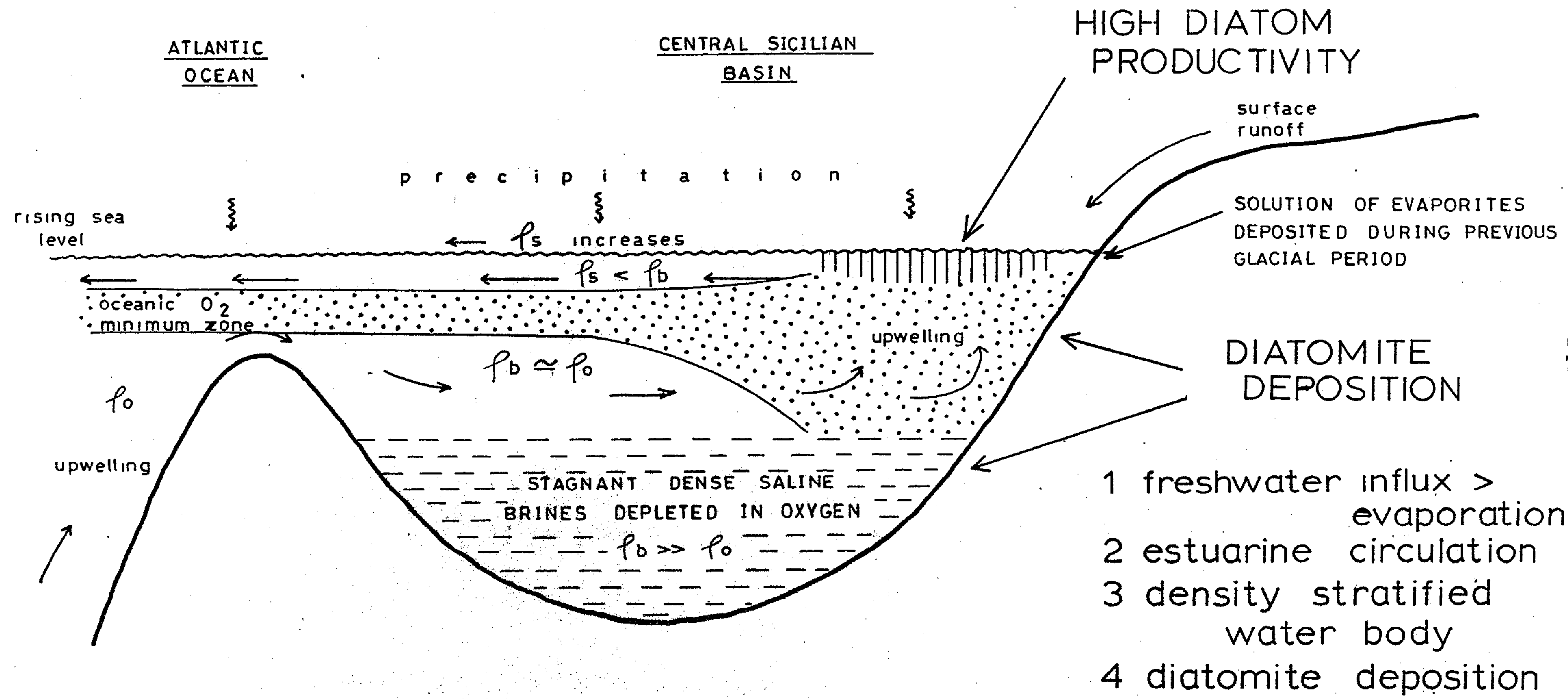
KEY : see fig. 3·32

FIG. 3.33 THE PALAEO-OCEANOGRAPHY OF THE CENTRAL SICILIAN BASIN DURING INTERGLACIAL PERIODS.



KEY: see fig. 3-32

FIG. 3.34 THE PALAEO-OCEANOGRAPHY OF THE CENTRAL SICILIAN BASIN DURING GLACIAL PERIODS



KEY: see fig. 3.32

FIG. 3.35 THE PALAEO OCEANOGRAPHY OF THE CENTRAL SICILIAN BASIN DURING A DEGLACIATION NEAR THE END OF TRIPOLI DEPOSITION interglacial period. This is only slightly later in the glacial cycle than the Tripoli diatomites are believed to have been deposited and in view of the difficulties encountered by Goll (1969) in establishing the age of the invasion, the difference may well be due to dating inaccuracies.

The grey dolomitic marls and brown shales are less easy to assign to particular parts of the climatic cycle since these lithologies may be deposited under a variety of conditions. However, the dolomitic marls are thought to have been deposited as foraminiferal-coccolith muds and therefore probably resemble sediments accumulating in parts of the Mediterranean today (Ryan et al.1966). This, together with their stratigraphic position overlying the diatomites, suggests they must represent sedimentation under "interglacial" conditions (Fig 3.31). At this time the oceanographic processes which produced the diatomites had waned and the existence of ventilated bottom conditions implies that an anti-estuarine circulation pattern had been established (Fig 3.33). The brown shales must therefore have been deposited under "glacial" conditions (Figs 3.31 & 3.34) since Pleistocene glacial periods were characterised by an increase in wind transported terrigenous sediment due to the cold arid climate and lowered sea levels (Fairbridge 1972, Huang and Stanley 1972).

Although many aspects of the Tripoli sedimentation can be explained by relating the rhythms to climatic cycles, there are other problems which remain unsolved. For example, the climatic cycles alone cannot account for the selective dolomitisation of the grey marls nor for the barren nature of the brown shales which were deposited when carbonate productivity should have been at a maximum. It has already been suggested (Sections 3.10.1 and 3.10.3) that salinity and the presence of a shallow sill have played an important roll in determining the nature of the Tripoli sediments. How these affected sedimentation and their influence on the build up to the Salinity Crisis will be discussed in the following section.

3.11. The Pre-Salinity Crisis Mediterranean.

Grasshoff (1975) has shown the salinity distribution in an enclosed sea such as the Mediterranean will be strongly influenced by the nature of any sill connecting it with the open ocean. The shallower the sill and the more restricted the circulation, the shallower will be the halocline and the greater will be the surface salinity gradient away from the source of oceanic water. Glacio-eustatic variations in sea level during the Messinian are thought to have been in the order of 50-70 metres (Adams et al.1977). Therefore, although such sea level changes would have been negligible when compared to the water depths of 2400 metres or more at Capodarso, they could have had a profound effect on salinities within the Mediterranean had it been separated from the Atlantic by a shallow sill at this time. The existence of such a sill has been suggested above (Section 3.10.1) and need not have been a barrier to the influx of deep nutrient rich waters from the Atlantic, since both the Sea of Japan and Saanich Inlet in British Columbia have an adequate supply of nutrients for sustaining diatomaceous sedimentation despite having sill depths of only 70 and 90 metres respectively (Solov'yev 1962, Gucluer and Gross 1964, Adams et al. 1977). Furthermore, a close relationship between Pleistocene foraminiferal assemblages and glacioeustatic fluctuations in sea level has been reported from the Red Sea which was also connected to the open ocean via a shallow sill at this time. It has been shown that a species able to withstand cold and highly saline conditions was particularly abundant during periods of lowered sea level while less tolerant species predominated at other times (Berggren and Boersma 1969). It is therefore proposed that during the Messinian a shallow sill existed between the Mediterranean and the Atlantic and as a result, the salinity of the Mediterranean waters was controlled primarily by the sea level changes associated with the climatic/glacial cycles.

The way in which salinity, circulation patterns and sedimentation in the Mediterranean are thought to have varied in relation to succeeding glacial/climatic cycles can be summarised as follows:

A) GLACIAL-INTERGLACIAL (Fig 3.32): The freshwater supply to the Mediterranean from surface runoff and precipitation exceeded losses through evaporation. The surface waters were therefore less saline and less dense than oceanic waters and floated on top of them, thereby establishing estuarine circulation. The Mediterranean received dense nutrient rich oceanic water over the sill and a density stratification therefore developed. Since there was little vertical exchange between the various layers poorly ventilated or anoxic bottom conditions eventually resulted. Where local topography and wind directions were favourable(e.g. the Central Sicilian Basin), upwelling brought the nutrient rich deep water to the surface and high surface productivities led to diatomite deposition and the expansion of the oceanic oxygen minimum layer.

B) INTERGLACIAL (Fig 3.33): Surface evaporation exceeded freshwater influx to the Mediterranean and anti-estuarine circulation was established. A surface salinity gradient increasing away from the supply of oceanic water was also produced. The denser and more saline of the surface waters sank into the basin, thereby raising oxygen levels but enhancing the density stratification. However, this was partially offset by a warmer climate making the surface waters less dense. Nevertheless, dense saline brines eventually accumulated below sill depth. Productivity in the surface waters was comparable to that of today, although in the Central Sicilian Basin it was sufficient to allow the accumulation of pelagic carbonate sediments. As sea-level declined, gypsum precipitated on tidal flats around the margins of the basin and dolomitising brines were generated which sank into the basin and produced the grey dolomitic marls.

C) GLACIAL (Fig 3.34): The influx of freshwater to the Mediterranean was severely reduced or even non-existent. The influx of surface oceanic waters was also much reduced due to the glacio-eustatic lowering of sea level, hence the surface salinity gradient was correspondingly greater. The colder climate also meant that the warming of surface waters which counteracted the density increase due to evaporation was less effective. There was therefore a more rapid accumulation of brines that were both more saline and more dense than those accumulating during the Interglacial period. The intensified atmospheric processes and the increased salinity of the basin waters must together have favoured evaporation and the precipitation of gypsum around the basin margins. The maximum generation of dolomitising brines would therefore have taken place at this time. Another effect of the increased salinities would have been to severely restrict the productivity of calcareous planktonic organisms so that the sediments accumulating in the Central Sicilian Basin were predominantly terrigenous mudstones. Towards the end of the deposition of the Tripoli Formation it is possible that a combination of glacioeustatically lowered sea levels and evaporitic drawdown could have resulted in the Mediterranean being temporarily isolated from the Atlantic.

D) GLACIAL-INTERGLACIAL (Fig 3.35): As in A) except that the deeper parts of the basin contained dense saline brines. The fertile ocean water entering the basin therefore floated on top of this dense water and a separate convection cell was set up with the surface waters. The deeper basin waters were therefore isolated and in the absence of any vertical water movement poorly oxygenated bottom conditions developed. Surface productivities were again high and diatomaceous sediments accumulated as before. The rise in sea level and less restricted communication with the open ocean would result in an overall lowering of the salinity of the basin waters and the dissolution of most of the evaporites deposited around the basin margins. As a result little evidence of Tripoli evaporite deposition now remains.

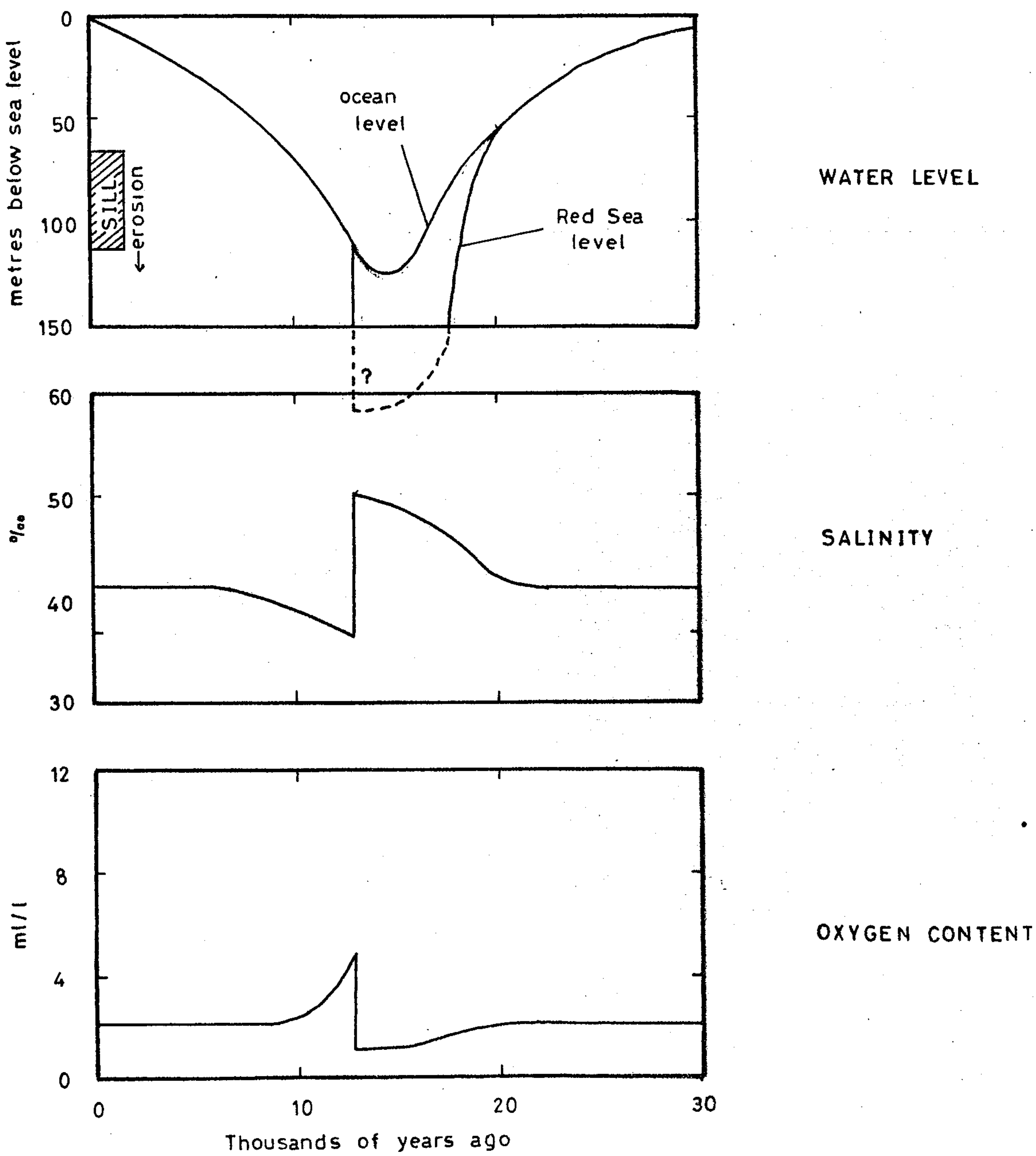
Today, both the Mediterranean and the Red Seas are connected to the ocean via a sill and both have a negative water balance which results in an anti-estuarine circulation pattern. They are therefore both characterised by higher salinities than the open ocean (Grasshoff 1975). This is particularly so for the Red Sea which, due to its particularly low freshwater input and high evaporation rates, has salinities ranging from just less than 38‰ at the surface to values of 40‰ to just over 40.6‰ in the virtually isohaline deep waters (Siedler 1969). Salinities at least as high as those in the Red Sea and probably much higher could therefore have been attained in the Mediterranean during the deposition of the Tripoli's dolomitic marls and terrigenous shales .

As the Messinian progressed and the climate gradually became colder an overall glacioeustatic lowering of the sea level would have been superimposed upon the fluctuations associated with the individual cycles. This would have led to increasingly restricted communications between the Mediterranean and the Atlantic and a corresponding increase in the overall salinity of Mediterranean waters. The build up of salinity during the deposition of the Tripoli sediments is reflected in the increasing abundance of dolomite towards the top of the formation and must certainly have been one of the major controls on organic productivity in the waters of the Central Sicilian Basin.. It accounts not only for the scarcity of biogenic material in the brown shale horizons but also for the increasing importance of the brown shales in the upper part of the section at Camastra and the decrease in the diversity of diatom assemblages at the top of the Tripoli Formation recognised by Gersonde (1978).

The combination of the increasing salinity of the basin waters and increasingly restricted communication with the Atlantic must have eventually eliminated the high surface productivities

FIG. 3.36 WATER LEVEL SALINITY AND OXYGEN CONTENT IN THE RED SEA DURING THE PAST 35,000 YEARS

(after Emery & Hunt 1974)



necessary for diatomite deposition. A marked change in dolomite composition also occurred at the top of the Tripoli Formation which is thought to have marked the ending of open marine influence in the Central Sicilian Basin (Section 3.10.3). Faunal studies by Cita et al. (1978) have also shown that dramatic environmental changes took place throughout the whole of the Mediterranean prior to the deposition of the evaporite unit. It is therefore suggested that the ending of Tripoli sedimentation in the Central Sicilian Basin coincided with the termination of marine communication across the shallow sill separating the Mediterranean from the Atlantic. At times during the Pleistocene the Red Sea is also thought to have become completely isolated from the Indian Ocean (Emery et al. 1969). This resulted in sharp falls in sea level within the basin and correspondingly sharp increases in salinity as shown in Fig 3.36 (Emery and Hunt 1974). The effect that the isolation of the Messinian Mediterranean would have had on sea levels and salinities must have been similar to that observed in the Red Sea during the Pleistocene. The severing of communication between the Mediterranean and the Atlantic must therefore have been closely followed by a rapid drawdown of sea level within the Mediterranean, a dramatic rise in salinity and the inevitable onset of the Messinian Salinity Crisis.

CHAPTER 4.

SUMMARY OF CONCLUSIONS.

Diatomaceous sediments of Aquitanian/Burdigalian and Messinian ages are found in Sicily.

The Lower Miocene siliceous sediments are not well exposed and are often in an advanced stage of diagenesis. There is no evidence to suggest a volcanic source for the silica in these deposits and a diatomaceous origin can be inferred from the occasional presence of corroded diatom frustules.

The stratigraphic setting of these diatomaceous sediments is obscure since some appear to occur as olistoliths within the Numidian Flysch or the Argille Scagliose while others have apparently conformable contacts. It is suggested that they accumulated in the deep narrow seaways in which the flysch and Argille Scagliose were also accumulating. They then underwent rapid burial beneath a pile of nappes as the Calabrian Massif moved against the African Foreland during the tectonic upheavals of the early to middle Miocene. As a result, some diatomaceous accumulations apparently became detached from their immediate stratigraphic surroundings.

It appears that a "diagenetic gradient" exists across Sicily since the deposits in the north and northeast of the island are exclusively quartzitic, those in central Sicily are composed of opal-CT and there is one reported occurrence of an unaltered early Miocene diatomite from the south coast. A similar gradient also appears to exist in southern Spain and it is suggested that this mineralogical zonation reflects the amount of burial which the sediments have undergone.

The opal-CT sediments in central Sicily occur both as porcelanites and cherts. However, the transition from porcelanite to chert is not simply due to increasing diagenetic alteration since the diatom frustules in the opal-CT cherts show far less evidence of dissolution than their counterparts in the porcelanites.

It is proposed that the cherts and porcelanites belong to different diagenetic "pathways" and that the textural variations are due primarily to compositional differences in the original sediment. The cherts were relatively pure diatomites, rich in opaline silica which underwent diagenesis mainly by in situ replacement. The porcelanites on the other hand, were rich in calcium carbonate and more porous so that their diagenesis was dependent on the passage of interstitial fluids causing the dissolution and re-precipitation of the various silica phases.

The quartzitic deposits also occur both as cherts and porcelanites. Chert development appears to be controlled primarily by the availability of silica required for the precipitation of cryptocrystalline quartz. Argillaceous horizons therefore inhibit chert growth since they act as permeability barriers.

The Messinian diatomaceous horizons belong to the Tripoli Formation which comprises cyclic alterations of diatomites and claystone horizons. It occurs in the Central Sicilian Basin overlying hemipelagic Tortonian marls and is itself overlain by the Mediterranean Evaporites. The Tripoli Formation therefore represents a broadly regressive sedimentary sequence.

The diatomites accumulated on the basin flanks while foraminiferal marl deposition prevailed in the deepest parts of the basin. They were deposited under normal marine conditions in response to the intermittent upwelling of deep nutrient-rich oceanic waters. Their finely laminated appearance also indicates that they accumulated in an oxygen deficient environment. It is suggested that the Guaymas Basin in the Gulf of California provides the closest modern analogy to the Central Sicilian Basin during the deposition of the Messinian diatomites. However, bottom conditions in the Central Sicilian Basin were less well ventilated than those existing today in the Guaymas Basin and it is therefore suggested that there was a physical barrier restricting circulation between the Mediterranean and the Atlantic during the late Miocene.

The interbedded claystone horizons each comprise a grey dolomitic marl overlain by a brown terrigenous shale. The dolomitic marls were probably deposited as foraminiferal marls, which were similar to those accumulating in the deepest parts of the basin and then underwent dolomitisation prior to burial. Productivity in the surface waters of the basin were clearly lower than during the deposition of the diatomites and it must have been very low indeed while the terrigenous shales were accumulating. Stable isotope studies show that the dolomitisation took place in highly evaporated, poorly oxygenated conditions possibly comparable to those existing today in the Dead Sea. Dense, saline, Mg^{2+} - rich brines are thought to have been generated round the margins of the basin where gypsum was probably precipitating and then to have descended into the basin dolomitising the sediments on the basin flanks. The generation of these dolomitising brines was clearly more active during the deposition of the grey marls than the diatomites, although both the interbedded claystones and the diatomites become increasingly dolomitic towards the top of the formation. Concurrent with the increase in dolomitisation the basin waters must have become increasingly saline. A change in the dolomite composition also coincides with the termination of diatomite deposition and their replacement by shallow water, evaporitic carbonates of the Calcare di Base. This is thought to indicate the severance of communication between the Mediterranean and Atlantic and the beginning of widespread gypsum precipitation within the basin.

The following model is proposed to account for Tripoli sedimentation in the Central Sicilian Basin : The alternating diatomite and claystone horizons are thought to reflect reversals in the exchange of water between the Atlantic and the Mediterranean. Anti-estuarine circulation being required to bring deep nutrient-rich waters into the Mediterranean in order to sustain diatom productivity and estuarine circulation accounting for the lower productivities and better ventilated conditions at other times. By analogy with Pleistocene events in the Mediterranean, these circulation reversals are thought to have been brought about by glacioclimatic fluctuations related to the late Miocene advance of the Antarctic Icecap. As a result of the overall glacioeustatic lowering of sea levels during the late Miocene, the exchange of waters over the shallow sill which separated the Mediterranean and the Atlantic became increasingly restricted. Hence the basin waters became increasingly saline and the Tripoli sediments increasingly dolomitic until communication was eventually severed and the Messinian Salinity Crisis ensued.

PLATE 2.1

Monte Caolina from near Santa Venera.
(the outcrop is visible on the right-
hand skyline.)

PLATE 2.2

Quartzitic porcelanites interbedded
with thin argillaceous horizons,
Monte Caolina.
(scale: compass is 7cms x 6cms.)

PLATE 2.3

Quartz chert nodules growing within the quartzitic porcelanites and causing the beds to pinch and swell, Monte Caolina.

PLATE 2.4

Thinly bedded and highly fractured quartzitic cherts, Sperlinga Quarry road.

PLATE 2.5

Quartzitic porcelanite showing crinkled laminae continuing into a chert nodule, Sperlinga River.
(scale is in centimetres)

PLATE 2.6

Photomicrograph of a quartzitic porcelanite showing foraminiferal tests (FT) and detrital grains (DG) set in a fine-grained, mainly siliceous groundmass, Monte Caolina.
(XP x50)

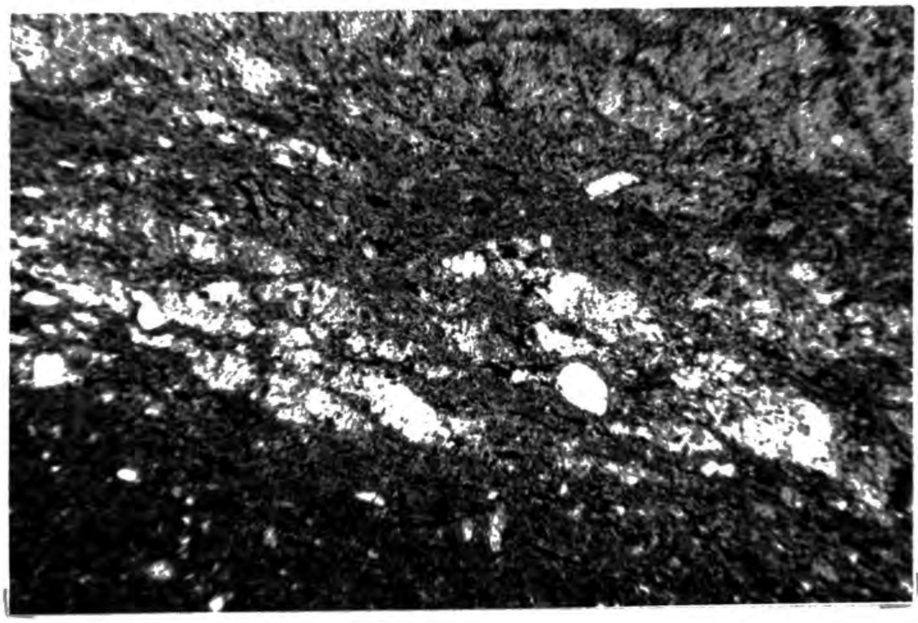
DG

PLATE 2.7

Photomicrograph of the contact between a quartzitic porcelanite (top) and an argillaceous horizon, Monte Caolina.
(PP x25)

PLATE 2.8

Light brown (lower left) and grey (top) opal-CT porcelanites, Dittaino.
(Scale in centimetres)



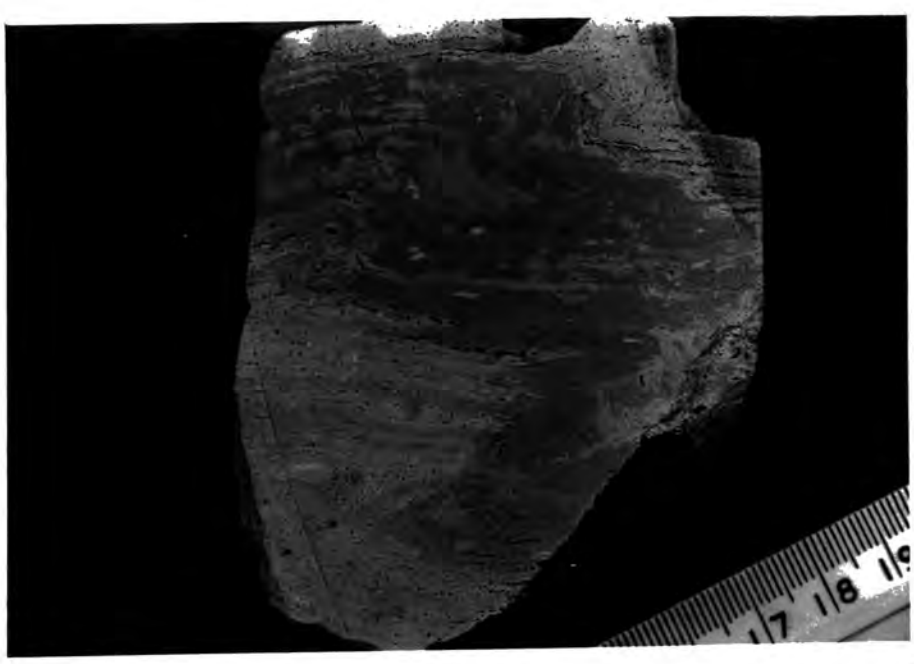
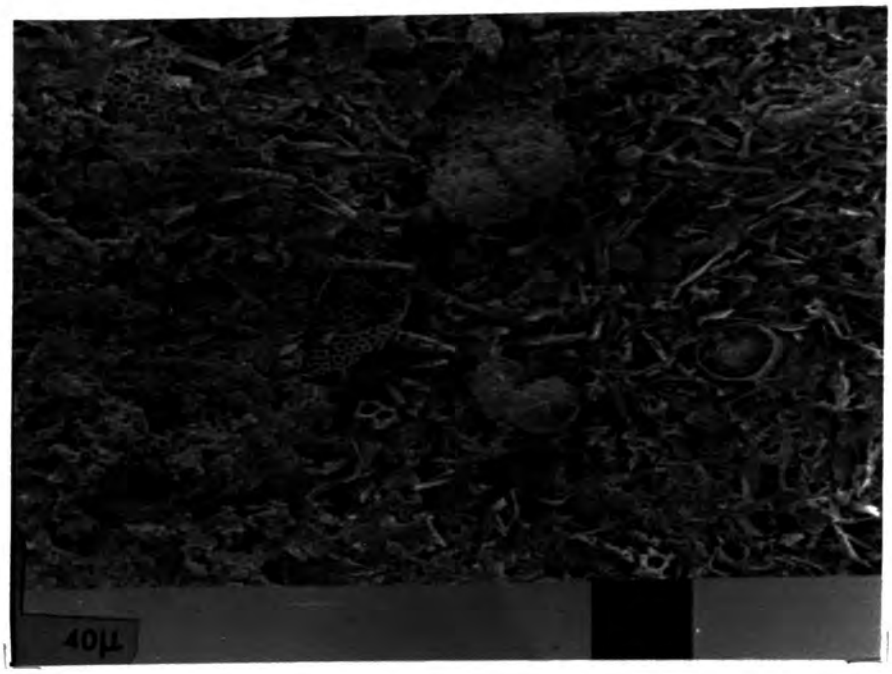

17
18
19

PLATE 2.9

Scanning electron micrograph of opal-CT chert showing diatomaceous debris, Antinello.
(Etched for 60 secs. in HF)

PLATE 2.10

Photomicrograph of opal-CT porcelanite showing crenulated laminae, Dittaino.
(PP x8)


40μ

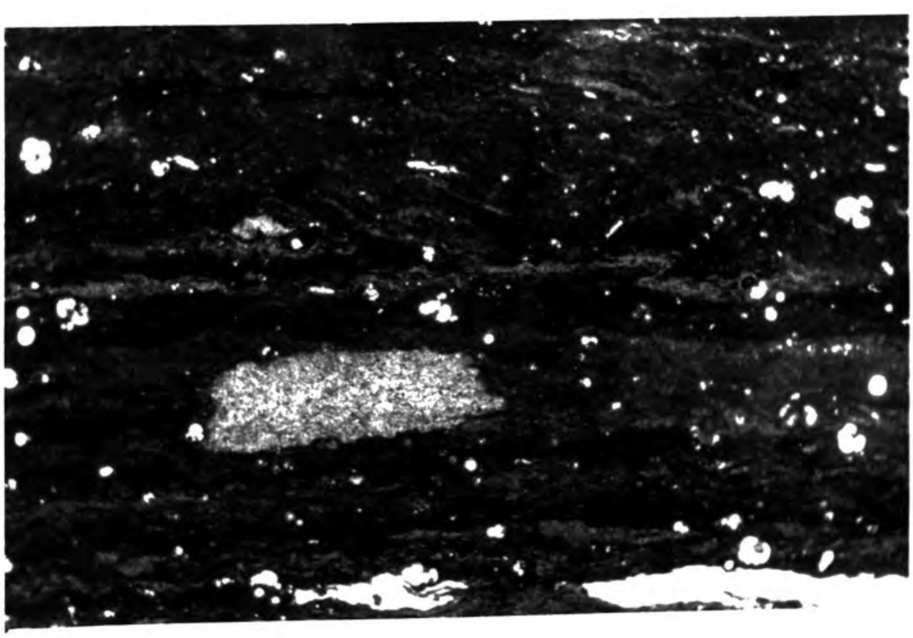
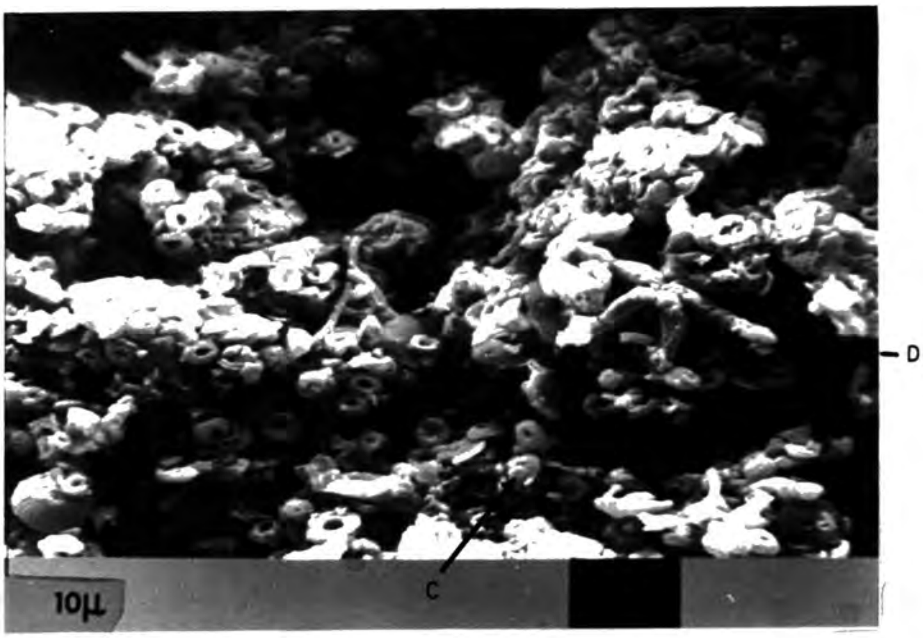


PLATE 2.11

Scanning electron micrograph of discoasters (D) and coccoliths (C) in an opal-CT porcelanite, Dittaino.

PLATE 2.12

Scanning electron micrograph of lepispheres (L) in opal-CT porcelanite, Dittaino.


10μ
C
D

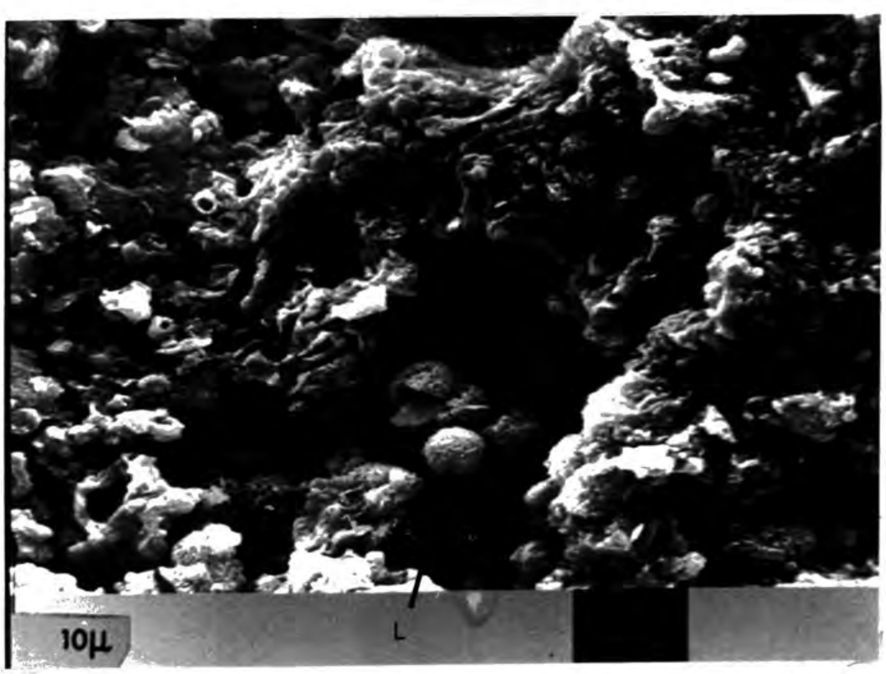

10μ
L

PLATE 2.13

Scanning electron micrograph of lepispheres in opal-CT porcelanite, Dittaino.

PLATE 2.14

Nodular quartzitic cherts growing in quartzitic porcelanite beds, Monte Caolina.

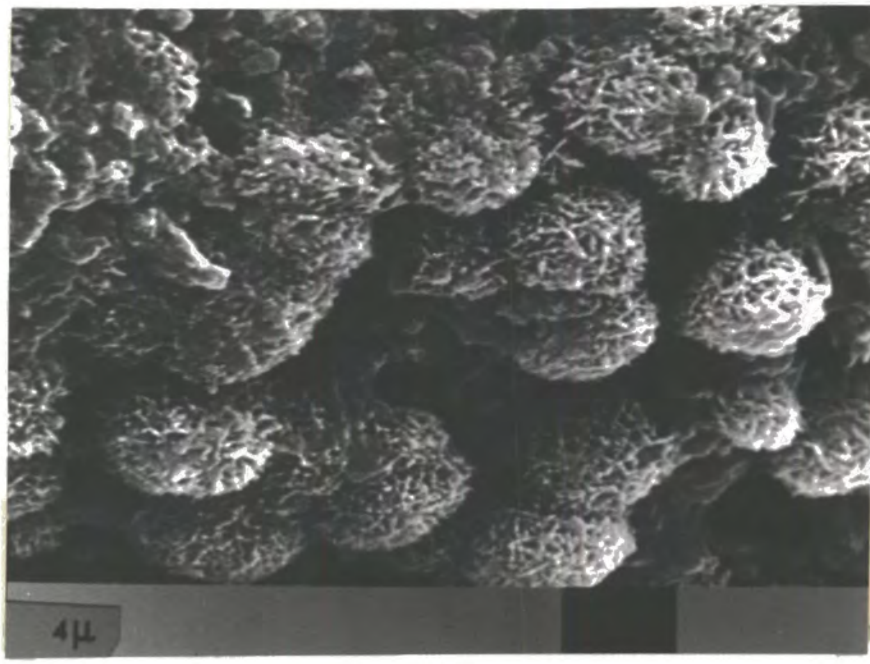

4μ

PLATE 2.15

Argillaneous partings constraining the growth of chert nodules, Monte Caolina.
(Scale: lens cap is 5.5 cms. in diameter)

PLATE 2.16

Cracks in a quartzitic chert, Sperlinga River.
(PP x8)

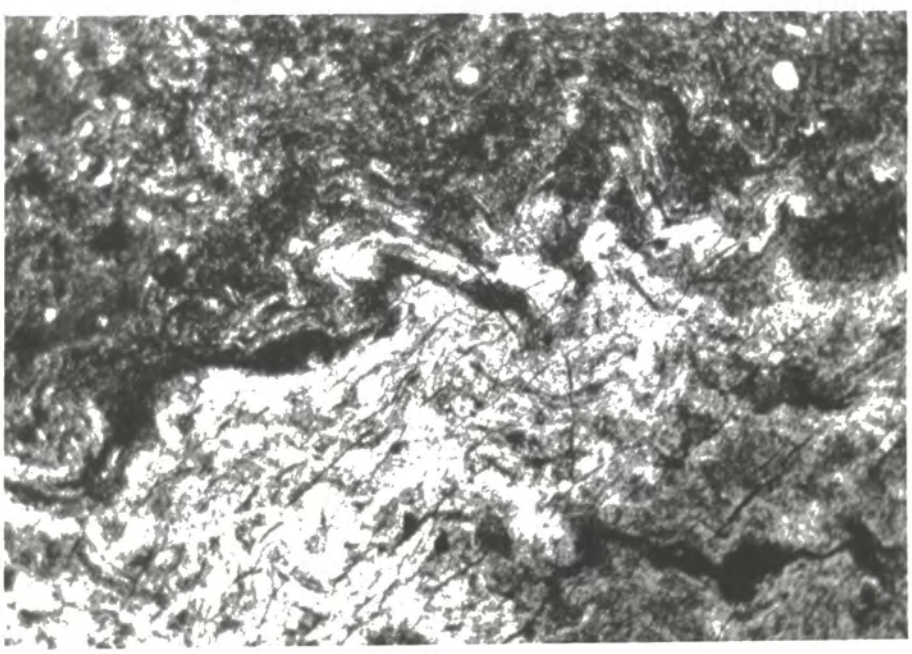
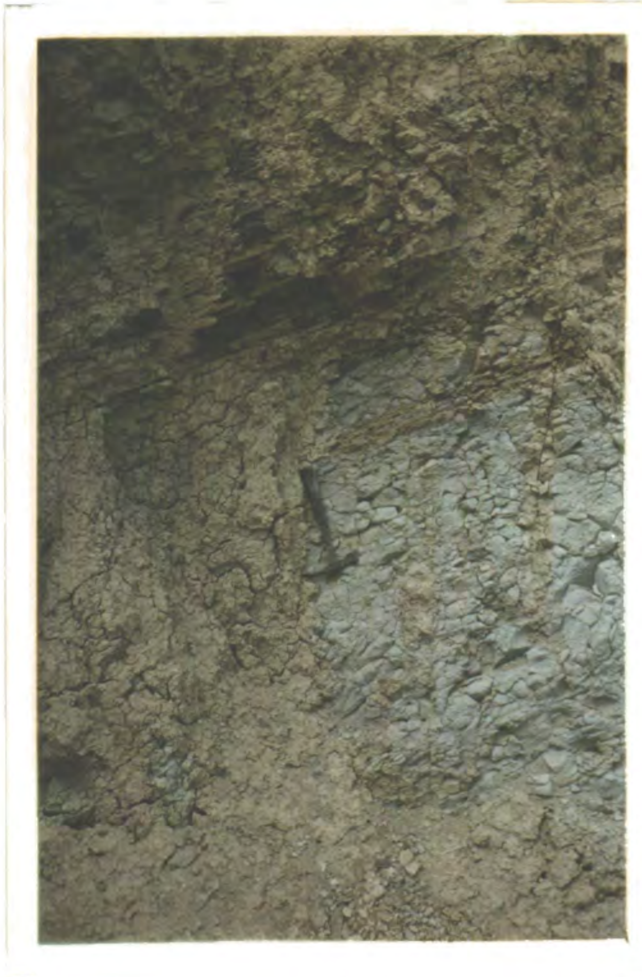


PLATE 3.1

Tortonian blue marls overlain by the fissile, basal Tripoli diatomites, Camastra.

PLATE 3.2

Graded intervals in a shaley diatomite from near the base of the Tripoli Formation, Camastra. (Scale in centimetres)




9 10 11 12 13 14 15 16 17 18 19

PLATE 3.3

A Tripoli rhythm : diatomite overlying brown shale overlying grey dolomitic marl, Camastra.

PLATE 3.4

Scoured contact between diatomite and the overlying grey dolomitic marl, Falconara.

PLATE 3.5

Conspicuously parallel laminated diatomite overlain by foraminifera-rich limestone, Campobello di Licata.

PLATE 3.6

Diatomite showing parallel laminated and homogenous horizons, Aragona.
(Note the convoluted laminae at the base of the homogenous horizon.)
(Scale in millimetres.)

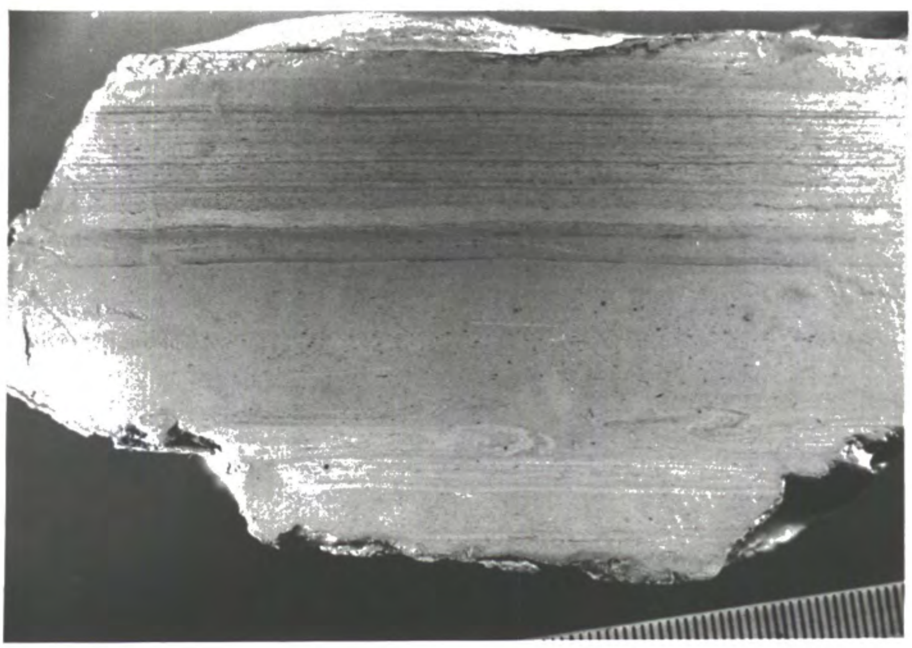


PLATE 3.7

Diatomite showing parallel laminae and homogenous intervals, Montedoro.
(Note disturbed horizon near base)
(Scale in millimetres)

PLATE 3.8

Scanning electron micrograph of Centric diatom (Coscinodiscus Sp. ?) set in a mass of diatom debris.
(x 1000)

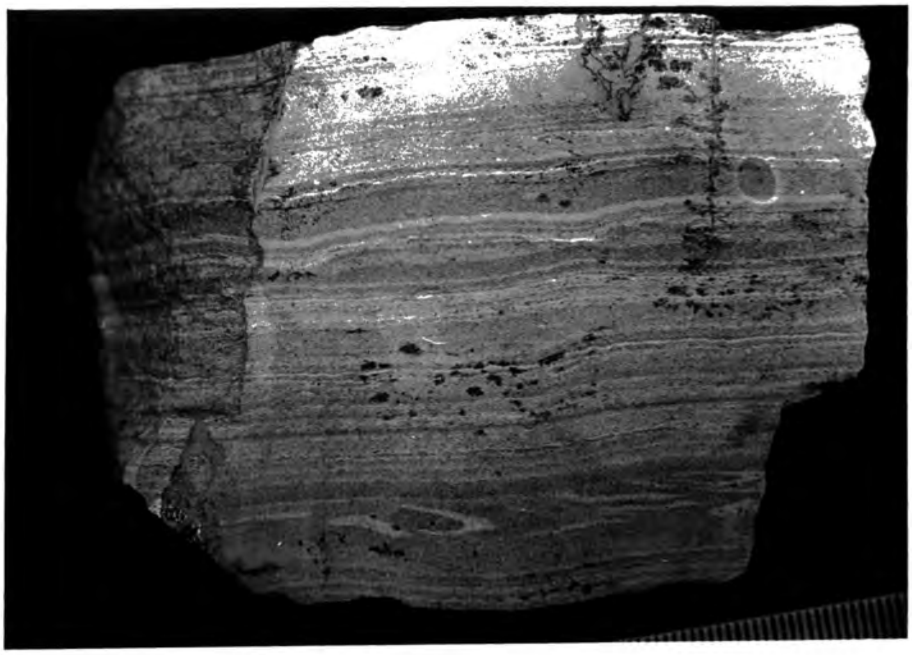
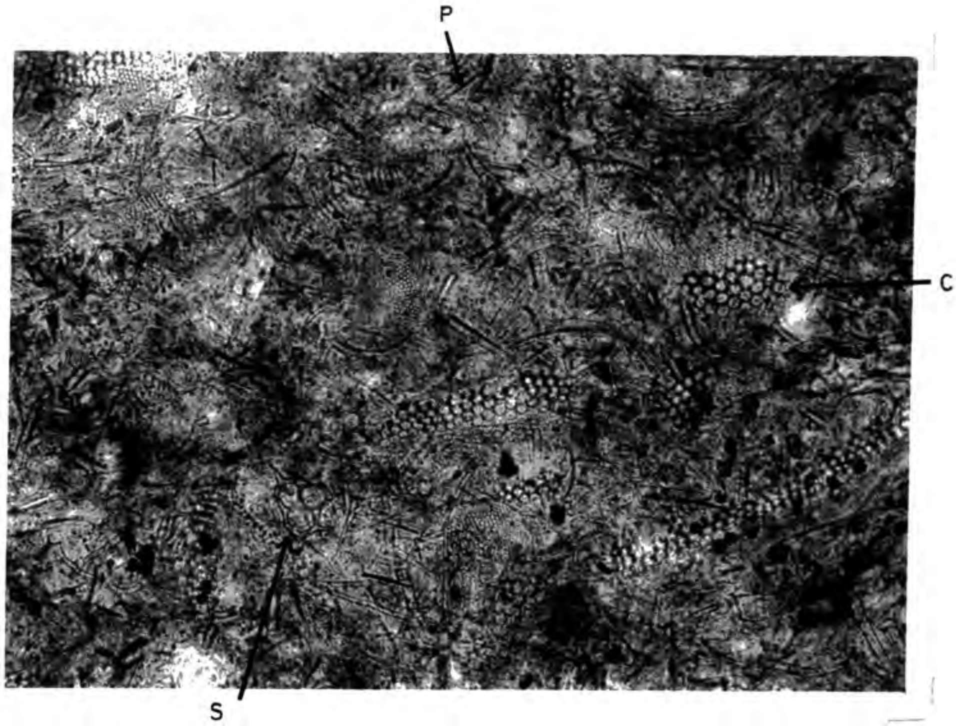


PLATE 3.9

Photomicrograph of diatomite. Groundmass consists of pennate (P) and centric (C) diatoms and silicoflagellates (S). Bompensiere. (PP x200)

PLATE 3.10

Photomicrograph of a smear slide of a diatomite showing pennate (P) and centric (C) diatoms, silicoflagellates (S) and discoasters (D), Campobello di Licata. (PP x200)


P
C
S

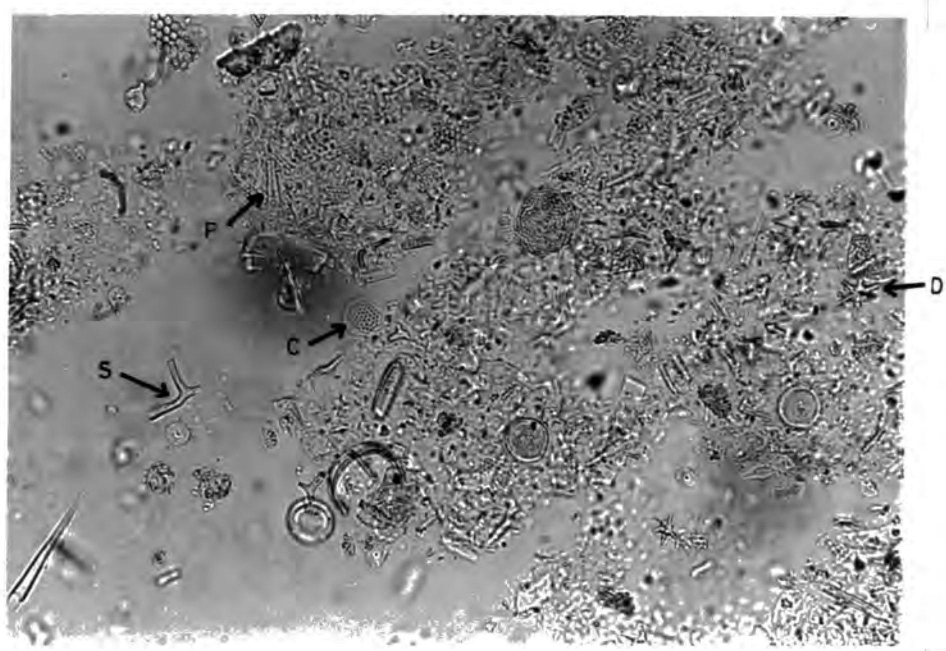
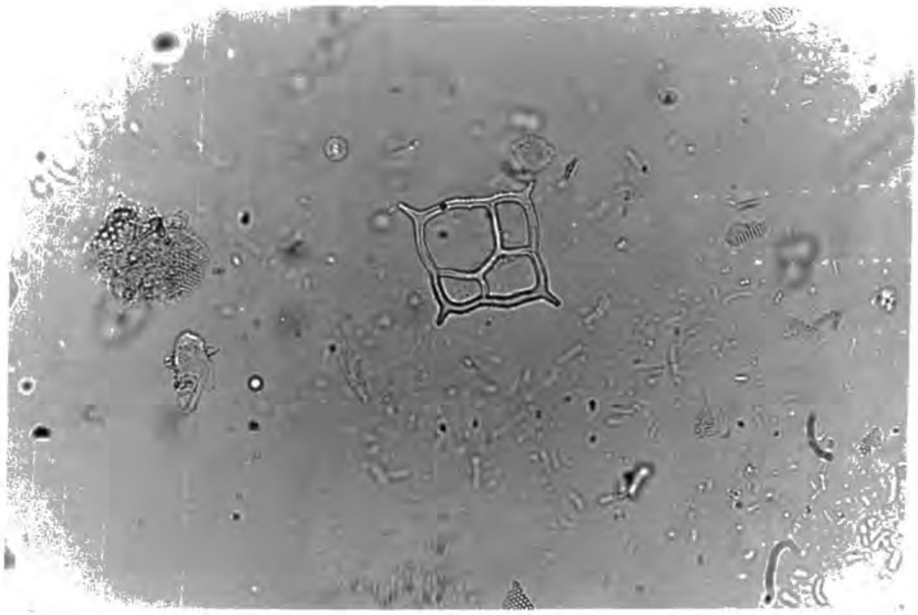

P
D
C
S

PLATE 3.11

Photomicrograph of a smear slide of a diatomite showing a silicoflagellate. Campobello di Licata. (PP x200)

PLATE 3.12

Photomicrograph of diatomite showing a radiolarian (R), foraminiferal tests (FT) and diatoms (D). Camastra.
(PP x125)



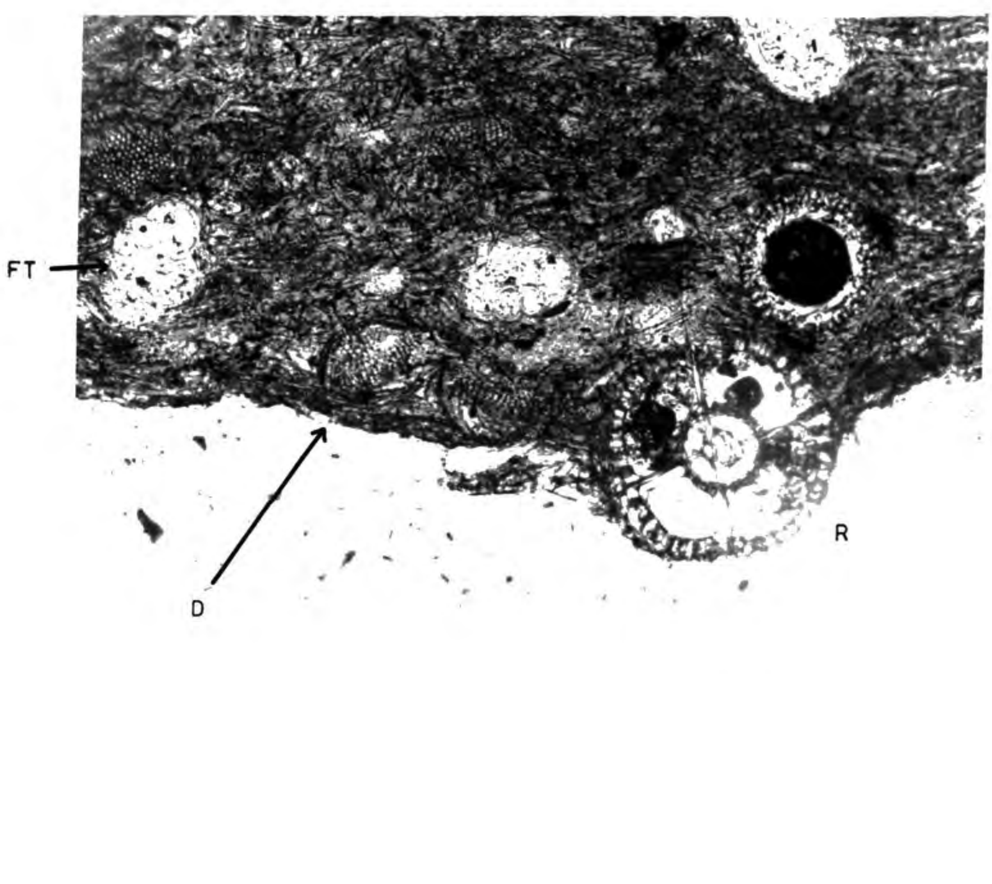
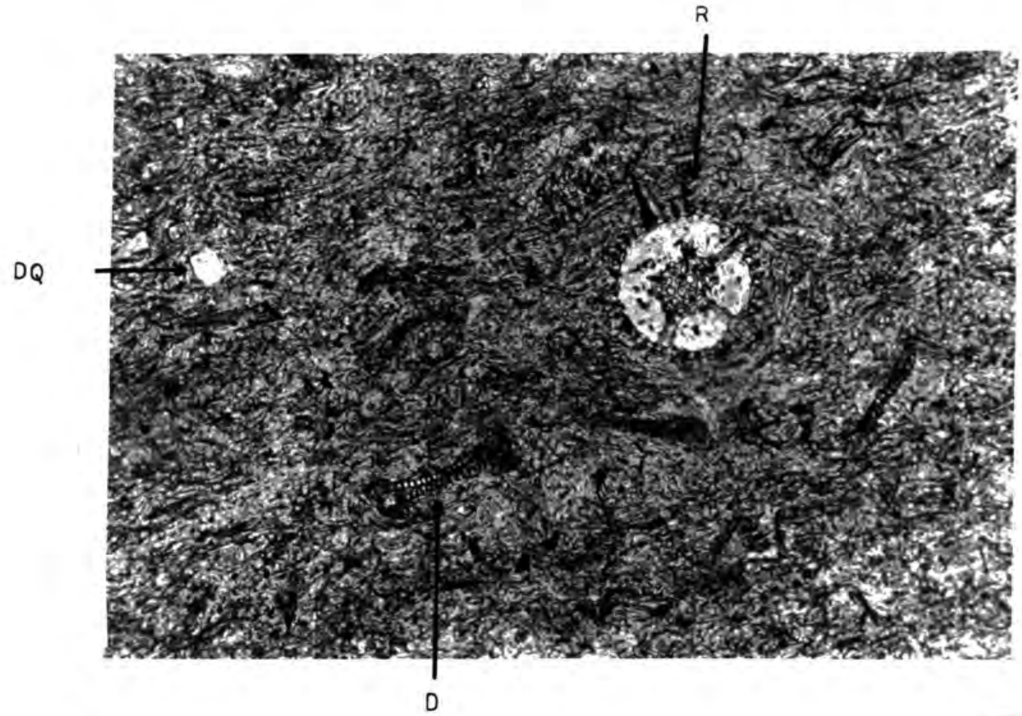

FT
D
R

PLATE 3.13a

Photomicrograph of diatomite showing a radiolarian (R), diatom remains (D) and detrital quartz (DQ), Camastra.
(PP x125)

PLATE 3.13b

As above, calcareous matter is recognisable by its high birefringence.
(XP x125)


R
DQ
D

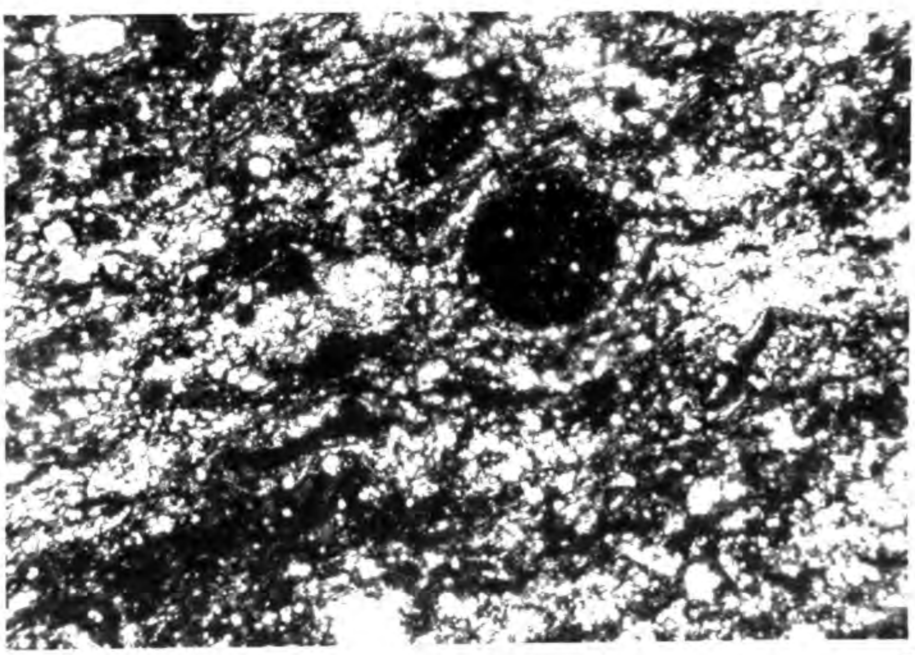


PLATE 3.14

Disturbed horizon in a diatomite, Campobello di Licata.

PLATE 3.15

Photomicrograph of a large dolomitic rhomb set in the micritic groundmass of a grey dolomitic marl,Camastra.
(XP x200)

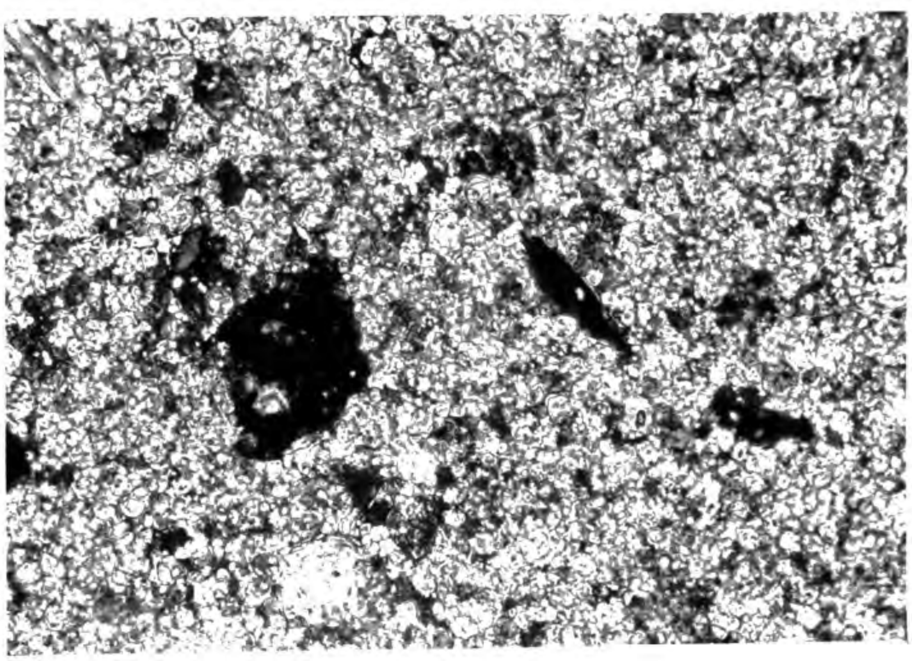
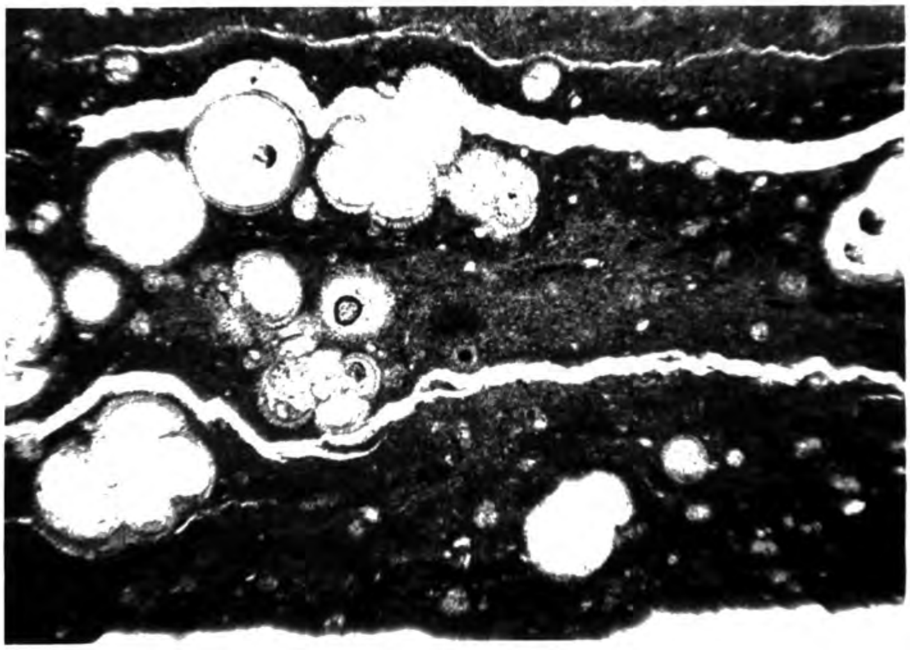


PLATE 3.16

Photomicrograph of a fissile, brown shale
with foraminiferal tests set in a fine terrigenous
matrix, Camastra.
(PP x 25)

PLATE 3.17

Scanning electron micrograph of gypsum(?)
crystals growing within a foraminiferal test,
Camastra.



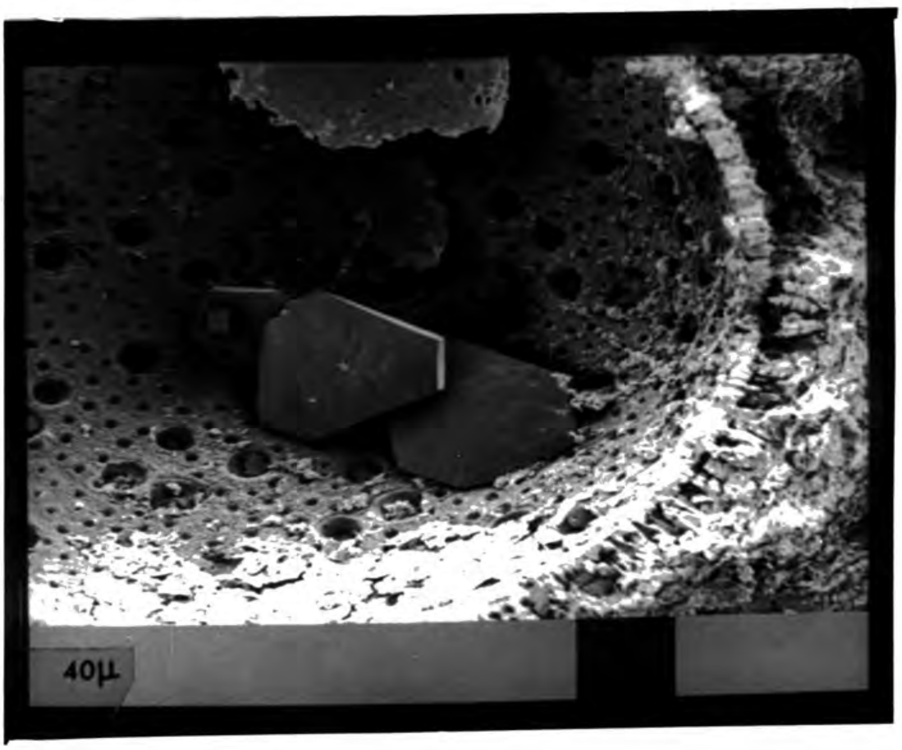
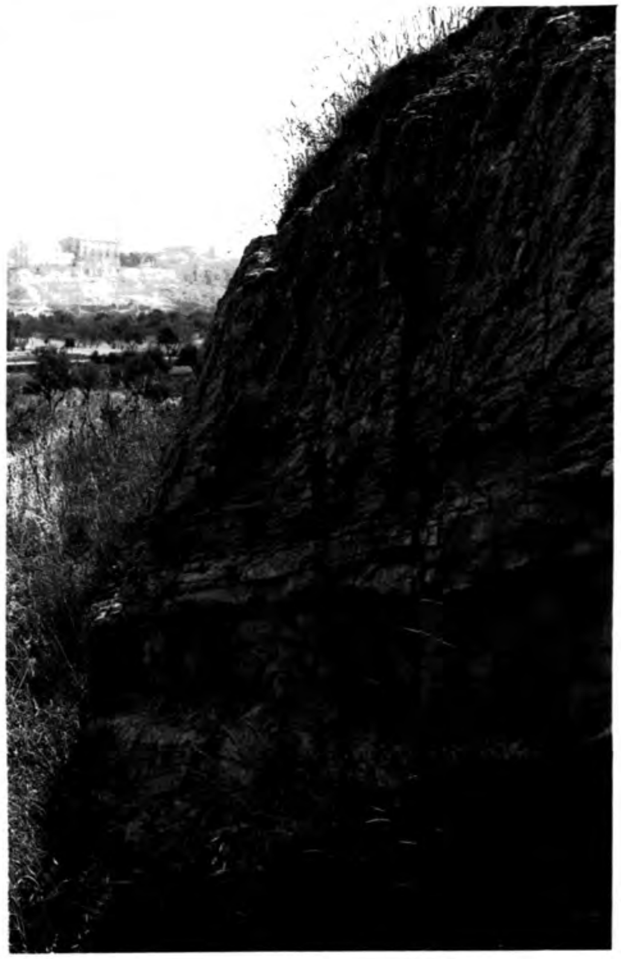

40µ

PLATE 3.18

The "Whitish Marls" at Palma di Montechiaro.
(The village is seen in the background.)

PLATE 3.19

Photomicrograph of cubic opaque minerals (formerly pyrite) within foraminiferal tests in a whitish marl, Marina di Palma.
(PP x50)



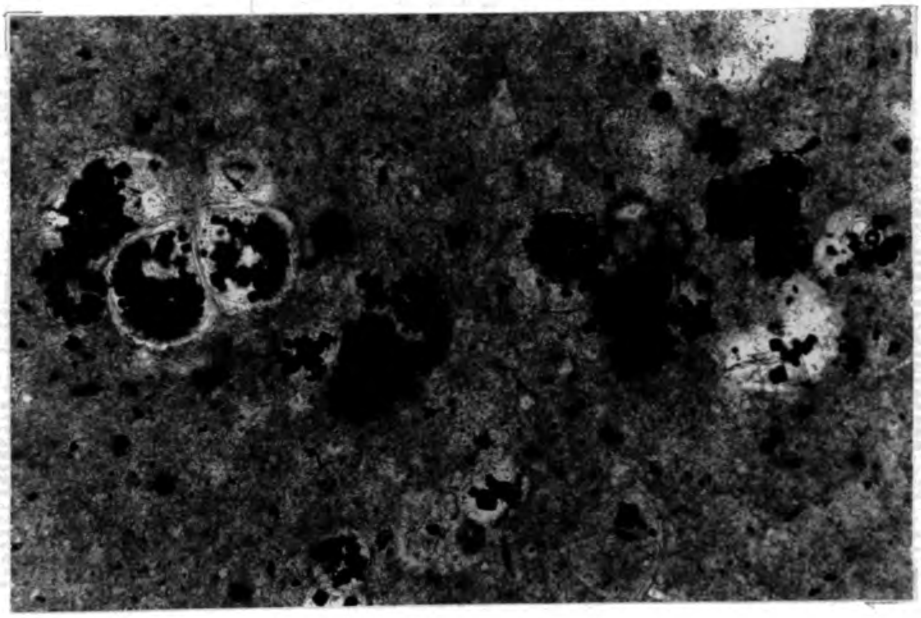
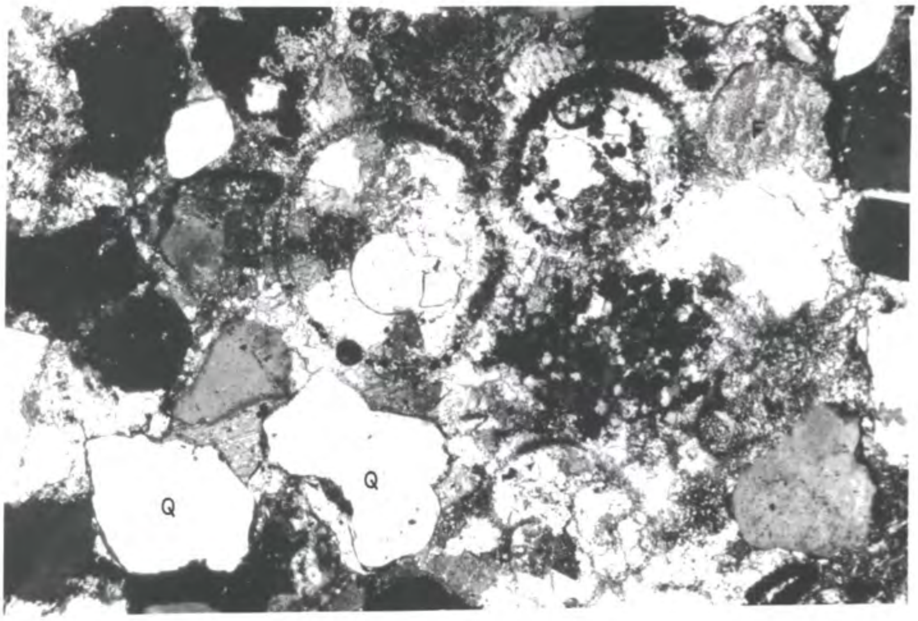


PLATE 3.20

Photomicrograph of a sandstone showing ghosts of foraminiferal tests that have been replaced by a calcite cement. Other grains include quartz (Q) and altered feldspars (F), Bompensiere. (XP x50)

PLATE 3.21

The dolomitic, lower Calcare di Base, Enna.


Q
Q

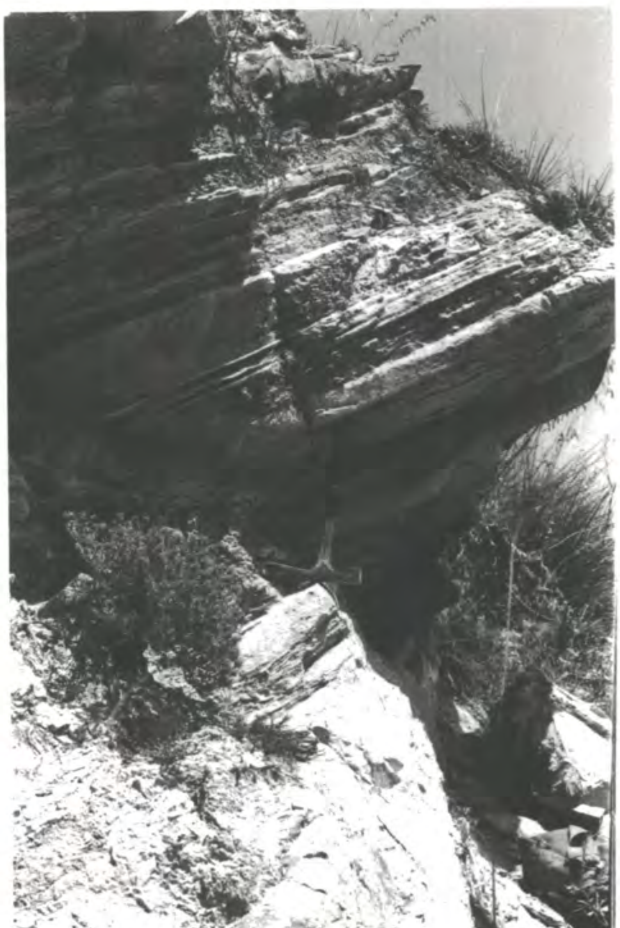
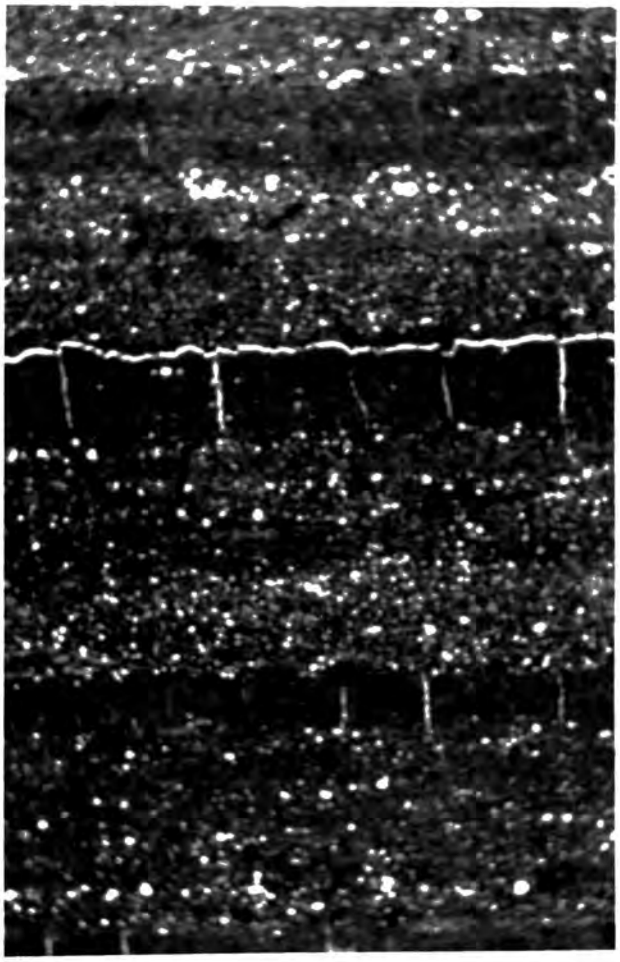


PLATE 3.22

Graded horizons in laminated dolomitic sediments, lower Calcare di Base, Antinello.
(PP x8)

PLATE 3.23

Grumeleuse structure in dolomitic sediments of the lower Calcare di Base, Enna.
(XP x200)



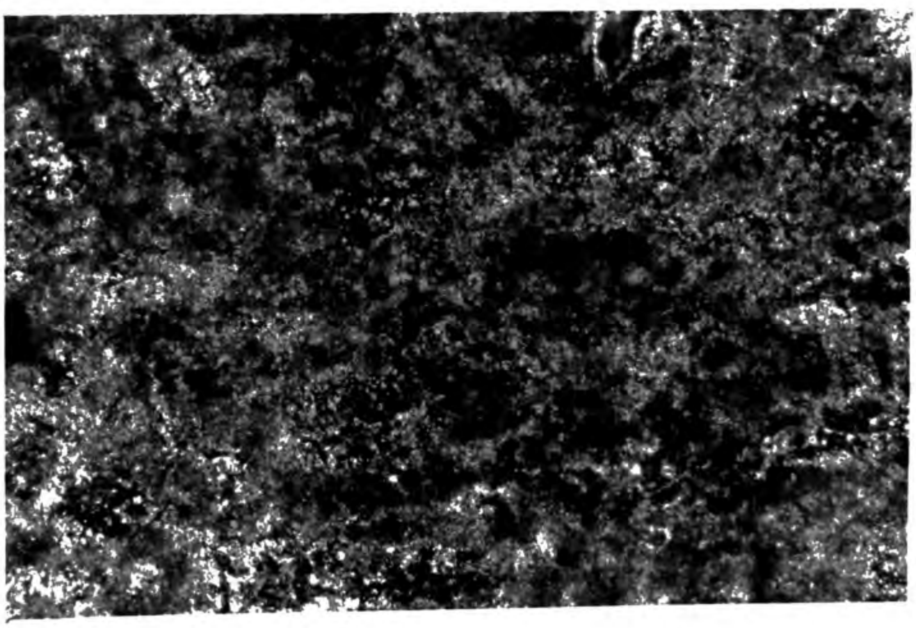


PLATE 3.24

Scanning electron micrograph of radiating aragonite needles. Sutera.

PLATE 3.25

Celestine (C) infilling pore space in a dolomitic Calcare di Base sediment, Enna.
(XP x50)


4μ

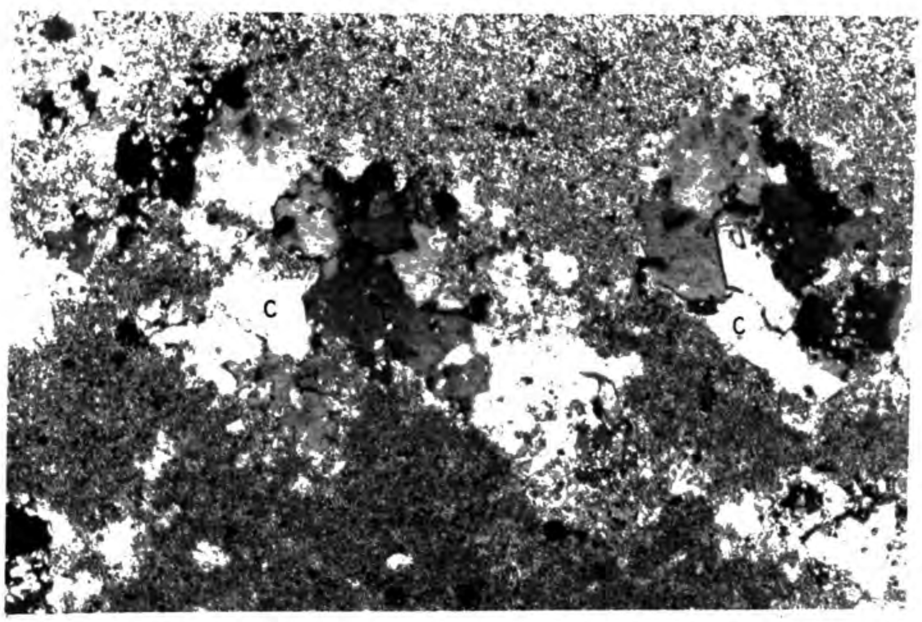
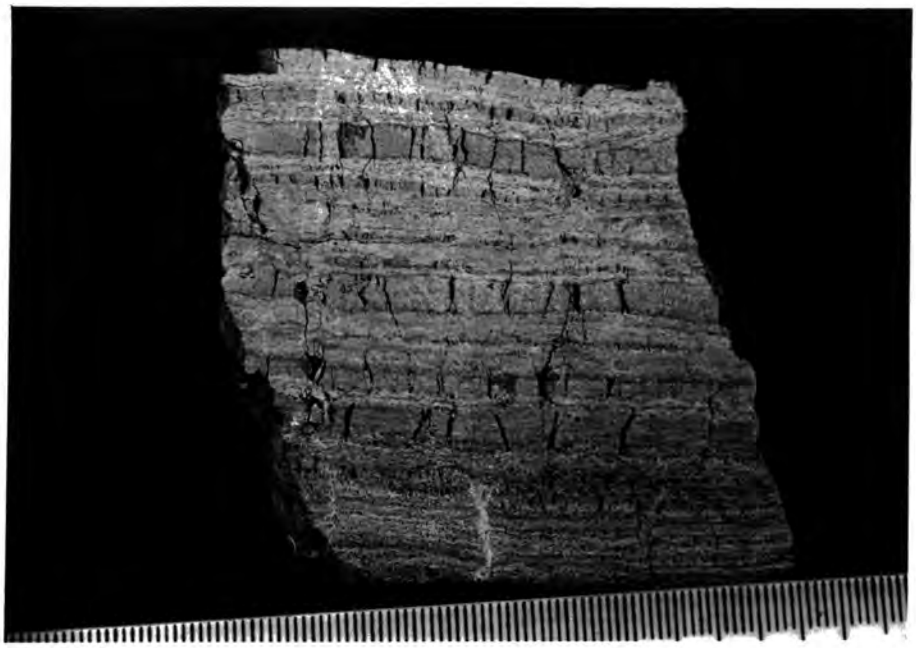

C
C

PLATE 3.26

Thinly bedded Calcare di Base dolomites,
Marina di Palma.
(Scale in centimetres)

PLATE 3.27

Angular clasts and vugs in a brecciated
Calcare di Base dolomite, Marina di Palma.
(Scale in centimetres)



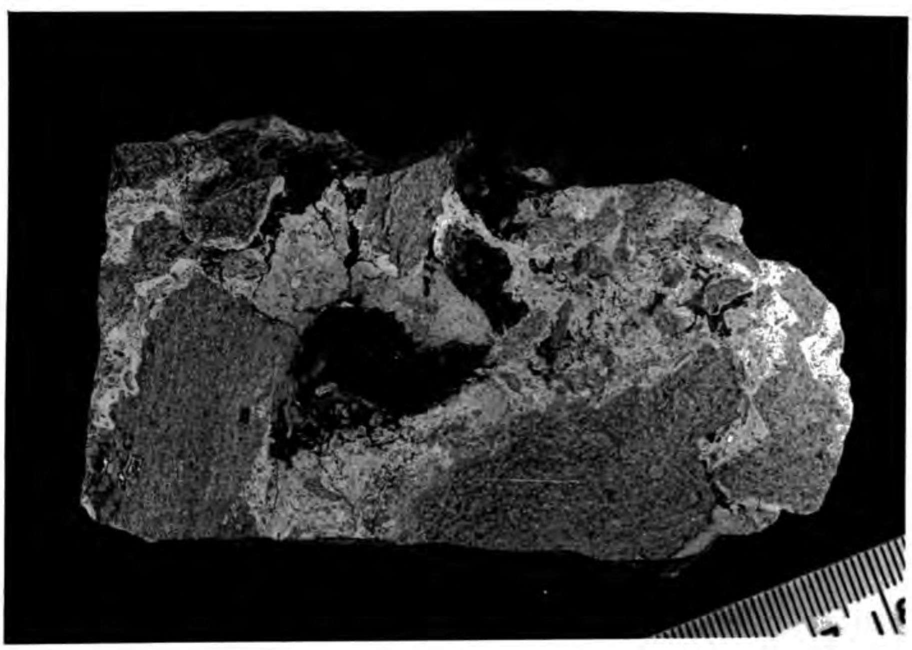


PLATE 3.28

Photomicrograph of calcite microspar developing in a micritic dolomite, Calcare di Base, Calascibetta. (XP x50)

PLATE 3.29

Photomicrograph of an anhedral calcite mosaic formed by a calcite cement infilling veins and the pore space of a micritic dolomite, Calcare di Base, Camastra. (XP x25)

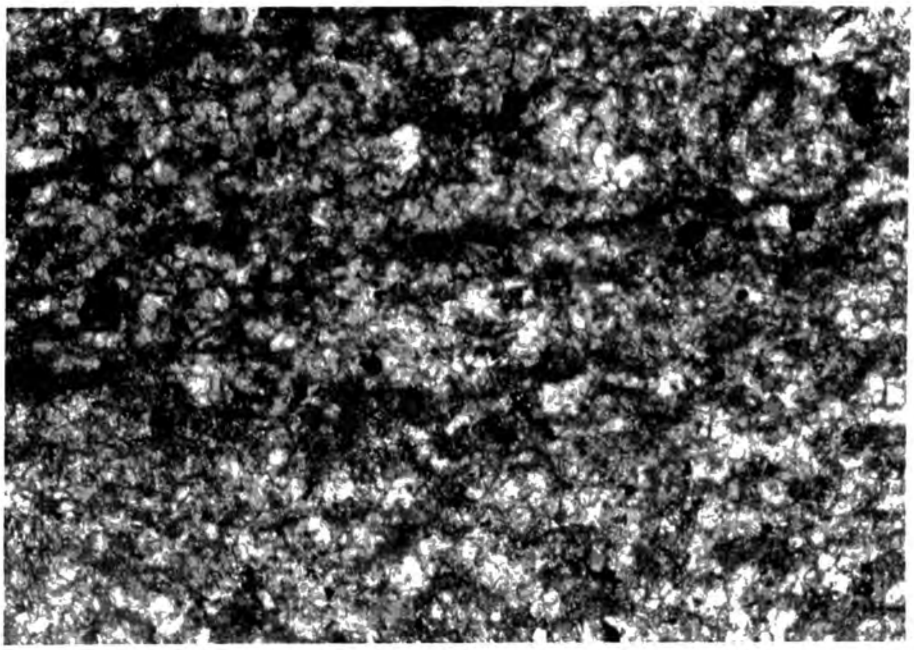


PLATE 3.30

Calcare di Base at Camastra.
(note the undulating dark bentonite bed and the massive nature of the Calcare di Base.)

PLATE 3.31

Photomicrograph of solution horizons (S) in a clast of a pellety limestone in a Calcare di Base breccia, Camastra.
(PP x8)

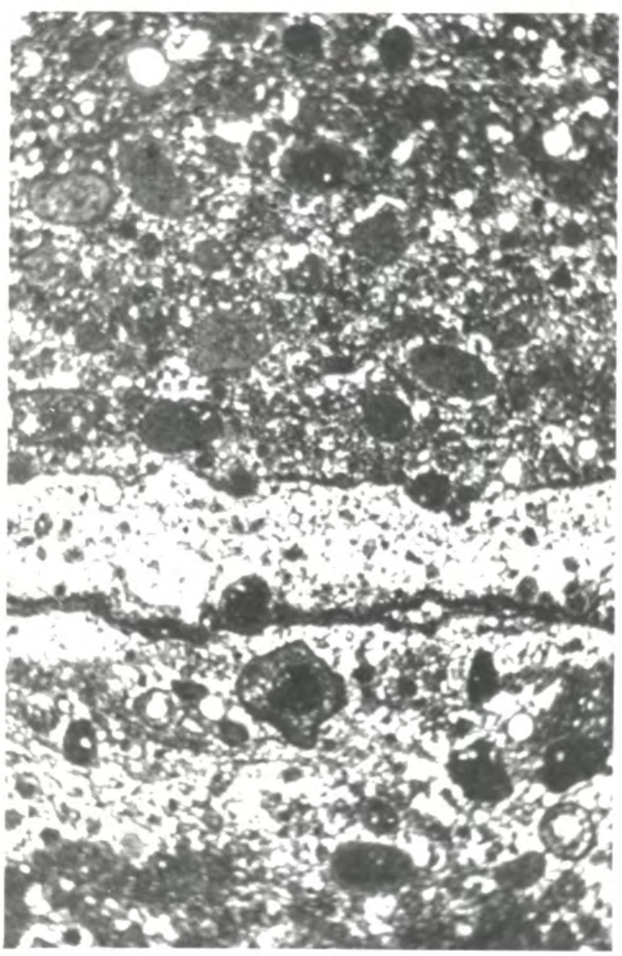

S
S

PLATE 3.32

A pseudomorph of a cubic mineral (halite),
Falconara.
(Scale in centimetres)

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APPENDIX I

X-RAY FLUORESCENCE ANALYSIS

The sediments' major and minor elements (Si, Al, Fe, Mg, Ca, Na, K, Ti, S and P) were determined by x-ray fluorescence analysis. Samples were prepared according to the method described by Beddoe-Stephens (1977). All analyses were performed on a PW1212 sequential x-ray spectrometer with a TE108 automatic sample loader using a Cr target and an evacuated tube.

International and departmental sedimentary standards were used to construct a calibration curve of number of counts against weight percent for each element. Where the data points approximated to a straight line (Al, Mg, Ca, Na, Ti, S and P), the curve was obtained by applying a linear regression. For Si, Fe and K the curve was drawn by hand. The compositions of the 'unknown' sediments were then obtained directly from these calibration curves. The accumulation of counts for the unknowns was based on a 'fixed count' time for a monitor. This minimises machine drift or instability.

No corrections were applied for interference effects neither were any independant analyses performed to determine the amounts of H_2O and CO_2 in the samples. However, a theoretical estimate of the CO_2 content could be made by assuming that it occurred solely in dolomite and calcite. This was thought to be a reasonable assumption since the only other common minerals are opal-A, quartz and clays. The percentages of calcite and dolomite in the sediments were calculated assuming that all the MgO was present as dolomite and all the CaO not incorporated in the dolomite occurred as calcite. This too, was thought to be a reasonable assumption since calcite and dolomite comprised the bulk of the non-siliceous material in the sediments. It also provided a quick and convenient method of estimating the sediments' mineralogical composition.

The summation of the percentages of calcite, dolomite, Si, Al, Fe, Na, K, Ti, S and P should approximate to 100% and therefore provides a guide to the likely accuracy of the analysis of each sample. It can be seen from the results presented below that in many cases the summation is substantially less than 100%. This is probably due to an underestimation of the percentage of calcite since the method of estimating dolomite and calcite necessitates that the dolomite percentage is a maximum value and the calcite percentage a minimum value. Summations that substantially exceed 100% are almost certainly due to interference effects.

Camastra:

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	Dol. %	Cte. %	Total
B006/06	44.60	13.23	3.73	3.44	16.16	0.29	2.76	0.57	0.21	-	15.32	20.30	101.91
B006/09	53.60	7.29	2.48	2.52	20.24	0.22	1.38	0.32	0.55	-	11.59	29.91	107.34
B006/11	34.00	10.01	2.54	2.44	26.30	0.36	2.06	0.37	0.72	0.05	11.22	40.96	102.29
B006/14	41.40	13.16	4.85	2.63	16.31	0.25	2.35	0.59	2.28	-	12.33	35.91	113.12
B006/21	46.50	14.61	6.40	3.49	9.95	0.31	2.63	0.71	1.11	0.19	16.05	9.06	97.57
X006/01	65.50	5.80	1.34	1.23	16.14	0.33	0.97	0.26	-	-	5.60	22.05	101.91
B006/25	43.30	12.57	4.45	3.78	16.76	0.28	2.63	0.58	-	-	17.39	20.53	102.23
B006/28	41.70	13.07	5.33	2.78	14.93	0.25	2.44	0.58	3.03	-	12.79	19.76	98.95
X006/02	49.35	6.32	2.04	1.55	26.00	0.46	1.12	0.26	-	0.03	7.13	40.11	106.82
X006/03	43.40	5.38	2.12	1.64	26.96	0.45	1.15	0.23	-	0.04	7.54	42.32	103.13
X006/04	78.80	4.05	1.99	1.06	7.96	0.15	0.58	0.23	-	0.10	4.88	9.43	100.21
X006/05	69.80	4.66	1.72	1.24	14.94	0.42	0.62	0.20	-	-	5.70	19.19	102.31
X006/06	74.80	6.18	2.70	3.12	5.15	0.58	0.95	0.34	-	0.16	11.65	0.00	97.36
X006/07	70.00	7.17	3.34	4.09	6.46	0.22	1.10	0.38	-	0.16	17.70	0.00	100.07
X006/08	67.10	2.85	1.39	-	9.42	18.02	0.35	0.17	-	0.12	0.00	12.42	102.49
X006/09	76.70	5.76	2.81	2.97	5.03	0.61	0.80	0.32	-	0.10	13.66	0.17	100.93
X006/10	52.80	6.48	3.08	8.01	14.29	0.57	1.12	0.31	-	-	36.85	2.19	103.40
X006/11	74.20	2.71	1.39	4.18	8.08	2.97	0.30	0.17	-	0.12	19.23	1.25	102.34
B006/31	21.10	4.99	1.83	15.31	25.29	0.42	1.16	0.27	-	0.03	70.43	6.91	107.19
B006/32	53.30	16.83	9.49	3.62	1.84	0.54	2.83	0.93	-	0.11	6.04	0.00	92.88
X006/12	49.40	4.45	2.01	9.54	17.27	0.39	0.70	0.24	-	-	43.83	3.34	104.41
X006/13	65.70	6.27	3.05	5.59	8.20	0.46	0.93	0.35	-	0.15	22.87	0.00	99.78

Camastra (cont.):

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	Dol. %	Cte. %	Total
X006/14	71.50	3.03	1.69	5.29	9.33	0.42	0.36	0.19	–	0.07	24.24	1.33	102.83
B006/01	35.00	8.46	3.67	11.42	17.15	0.29	1.96	0.46	–	0.01	52.53	2.08	104.46
X006/15	81.40	2.26	1.42	3.08	5.76	0.32	0.22	0.17	–	0.09	14.17	0.77	100.82
X006/16	79.00	3.28	2.16	3.19	5.89	0.17	0.43	0.23	–	0.10	14.67	0.90	100.94
B006/34	52.40	6.41	3.05	8.49	14.13	0.24	1.17	0.38	–	–	39.05	4.01	106.71
B006/35	11.00	2.54	0.77	15.02	31.02	0.68	0.50	0.14	0.10	0.18	69.09	17.33	102.88
B006/37	4.30	1.73	0.54	6.29	47.77	0.81	0.17	0.08	–	0.22	28.93	69.58	106.36
B006/39	2.50	1.41	0.43	7.90	47.30	0.93	0.04	0.06	–	0.22	36.34	64.71	106.64
B006/40	13.40	1.92	0.57	2.72	44.69	0.65	0.16	0.09	–	0.16	12.51	73.00	102.46
B006/41	5.80	2.58	0.66	1.12	50.29	0.70	0.31	0.09	–	0.21	5.15	87.00	102.50
B006/42	56.90	13.97	10.40	3.69	1.61	0.17	2.64	0.84	–	0.14	5.29	0.00	92.89
B006/43	2.60	1.14	0.23	0.81	57.48	0.74	0.00	0.05	–	0.20	4.09	100.62	107.67

Montedoro:

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	Dol. %	Cte. %	Total
X007/01	46.60	2.74	1.19	1.18	30.11	0.06	0.46	0.11	<0.01	0.17	5.43	50.82	107.59
B007/03	35.10	9.00	4.98	1.96	21.15	0.15	1.81	0.44	<0.01	0.15	9.02	32.95	93.61
B007/04	41.40	9.24	4.86	1.93	18.04	0.17	1.76	0.48	0.16	0.15	8.88	27.46	94.56
X007/02	80.90	3.38	1.91	0.82	5.75	0.24	0.45	0.23	<0.01	0.08	3.77	8.22	99.19
B007/08	67.30	4.72	3.18	1.06	13.00	0.20	0.72	0.32	<0.01	0.11	4.88	20.62	102.58
X007/03	84.30	1.96	1.13	0.60	5.41	0.38	0.28	0.12	<0.01	0.08	2.76	3.16	99.13
B007/11	77.70	3.56	2.14	0.85	8.04	0.25	0.51	0.21	<0.01	0.10	3.91	12.26	100.65

Montedoro (cont.):

Sample no.	SiO_3	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	Dol. %	Cte. %	Total
X007/04	79.40	3.19	2.08	0.70	6.46	0.21	0.42	0.21	< 0.01	0.11	3.22	9.79	93.64
B007/13	36.40	9.62	4.70	2.06	20.83	0.20	1.78	0.43	< 0.01	0.18	9.48	32.13	94.93
X007/05	66.70	4.13	2.25	1.12	16.36	0.30	0.62	0.18	< 0.01	0.08	5.15	26.41	105.83
X007/06	73.50	2.62	1.50	0.79	13.00	0.24	0.40	0.14	< 0.01	0.12	3.63	21.24	103.40
B007/14	41.70	10.87	4.43	2.53	18.65	0.16	2.10	0.50	< 0.01	0.26	11.64	27.12	98.79
X007/07	68.50	3.70	1.81	1.15	22.69	0.23	0.59	0.16	< 0.01	0.14	5.29	37.64	118.07
X007/08	53.30	4.86	2.00	1.34	22.30	0.13	0.76	0.22	< 0.01	0.17	6.16	36.47	109.08
X007/09	31.00	1.30	1.12	0.60	8.27	0.17	0.26	0.10	< 0.01	0.09	2.76	13.27	100.58
X007/11	46.00	4.33	1.88	1.59	27.62	-	0.69	0.18	< 0.01	0.14	7.31	45.35	105.89
B007/15	30.00	7.40	3.61	3.37	23.49	0.20	1.61	0.37	< 0.01	0.25	15.50	33.60	92.55
B007/18	14.90	4.07	1.74	10.04	31.18	0.17	0.89	0.20	< 0.01	0.24	46.18	30.64	99.04
B007/19	6.80	1.78	0.78	8.21	43.37	0.04	0.42	0.09	0.19	0.25	37.77	57.07	105.19
B007/20	71.80	2.90	2.74	7.62	12.41	0.31	0.41	0.15	< 0.01	0.10	35.05	3.11	116.58
X007/13	54.60	7.37	5.60	1.56	14.99	0.24	1.20	0.39	< 0.01	0.14	7.18	22.87	99.59

Campobello di Licata:

Sample no.	SiO_3	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	Dol. %	Cte. %	Total
B010/01	24.40	6.13	2.50	8.25	25.70	0.25	1.34	0.27	<0.01	0.17	37.95	25.27	98.29
B010/02	38.10	10.24	5.42	2.59	17.10	0.30	2.19	0.50	<0.01	0.13	11.91	24.05	92.67
B010/03	40.00	10.12	4.53	3.06	18.81	0.32	1.95	0.46	<0.01	0.21	14.08	25.95	97.63
X010/01	75.90	2.20	1.53	1.18	9.91	0.77	0.33	0.12	<0.01	0.11	5.43	14.75	101.15
B010/05	44.70	12.10	6.15	3.00	12.89	0.38	2.43	0.59	<0.01	0.15	13.80	15.52	95.83
B010/06	64.30	5.98	3.00	1.84	16.02	0.25	0.95	0.28	<0.01	0.16	8.46	24.00	107.39

Campobello di Licata (cont.):

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	Dol. %	Cte. %	Total
X010/02	76.10	2.95	1.64	1.14	10.60	0.27	0.43	0.15	<0.01	0.09	5.24	16.08	102.96
B010/07	41.20	8.30	4.47	2.77	14.39	5.35?	1.56	0.42	<0.01	0.14	12.74	18.77	92.96
X010/03	60.70	4.63	2.68	1.69	18.18	0.51	0.83	0.24	<0.01	0.14	7.77	28.24	105.75
B010/08	35.40	7.01	3.29	5.97	22.09	0.64	1.45	0.35	<0.01	0.17	27.46	24.52	100.30
B010/09	52.80	14.72	8.13	3.23	5.69	0.57	2.81	0.83	<0.01	0.14	14.86	2.09	96.95
X010/04	62.30	4.21	2.10	1.37	19.08	0.16	0.65	0.18	<0.01	0.14	6.30	30.65	106.70
B010/10	39.30	10.16	5.19	2.51	17.70	0.38	2.10	0.50	<0.01	0.13	11.55	25.34	94.66
X010/05	72.40	4.31	2.45	1.29	9.34	0.84	0.60	0.23	<0.01	0.11	5.93	13.45	100.33
X010/06	71.70	2.26	1.30	0.92	14.50	0.32	0.35	0.11	<0.01	0.10	4.23	23.59	103.97
B010/11	32.00	8.13	3.30	2.36	25.83	1.86	1.72	0.35	<0.01	0.18	10.86	40.18	98.59
B010/12	23.70	5.80	2.00	2.84	34.20	0.13	1.30	0.23	<0.01	0.13	13.06	53.96	100.37
B010/13	27.20	7.14	4.01	2.13	28.50	0.19	1.49	0.31	<0.01	0.16	9.80	45.04	95.35
X010/07	61.90	5.65	3.32	1.72	16.28	0.22	0.95	0.28	<0.01	0.12	7.91	24.77	105.13
B010/14	50.80	12.39	5.23	3.98	10.36	0.32	2.38	0.57	<0.01	0.15	18.31	8.55	98.71
X010/08	64.50	3.77	2.06	1.27	18.29	0.20	0.61	0.18	<0.01	0.12	5.84	29.49	106.78
B010/15	18.40	4.42	1.49	3.46	36.83	0.07	1.02	0.18	<0.01	0.20	15.92	57.13	98.84
B010/16	43.20	10.19	5.40	2.79	16.18	0.30	1.88	0.49	<0.01	0.15	12.83	21.91	96.36
X010/09	50.80	7.02	3.48	2.14	19.38	0.26	1.17	0.33	<0.01	0.14	9.84	29.26	102.31
X010/10	27.00	5.48	2.73	1.94	29.65	0.47	1.21	0.27	<0.01	0.16	8.92	43.10	94.35
B010/17	44.80	5.86	2.77	1.82	23.07	0.35	1.02	0.23	<0.01	0.16	8.37	36.64	100.26
X010/11	73.30	1.79	1.06	1.34	13.06	0.42	0.30	0.09	0.07	0.10	6.16	10.97	103.20
B010/18	28.80	6.52	3.36	4.51	14.63	16.18?	1.20	0.39	<0.01	0.17	20.75	37.05	114.43

Campobello di Licata (cont.):

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	Dol. %	Cte. %	Total
X010/12	76.80	3.15	2.00	1.16	7.85	0.55	0.44	0.19	<0.01	0.04	5.34	11.12	99.64
X010/13	58.20	3.35	1.79	1.37	22.80	0.24	0.59	0.15	<0.01	0.14	6.30	37.29	108.26
X010/14	81.10	2.20	1.49	1.68	6.05	0.67	0.29	0.13	<0.01	0.08	7.73	6.60	100.30
Calascibetta:													
B025/05	45.50	4.33	2.00	1.73	24.78	0.39	1.87	0.20	<0.01	0.16	7.96	40.02	102.44
B025/06	48.90	6.53	3.82	2.20	19.74	0.42	1.20	0.31	0.59	0.15	10.12	29.82	101.86
B025/07	50.40	5.62	2.63	2.06	19.38	0.45	0.91	0.25	3.92	0.16	9.48	29.54	103.36
B025/08	73.80	3.25	2.00	1.17	11.67	0.25	0.48	0.17	<0.01	0.12	5.38	17.95	103.41
B025/09	63.80	10.33	4.72	2.52	8.13	0.28	1.79	0.57	<0.01	0.15	11.59	8.23	101.47
B025/10	55.20	10.63	4.97	2.91	10.43	0.27	2.18	0.56	<0.01	0.13	13.39	11.47	98.86
B025/11	74.40	4.25	2.73	1.72	7.38	0.88	0.66	0.26	0.30	0.09	7.91	8.90	100.38
B025/12	80.60	3.01	2.41	1.46	4.43	0.44	0.45	0.20	0.07	0.03	6.72	4.28	98.26
B025/13	71.70	2.59	1.74	1.56	11.61	0.18	0.46	0.14	1.67	0.10	7.13	16.88	102.64
B025/14	26.00	6.93	3.55	10.95	20.06	0.32	1.46	0.34	<0.01	0.13	50.37	8.47	97.63
B025/15	69.60	6.54	5.61	2.27	5.99	1.03	1.02	0.39	0.27	0.10	10.44	5.03	100.03
B025/16	57.30	2.31	1.94	8.04	16.44	0.27	0.41	0.12	<0.01	0.16	36.94	9.31	108.77
B025/17	15.30	3.67	2.51	14.39	25.08	0.08	0.62	0.21	<0.01	0.25	66.19	8.82	97.65
B025/18	74.20	3.15	2.41	2.35	8.24	0.30	0.54	0.19	0.02	0.10	10.81	8.86	100.58
B025/19	52.80	9.03	3.91	3.04	14.11	0.24	1.84	0.44	<0.01	0.20	13.93	17.63	100.08
B025/20	53.20	8.73	4.07	3.06	12.74	0.24	1.79	0.44	<0.01	0.17	14.03	15.14	97.87
B025/21	49.10	10.54	4.65	3.79	13.34	0.26	2.11	0.53	<0.01	0.20	17.43	14.37	99.20

Calascibetta (cont.):

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	Dol. %	Cte. %	Total
B025/22	66.90	8.34	5.52	2.24	6.47	1.50	1.83	0.48	<0.01	0.11	10.30	5.96	100.95
B025/23	51.50	4.41	2.29	2.91	19.99	0.70	0.77	0.20	1.01	0.17	13.39	28.50	102.94
B025/25	76.00	3.41	2.41	3.17	5.16	0.89	0.54	0.21	0.66	0.09	14.58	1.29	100.08
B025/28	59.40	6.27	5.06	2.85	10.41	0.81	1.23	0.36	0.79	0.17	13.11	11.49	98.69
B025/30	76.80	3.47	2.42	1.47	5.81	0.55	0.54	0.20	1.99	0.12	6.76	6.71	99.56
B025/31	53.00	7.46	3.32	2.87	17.01	0.44	1.52	0.36	<0.01	0.16	13.20	23.25	102.72
B025/32	11.70	2.44	2.15	14.50	27.63	0.17	1.65	0.14	0.35	0.34	66.70	13.12	98.76
B025/33	81.10	2.60	2.41	0.98	5.93	0.41	0.38	0.16	<0.01	0.08	4.51	8.16	99.82
B025/34	72.70	4.70	2.39	1.89	8.02	0.53	0.73	0.25	<0.01	0.11	8.69	9.61	100.22
B025/36	85.90	1.50	0.73	0.78	3.46	1.48	0.23	0.09	0.14	0.07	3.59	4.24	97.97
B025/37	22.80	3.42	1.52	12.24	24.54	0.10	0.55	0.18	<0.01	0.26	56.30	13.25	98.39
B025/38	82.80	1.26	0.92	0.73	5.94	0.39	0.22	0.09	<0.01	0.10	3.36	14.39	104.04
B025/39	70.60	6.18	3.73	2.46	5.10	2.91	1.06	0.35	0.15	0.14	11.32	2.97	99.41
B025/40	9.70	2.45	1.67	16.47	23.42	0.23	0.67	0.14	0.28	0.21	75.76	9.59	100.70
B025/41	4.60	1.20	0.70	18.02	32.21	0.14	0.32	0.06	1.19	0.22	82.89	12.33	103.65
B025/42	8.20	1.72	1.13	17.96	28.65	0.30	0.48	0.09	0.59	0.22	82.62	6.28	101.63
B025/43	4.20	1.02	0.80	18.48	32.23	0.15	0.31	0.05	0.46	0.21	85.01	11.38	103.59
B025/44	13.40	3.02	2.31	16.57	24.06	0.35	0.77	0.17	0.65	0.21	76.22	1.54	98.64
B025/45	2.80	0.85	0.38	5.34	47.69	–	0.20	0.03	5.00	0.21	24.56	71.98	106.01

Falconara:

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	Dol. %	Cte. %	Total
B065/01	52.70	7.86	3.25	2.35	17.27	0.69	1.45	0.37	<0.01	0.12	10.81	25.02	102.28
B065/02	59.30	7.06	2.69	2.22	16.63	0.65	1.26	0.32	<0.01	0.13	10.21	24.20	106.15
B065/04	80.20	2.72	1.70	1.02	7.00	0.52	0.44	0.16	<0.01	0.09	4.69	9.97	100.50
B065/05	30.10	3.17	3.14	9.42	19.49	0.85	1.70	0.35	<0.01	0.15	43.33	11.28	99.09
B065/06	41.70	11.57	5.89	3.94	12.63	0.82	2.45	0.57	<0.01	0.11	13.12	12.73	93.97
B065/07	11.00	2.79	0.97	3.39	41.27	0.14	0.73	0.11	<0.01	0.20	17.39	64.12	97.96
B065/12	40.10	5.01	2.89	3.26	13.55	0.48	0.98	0.26	<0.01	0.30	38.00	12.51	108.82
B065/03	7.40	1.88	0.71	13.20	30.07	0.16	0.46	0.10	0.06	0.17	33.72	3.66	103.32
B065/11	1.20	0.19	0.16	0.92	22.01	0.04	0.05	0.04	0.12	0.09	4.23	37.09	43.21
B065/09	1.40	0.45	0.23	1.64	55.10	–	0.14	0.02	<0.01	0.22	7.54	94.51	104.52

Favara:

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	Dol. %	Cte. %	Total
B067/01	44.40	12.62	6.45	3.11	11.45	0.52	2.45	0.62	0.55	0.11	14.31	12.67	94.70
B067/02	77.30	3.55	2.10	1.04	8.04	0.27	0.54	0.20	<0.01	0.10	4.78	11.76	100.61
B067/07	33.60	3.60	5.21	1.62	11.26	14.82?	1.52	0.46	<0.01	0.13	7.45	16.06	87.96
B067/06	60.00	4.39	2.44	1.26	18.39	0.26	0.80	0.22	<0.01	0.14	5.30	30.58	105.14
B067/05	20.50	4.90	1.96	1.70	26.44	11.24?	0.97	0.21	<0.01	0.18	7.32	42.96	90.75
B067/04	12.20	3.06	1.04	1.77	43.46	0.04	0.80	0.12	<0.01	0.19	3.14	73.18	93.73

Capodarso:

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	Dol. %	Cte. %	Total
B068/06	40.40	10.15	4.62	6.83	14.72	0.26	2.25	0.50	<0.01	0.21	31.42	9.21	99.03
B068/05	75.80	2.42	1.54	1.72	9.70	1.96	0.46	0.14	0.18	0.10	7.91	13.02	103.53
B068/04	40.20	11.43	5.99	7.67	11.10	0.21	2.10	0.60	0.13	0.15	35.26	0.65	96.77
B068/03	75.60	4.61	2.83	3.01	4.99	0.27	0.68	0.27	<0.01	0.11	13.85	1.39	99.62
B068/02	2.30	0.64	0.52	17.62	33.47	0.08	0.20	0.03	2.86	0.19	81.05	15.72	103.59
B068/01	4.20	1.01	0.65	19.19	32.30	0.05	0.31	0.05	0.22	0.17	88.27	9.70	104.63

Monte Giammoia:

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	Dol. %	Cte. %	Total
B074/02	7.20	1.39	0.33	2.21	42.75	1.40	0.57	0.03	<0.01	0.17	10.17	70.81	93.13
B074/03	75.20	1.62	0.98	1.23	11.68	0.30	0.29	0.08	0.01	0.08	5.66	17.78	102.00
B074/04	40.20	9.29	4.02	5.65	14.72	1.60	1.89	0.51	<0.01	0.16	25.58	12.16	95.42
B074/05	83.80	1.66	0.63	1.41	4.70	0.71	0.27	0.10	<0.01	0.08	6.49	4.87	98.62
B074/06	6.30	1.49	0.88	18.50	29.61	0.21	0.44	0.09	0.23	0.20	85.10	6.63	102.70
B074/07	44.20	6.56	2.51	10.36	13.95	0.53	1.30	0.37	<0.01	0.23	45.84	0.00	101.95
B074/08	6.70	1.48	0.73	18.24	29.18	0.25	0.43	0.08	0.25	0.19	83.90	6.51	100.52
B074/09	13.00	3.55	2.46	12.45	17.09	11.07?	0.78	0.23	<0.01	0.33	56.15	0.00	92.32?

Monte Caolina:

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	CO_2	Total
B028/01	76.90	2.63	1.09	0.61	12.29	0.38	0.40	0.41	–	0.14	9.71	104.29
B028/02	67.20	8.85	3.06	1.75	10.28	0.61	1.79	0.37	–	0.20	8.21	102.32
B028/03	80.20	2.36	0.98	0.53	11.15	0.20	0.30	0.12	–	0.13	8.81	104.78
B028/03b	73.30	8.22	3.28	1.65	6.93	0.47	1.91	0.39	–	0.18	5.47	101.80
B028/04	69.80	8.59	3.12	1.70	8.74	0.60	1.94	0.36	–	0.18	7.87	102.90
B028/05	81.30	2.34	0.96	0.50	9.86	0.42	0.27	0.13	–	0.13	7.79	103.70
B028/06	81.50	2.23	0.98	0.49	10.49	0.20	0.25	0.12	–	0.14	8.29	104.69
B028/07	89.20	1.89	0.81	0.34	4.61	0.39	0.29	0.12	–	0.07	3.64	101.36
B028/08a	90.60	1.31	0.72	0.29	4.75	0.30	0.16	0.12	–	0.08	3.75	102.65
B028/08b	92.50	1.27	0.63	0.27	3.99	0.15	0.02	0.10	–	0.06	3.15	102.14
B028/09	93.20	1.10	0.58	0.23	3.21	0.07	–	0.09	–	0.03	2.54	101.05
B028/10	82.10	1.87	0.96	–	8.10	4.40	0.34	0.12	–	0.10	6.40	104.39
B028/11	78.50	2.82	1.34	0.56	11.96	0.11	0.30	0.15	–	0.14	9.45	105.33
B028/12	73.00	3.32	1.55	0.61	11.30	0.09	0.41	0.17	–	0.13	8.93	98.51
B071/01	68.90	7.64	2.69	1.48	10.52	0.64	1.62	0.33	–	0.20	8.31	102.33
B071/02	78.30	2.61	1.11	0.53	11.54	0.61	0.26	0.14	–	0.15	9.12	104.37

Sperlinga Quarry:

Sample no.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	S	P_2O_5	CO_2	Total
B072/01	95.70	0.64	0.54	0.23	1.58	–	–	0.07	–	0.04	1.25	100.05

APPENDIX II

X-RAY DIFFRACTION ANALYSIS.

II.i. Qualitative X.R.D.

X-ray diffraction has been used extensively for the routine identification of the minerals that make up the Tripoli sediments. All of these and other analyses were performed on a Philips PW 1130 Generator with a PW 1050 Diffractometer utilizing Co K_α radiation.

II.ii. Quantitative X.R.D.

A quantitative x-ray diffraction analysis was attempted in order to determine the amounts of quartz, calcite and dolomite in the carbonate sediments of the Tripoli Formation and Calcare di Base. The method was based on the Internal Standard Method described by Diebold et al. (1963) with boehmite being used as an internal standard. Other modifications to the original method were as follows:

The calibration curves for quartz, calcite and dolomite were constructed using National Bureau of Standards No. 88a Dolomitic Limestone and euhedral crystal samples of both quartz and calcite. Samples were prepared by being crushed in a Tema Laboratary Disc Mill, then sieved through 122 mesh before being added to the internal standard and mixed for 20 minutes in a Spex Mixer Mill. A cavity mount was then prepared according to the method described by Diebold et al. (1963).

The intensities of the quartz 4.26 Å, calcite 3.04 Å and dolomite 2.89 Å peaks relative to both the boehmite 3.16 Å and 6.11 Å peaks were calculated by the peak area count method. These relative intensities were then plotted against weight percent and a curve drawn through the data points using a linear regression by the method of least squares. Two calibration curves were thus obtained for each mineral. The unknown samples were prepared in the same way and the intensities of each mineral peak to both boehmite peaks were determined. Two independant values for the weight percent of each mineral in the sample could therefore be obtained from the calibration curves.

The results of this quantitative analysis are presented below. Unfortunately, the reproducibility of these results was found to be poor and to vary considerably more than 10% on occasions. There were thought to be primarily two reasons for this :

1) Poor cavity mount preparation resulting in the non-random orientation of the crystallites. This problem was minimised by the following method : A mean value for the relative intensity of the two boehmite peaks was established while constructing the calibration curves. This ratio was subsequently measured during each unknown sample run and if it deviated from the mean by more than 10%, the quality of that sample was considered to be unacceptable and a new mount was prepared.

2) Sieving irregularities. Quartz is harder and more resistant to crushing than either calcite or dolomite. Sieving may therefore result in the quartz being preferentially retained on the sieve screen. On the other hand, if crushing is too severe, the calcite and dolomite may become so fine grained that it is amorphous to x-rays.

This problem would be lessened by using a less severe method of crushing than the Tema mill, as recommended by Diebold et al. (1963).

The unsatisfactory results obtained by this method of quantitative analysis together with its time consuming and tedious nature led to its being abandoned in favour of x-ray fluorescence analysis. However, estimates of dolomite and calcite contents made from thin sections suggest that the results may be more accurate than the X.R.F. results where only small amounts (10%) of the mineral are present in the sediment. This method also provides a means of estimating the detrital quartz content of the sediment rather than the total SiO_2 content which includes amorphous silica in the form of diatom frustules. The difference in the SiO_2 content of the sediment (as measured by X.R.F.) and the quartz content (as measured by X.R.D.) therefore provides a means of estimating the diatom content of a sediment.

Results :

Camastra :

Sample no.	% Quartz	% Calcite	% Dolomite
B006/06	7.62	26.63	2.04
B006/08	5.35	22.60	6.45
B006/09	2.20	21.63	4.80
B006/11	6.99	48.17	0.68
B006/14	6.43	34.19	0.46
B006/15	11.07	33.37	1.14
B006/18	8.67	32.60	0.28
B006/21	17.26	15.65	1.13
B006/22	4.37	25.55	0.82
B006/25	8.03	32.97	2.30
B006/28	8.22	21.62	4.16
B006/31	4.34	0.00	47.16
B006/33	4.06	0.00	8.39
B006/03	12.48	0.00	22.15
B006/01	9.75	0.00	28.75
B006/05	7.19	0.53	24.57
B006/34	3.85	0.00	22.60
B006/35	3.22	17.45	40.46
B006/37	3.69	72.10	12.05
B006/39	1.18	62.14	13.06
B006/40	0.00	80.28	4.90
B006/41	4.07	99.88	0.00
B006/43	0.83	114.17	0.00

II.iii. Mole % Ca in Dolomite.

The mole % Ca in dolomite was determined by an x-ray diffraction method using quartz or cadmium fluoride as an internal standard. The d – spacing of the dolomite crystal lattice varies in proportion to the amount of Mg present, being 2.89 Å in stoichimetric dolomite and 3.04 Å in calcite. The mole % Ca can therefore be determined by measuring the dolomite's d – spacing. This was done by comparing with an internal standard and averaging the results of two runs (one in either direction). The results are presented over.

Mole % Ca^{++} in Dolomite

Camastra:

Sample no.	% Ca^{++}
B006/06	55.2
B006/09	55.0
B006/21	54.1
B006/25	53.8
X006/06	54.7
X006/07	54.7
X006/09	54.7
X006/10	54.3
X006/11	53.0
B006/31	52.9
X006/12	53.3
X006/13	52.7
X006/14	52.7
B006/0	53.4
B006/05	52.0
X006/15	53.7
X006/16	53.0
X006/34	53.0
X006/35	52.4
X006/37	53.7
X006/39	50.7
X006/40	51.0

Campobello di Licata:

Sample no.	
B010/01	56.0
B010/03	54.7
B010/08	56.0
B010/09	53.0
B010/12	54.7
B010/14	54.3
B010/15	55.0
B010/18	55.7

Calascibetta:

Sample no.	% Ca^{++}
B025/17	54.3
B025/25	53.3
B025/32	53.3
B025/37	54.3
B025/39	57.3
B025/40	55.7
B025/42	54.7
B025/45	52.0

Marina di Palma:

Sample no.	
B063/04	54.3
B063/05	54.0
B063/06	53.7
B063/07	54.3
B063/08	53.0
B063/09	52.0
B063/10	52.3

Falconara:

Sample no.	
B065/05	54.3
B065/06	55.0
B065/07	54.0
B065/12	52.7
B065/08	52.7

Capodarso:

Sample no.	
B068/06	56.3
B068/04	55.7
B068/03	55.7
B068/02	53.3
B068/01	54.0

Mole % Ca^{++} in Dolomite.

Monte Giammoia:

Sample no.	% Ca^{++}
B074/04	55.0
B074/06	53.3
B074/07	54.0
B074/08	53.3
B074/09	51.7

APPENDIX III

LOCALITIES VISITED AND REFERRED TO IN THE TEXT.

(Map references refer to the 4th Edition of the 1:25,000 map of Italy, series M.891 published by the Italian Military Geographic Institute.

ANTINELLO :

Calcare di Base dolomites. The outcrop lies approximately 100 metres along the track to Antinello which leaves the San Cataldo - Mimiani/Marianopoli road about 10 kms. NNW of San Cataldo. Opal-CT cherts were found in a nearby ploughed field.

ARAGONA :

Tripoli diatomites and marls. A small roadside outcrop located about 6 kms. NW of Aragona on the road to S. Elisabetta.

BOMPENSIERE :

Tripoli diatomites, marls and sandstone. A small roadside outcrop by the road between Montedoro and Bompensiere, approximately 3 kms. from Bompensiere.

CALASCIBETTA :

Tripoli diatomites and marls, Calcare di Base and gypsum deposits. An extensive outcrop located by the side of the road between Calascibetta and Alimena, approximately 8 kms. NW of Calascibetta.

CAMASTRA :

Tortonian marls, Tripoli Formation and Calcare di Base. An extensive outcrop on the west side of the road between Palma di Montechiaro and Naro, about 7 - 8 kms. south of Camastra.

CAMPOBELLO DI LICATA :

Tripoli Formation and Calcare di Base. An outcrop on the west side of the road between Canicatti and Licata, about 15 kms. south of Campobello di Licata.

CAPODARSO :

Tortonian marls, Tripoli Formation and Calcare di Base. The outcrop is located behind a sulphur mine (Miniera Giumentaro) in the valley of the Fiume Salso, about 3 kms. north of where it is crossed by the Caltanissetta - Enna road. (Sheet : Staz. di Imera, 268, IV, SE. Grid Ref: 242523)

CASTROFILIPPO :

Upper Tripoli Formation and Calcare di Base. A small exposure located behind a housing development on the outskirts of the village on the road to Favara. It is unlikely that this outcrop is still accessible.

DITTAINO :

Opal-CT porcelanites. A poor exposure on a rocky knoll lying on the north side of the road (not the autostrada) between Enna and Catenanuova, near the St. di Dittaino approximately 21 kms. east of Enna.

ENNA :

Tripoli diatomites, Calcare di Base dolomites and gypsum. An extensive exposure on a hillside overlooking and lying to the NW of the Enna - Caltanissetta road some 8 kms. from Enna. (Sheet : Enna, 268, I, SW. Grid. Ref: 351548)

FALCONARA :

Tortonian marls, Tripoli Formation and Calcare di Base. An extensive outcrop on the south side of Monte Cantigaglione. Access is via a minor road which leaves the Licata - Gela road 6 kms. west of Castello di Falconara. (Sheet : Castello di Falconara, 272, III, SW. 37° 7' 35" N, 1° 34' 10" E.)

FAVARA :

Tripoli diatomites and marls. A large exposure in a quarry behind a housing development on the edge of the town on the road to Agrigento. This outcrop may no longer be accessible.

GROTTE :

Whitish marls. A small roadside outcrop between Comitini and Grotte about 2 kms. from Grotte.

:

Calcare di Base. A small quarry about 5 kms. south of Grotte on the road to Favara.

MARCATO BIANCO :

Whitish marls and Tripoli diatomites. A road cutting about 1 km. north of Marcato Bianco and 6 kms. NE of Pietraperzia.

MARIANOPOLI :

Messinian clastics and Calcare di Base. A roadcutting near the crest of the ridge about 1 km. east of Marianopoli on the road to San Cataldo.

MARINA DI PALMA :

Tripoli Formation and Calcare di Base. The first small headland along the coast west of the village. Several other small outcrops of early Messinian and Tortonian sediments occur further west along the coast.

MONTALLEGRO :

Calcare di Base intercalated with gypsum horizons. The outcrop lies on a hillside overlooking the main Sciacca - Agrigento road near the tunnel about 5 kms. SW of Montallegro.

MONTE CAOLINA :

Quartzitic porcelanites and cherts. An outcrop on the flank of Monte Caolina which overlooks the Santa Venera valley. (see Plate 2.1) (Sheet ; Gangi, 260, II, NW. Grid. Ref: 365829)

MONTEDORO :

Tripoli Formation. A section by the side of the road a kilometre south of Montedoro on the road to Serradifalco. A good exposure of laminated gypsum deposits occurs some 100 metres nearer Montedoro.

MONTE GIAMMOIA :

Tortonian marls, Tripoli Formation and Calcare di Base. An extensive outcrop on the southern side of Monte Giammoia which lies about 1 km. west of the Niscemi - S. Michele di Ganzaria road, 5 kms. north of where it is joined by the road from Caltagirone. (Sheet ; Passo di Piazza, 272, I, SE. 37° 14' 30" N, 1° 55' 15" E)

PALMA DI MONTECHIARO :

Whitish marls. A few metres along the road to Marina di Palma from its junction with the Agrigento - Licata road near Palma di Montechiaro.

SAN CATALDO :

Calcare di Base. The outcrops lie at the top of the hairpin bends on the road between San Cataldo - Caltanissetta, about 4 kms. from San Cataldo.

SANTA VENERA :

Quartzitic porcelanites and cherts. There are two good exposures near the hamlet of Santa Venera. (Sheet ; Gangi, 260, II, NW. Grid. Ref: 369824)

SPERLINGA QUARRY :

Quartzitic cherts. A small roadside outcrop (see Plate 2.4) about 1½ kms. NE of Sperlinga village. (Sheet : Sperlinga, 260, II, NE. Grid. Ref: 437813)

SPERLINGA RIVERSIDE :

Quartzitic cherts and porcelanite. An outcrop by the Fiume Sperlinga about a kilometre NW of the village. (Sheet : Sperlinga, 260, II, NE. Grid.Ref: 421809)

SUTERA :

Diatomites and Calcare di Base dolomites. Several outcrops lie to the north of the hairpin bends just outside Sutera on the road to Campofranco. (Sheet : Mussomeli, 267, I, SW. Grid. Ref: 875546)