Zeitschrift: Eclogae Geologicae Helvetiae
Herausgeber: Schweizerische Geologische Gesellschaft
Band: 63 (1970)
Heft: 2

Artikel: Submarine volcanism and the toarcian iron pisolites of western Sicily
Autor: Jenkyns, Hugh C.
DOI: https://doi.org/10.5169/seals-163860

Eclogae geol. Helv.	Vol. 63/2	Pages 549–572	With 18 figures	Basle, Juli 1970

Submarine Volcanism and the Toarcian Iron Pisolites of Western Sicily

By HUGH C. JENKYNS

Geologisch-paläontologisches Institut der Universität Basel

ABSTRACT

Some marine iron pisolite beds from the Toarcian of western Sicily are described for the first time. These beds, which generally overlie the Liassic platform carbonates, are usually chocolate-brown in colour; they attain a maximum thickness of about 40 cm at one locality but are often tracable as centimetre-thick remanié horizons elsewhere. Their fauna comprises Tethyan ammonites, belemnites, gastropods, rare brachiopods, fish teeth, foraminifera and crinoid ossicles.

The pisoliths themselves contain calcite, limonite (goethite), haematite and, in rare cases, chamosite; electron-probe microanalysis shows that they are enriched in certain trace elements, particularly manganese, relative to many iron ooliths. The high content of trace elements suggests deposition in a pelagic environment, as do the faunal associations of this deposit; and, since fragments of sanidine trachyte are invariably associated with this lithology – sometimes even forming the cores of the pisoliths themselves – submarine volcanism and exhalations seem a likely source for the ferruginous and manganiferous material.

The stratigraphical position of the iron pisolite, often between two stromatolitic sediments, and the traces of boring algae in the pisoliths, suggest deposition within the photic zone, probably some tens of metres deep.

ZUSAMMENFASSUNG

In der vorliegenden Arbeit werden zum erstenmal marine Eisen-Pisolithe aus dem Toarcien von Westsizilien beschrieben. Die Pisolithe überlagern in der Regel Plattform-Karbonate des mittleren Lias; sie sind von schokoladebrauner Farbe und erreichen eine maximale Mächtigkeit von 40 cm. Meist sind sie jedoch nur als zentimeterdicke Aufarbeitungshorizonte nachweisbar. Ihre Fauna umfasst Ammoniten von mediterranem Gepräge, Belemniten, Gastropoden, seltene Brachiopoden, Fischzähne, Foraminiferen und Crinoiden-Skelettelemente.

Die Pisoide selbst enthalten Kalzit, Limonit (Goethit), Haematit und in seltenen Fällen Chamosit. Analysen mit der Röntgen-Mikrosonde zeigen in vielen Fällen Anreicherung von Spurenelementen; insbesondere die Mangan-Gehalte sind im Vergleich mit anderen Eisen-Oolithen beträchtlich. Der hohe Anteil von Spurenelementen spricht für eine Entstehung in einem pelagischen Ablagerungsbereich, was durch die Fauna bestätigt wird. Da sämtliche Eisenpisolith-Vorkommen Fragmente von Sanidin-Trachyt enthalten – diese bilden manchmal auch den Kern der Pisoide –, lassen sich Eisen und Mangan mit grosser Wahrscheinlichkeit von submarinen vulkanischen Ergüssen und Exhalationen herleiten.

Die Eisen-Pisolithe überlagern oft stromatolitische Sedimente des Gezeitenbereichs und werden ihrerseits meist von pelagischen stromatolitischen Sedimenten überlagert. Ausserdem treten in den Pisoiden Spuren von Bohralgen auf, welche ihrerseits eine Ablagerung innerhalb der photischen Zone, vermutlich in einigen zehn Metern Wassertiefe, anzeigen.

Introduction

Oolitic iron deposits are well developed throughout the north European Jurassic (HALLAM, 1967a) and also occur as very minor constituents of the Jurassic of North Africa (LUCAS, 1942): in both cases the depositional site may be related to the proximity of a large landmass. However, in the Toarcian of western Sicily thin iron-pisolite beds occur associated with red limestones of pelagic facies, and an origin other than continental must be sought for the limonitic material. These deposits, previously undescribed, are most spectacularly developed at Monte and Rocce Maranfusa and can also be traced, usually as centimetre-thick remanié horizons, at other localities. Such pisolite horizons are not confined entirely to the Toarcian, occurring also as minor developments within the main ferromanganiferous condensed sequences of the Middle Jurassic. The Toarcian, however, seems to have been their optimum period of formation.

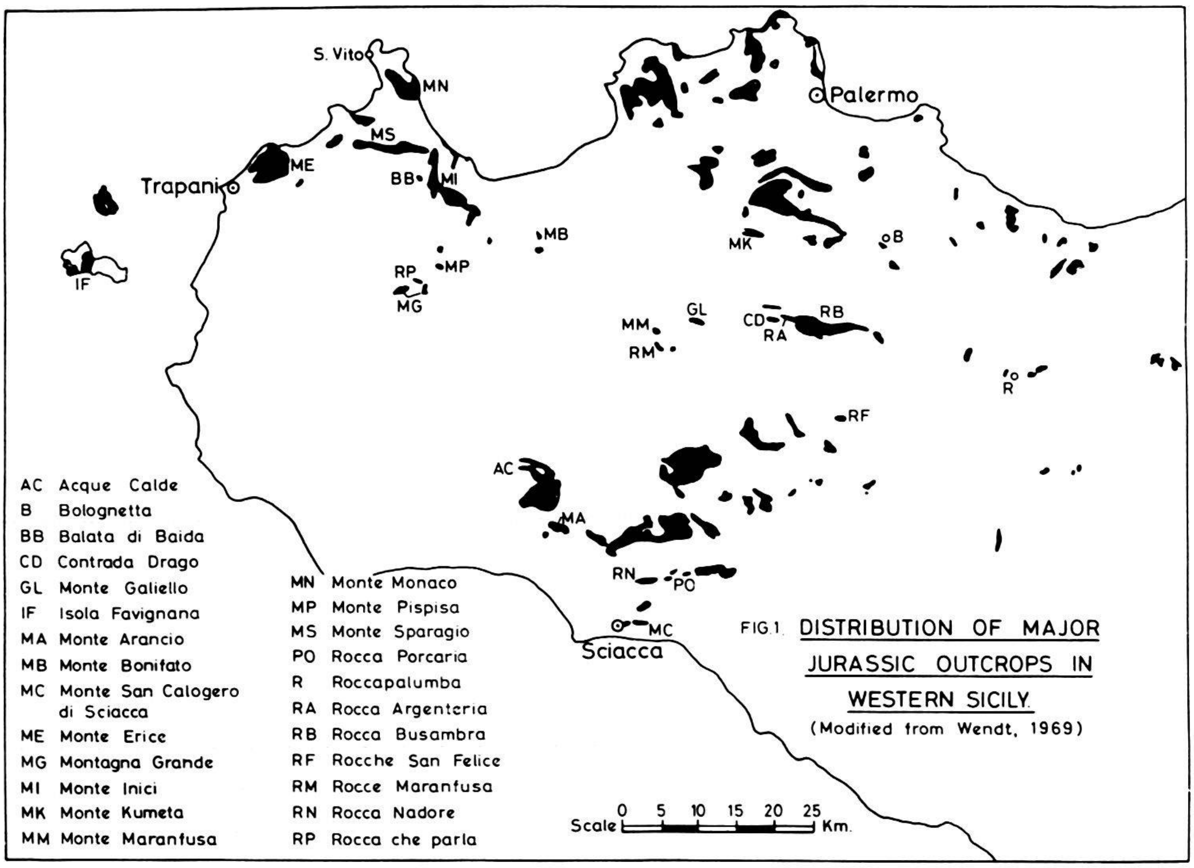

Fig. 1. Locality map.

Occurrence and Description of Iron-pisolite Horizons

Iron pisolites occur in well-developed but discontinuous sequences throughout the group of mountains known as Rocce and Monte Maranfusa, west-central Sicily (see Fig. 1 and 2). This group of mountains has recently been interpreted as a sedimentary klippe (BROQUET, CAIRE, MASCLE, 1966). In these localities the pisolite bed is richly

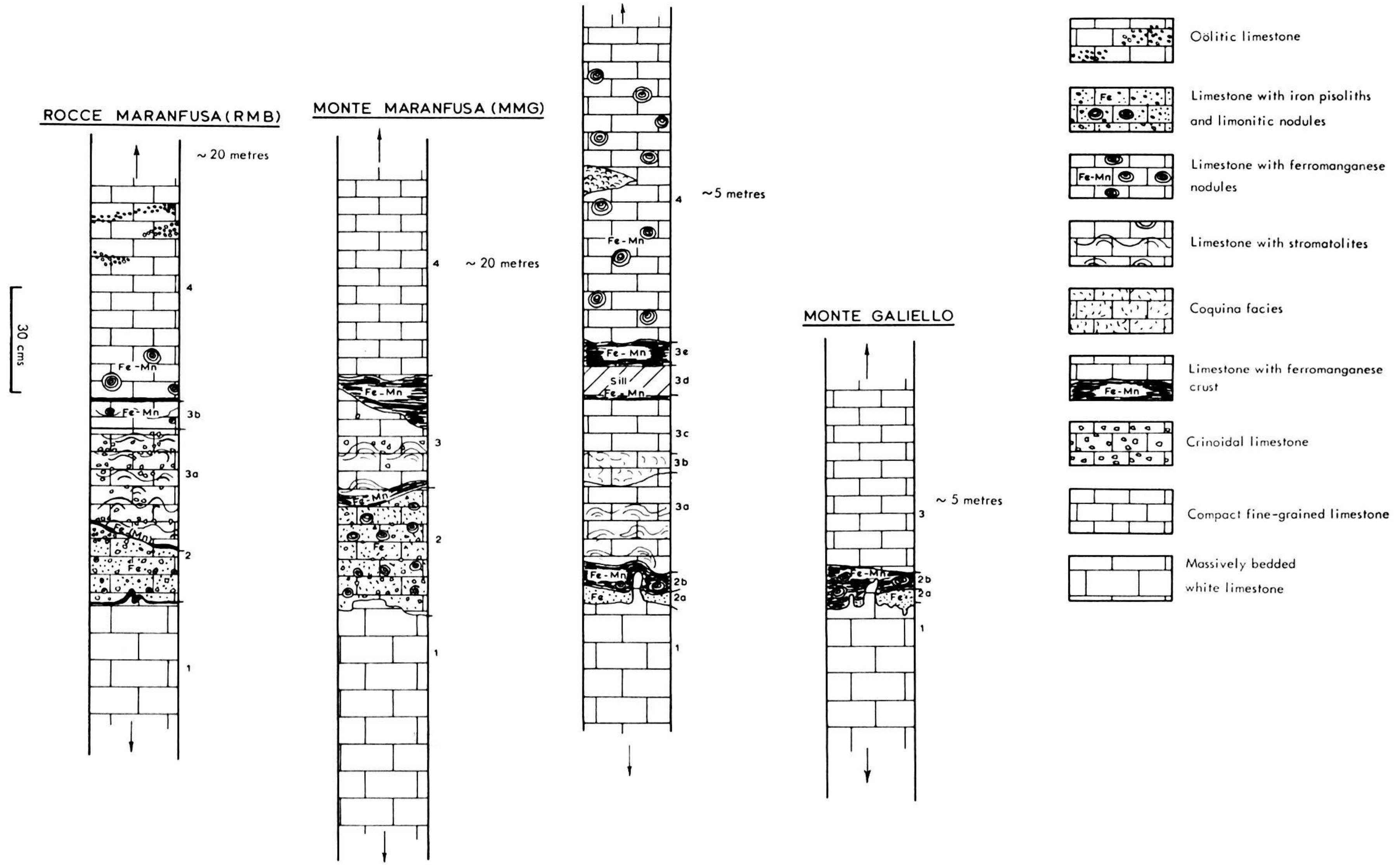

Fig. 2. Sections at four Jurassic localities in western Sicily showing the stratigraphical relationship of the Toarcian iron pisolite. Bed 1, the Liassic platform carbonates, consist of light-coloured oolitic, pelletal and stromatolitic sediments; its upper (karst) surface is assumed to be Upper Pliensbachian in age. Bed 2 is the Toarcian iron pisolite. Bed 3 consists of fine-grained red pelagic limestone with crinoids, lenses of coquina, stromatolites, and ferromanganese nodules and crusts; approximately Middle Jurassic in age. Bed 4 consists of grey to pink fine-grained, pelletal or oolitic limestone with some coquina lenses, and ferromanganese nodules at base. Data from JENKYNS and TORRENS, personal observations, 1966–1967.

crinoidal and varies in colour from chocolate brown through shades of red and yellow to, in rare circumstances, green. It is capped by a ferromanganese crust. The bed directly overlies the stromatolitic and oolitic Liassic platform carbonates (see JENKYNS and TORRENS, 1969) and its thickness, varying from nothing up to about 40 cm, is considerably affected by syn-sedimentary faults and surface topography of the underlying formation; lensing out where the Lias bulges upwards, or infilling karstic cavities within it. The pisoliths themselves vary in colour from yellow-brown to green and tend to occur in bundles within the crinoidal sediment. At Monte Maranfusa larger (2–3 cm) calcareous ferromanganese nodules, associated with the pisoliths, are particularly conspicuous.

At Rocca Busambra, and its off-faulted blocks Rocca Argenteria and at Contrada Drago (Fig. 1 and 2), the iron pisoliths occur as small lenses in the same stratigraphic position, and are intimately associated with the ferromanganese crust which usually directly overlies the white Liassic limestones. Although the pisoliths are concentrated at the contact, a few range as high as 30 cm into the bed above, presumably a result of continual reworking. At Monte Galiello (Fig. 1 and 2) the exposure is similar with pisoliths occurring sporadically in a lensing red limestone (Fig. 3) that generally underlies the ferromanganese crust.

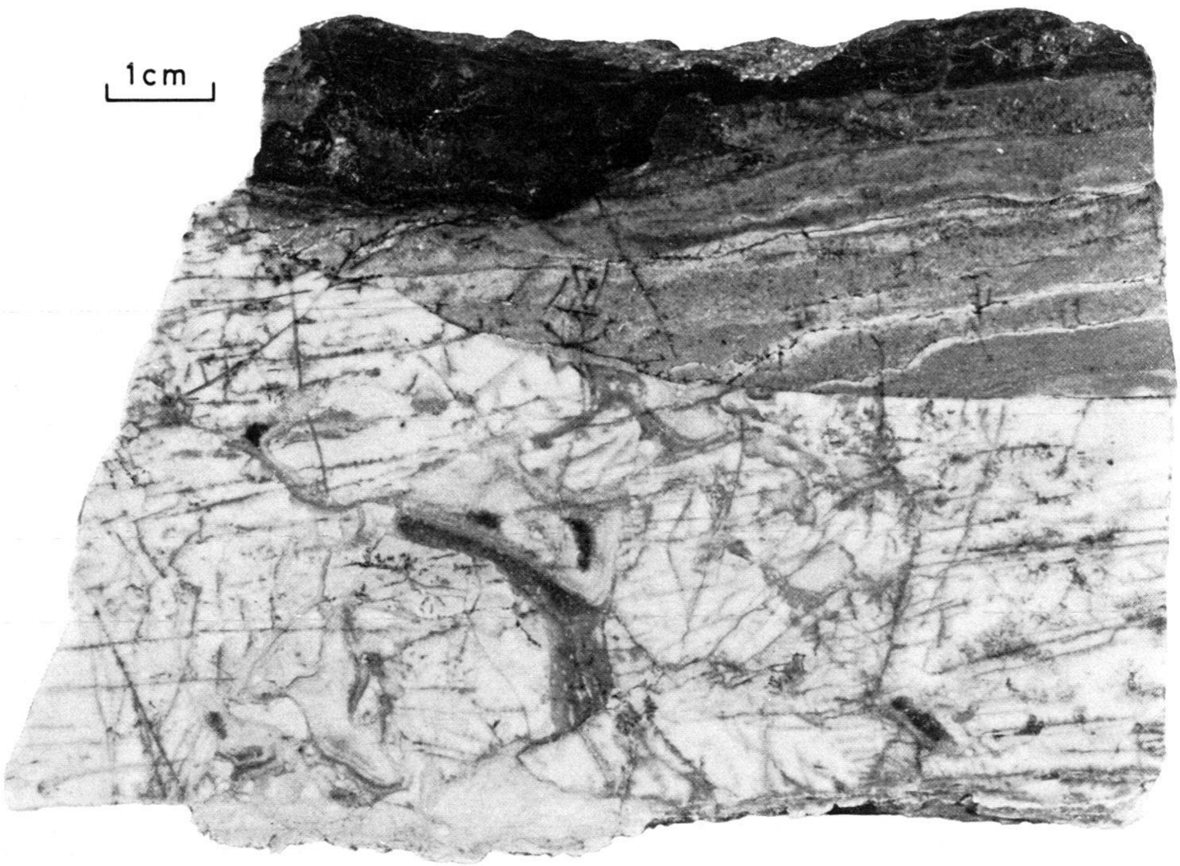

Fig. 3. White Liassic limestone with *Stromatactis* cavities, overlain by lensing Toarcian iron pisolite which is, in turn, capped by ferromanganese crust. Polished block. Monte Galiello, western Sicily.

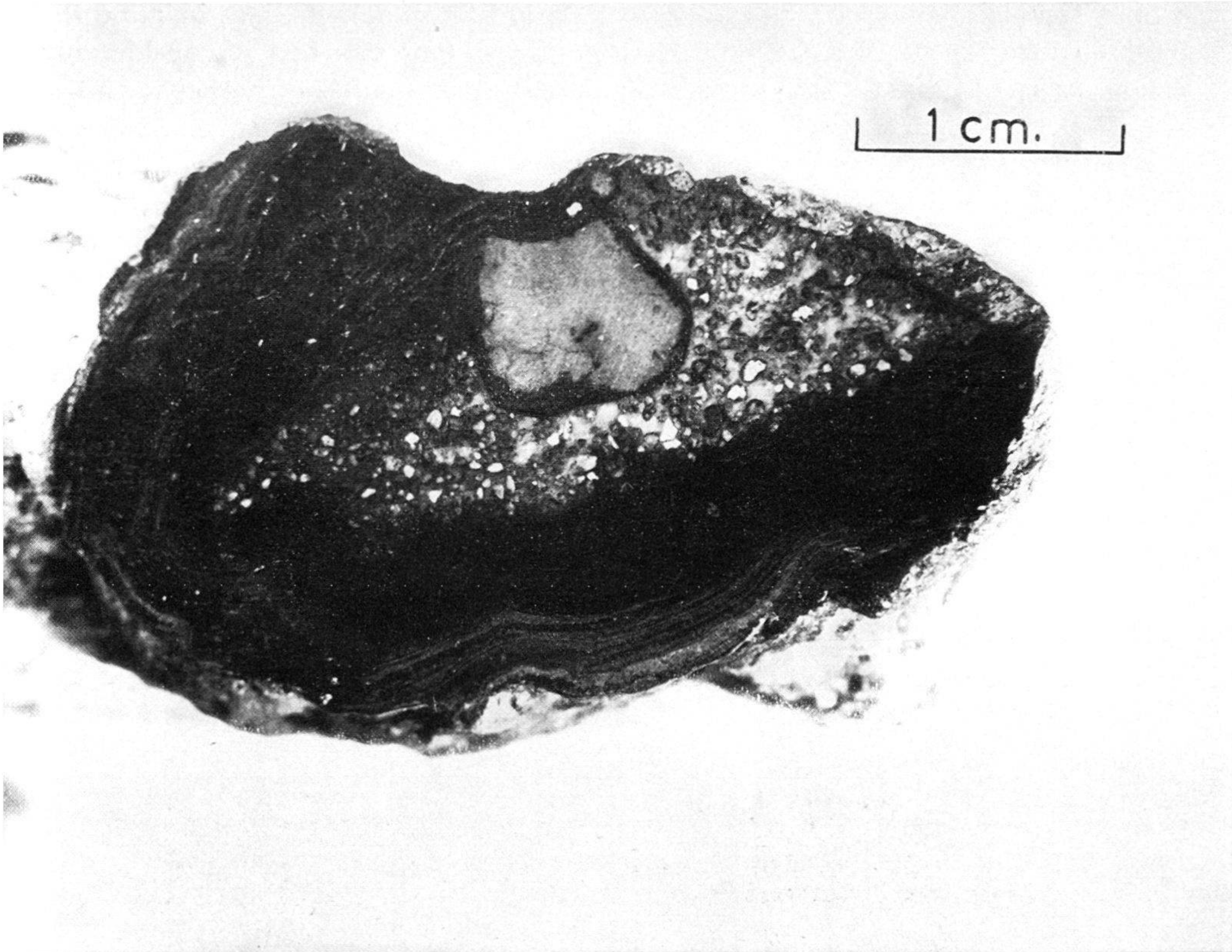

Fig. 4. Iron pisolite forming the core of a ferromanganese nodule. Polished block. Monte Arancio, south-west Sicily.

At Monte Arancio iron pisoliths have been found forming the core of a ferromanganese nodule (Fig. 4), demonstrating that the pisoliths were formed earlier in time. A few pisoliths also occur scattered through the basal horizons of the red limestone at this locality.

At Monte Monaco (Fig. 1), north-western Sicily, pisoliths are amply distributed through the condensed horizon and are intimately intermixed with the later ferromanganese crust; the pisoliths, however, are notably associated with yellow-stained fossils and matrix, in contrast to the red limestone and its black mineral crust. The same is also true at Monte Kumeta where a yellow ferruginous deposit, with some large pisoliths, infills solution hollows in the crinoidal limestone beneath. Only at this locality does the pisolitic horizon not rest directly on the Liassic platform carbonates.

At some of these localities the iron pisolites occur as fissure infillings.

Fauna and Age of the Iron-pisolite Horizons

The iron-pisolite horizons at Rocce and Monte Maranfusa have yielded a number of ammonites (see Jenkyns and Torrens, 1969) that indicate an age at the Lower-

Upper Toarcian boundary (Erbaense Zone, Bayani Subzone). Bearing in mind the diminutive thickness of the deposit, it is apparent that this bed is considerably condensed. At Monte Galiello some badly preserved ammonites of probable Liassic age have also been obtained from this horizon (H. S. TORRENS, personal communication). Ammonites of Upper Toarcian age have also been found at Monte Kumeta (WENDT, 1963) and Monte Monaco (WENDT, 1969a).

Apart from ammonites, other macrofauna in these beds include belemnites, gastropods, rare brachiopods, and fish teeth: the latter weather out conspicuously.

Petrology

The most obvious feature of the Toarcian iron pisolites is that they all contain igneous material, and this will be discussed later. Petrographically, the rocks are highly ferruginous biomicrites, containing considerable echinoderm debris, chiefly crinoidal, and foraminifera, broken lamellibranch shells, and ostracods. Fish teeth are as noticeable in thin section as they are in the field. Subsolved aragonitic fossils are common (HOLLMANN, 1964).

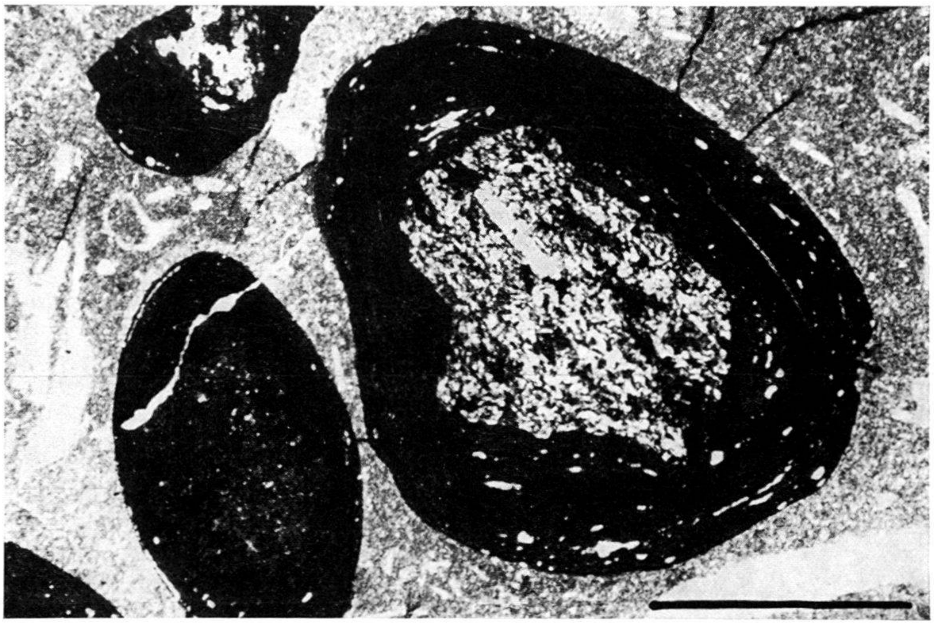

Fig. 5. Trachyte with flow structure forming the core of an iron pisolith. Thin section. Rocca Busambra, western Sicily. Scale bar = 1 mm.

The pisoliths are usually 0.2–0.5 mm in diameter but may range as large as 4 mm across; they are sporadically distributed in the ground-mass. They usually consist of a concentric limonitic rind (20–500 μ thick) round a variety of nuclei; these include dolomitised micrite, calcitised igneous material, felspar crystals (Fig. 5), crinoid ossicles and spines, foraminifera, fish teeth, chamosite flakes, often highly distorted, and micrite intraclasts which may or may not be limonitised. Compound nuclei occur; and some pisoliths have been broken and show regeneration coatings.

The yellow-brown pisolith material, although giving a goethite X-ray powder pattern, can probably be best described as limonite; the optical identification of the yellow-green mineral as chamosite, confirmed by its X-ray powder pattern, is further borne out by the electron-probe analysis (Fig. 14). X-ray patterns of all pisoliths gave goethite and calcite; some contained haematite; chamosite has only been identified at a few localities. The large nodules that occur at Monte Maranfusa have only yielded patterns of goethite and calcite.

Insoluble Residues

Insoluble residues of these Toarcian facies varied from 5–30% depending on the amount of limonitic material present. Clay minerals present included illite and kaolinite in varying amounts, with montmorillonite.

Illite and montmorillonite are common constituents of modern oceanic sediments (GRIFFIN, WINDOM and GOLDBERG, 1968), whereas kaolinite tends to be localised around continental margins, being derived from weathering products on land. Illite is probably detrital. Montmorillonite is commonly regarded as being a breakdown product of volcanic material, and its presence is not surprising since the iron pisolites contain considerable amounts of igneous fragments. The presence of kaolinite, even in the non-chamositic sediments, is a little more puzzling; according to VAN HOUTEN (1964), the occurrence of this mineral in a red sediment presupposes the proximity of lateritic soils, but there is certainly no evidence of a continental landmass in this area during Toarcian times. However, the iron pisolite beds are very close to the top of the Liassic platform carbonates and parts of this surface may have been lateritised with the production of kaolinite (JENKYNS, 1969) – and this weathered mantle could have been later incorporated into the Toarcian sediments. Nevertheless, it is not by any means inconceivable that there were some oceanic limestone islands providing kaolinite from exposed weathered surfaces at this time (see JENKYNS, 1969).

Chamosite

Chamosite has only been identified from Rocce and Monte Maranfusa. In thin section it exhibits typical properties: good spherulitic structure with an extinction cross shown under cross-nicols, and it commonly occurs as bent flakes or spastoliths (see RASTALL and HEMINGWAY, 1939), and may alternate in layers with limonite. Almost invariably it is outlined by a "protective" limonite coating. The origin of chamosite presents something of a problem since it is a divalent iron compound, presumably only stable at negative values of Eh, and yet it occurs in rocks that must have been laid down in oxidising conditions. Two main possibilities seem feasible for the origin of chamosite ooliths: either they formed below the sediment-water interface by some concretionary mechanism producing a "pseudo-oolitic" structure, or they were formed, in the same way as aragonite ooliths, but were originally composed of some substance, stable at positive Eh values, that crystallised diagenetically to chamosite. HALLAM (1967b), CURTIS and SPEARS (1968) and SCHELLMANN (1969) deal with these problems. PORRENGA (1965, 1966) has recorded modern chamosite replacing faecal pellets, and

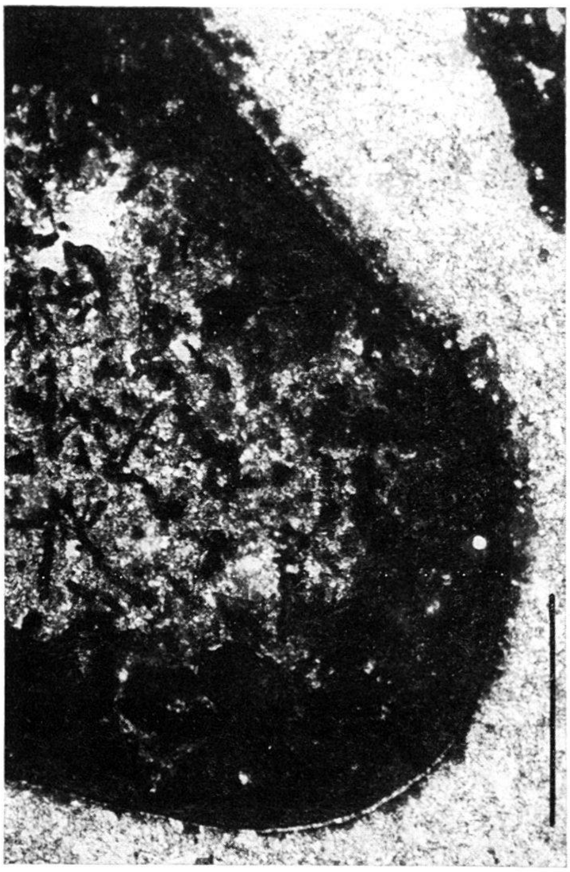

Fig. 7

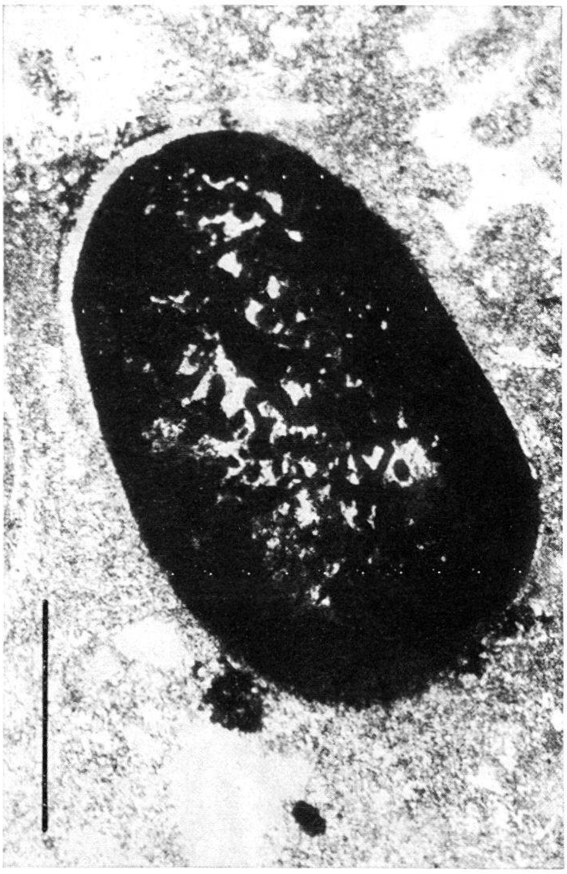

Fig. 9

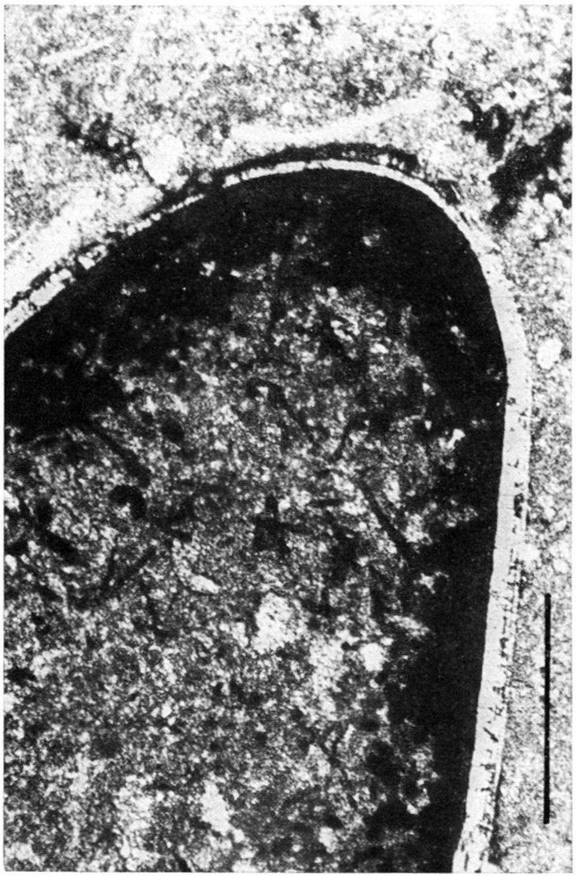

Fig. 6

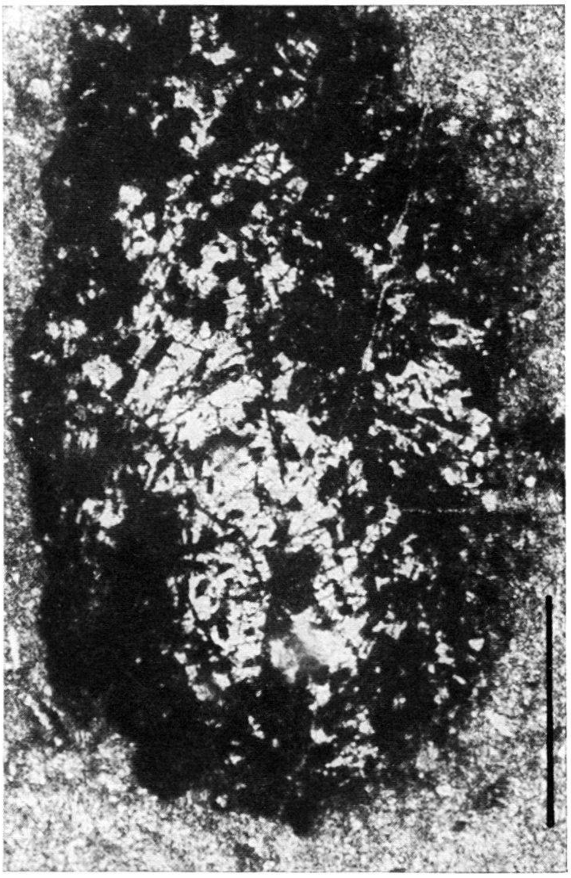

Fig. 8

in the tests of organisms, in some tropical shallow-water shelf regions; here the close association with organic matter suggests that reducing environments have been influential in the genesis of this mineral. Furthermore, ROHRLICH, PRICE and CALVERT (1969) have described early diagenetic chamosite from a Scottish loch; here the crystals occur arranged tangentially around detrital minerals and faecal pellets – and this concentric structure may be "proto-oolitic".

The Toarcian iron pisolites are condensed, and thus in this environment of minimal sedimentation any organic matter is liable to be oxidised before it becomes buried. The concentration of manganese in this bed (see Figs. 14 to 17) and its prevailing chocolate-brown colour all suggest a realm of positive Eh. Nevertheless, rare patches of green do occur in this ferruginous limestone and if these are primary, it is conceivable that small areas of reducing conditions did exist below the sediment-water interface. However, although chamositic pisoliths are more prominent in these green patches, they occur with equal frequency in the chocolate-brown matrix. The pisolith from Rocce Maranfusa contains considerably more silica than those from Monte Galiello and Monte Monaco, and these latter may be primary limonite precipitates rather than oxidation products of chamosite.

The formation of chamosite does not seem to be restricted to any depths or temperatures of water (ROHRLICH, PRICE and CALVERT, 1969; cf. PORRENGA, 1967), although it does not seem to have been recorded deeper than 150 metres.

Boring Algae and Limonitisation

It is apparent that although a few of the pisolith nuclei are composed of grey micrite or sparite, many of them are limonitised to a considerable degree. The formation of this limonitic material can be best interpreted as due to the activities of boring algae or boring fungi. Thus the limonitisation process is an absolute parallel to the micritisation described by BATHURST (1966); only in this case the algal (or fungal) bores are filled with precipitated limonite or at least limonitic micrite. Various stages can be observed in this process, as illustrated by Figures 6 to 9. The first state is the invasion of filaments (diameter commonly 5–10 μ) round the periphery of the particle, then further advance, until a uniformly dense limonitic area is eventually produced. In most cases this limonitisation process took place before the formation of the pisolitic coating, as this outer limonitic ring is not usually bored (cf. HESSLAND, 1949, for comparable observations).

Fig. 6. Slightly limonitised micritic pisolith, with traces of algal tubules towards the centre. Thin section. Monte Monaco, north-west Sicily. Scale bar = 0.25 mm.

Fig. 7. Moderately limonitised micritic pisolith. Thin section. Monte Monaco, north-west Sicily. Scale bar = 0.25 mm.

Fig. 8. Skeletal calcite or calcitised igneous fragment showing partial limonitisation. Thin section. Monte Monaco, north-west Sicily. Scale bar = 0.25 mm.

Fig. 9. Iron pisolith showing virtually complete limonitisation. Thin section. Monte Monaco, north-west Sicily. Scale bar = 0.25 mm.

The boring organisms choose various hosts to invade, including calcitised igneous material, skeletal calcite, fish teeth, crinoid ossicles and micrite intraclasts. The most frequently chosen hosts are those composed of sparry calcite; unaltered felspars are not attacked to any great extent.

If these boring organisms are algal, then their activities will be limited to environments where sufficient light is present for them to photosynthesise. As HOLMES (1957) has remarked, it is impossible to set a depth limit to the photic zone, but in low latitudes with clear "oceanic" water a maximum figure around 150–200 metres is perhaps reasonable; although NADSON (1927) found no boring algae living deeper than 50 metres.

"Limonitic Cauliflower Structures"

Small limonitic "cauliflower" structures occur "growing" in limestone at many ferruginous horizons in the west Sicilian Jurassic, but they are particularly well developed in the Toarcian facies (Fig. 10 and 11). Such structures, commonly of a millimetre scale, have been interpreted as either organic or inorganic. FARINACCI (1967) considered similar ferruginous segregations as stromatolites, and indeed such dendritic patterns have been recorded by RADWANSKI and SZULCZEWSKI (1965), and SZULCZEWSKI (1963, 1967, 1968), from undoubted algal-mat structures. In these latter examples the dendrites are tentatively interpreted as being formed after blue-green algal colonies.

Similar structures occur within ancient and modern ferromanganese nodules (WENDT, 1969b; CRONAN and TOOMS, 1968; FRIEDRICH, ROSNER and DEMIRSOY, 1969); and CRONAN and TOOMS interpret them as being due to early diagenetic re-arrangements, since the segregations may also occur in the volcanic cores of some nodules (BONATTI and NAYUDU, 1965).

In some cases these segregations may cross-cut calcite skeletons and veins which proves their non-syngenetic origin, and they are probably best interpreted as products of the diagenetic mobility of iron (and manganese).

Volcanism

Fragments of porphyritic trachyte have been identified in the iron pisolite horizon, immediately above the Liassic platform carbonates, at Monte Maranfusa, Rocce Maranfusa, Rocca Busambra and its off-faulted blocks, Rocca Argenteria and at Contrada Drago; Monte Galiello, Monte Arancio, Monte Kumeta, Monte Monaco, and Bolognetta. The spatial distribution of this igneous material is plotted in Figure 12, and it is evident that the effects of this volcanic episode were felt over a considerable area. This extrusion is presumably pre-Erbaense Zone, since the ammonite fauna at Rocce Maranfusa is of this age.

The lava type is an alkali trachyte with phenocrysts of sanidine set in a felspathic groundmass showing well-developed flow structure (Fig. 13). In general, the felspars are not greatly altered, but some show varying degrees of replacement by sericite and carbonate, usually with preservation of the original structure. Ferromagnesian minerals are usually completely altered and only biotite has been positively identified.

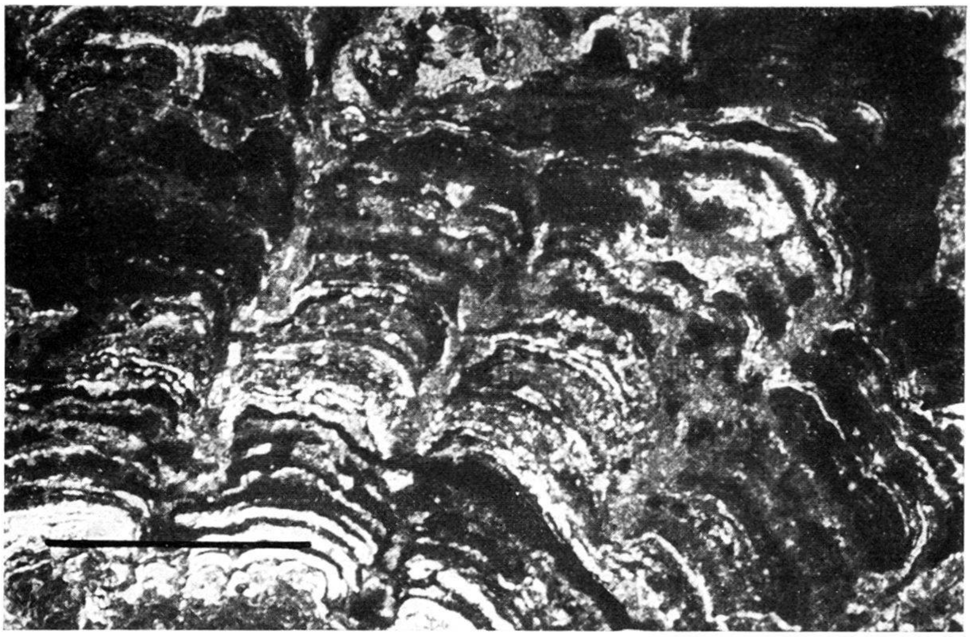

Fig. 10. Limonitic "cauliflower" structures showing massive columnal development. Thin section. Contrada Drago, western Sicily. Scale bar = 0.25 mm.

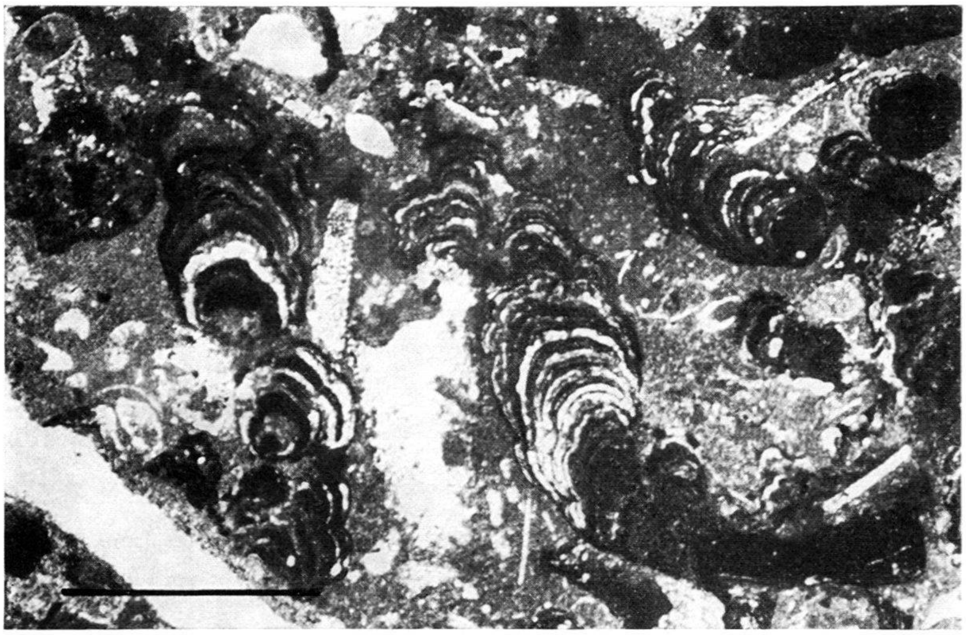

Fig. 11. Single limonitic segregations. Thin section. Contrada Drago, western Sicily. Scale bar = 0.25 mm.

In some cases the felspathic matrix is completely glassy, and various stages of crystallisation can be seen.

This type of alkali volcanism is very rare in the Jurassic of western Sicily – most extrusions are described as basaltic – and it is probable that these trachytic fragments

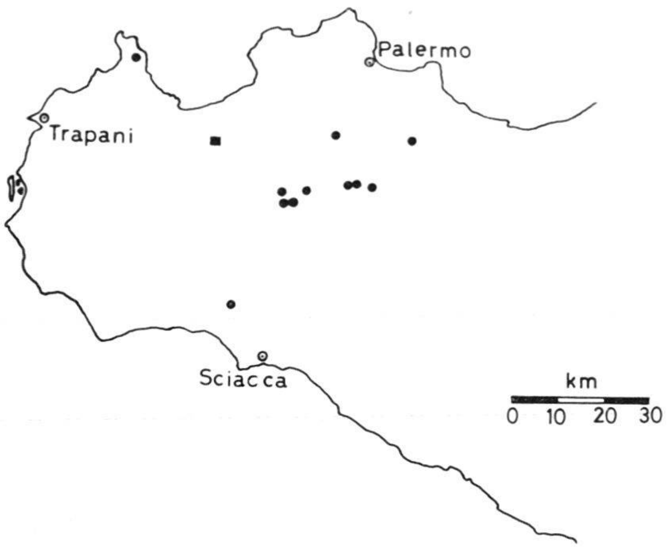

Fig. 12. Toarcian igneous localities, western Sicily. The infilled circles indicate localities where trachytic fragments have been found associated with iron pisolites, immediately above the top of the white Liassic limestones. The black oblong indicates the position of Monte Bonifato where a large-scale trachytic extrusion is present.

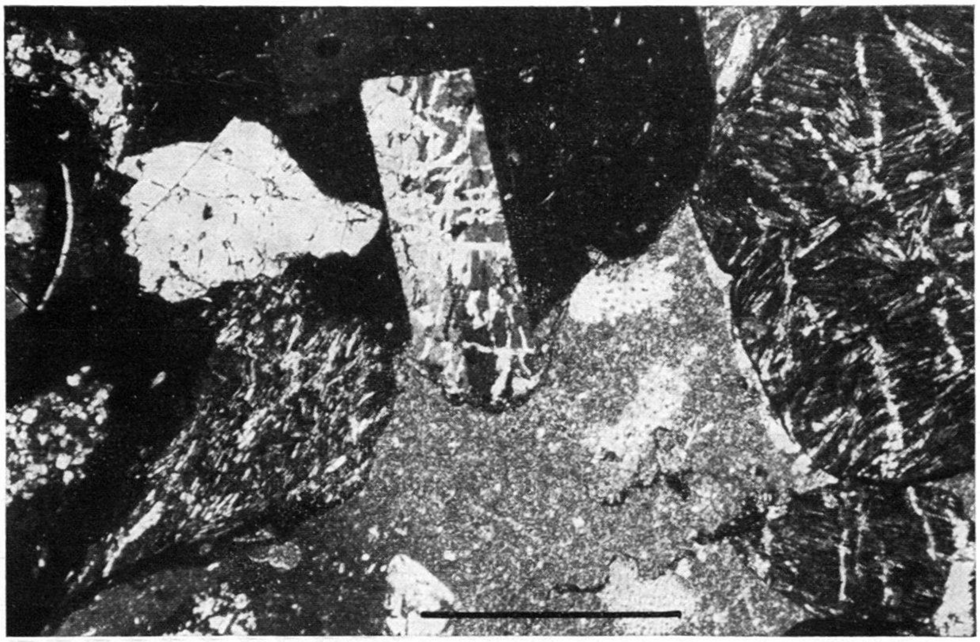

Fig. 13. Phenocrysts of sanidine and fragments of trachytic groundmass with flow structure set in ferruginous limestone. Crossed nicols. Monte Monaco, north-west Sicily. Scale bar = 1 mm.

provide a good marker horizon. However, a thick extrusion of biotite-hornblende trachyte has also been described from Monte Bonifato by WENDT (1963) who considered it to be Bajocian; but there is a possibility that this may also be of Toarcian age (JENKYNS and TORRENS, 1969) and the similarity in texture between this lava and the igneous fragments described here is consistent with a genetic relationship.

Rounded quartz fragments (up to 1 mm diameter) have been found at Rocce che Parla just above the top of the Liassic platform carbonates in a bed dated as Lower Bathonian by WENDT (1963). These fragments are probably also of volcanic origin, but it is impossible to assign them to a known phase of volcanism, since they may have been extensively reworked, and preserved, whilst zonal ammonites have been dissolved. Their age must lie between Pliensbachian and Bathonian, as delimited by the succession (WENDT, 1963, 1969); no quartz phenocrysts have been found associated with the trachytes, so this Rocca che Parla example may record a separate period of acidic volcanism.

Comparison with Modern Submarine Volcanism

A region of submarine acid and intermediate volcanism has been recorded from the East Pacific Rise (ARRHENIUS and BONATTI, 1965); in this area the alkali felspars are relatively little altered (PETERSON and GOLDBERG, 1962), which is consistent with the observations on the Sicilian examples. In other respects, the various secondary products – carbonate, limonite, chlorite – are in agreement with descriptions of altered submarine flows (MATTHEWS, 1961, 1962; NAYUDU, 1964; CRONAN and TOOMS, 1968).

Geochemistry

Electron-microprobe analyses have been undertaken on some of the Toarcian iron pisoliths, and the data is presented in Figures 14 to 16. One of the larger ferromanganese nodules from the pisolite horizon at Monte Maranfusa has also been analysed (Fig. 17), as well as an iron oolith from the Bathonian Twinhoe Beds of Somerset, England (Fig. 18).

Methods

The analyses were obtained by taking 125-second scans across 375 μ traverses in selected parts of the specimen. Errors were minimised by using composite oxide standards for the analyses, but the results have been presented as weight percentages of the elements, except for calcium which has only been analysed semi-quantitatively using a pure limestone standard.

With the graphs presented in Figures 14 to 18, the zero percentage has been calculated for the iron-rich area and since the background is lower for the calcareous phase, this accounts for the scan-line falling below zero in this part of the traverse.

Accuracy for the major element analyses should lie in the range $\pm 5\%$. Errors increase as the amount detected decreases, and for the minor elements an uncertainty value of $\pm 20\%$ is probably suitable. The detection limits, in per cent, of the various elements are set out below:

P	.012	Ti	.011	Mn	.016	Ni	.026	Ba	.028
Si	.027	V	.012	Fe	.023	Cu	.038	$CaCO_3$	.097
Al	.037	Cr	.012	Co	.038	Zn	.034	(Ca)	.039

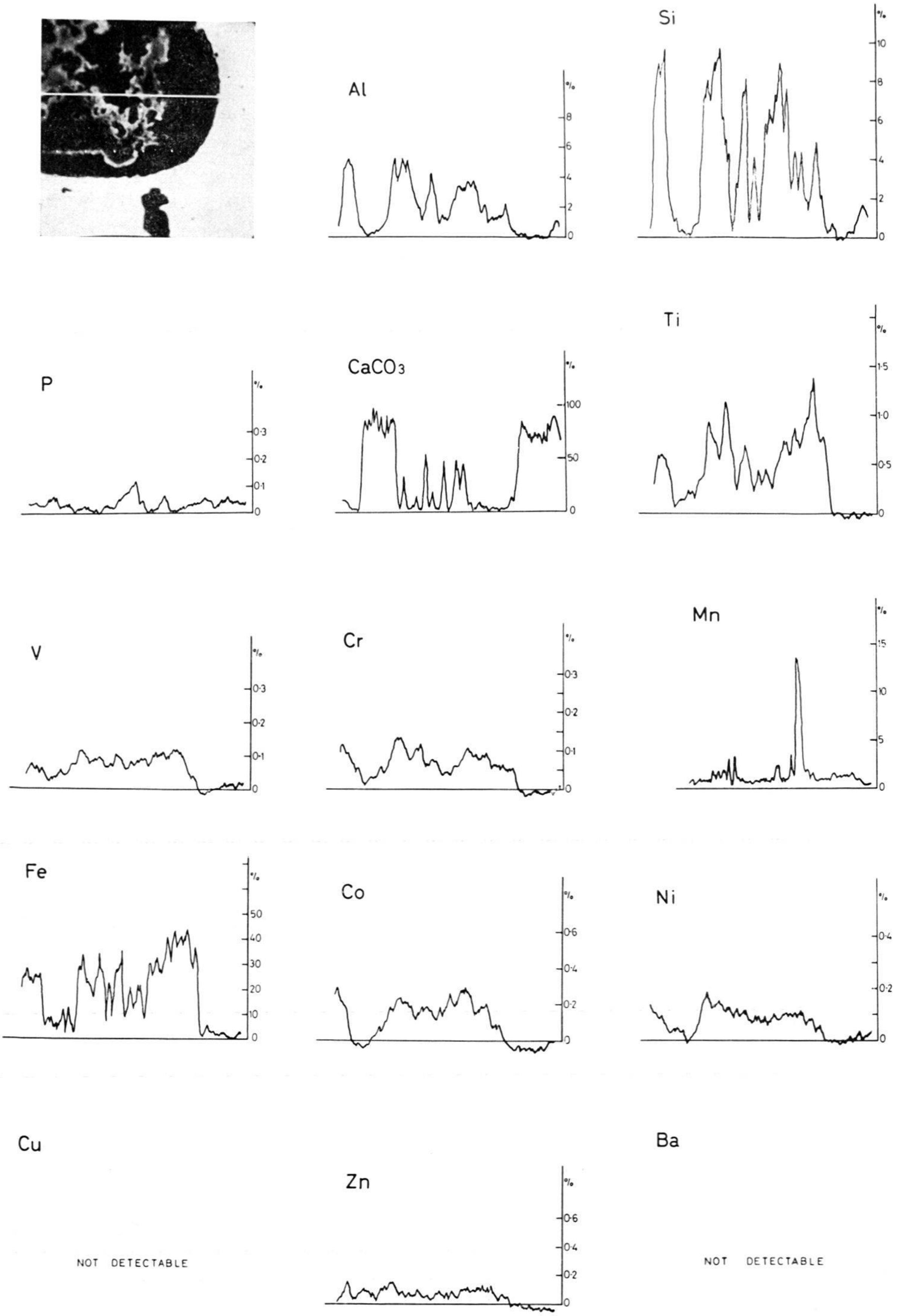

Fig. 14. Electron-probe microanalysis of an iron (chamosite-goethite-haematite) pisolith from the Toarcian of Rocce Maranfusa, western Sicily. Length of scan line = 375 μ.

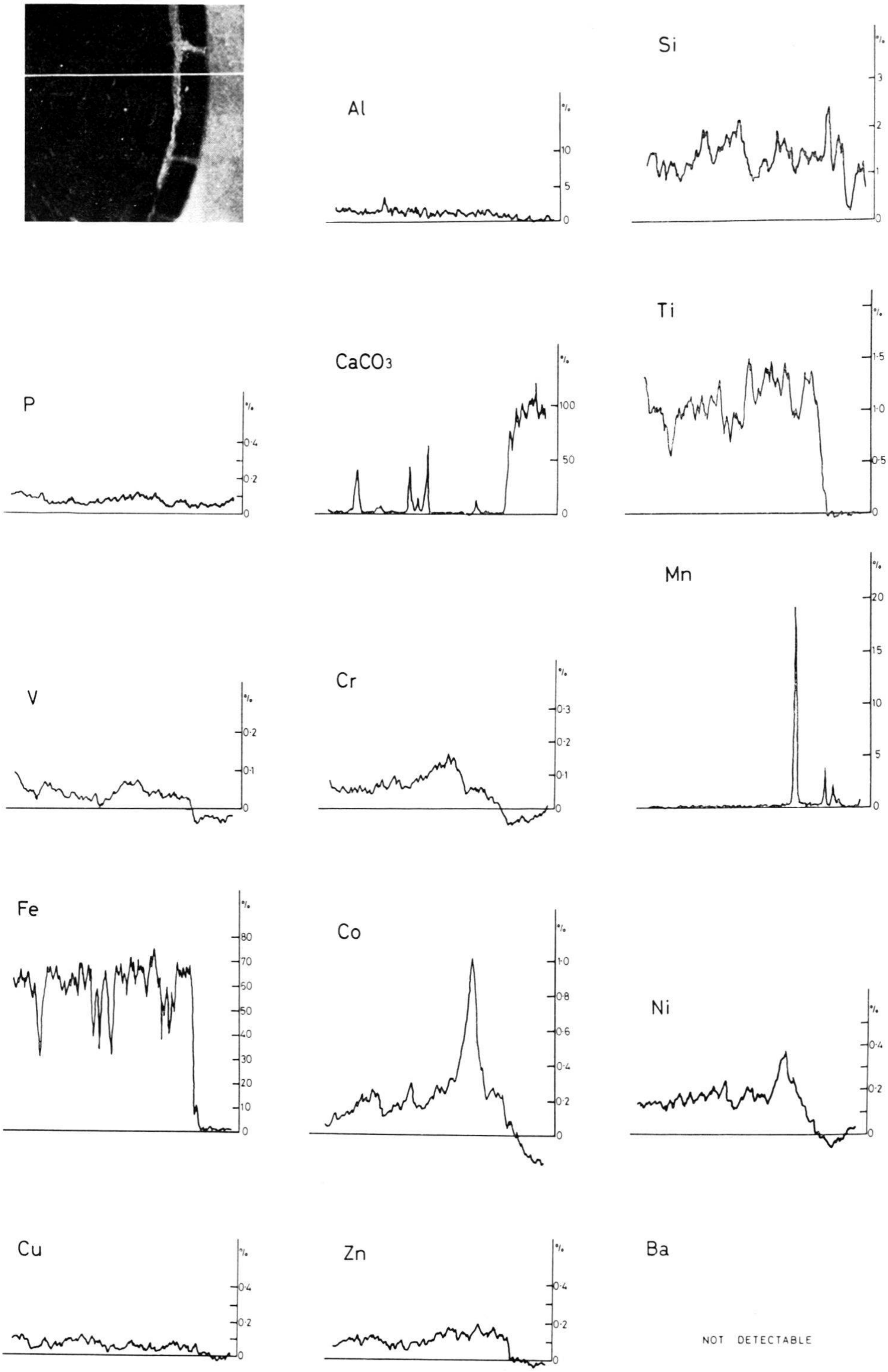

Fig. 15. Electron-probe microanalysis of an iron (goethite-haematite) pisolith from the Toarcian of Monte Galiello, western Sicily. Length of scan line = 375 μ.

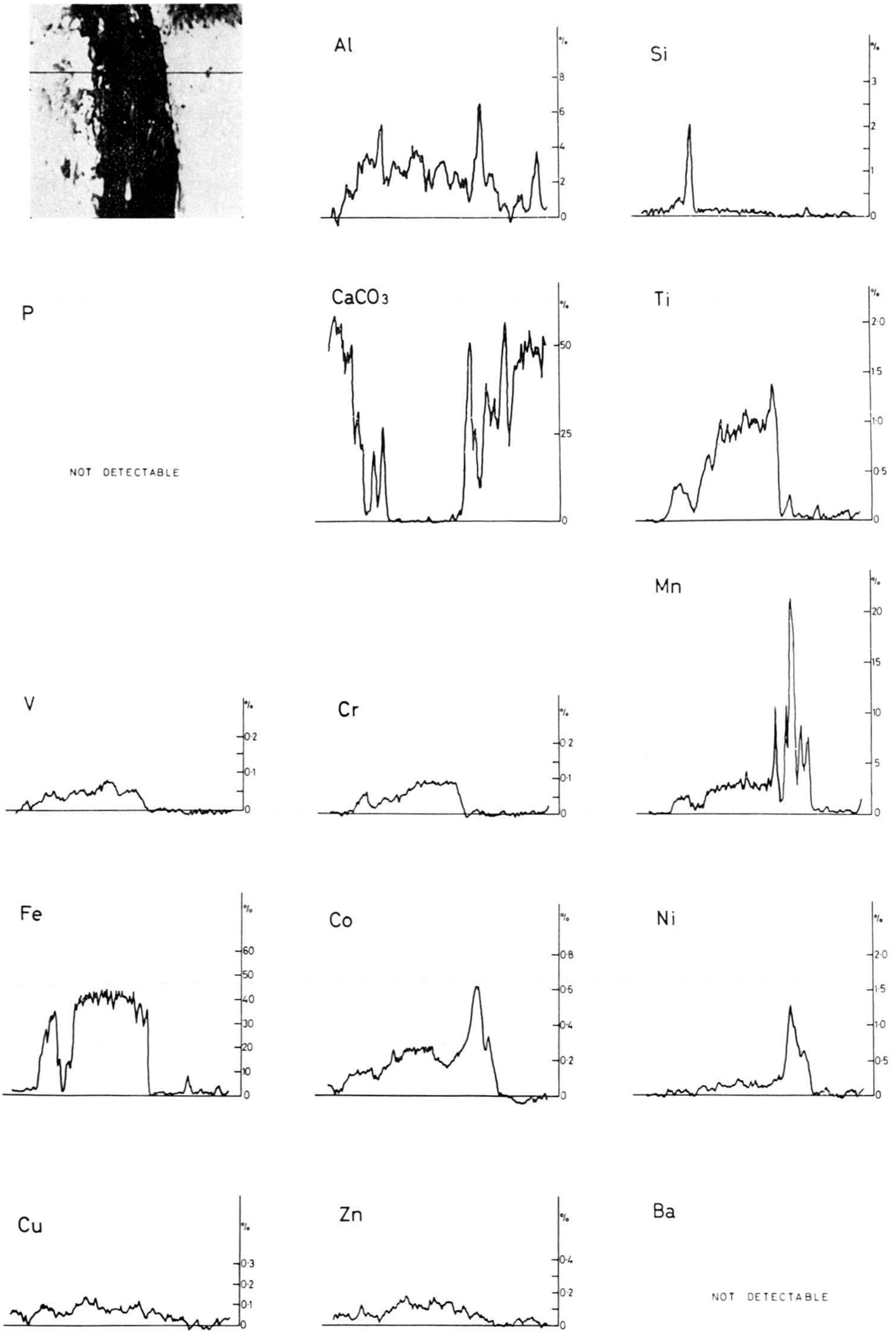

Fig. 16. Electron-probe microanalysis of an iron (goethite) pisolith from the Toarcian of Monte Monaco, north-west Sicily. Length of scan line = 375 μ.

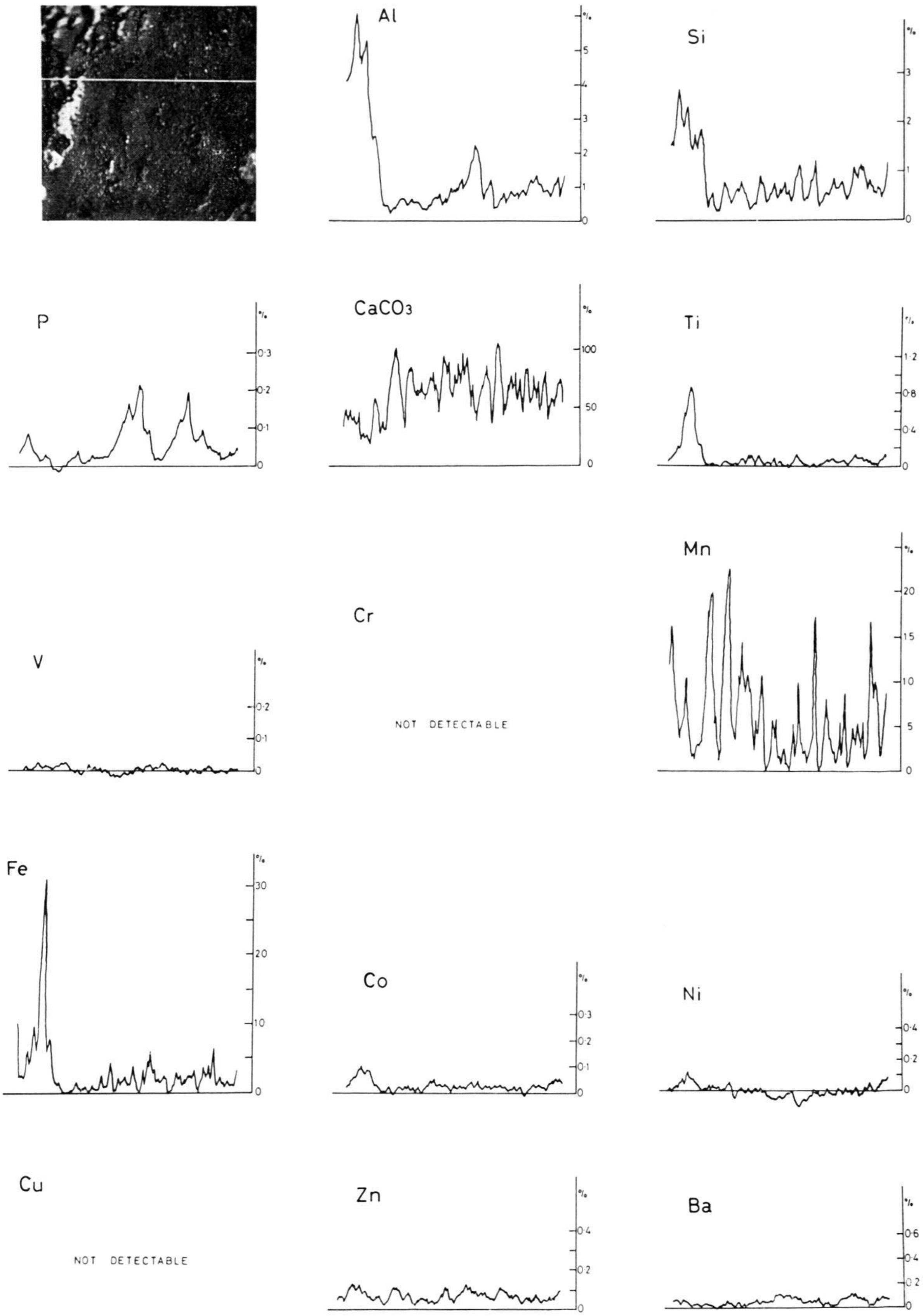

Fig. 17. Electron-probe microanalysis of calcareous ferromanganese nodule from the Toarcian of Monte Maranfusa, western Sicily. Length of scan line = 375 μ.

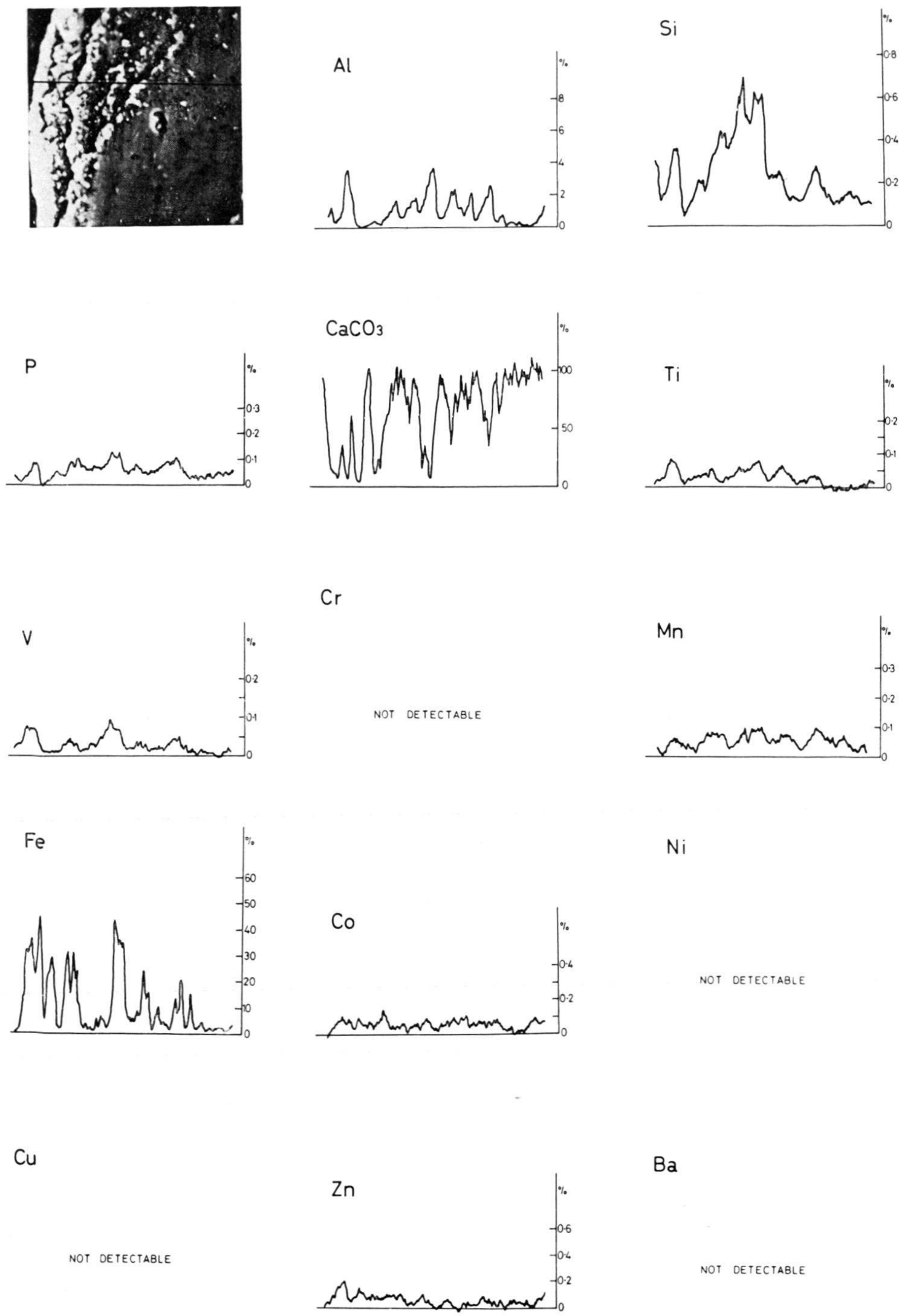

Fig.18. Electron-probe microanalysis of an iron oolith from the Bathonian Twinhoe Beds of Somerset, England. Length of scan line = 375 μ.

Results

It is apparent that the Toarcian iron pisoliths are considerably enriched in trace elements. Perhaps the most striking feature is that all show thin bands (10–15 μ) considerably enriched in manganese. With the samples from Monte Monaco and Monte Galiello, cobalt and nickel are obviously sympathetic with manganese, whereas chromium, titanium and vanadium are covariant with iron. Zinc and copper seem also to be sorbed in the iron-rich phase. These selective sorption phases are less obvious with the Rocce Maranfusa pisolith, where all of the ferromanganiferous material is concentrated in a central band. In all cases the ferromanganese phase is antipathetic to the calcareous matrix.

These results may be compared with electron-probe investigations on modern ferromanganese nodules: BURNS and FUERSTENAU (1966), CRONAN and TOOMS (1968), AUMENTO, LAWRENCE and PLANT (1968) and FRIEDRICH, ROSNER and DEMIRSOY (1969) have reported differing inter-element relationships in the material investigated and it is apparent that sorption phases can be highly variable. All authors are agreed on the association of nickel with manganese, and AUMENTO, LAWRENCE and PLANT found cobalt also sorbed in this phase. BURNS and FUERSTENAU recorded an association of titanium with iron, whereas their other data is not in agreement with that presented here. In modern ferromanganese nodules, there are variations in the relative amounts of iron and manganese, but this variation is not as spectacular as with the Toarcian iron pisoliths.

The concretion from Monte Maranfusa is rather calcareous, with interlayered ferromanganese bands; in most parts of the nodule analysed manganese is present in greater quantities than iron. As with the pisoliths, titanium is obviously covariant with the ferruginous phase.

HALLAM (1966, 1967a, 1969) has proposed a model of Jurassic palaeogeography where a northern area dominated by river drainage was the depositional site of a variety of facies, including ironstones; whereas in a southern domain, in at least some areas, more manganiferous red limestones were laid down. The Sicilian iron pisoliths are associated with the red limestone facies; so, bearing in mind these two depositional provinces, one epicontinental, one "oceanic", it is instructive to compare the chemical composition of a "northern" iron oolith with the more pelagic Sicilian specimens. The Twinhoe oolith was chosen because it comes from a calcareous facies in which ooliths are, as with the Sicilian examples, only sporadically distributed.

From an examination of the chemistry of other sedimentary iron deposits (TAYLOR, 1949; HEGEMANN and ALBRECHT, 1954; KREJCI-GRAF, 1964; HALBACH, 1968; SCHELLMANN, 1969), it is clear that the Twinhoe iron oolith is typical of a Minette ore, although local sources can greatly affect elemental abundance. Comparing the analysis of this oolith (Fig. 18) with the Sicilian iron pisoliths (Figs. 14 to 17), a considerable difference in trace-element abundance can be seen. This bears out the idea that the Sicilian pisoliths were deposited in a more "oceanic" regime, since, by comparison with modern ferromanganese nodules, the pelagic concretions are notably more enriched in minor elements than their epicontinental counterparts (PRICE, 1967). The presence of manganese, also essentially a "pelagic" element, in these pisoliths, and in the nodule from Monte Maranfusa, reinforces this interpretation.

Origin of Iron

With the ferromanganese nodules of the present oceans, two primary elemental sources are postulated (see MERO, 1965): 1. from continental run-off; 2. from leaching of volcanic rock on the sea floor, and direct supply from volcanic effusions. A secondary remobilisation of manganese from the reduced zone below the sediment-water interface has also been suggested (LYNN and BONATTI, 1965). These mechanisms have all been proposed for the origin of the iron in oolitic iron deposits. TAYLOR (1949) suggested that a continental source would be sufficient to account for all of the iron in the Northampton Sand Ironstone, and HALLAM (1966), in a useful review of British Liassic ironstones, accepted this view, as does BUBENICEK (1968). HUMMEL (1922) in a classic paper dealing with the origin of iron-rich rocks through halmyrolysis (submarine leaching) suggested that the iron in iron ooliths could come from oceanic sources: it is essentially this idea, that iron is remobilised from the oceans, albeit in a more sophisticated form, that has been adopted by BORCHERT (1960, 1965). ALDINGER (1955) has suggested that as some iron ooliths are deposited at great distances from land (more than 100 kilometres) a continental source is by no means obvious; and that (1957) iron must be remobilised from a reduced zone to the sediment-water interface to form ooliths.

Reviews on the origin of iron ooliths have been given by DUNHAM (1960), KREJI-GRAF (1964) and HALLAM (1966).

It is obvious that the Toarcian iron pisoliths constitute a special case. KRAUSKOPF (1956, 1957) has shown that, relative to manganese, iron is much less mobile and will thus tend to precipitate near its source; this is in agreement with the continental derivation proposed for the iron in most iron-oolite deposits, but makes a large-scale continental supply of this element less likely as a source for the Sicilian pisoliths. Their high iron content (relative to manganese) is still indicative of a local origin, however, and the association of the rocks with submarine effusives suggests an obvious source.

The iron may have been derived from leaching of the lava or from hydrothermal effusions accompanying the extrusion (see ZELANOV, 1964, for a Recent parallel), and both sources seem likely. The fact that some of the lava, particularly the mafic minerals, has been replaced by carbonate shows that some of the ferromagnesian material must have gone rapidly into solution. The high content of chromium and titanium in the pisoliths may also be indicative of volcanic influences (GOLDBERG and ARRHENIUS, 1958); however, chromium is usually very low in ferromanganese nodules (but may be present in greater amounts in some iron ooliths; see for example, SCHELLMANN, 1969), since this element tends to remain locked up in spinels and end up among the resistates (ARRHENIUS and BONATTI, 1965). High chromium does occur, however, in the hydrothermal precipitates on the East Pacific Rise (BOSTROM and PETERSON, 1966) and in this region BONATTI and JOENSUU (1966) have also recorded pelagic high-iron deposits associated with manganiferous material – and assume a local source for this poorly crystalline and rapidly precipitated goethitic matter. This suggests that direct hydrothermal supply has played a major part in the formation of the Toarcian iron pisoliths.

If the iron was deposited relatively quickly, then it is clear that the manganese-rich bands in the pisoliths and the Monte Maranfusa ferromanganese nodule – representing the normal pelagic "input" – must have been formed more slowly (GOLDBERG and ARRHENIUS, 1958), allowing, in some cases, a greater uptake of some minor elements, possibly by the scavenging mechanism of GOLDBERG (1954). RONA, HOOD, MUSE and BUGLIO (1963) have demonstrated that the amount of manganese coprecipitated with iron is inversely proportional to the rate of precipitation, which is consistent with this. ARRHENIUS, MERO and KORKISCH (1964) have suggested a criterion for distinguishing ferromanganese material deposited by submarine volcanism from that formed from dilute solutions of continental origin: they propose that a manganese to cobalt ratio of less than 300 is probably indicative of volcanic origin. From a study of the cobalt and manganese concentrations in the manganese-rich regions of the iron pisoliths (Figs. 14 to 16), it is clear that a ratio considerably less than 300 is obtained, which is further evidence for a volcanic origin – although this type of numerical exercise must clearly be treated with some caution.

Thus a local volcanic source, leading to relatively early precipitation of iron, seems the best explanation of the origin of the west Sicilian iron pisolites.

Depositional Environment

As the Toarcian iron pisolites occur only as remanié beds, and are considerably condensed, it is obvious that currents have been instrument in their formation, and it is likely that deposition took place on open "ocean" seamounts after the Liassic carbonate platform had broken up (JENKYNS, 1969). The association of iron oolites with high-energy environments has been remarked upon by numerous authors and it is evident that an essentially non-depositional environment is required for the concentration of iron (HALLAM, 1967 b); and indeed BLACK, HILL, LAUGHTON and MATTHEWS (1964) have recorded a ferruginous limestone from Vigo Seamount, off the Iberian Coast.

Thus the depositional environment of the Toarcian iron pisolites is thought to be very similar to that of the main ferromanganiferous condensed sequences which overlie them (see JENKYNS, 1967), but in the former case with submarine effusives and exhalations playing a more immediate role. The environment was probably strongly oxidising in most places, although small reduction zones may have enabled chamosite to form: PALMER (1964) has recorded a comparable association of glauconite and ferromanganese crusts from Rodriguez Seamount.

The presence of probable traces of boring algae in the Toarcian iron pisolites, plus the fact that they are underlain and overlain by stromatolitic sediments, suggests that the tops of the seamounts probably reached to within tens of metres of the surface.

Further Examples of Pelagic Iron Ooliths

During the Jurassic there was large-scale formation of oolitic iron deposits in northern epicontinental regions (HALLAM, 1967 a) and this realm extended south to parts of the Alps (LUCAS, 1942, p. 79) and Carpathians (MIŠÍK, 1964) where chamositic and haematitic ooliths were also formed, particularly during the Lias. Epicontinental conditions also existed over parts of southern Spain and iron oolites also occur there (GEYER, 1967). In North Africa, also, small-scale oolitic iron bodies are not uncommon (LUCAS, 1942), and in this case deposition may be related to a southern epicontinental influence. However, in the pelagic red limestones of Tethyan facies such oolitic iron deposits are certainly very rare.

Geyer (1967) has, however, recorded the presence of sparse iron ooliths associated with a limonite crust in the subbetic zone of Spain: this horizon is developed in red limestone facies and contains a fauna of Toarcian-Bajocian age. Since this is a pelagic facies, it is likely that the "limonite" crust contains considerable quantities of manganese. It is also interesting to note that southern Spain was, like Sicily, a region of submarine volcanism during the Jurassic.

Conclusions

The Toarcian iron pisolites of western Sicily, which occur as remanié horizons at several Jurassic localities, contain limonite (goethite), haematite, and, in rare cases, chamosite. Since these iron pisoliths are developed in pelagic red limestones, a continental origin for the limonitic material seems unlikely; however, to produce high iron (relative to manganese) deposits in an "oceanic" realm it is still necessary to postulate a local supply, since iron will tend to precipitate near its source (Krauskopf, 1958).

The iron pisolites contain igneous material – sanidine trachyte – and it is probable that much of the iron and trace elements that compose the pisoliths were derived from hydrothermal effusions that accompanied the submarine extrusion.

The presence of chamosite, probable traces of boring algae, in the iron pisolites and the stratigraphic position of the bed between two shallow-water sediments suggests that deposition took place in water tens of metres deep, probably on "oceanic" limestone seamounts.

Acknowledgments

This work was carried out whilst the author held a NERC research studentship at the University of Leicester, Great Britain; and the paper completed at Basel University, Switzerland, during the tenure of a Royal Society European Fellowship. Both these awards are gratefully acknowledged.

I am grateful to Dr. J. A. Dixon for carrying out the microprobe analyses, and to Dr. J. D. Hudson and Dr. D. Bernoulli for advice and helpful comments on the manuscript. For help in the field my thanks go to Dr. H. S. Torrens.

REFERENCES

Aldinger, H. (1955): *Die Eisenoolithe aus dem Dogger der Bohrung Scherstetten 1.* Geol. Bav. *24*, 89–96.
– (1957): *Zur Entstehung der Eisenoolithe im Schwäbischen Jura.* Z. deutsch. Geol. Ges. *109*, 7–9.
Arrhenius, G., and Bonatti, E. (1965): *Neptunism and Vulcanism in the Ocean.* In: M. Sears (Editor), *Progress in Oceanography* (Hans Pettersson volume) *3*, 7–22.
Arrhenius, G., Mero, J., and Korkisch, J. (1964): *Origin of Oceanic Manganese Minerals.* Science *144*, 170–173.
Aumento, F., Lawrence, D. E., and Plant, A. G. (1968): *The Ferromanganese Pavement on San Pablo Seamount.* Pap. geol. Surv. Can. *68-32*, 1–30.
Bathurst, R. G. C. (1966): *Boring Algae, Micrite Envelopes and Lithification of Molluscan Biosparites.* Geol. J. *5*, 15–32.
Black, M., Hill, M. N., Laughton, A. S., and Matthews, D. H. (1964): *Three Non-magnetic Seamounts off the Iberian Coast.* Quart. J. geol. Soc. London *120*, 477–517.
Bonatti, E., and Joensuu, O. (1966): *Deep-sea Iron Deposit from the South Pacific.* Science *154*, 643–645.
Bonatti, E., and Nayudu, Y. R. (1965): *Origin of Manganese Nodules on the Ocean Floor.* Am. J. Sci. *263*, 17–39.

BORCHERT, H. (1960): *Genesis of Marine Sedimentary Iron Ores*. Trans. Inst. Min. Metal. *67*, 261–279.
– (1965): *Formation of Marine Sedimentary Iron Ores*. In: J. P. Riley and G. Skirrow (Editors), *Chemical Oceanography* (Academic Press, London and New York) *2*, 159–204.
BOSTROM, K., and PETERSON, M. N. A. (1966): *Precipitates from Hydrothermal Exhalations on the East Pacific Rise*. Econ. Geol. *61*, 1258–1265.
BROQUET, P., CAIRE, A., et MASCLE, G. (1966): *Structure et évolution de la Sicile occidentale (Madonies et Sicani)*. Bull. Soc. geol. Fr. *8*, 994–1013.
BUBENICEK, L. (1968): *Géologie des minerais de fer oolithiques*. Mineralium Depos. *3*, 89–108.
BURNS, R. G., and FUERSTENAU, D.W. (1966): *Electron-probe Determination of Inter-element Relationships in Manganese Nodules*. Am. Miner. *51*, 895–902.
CRONAN, D. S., and TOOMS, J. S. (1968): *A Microscopic and Electron Probe Investigation of Manganese Nodules from the Northwest Indian Ocean*. Deep-Sea Res. *15*, 215–223.
CURTIS, C. D., and SPEARS, D. A. (1968): *The Formation of Sedimentary Iron Minerals*. Econ. Geol. *63*, 257–270.
DUNHAM, K. C. (1960): *Syngenetic and Diagenetic Mineralisation in Yorkshire*. Proc. Yorks. geol. Soc. *32*, 229–284.
FARINACCI, A. (1967): *La serie giurassico-neocomiana di Monte Lacerone (Sabina). Nuove vedute sull'interpretazione paleogeografica delle aree di facies umbro-marchigiana*. Geologica Rom. *6*, 421–480.
FRIEDRICH, G., ROSNER, B., und DEMIRSOY, S. (1969): *Erzmikroskopische und mikroanalytische Untersuchungen an Manganerzkonkretionen aus dem Pazifischen Ozean*. Mineral. Deposita *4*, 298–307.
GEYER, O. F. (1967): *Zur faziellen Entwicklung des subbetischen Juras in Südspanien*. Geol. Rdsch. *56*, 973–992.
GOLDBERG, E. D. (1954): *Marine Geochemistry. I. Chemical Scavengers of the Sea*. J. Geol. *62*, 249–265.
GOLDBERG, E. D., and ARRHENIUS, G. (1958): *Chemistry of Pacific Pelagic Sediments*. Geochim. Cosmochim. Acta *13*, 153–212.
GRIFFIN, J. J., WINDOM, H., and GOLDBERG, E. D. (1968): *The Distribution of Clay Minerals in the World Ocean*. Deep-Sea Res. *15*, 433–459.
HALBACH, P. (1968): *Zum Gehalt von Phosphor und anderen Spurenelementen in Braueneisenerzooiden aus dem fränkischen Dogger beta*. Contr. Mineral. Petrol. *18*, 241–251.
HALLAM, A. (1966): *Depositional Environment of British Liassic Ironstones Considered in the Context of Their Facies Relationships*. Nature London *209*, 1306–1307.
– (1967a): *Sedimentology and Palaeogeographic Significance of Certain Red Limestones and Associated Beds in the Lias of the Alpine Region*. Scott. J. Geol. *3*, 195–220.
– (1967b): *An Environmental Study of the Upper Domerian and Lower Toarcian in Great Britain*. Phil. Trans. R. Soc., Ser. B *252*, 393–445.
– (1969): *Faunal Realms and Facies in the Jurassic*. Palaeontology *12*, 1–18.
HEGEMANN, F., und ALBRECHT, F. (1954): *Zur Geochemie oxydischer Eisenerze*. Chemie Erde *17*, 81–103.
HESSLAND, I. (1949): *Lower Ordovician Penetrative and Enveloping Algae from the Siljan District. Investigations of the Lower Ordovician of the Siljan District, Sweden*. Bull. Geol. *33*, 409–428.
HOLLMANN, R. (1964): *Subsolutions-Fragmente (Zur Biostratinomie der Ammonoidea im Malm des Monte Baldo/Norditalien)*. Neues Jb. Geol. Paläont. Abh. *119*, 22–82.
HOLMES, R. W. (1957): *Solar Radiation, Submarine Daylight and Photosynthesis*. In: J. W. Hedgpeth (Editor), *Treatise on Marine Ecology and Palaeoecology. I. Ecology*. Geol. Soc. Am. Mem. *67*, 109–128.
HUMMEL, K. (1922): *Die Entstehung eisenreicher Gesteine durch Halmyrolyse*. Geol. Rdsch. *13*, 41–81, 97–136.
JENKYNS, H. C. (1967): *Fossil Manganese Nodules from Sicily*. Nature London *216*, 673–674.
– (1969): *Sedimentology of the West Sicilian Jurassic*. Thesis (University of Leicester), 279 pp.
JENKYNS, H. C., and TORRENS, H. S. (1969): *Palaeogeographic Evolution of Jurassic Seamounts in Western Sicily*. Preprint, Colloquium on Mediterranean Jurassic Stratigraphy, Budapest 1969, 19 pp.
KRAUSKOPF, K. B. (1956): *Separation of Manganese from Iron in the Formation of Manganese Deposits in Volcanic Associations*. In: J. G. Reyna (Editor), *Symposium sobre yacimientos de manganeso. I. El manganeso en general*. XX. Int. geol. Congr., 119–131.

– (1957): *Separation of Manganese from Iron in Sedimentary Processes*. Geochim. Cosmochim. Acta *12*, 61–84.

KREJI-GRAF, K. (1964): *Geochemical Diagnosis of Facies*. Proc. Yorks. geol. Soc. *34*, 469–521.

LUCAS, G. (1942): *Description géologique et pétrographique des Monts de Ghar Rhouban et du Sidi el Abed (frontière algero-marocaine)*. Bull. Serv. Carte geol. Alger., 2e s., *16*, 2 vols.

LYNN, D. C., and BONATTI, E. (1965): *Mobility of Manganese in Diagenesis of Deep-sea Sediments*. Mar. Geol. *3*, 457–474.

MATTHEWS, D. H. (1961): *Lavas from an Abyssal Hill on the Floor of the North Atlantic Ocean*. Nature London *190*, 158–159.

– (1962): *Altered Lavas from the Floor of the Eastern North Atlantic*. Nature London *194*, 368–369.

MERO, J. L. (1965): *The Mineral Resources of the Sea* (Elsevier, Amsterdam), 312 pp.

MIŠÍK, M. (1964): *Lithofazielles Studium des Lias der Grossen Fatra und des westlichen Teils der Niederen Tatra*. Sbornik Geol. Vied: Západné Karpaty; Rad ZK-Zväzok, *1*, 9–92.

NADSON, G. (1927): *Les algues pérforantes, leur distribution et leur rôle dans la nature*. C. r. Acad. Sci. *184*, 1015–1017.

NAYUDU, Y. R. (1964): *Palagonite Tuffs (Hyaloclastites) and the Products of Post-eruptive Processes*. Bull. volcan. *27*, 391–410.

PALMER, H. D. (1964): *Marine Geology of Rodriquez Seamont*. Deep-Sea Res. *11*, 737–756.

PETERSON, M. N. A., and GOLDBERG, E. D. (1962): *Felspar Distribution in South Pacific Pelagic Sediments*. J. geophys. Res. *67*, 3477–3492.

PORRENGA, D. H. (1965): *Chamosite in Recent Sediments of the Niger and Orinoco Deltas*. Geol. Mijnbouw *44*, 400–403.

– (1966): *Clay Minerals in Recent Sediments of the Niger Delta*. Clays, Clay Minerals, Proc. 14th Natl. Conf. Clays, Clay Minerals, 221–233.

– (1967): *Glauconite and Chamosite as Depth Indicators in the Marine Environment*. Mar. Geol. *5*, 495–501.

PRICE, N. B. (1967): *Some Geochemical Observations on Manganese-iron Oxide Nodules from Different Depth Environments*. Mar. Geol. *5*, 511–538.

RADWANSKI, A., and SZULCZEWSKI, M. (1965): *Jurassic Stromatolites of the Villány Mountains (Southern Hungary)*. Annls Univ. Scient. bpest. Rolando Eötvös Sect. geol. *9*, 87–107.

RASTALL, R. H., and HEMINGWAY, J. E. (1939): *Black Oolites in the Dogger of North-east Yorkshire*. Geol. Mag. *76*, 225–233.

ROHRLICH, V., PRICE, N. B., and CALVERT, S. E. (1969): *Chamosite in Recent Sediments of Loch Etive, Scotland*. J. sediment. Petrol. *39*, 624–631.

RONA, E. D. W., HOOD, O. W., MUSE, L., and BUGLIO, B. (1962): *Activation Analysis of Manganese and Zinc in Sea Water*. Limnol. Oceanogr. *7*, 201–206.

SCHELLMANN, W. (1969): *Die Bildungsbedingungen sedimentärer Chamosit- und Hämatit-Eisenerze am Beispiel der Lagerstätte Eche*. Neues Jb. Miner. Abh. *111*, 1–31.

SZULCZEWSKI, M. (1963): *Stromatolites from the High-tatric Bathonian of the Tatra Mountains*. Acta geol. pol. *13*, 125–141.

– (1967): *Stromatolitic Structures within Middle Jurassic Transgressive Deposits at Wola Morawicka*. Annls Soc. geol. Pol. *37*, 515–528.

– (1968): *Jurassic Stromatolites of Poland*. Acta geol. pol. *18*, 1–99.

TAYLOR, J. H. (1949): *Petrology of the Northampton Sand Ironstone Formation*. Mem. geol. Surv. G.B., H.M.S.O., London, 111 pp.

VAN HOUTEN, F. B. (1964): *Origin of Red Beds – Some Unsolved Problems*. In: A. E. M. Nairn (Editor), *Problems in Palaeoclimatology* (Interscience London), 647–659.

WENDT, J. (1963): *Stratigraphisch-paläontologische Untersuchungen im Dogger Westsiziliens*. Boll. Soc. paleont. ital., *2*, 57–145

– (1969a): *Die stratigraphisch-paläogeographische Entwicklung des Jura in Westsizilien*. Geol. Rdsch. *58*, 735–755.

– (1969b): *Stratigraphie und Paläogeographie des Roten Jurakalks im Sonnwendgebirge (Tirol, Österreich)*. Neues Jb. Geol. Paläont. Abh. *132*, 219–238.

ZELANOV, K. K. (1964): *Iron and Manganese in Exhalations of the Submarine Banu Wuhu Volcano, Indonesia*. Dokl. Acad. Sci. U.S.S.R. Earth Sci. Sect. *155*, 94–96.