# Fossil managese nodules from the West Sicilian Jurassic

Autor(en): **Jenkyns, Hugh C.**

Objekttyp: **Article**

Zeitschrift: **Eclogae Geologicae Helvetiae**

Band (Jahr): **63 (1970)**

Heft 2

PDF erstellt am: **24.07.2024**

Persistenter Link: https://doi.org/10.5169/seals-163867

| Eclogae geol. Helv. | Vol. 63/3 | Pages 741–774 | With 24 figures and 1 table in the text | Basle, Dec. 1970 |
| --- | --- | --- | --- | --- |

# Fossil Manganese Nodules from the West Sicilian Jurassic

By HUGH C. JENKYNS

Department of Geology, University of Oxford, Great Britain

## ABSTRACT

Fossil ferromanganese crusts, nodules and pavements are contained in stratigraphically condensed pelagic limestones from the Middle Jurassic of western Sicily; and a similar association of iron-manganese deposits with condensed pelagic sequences is notable throughout the Tethyan region. The west Sicilian concretions contain goethite, haematite and todokorite as fine-grained phases; their internal structure consists of iron-manganese segregations in a calcite matrix. Electron-microprobe study indicates that the amount of iron and manganese varies considerably in nodules from different localities, notwithstanding the disparity in carbonate content; and the same is true of the minor elements. The most consistently established inter-element relationships are Ni, Ba with Mn, and Ti with Fe – but these associations are by no means invariably developed.

For western Sicily, submarine volcanism seems to have been the most immediate source of supply for the formation of the concretions; and this may well have been the case elsewhere in the Alpine-Mediterranean region; however, the Jurassic was a time of widespread sedimentary iron-ore formation in epicontinental northern Europe, and river drainage must have also supplied some manganese to the Tethyan Ocean. These mineral concretions are interpreted as being formed on ancient limestone (non-volcanic) seamounts. The presence of algal stromatolites in many of the condensed sequences suggests formation within the photic zone; and this relatively shallow-water origin may have affected the minor-element composition of the concretions, particularly with reference to copper and vanadium.

## RIASSUNTO

Le formazioni pelagiche condensate del Giurassico medio della Sicilia occidentale contengono spesso delle croste, dei noduli e degli estesi rivestimenti ferromanganesiferi che costituiscono degli equivalenti fossili dei depositi analoghi che si trovano negli oceani attuali. L'associazione di tali depositi con calcari pelagici condensati si trova frequentemente nella regione alpino-mediterranea. Le concrezioni della Sicilia occidentale contengono goetite, ematite e todocorite a grana molto fine: la loro struttura interna consiste di segregazioni laminate in una matrice di calcite. Lo studio alla microsonda elettronica ha rilevato delle variazioni considerovoli nei contenuti relativi di ferro e di manganese per i noduli provenienti da località differenti; queste variazioni sono indipendenti dalla quantità di carbonato. Le stesse relazioni si riscontrano per gli elementi minori. Nei casi più frequenti Ni e Ba sono associati con Mn, e Ti con Fe.

Nella Sicilia occidentale l'origine delle concrezioni sembra per lo più legata al vulcanismo sottomarino, e possibilmente questa relazione genetica esiste anche in altre parti della Tetide. Comunque nel Giurassico si sono formati dei giacimenti sedimentari di minerali di ferro nei mari epicontinentali de'l'Europa settentrionale, ed i fiumi hanno apportato sicuramente anche del manganese entro il bacino della Tetide. Le concrezioni ferromanganesifere sono interpretate come depositi di «seamounts.» La presenza di stromatoliti algali in molte serie condensate indica una deposizione nella zona della fotosintesi, e quest'ambiente non molto profondo può anche avere influenzato la distribuzione degli elementi minori, ed in particolare i contenuti di Cu e V.

## Introduction

Since the discovery of manganese nodules during the course of the "Challenger" expedition (1873–76), these concretions have constantly held a place in the pages of oceanographic literature. Fossil nodules, however, although recognised soon after the publication of the "Challenger's" results have received little attention, and although such concretions are by no means uncommon in the geological succession, and are often recorded, their true nature and significance has not always been realised. A brief review of documented occurrences of fossil nodules will therefore be given.

JUKES BROWNE & HARRISON (1892) in describing the Tertiary Barbados Earth referred, rather cryptically, to "hollow spaces ... which appear to be the casts of small manganese nodules". This seems to be the first reference to fossil concretions of this type. SOKOLOW (1901) described some irregular pyrolusite concretions, some of which had knobbly surfaces and concentric shells, from the Tertiary of Russia; they were associated with clays, sands, and shallow-water fossils, and were compared by SOKOLOW to the Recent nodules from the Black Sea and particularly to those of Loch Fyne, Scotland, where similar molluscan faunas and sediments occur (BUCHANAN, 1891; MURRAY & IRVINE, 1894).

MOLENGRAAF (1916, 1922) described what is probably the best-known occurrence of fossil nodules: those from the Cretaceous red clays of western Timor. AUDLEY-CHARLES (1965) has recently described and analysed similar concretions from the eastern part of this island. HEIM (1924), in a brilliant paper applying modern oceanographic evidence to the interpretation of Alpine geology, compared the manganese nodules from the Lower Jurassic limestones at Gosau, Austria, to those found in the deep sea. GRUNWALD (1964) interpreted some manganese carbonate concretions from the Pierre Shale of South Dakota, U.S.A., as fossil manganese (oxide-hydroxide) nodules that had undergone diagenetic alteration. SOREM & GUNN (1967) related some features of parts of the Tertiary manganese deposits of the Olympic Peninsular, Washington, U.S.A., to modern nodules.

JENKYNS (1967) briefly described and interpreted the nodules from western Sicily; JURGAN (1967, p. 46–47, 1969) compared the ferromanganese concretions from the Jurassic of the Berchtesgadener Alps, Germany, with those from the Baltic, Atlantic and Pacific, and considered that the fossil nodules signified slow sedimentation rates in oxidising environments. HURLEY (1966) and FISCHER & GARRISON (1967) have recorded some pancakes of ferromanganese partly embedded in hard Caenozoic limestones dredged from off Barbados: these may perhaps qualify as fossil nodules. FABRICIUS (1968) has figured a manganese nodule from the Sonnwend Mountains, Tirol, Austria, and WENDT (1969a) has further described the nodules from this area and related some of their structural features to those in modern concretions. GARRISON & FISCHER (1969) have also figured a ferromanganese nodule from the Adnet Beds of Austria. GULBRANDSEN & REESER (1969) have described and analysed some Permian manganese nodules from an argillaceous sandstone bed near Dillon, Montana, U.S.A.

In the present study fossil nodules from the west Sicilian Jurassic will be described further and details of their geochemistry will be presented; these concretions occur in comparable facies to those described by HEIM (1924), JURGAN (1967, 1969), FABRICIUS (1968), WENDT (1969a) and GARRISON & FISCHER (1969).

## Occurrence in western Sicily and stratigraphic relations

Ferromanganese nodules occur throughout western Sicily associated with the pelagic red limestone facies typical of the Tethyan Jurassic, and are invariably localised in extremely condensed sequences (WENDT, 1963; JENKYNS, 1967). The distribution of the nodule-bearing red limestones is shown in Fig. 1 as adapted from WENDT (1969b).

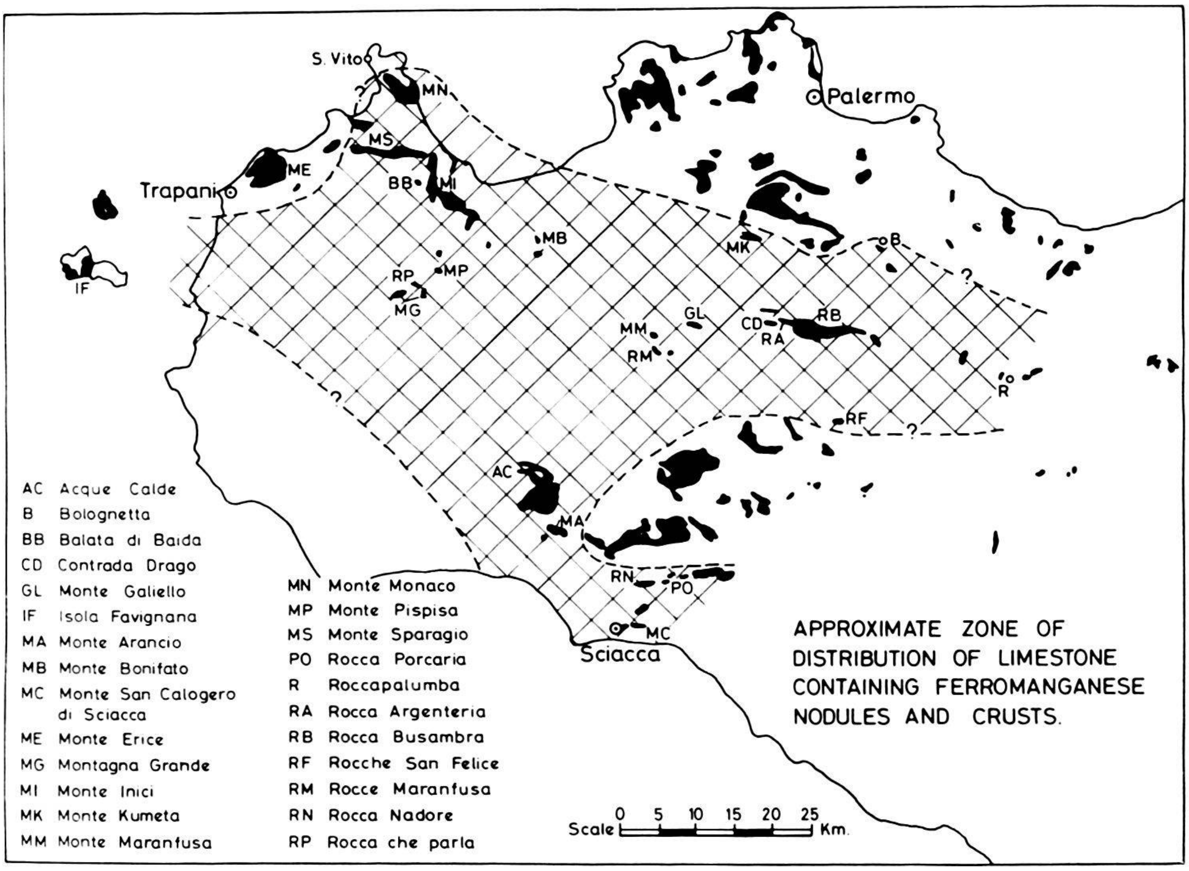


Fig. 1. Approximate zone of distribution of Jurassic red limestone containing ferromanganese crusts and nodules in western Sicily. Modified from WENDT, 1969b.

The ferromanganiferous condensed sequences can overlie a variety of facies, most commonly a shallow-water white limestone, but other deposits such as crinoidal limestones and iron pisolites may intervene between this white limestone and the beds containing ferromanganese nodules (Fig. 2). The condensed sequences are generally of Middle Jurassic age, sensu ARKELL (1956): for more precise data, see WENDT (1963) – and may be overlain by red marly nodular limestones and cherts, or by oolitic and pelletal deposits.

## Description of the ferromanganese nodules

A brief description of the nodules and crusts was given by JENKYNS (1967). Different characteristic forms occur at different localities: for example, at Rocca Busambra, Rocca Argenteria, and at Contrada Drago beds of concentric nodules and thin ferro-

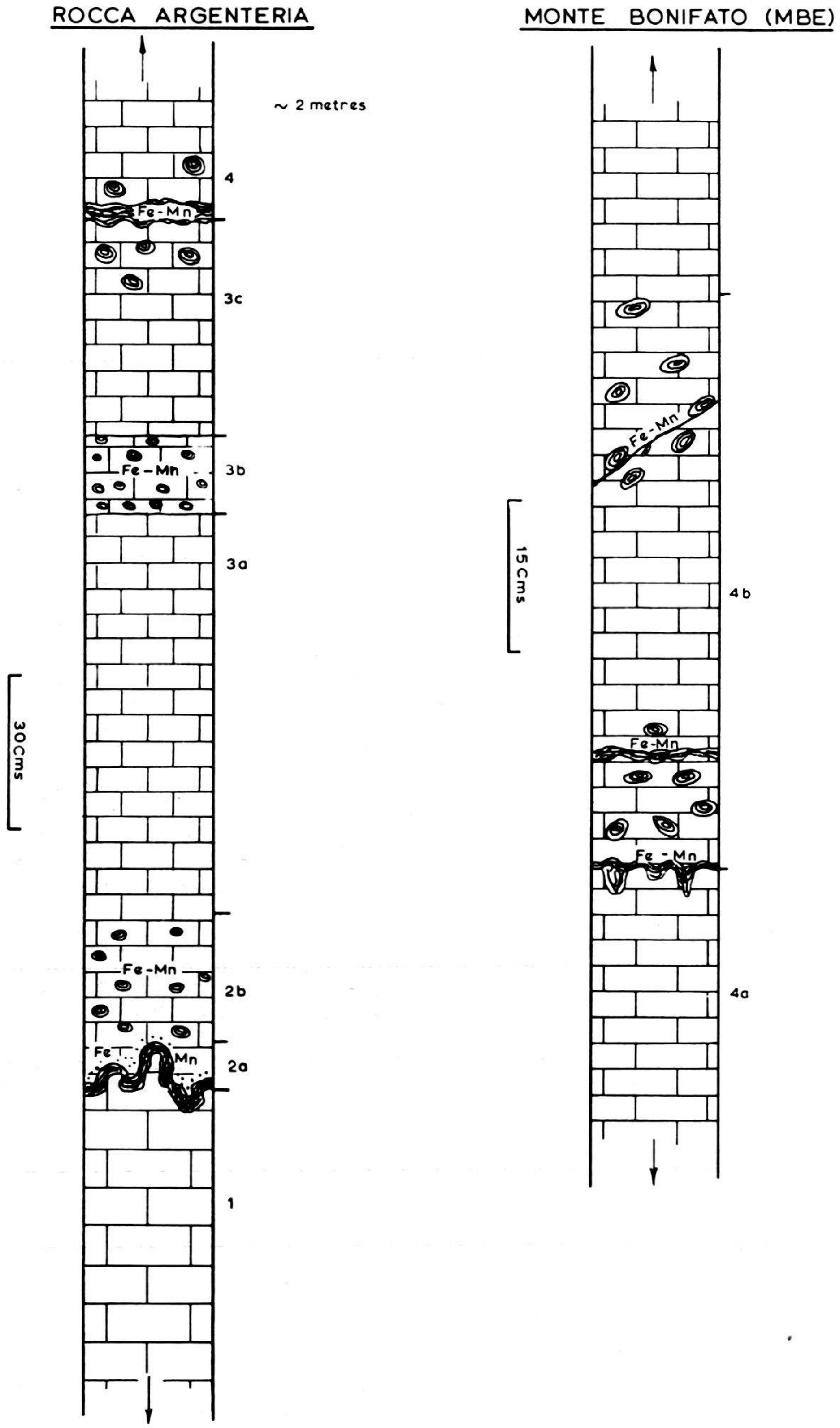


Fig. 2. Stratigraphical sections in condensed sequences from two localities in western Sicily showing vertical distribution of ferromanganese nodules and crusts. Rocca Argenteria: Bed 1, Liassic platform carbonates with upper karst surface; Bed 2, iron pisoliths and ferromanganese nodules in red pelagic limestone; Beds 3 and 4, pink pelagic limestone with ferromanganese nodules. Monte Bonifato: Bed 4, red pelagic limestone with ferromanganese nodules (see WENDT, 1963).

manganese pavements are well developed (Fig. 3 and 4); here distinct populations of nodules with particular size ranges are characteristic of each ferromanganese horizon and are usually separated by barren sediments (Fig. 2 ; see also JENKYNS, 1970, Fig. 2). The concentration of nodules in certain horizons has been observed by STRAKOV (1961) in present-day ocean sediments. The aforementioned localities also compare well with the Blake Plateau where both nodules and continuous pavements occur (MERO, 1965; PRATT & MCFARLIN, 1966). At Rocche San Felice and Monte Kumeta thick fused crusts occur (Fig. 5 and 6) and the Monte Kumeta deposit bears a quite striking resemblance to that on San Pablo seamount (AUMENTO, LAWRENCE & PLANT, 1968).

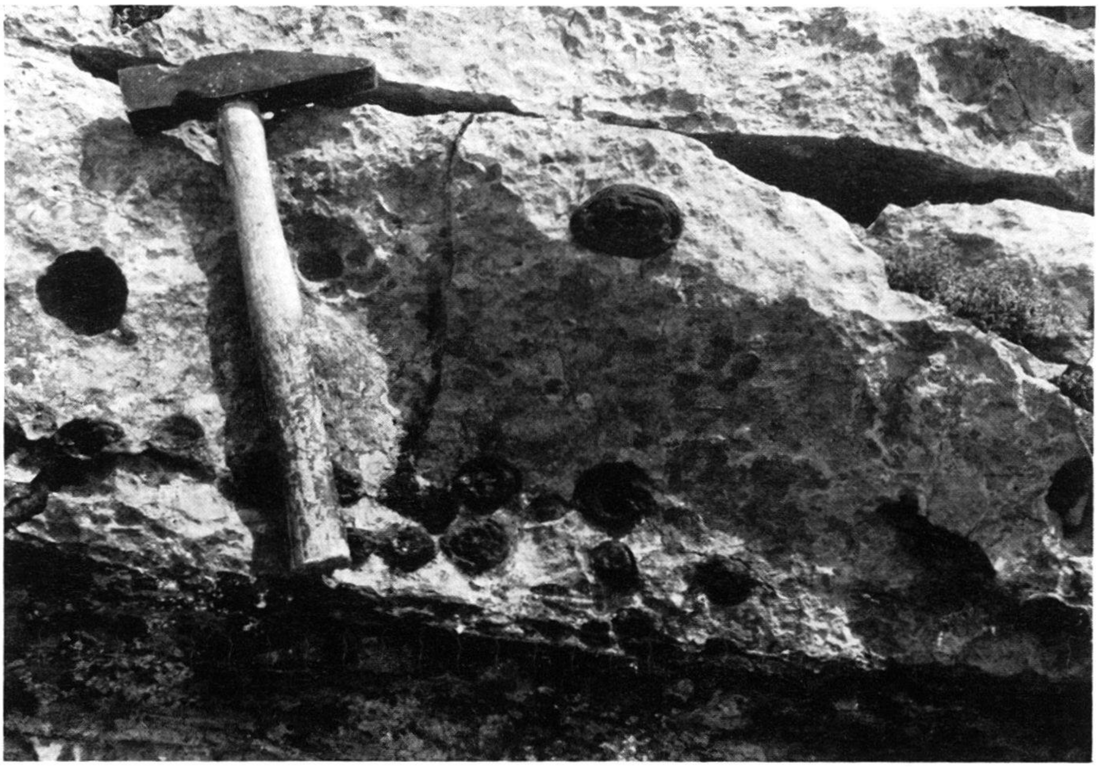

Fig. 3. Discrete, concentrically laminated ferromanganese nodules concentrated in one main horizon. Vertical section. Rocca Argenteria, western Sicily. Length of hammer handle = 36 cm.

The variation in form of modern ferromanganese concretions from locality to locality has also been remarked upon by MURRAY & RENARD (1891, p. 366), MURRAY & IRVINE (1894), MERO (1956, p. 132) and GRANT (1967). MURRAY, in fact, claimed that he could identify the source area of a manganese nodule by its characteristic shape, and to some extent this is also possible with the Sicilian deposits.

Ferromanganese crusts may also coat upstanding parts of the shallow-water white limestones that underlie the condensed sequences (Fig. 7; cf. FABRICIUS, 1968): these are probably karstic pinnacles that have acted as non-depositional points on the sea floor and have thus accreted mineral matter.

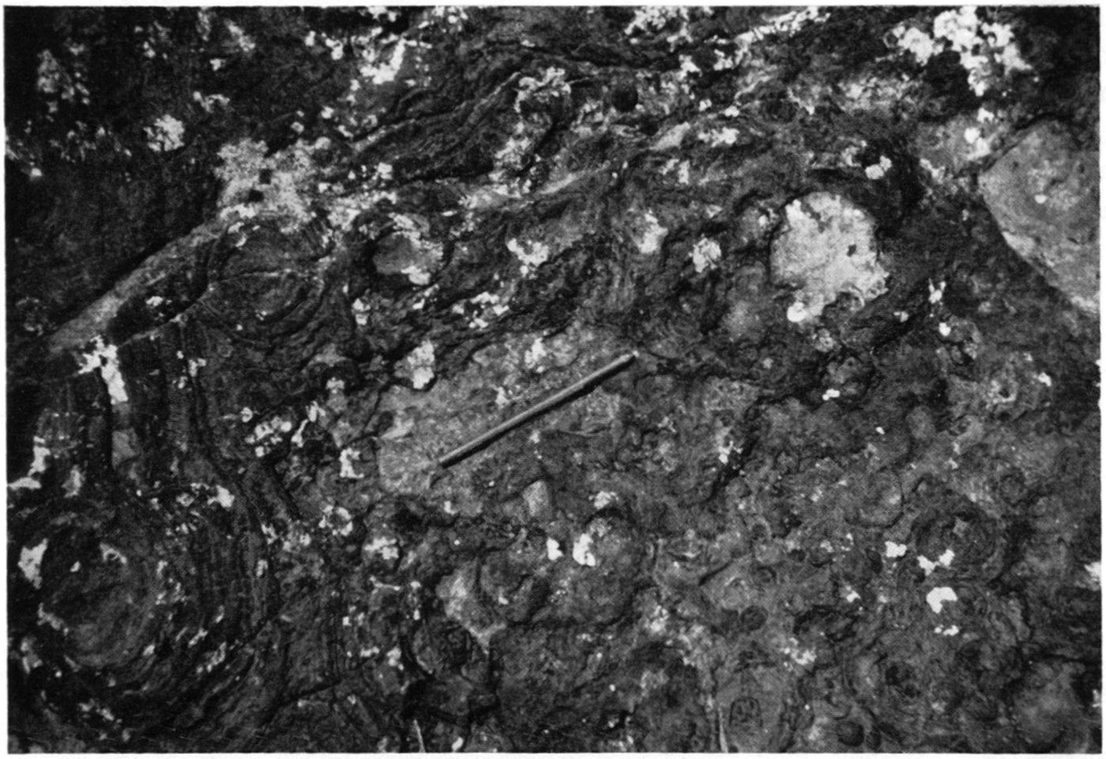

Fig. 4. Thin ferromanganese pavement formed by lateral accretion and fusion of nodules. Bedding surface. Rocca Argenteria, western Sicily. Approximate length of pencil = 15 cm.

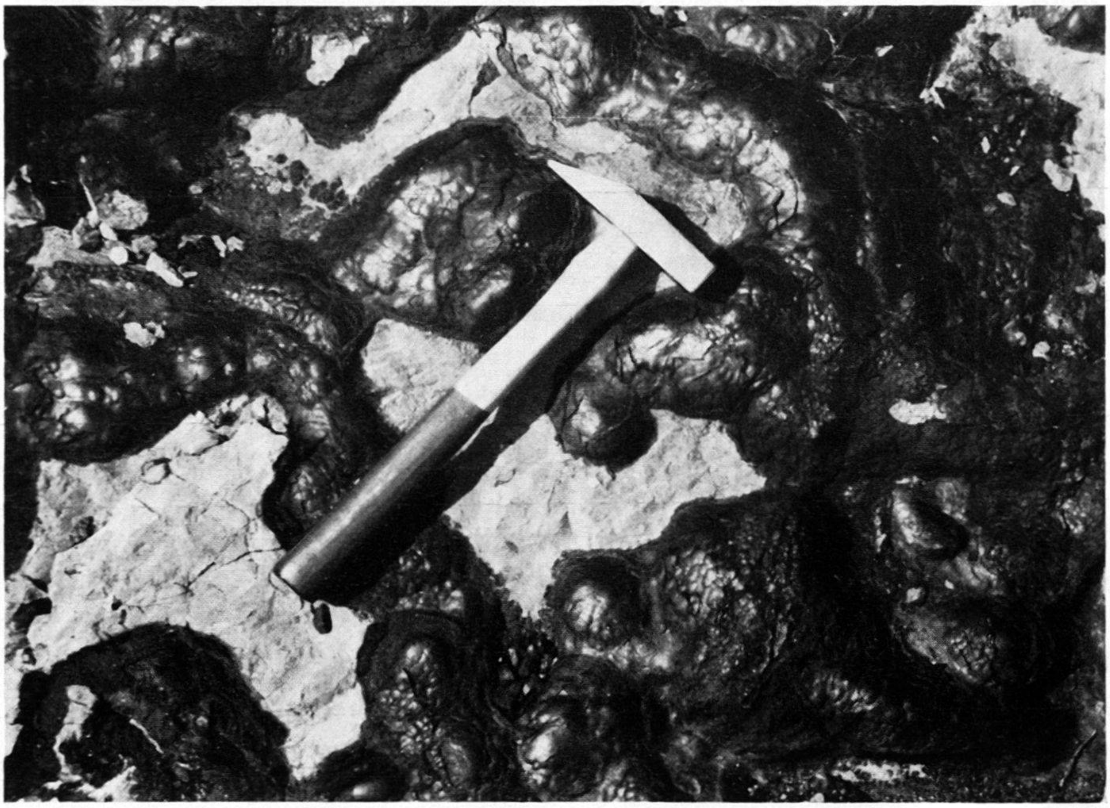

Fig. 5. Thick ferromanganese crust with limestone interstices. Bedding surface. Monte Kumeta, western Sicily. Length of hammer handle = 28 cm.


Fig. 6. Close-up view of the Monte Kumeta crust, showing fused "pancakes" of ferromanganese.

A few fossil nodules, extracted from their matrix, are shown in Fig. 8; their outer morphology varies from crenulate, or mammillated, to completely smooth. Concentric lamination is particularly well developed in the roughly spherical nodules found on Rocca Busambra and adjacent localities : with the crusts the lamination may only be developed as a lustrous outer skin with a more homogeneous earthy texture towards the centre. Some nodules show alternate light and dark bands. All

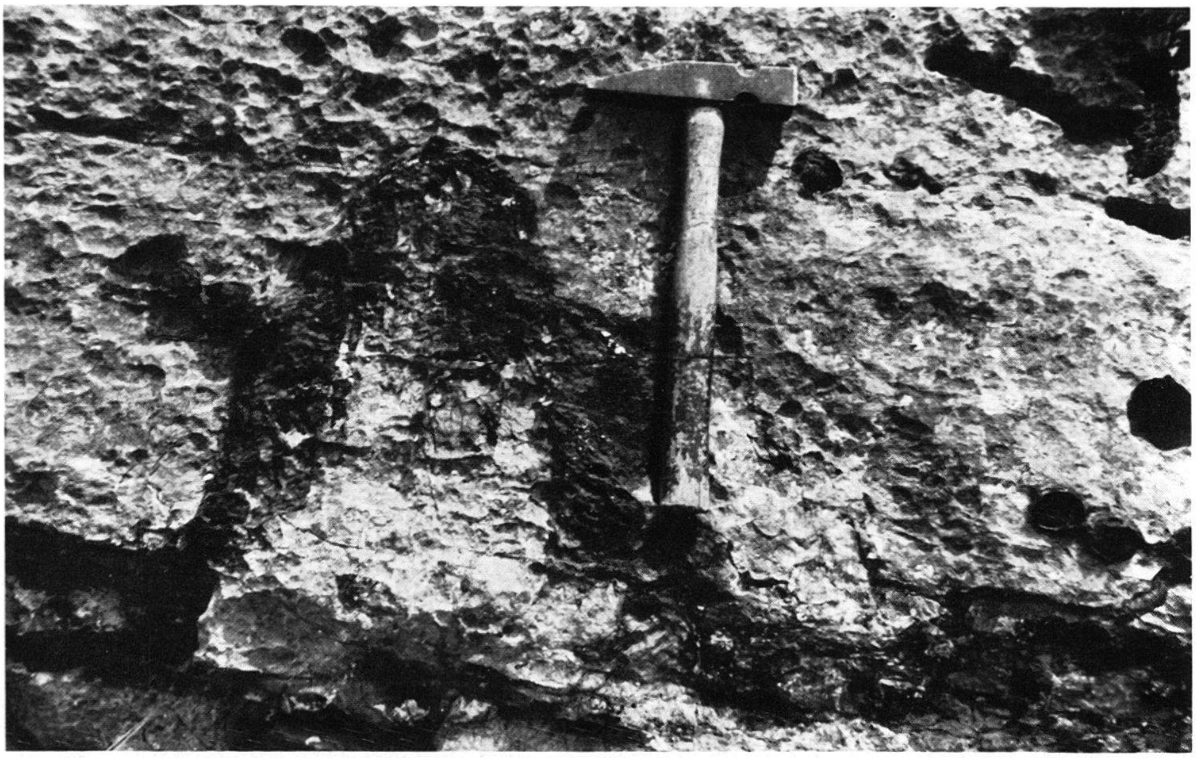

Fig. 7. Karstic pinnacle of white limestone (Liassic platform carbonates) coated with ferromanganese crust. Rocca Argenteria, western Sicily. Length of hammer handle = 36 cm.

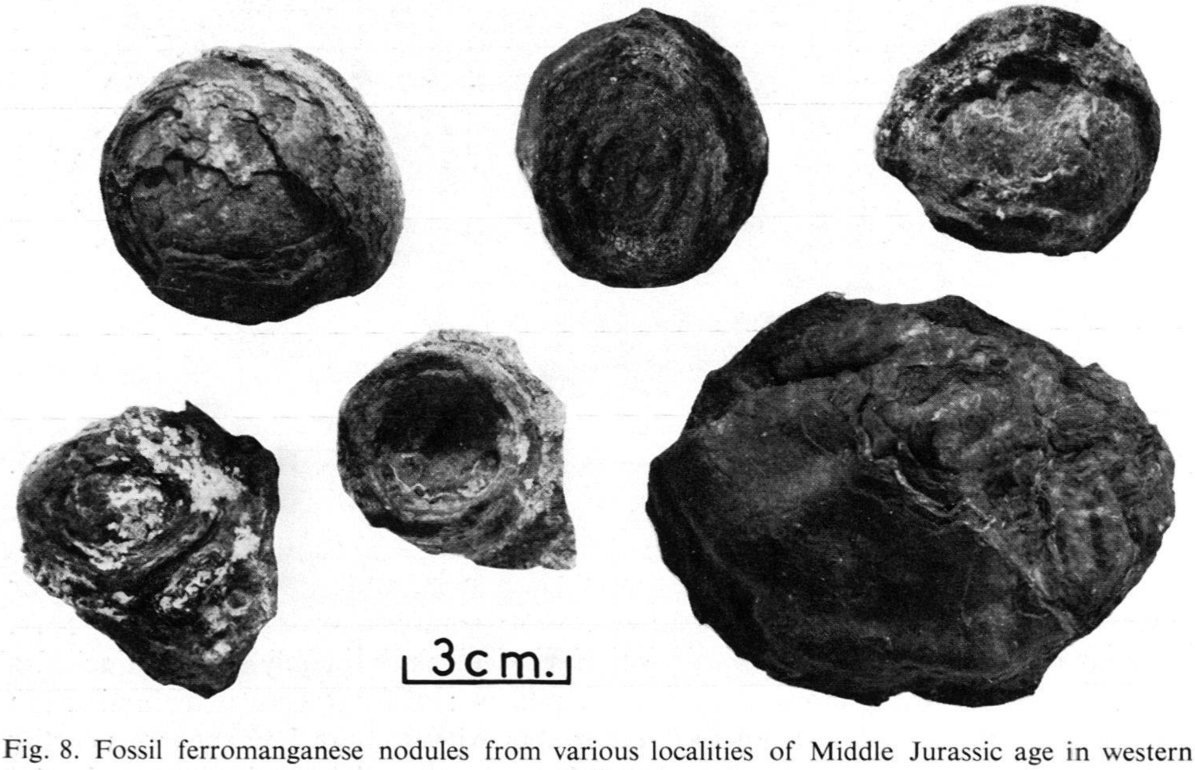


Fig. 8. Fossil ferromanganese nodules from various localities of Middle Jurassic age in western Sicily.

this is in accord with the observations of MURRAY & RENARD (1891, p. 344–366), PETTERSSON (1943) and RILEY & SINHASENI (1958) on modern iron-manganese concretions.

JURGAN (1967, 1969), when describing fossil Jurassic manganese nodules from the Berchtesgadener Alps, related the typical crinkled onion-skin structure of the fossil concretions to the dehydration of goethite to haematite during diagenesis as this would cause volume reduction. However, in the photograph of a modern nodule given by MERO (1965, p. 138), this structure is already apparent, so the crenulate arrangement of laminae is probably more or less primary.

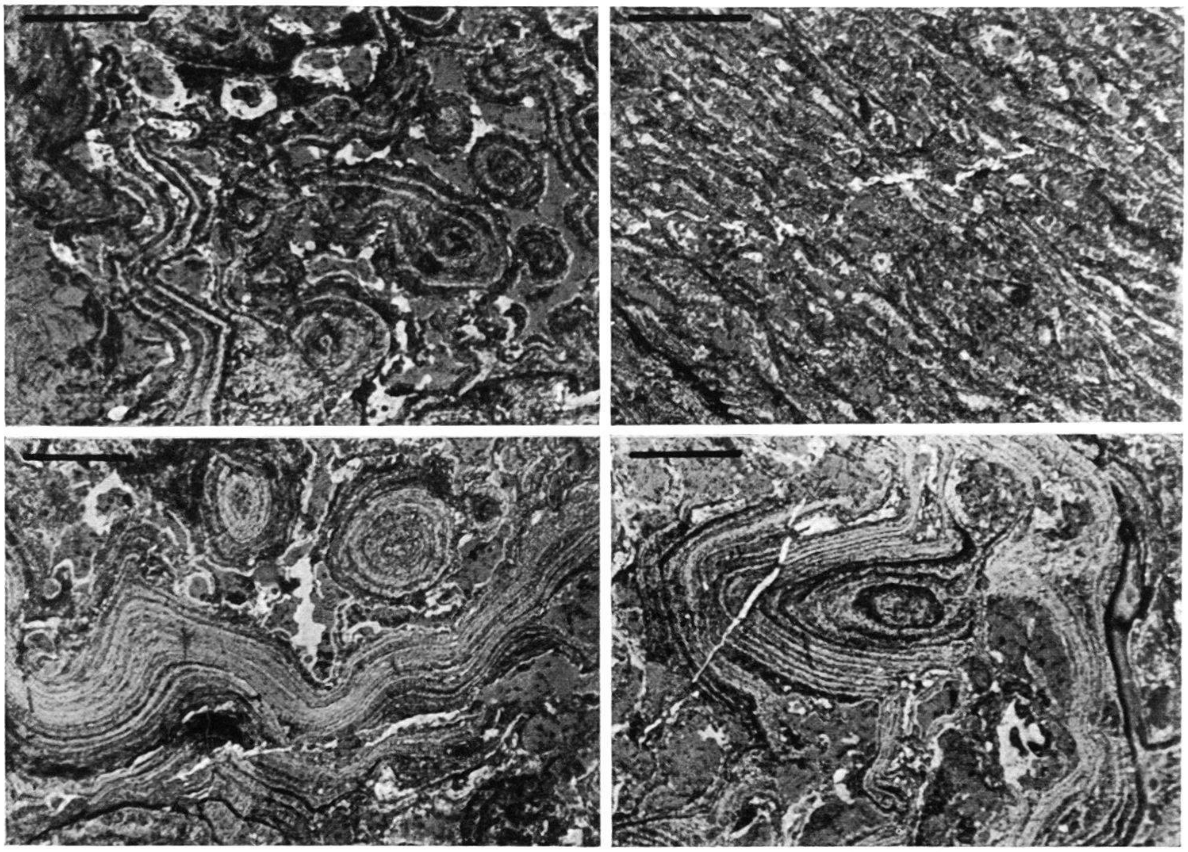

Fig. 9. Nodule textures. Iron-manganese segregations in calcareous matrix. Polished sections from the ferromanganese crust on Monte Kumeta, western Sicily. Scale bar = 0.1 mm.

A series of photographs of polished sections from the Monte Kumeta crust is illustrated in Fig. 9: these should be compared with those presented by SOREM (1967), CRONAN & TOOMS (1968), FRIEDRICH, ROSNER & DEMIRSOY (1969) and ANDRUSHCHENKO & SKORNYAKOVA (1969) for modern nodules. With the Sicilian concretions, however, the interstitial areas between the ferromanganese segregations are made up of carbonate as opposed to the aluminosilicate matrix of the Recent nodules described by CRONAN & TOOMS (1968). These authors suggest that the "cauliflower" structures are due to early post-depositional migration and precipitation of the ferromanganese, and that they are of certain diagenetic origin in the fossil nodules is shown by the

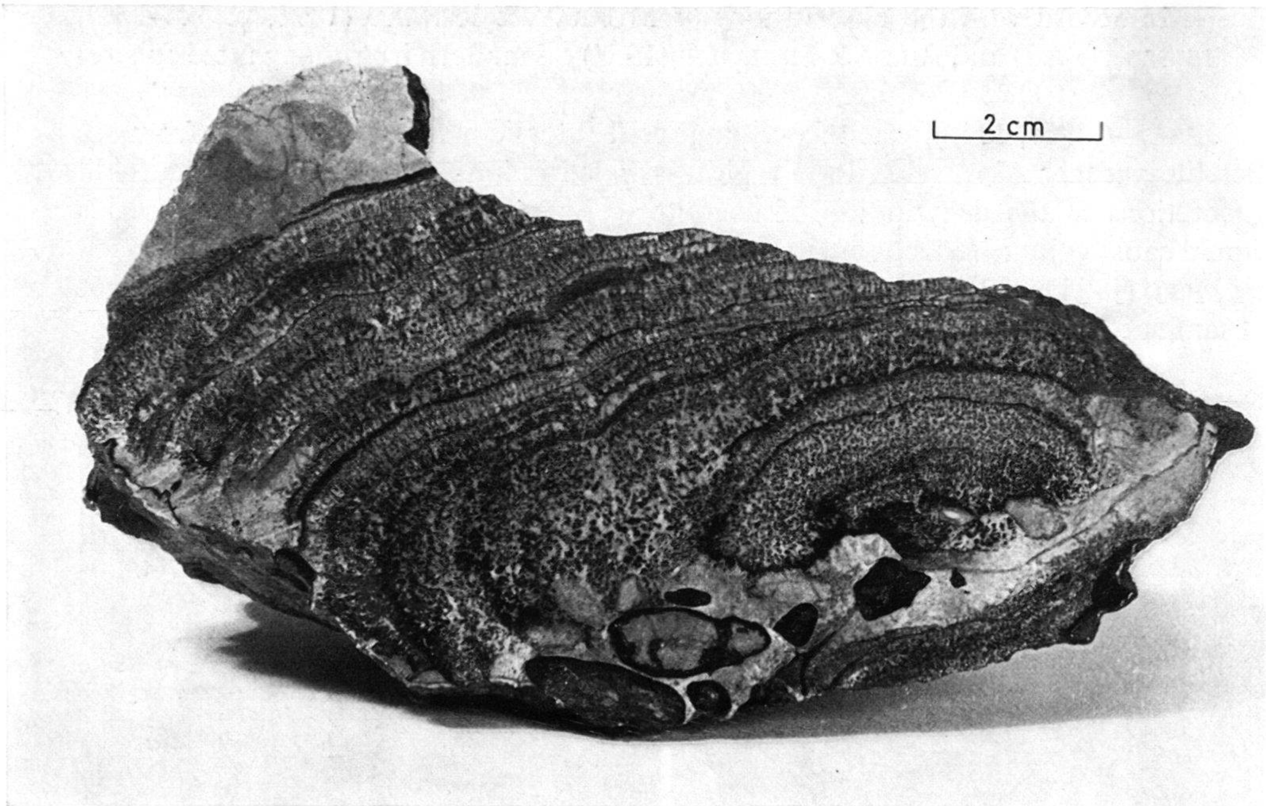


Fig. 10. Iron-manganese "cauliflower" structures in limestone. Vertical section. Monte Inici, western Sicily.

fact that they occur also in the limestone in which the nodules are embedded (Fig. 10). To some extent these migrating segregations may replace the limestone in the immediate vicinity of the nodules' periphery.

Calcite veins, both concordant and discordant with the lamination, occur in some crusts and nodules; some of these are probably of tectonic origin, but since aragonite vein fillings have been recorded from modern manganese nodules (MANHEIM, 1965; McFARLIN, 1967), a primary origin of some of these is possible. Micritic calcite is also often bound into the fossil nodules, as is the case with modern concretions formed in areas of carbonate accumulation: organic remains may also be found within the Sicilian nodules (cf. WENDT, 1970, for other Tethyan localities).

The fossil nodules are commonly around 0.5–5 cm in diameter but may range up to 30 cm across (Fig. 11); the colour of the concretions varies from black through brown to reddish purple: this variation is probably a function of the degree of hydration of the component iron oxides and is not a reliable indicator of the amount of manganese present. In fact, the opposite of that observed by MERO (1965, p.132) is often true: that is, brown or purple nodules are often higher in manganese than those of jet-black colour. The hardness of the fossil nodules is commonly around 3 Mohs scale, and increases with greater carbonate content (cf. MERO, 1965, p. 132). The density (minimum value) of one nodule tested was 2.3 gms/cc which is also comparable with the figure given by MERO (1965, p. 135).

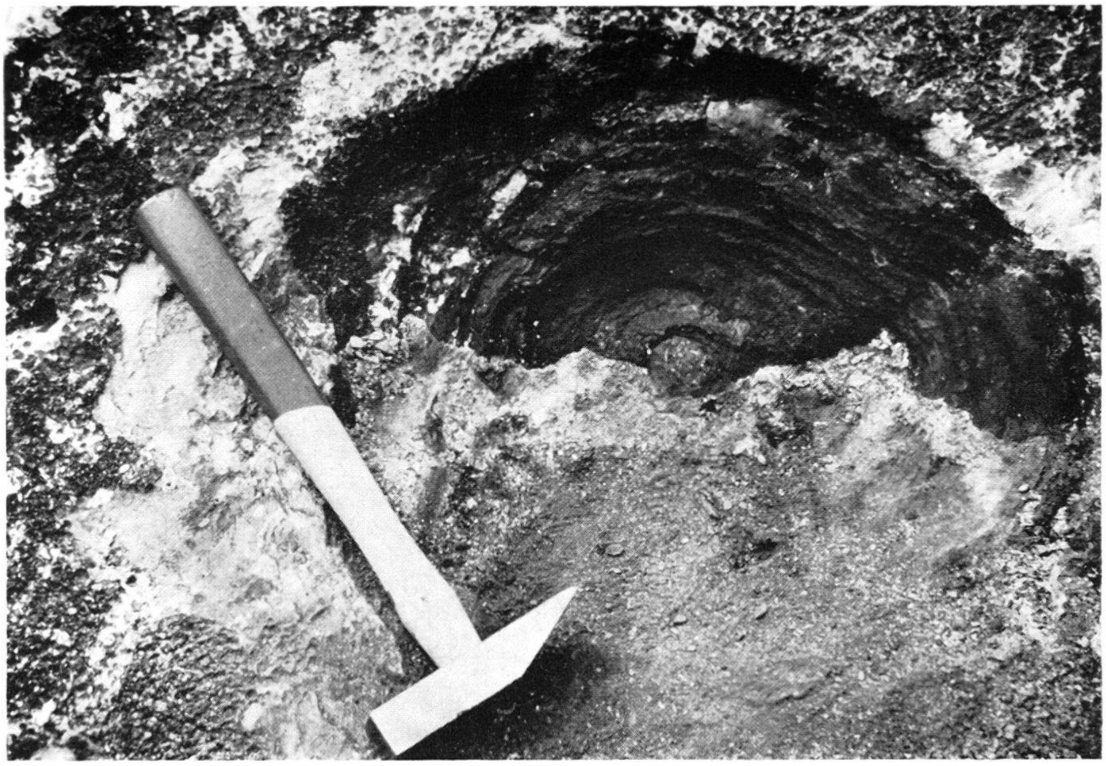

Fig. 11. Large discoid ferromanganese nodule. Bedding surface. Monte Inici, western Sicily. Length of hammer handle = 28 cm.

Some fossil nodules have no obvious nucleus, but most are formed either around a limestone intraclast or an ammonite (Fig. 12) which may or may not have been partially dissolved. In some cases the encrustation of ferromanganese has preserved the ammonite's outer shell, showing that the precipitation of the mineral matter proceeded faster than the solution of aragonite. KOVÁCS (1956) has described a similar mode of preservation for ferromanganese-coated ammonites from the Hungarian Jurassic; furthermore, seizing upon the association of the black oxide material with fossil shells, he assumed that the decay of the oiiginal organic body had caused precipitation of the mineral matter. This, as HOLLMANN (1964) has pointed out, seems unlikely; more probably the shells just acted as nuclei. Manganese coatings on both dead and *living* molluscs from the Clyde Estuary, Scotland, have been recorded by MURRAY & IRVINE (1894) and ALLEN (1960).

At Monte Bonifato the ferromanganese horizon overlies a submarine extrusion of hornblende-biotite trachyte, and the nuclei of some of the nodules above are formed of reworked volcanic material. Igneous material is the most common nucleus in modern concretions (MURRAY & RENARD, 1891, p. 367).

For estimates of the growth rate of Tethyan Jurassic ferromanganese nodules, see WENDT (1970).

## Mineralogy of fossil ferromanganese nodules

Although polished sections of the ferromanganiferous material are dominantly isotropic, X-ray powder patterns of virtually all crusts and nodules show the presence of goethite. Haematite is also detectable in some samples, usually those that are more

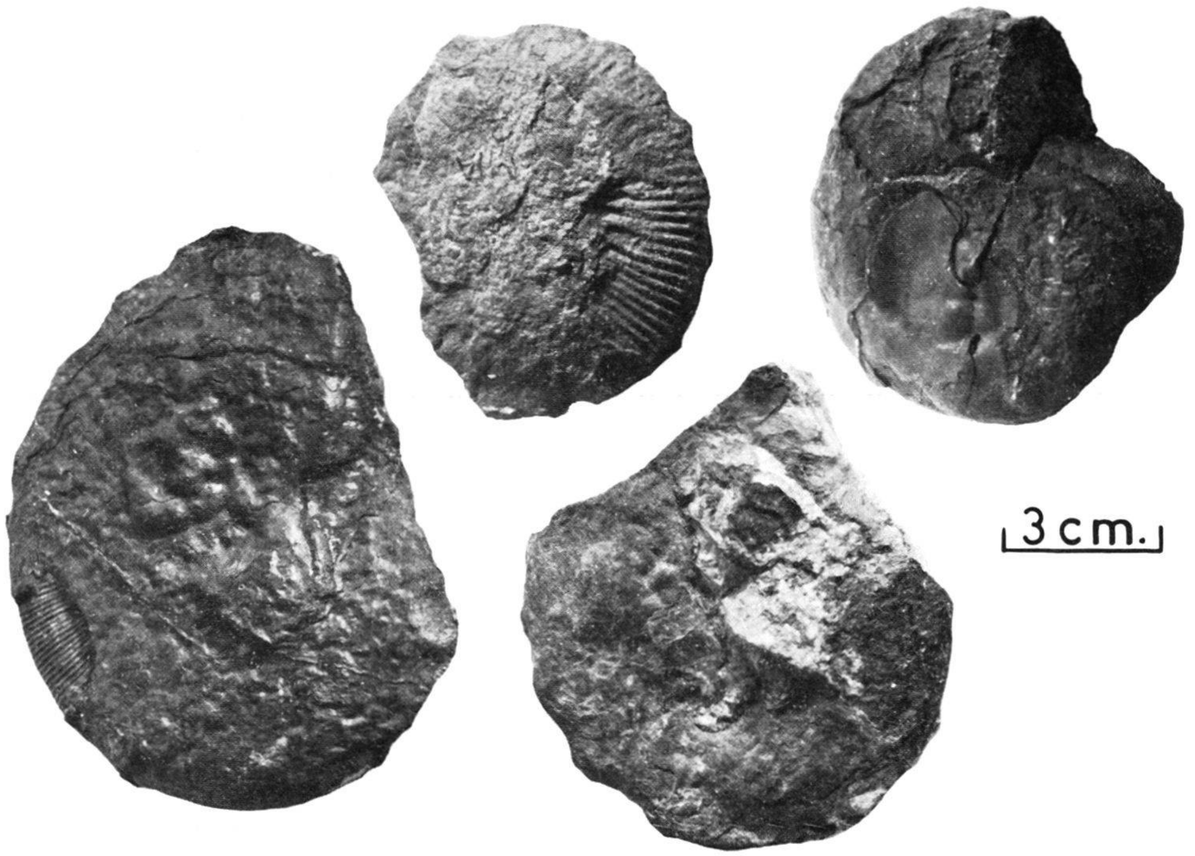


Fig. 12. Ferromanganese-encrusted ammonites from various localities of Middle Jurassic age in western Sicily.

reddish in colour. The only manganese mineral that has been identified with reasonable certainty is todokorite and this is a common component of modern nodules (SOREM, 1967; MEYLAN & GOODELL, 1967; GRILL, MURRAY & MACDONALD, 1968), and also occurs in the Permian examples described by GULBRANDSEN & REESER (1969). The todokorite lines, when present, are broad, so the mineral must be fine-grained. However, it must be stressed that in general the fossil nodules are not particularly crystalline, even after diagenesis, and presumably reflect an original dominantly colloidal nature. MERO (1965, p. 152) notes the ill-crystallinity of modern nodules and AUMENTO, LAWRENCE & PLANT (1968) found identifiable mineral phases only with difficulty. SMITH, GASSAWAY & GILES (1968) have recorded entirely X-ray amorphous manganese oxides from some modern nodules; only secondary goethite was detectable – and this iron mineral is not uncommon in deep-sea concretions (e.g. BUSER & GRÜTTER, 1957). Thus it seems as if the fossil nodules must also bear a very strong mineralogical resemblance to their modern counterparts. The only difference is the presence of haematite; however, as BERNER (1969) has recently pointed out, goethite is unstable relative to haematite in almost all geological conditions, so this latter mineral is of obvious diagenetic origin (see also JURGAN, 1967, p. 46, 1969). "Hydrohaematite" has, in fact, been mentioned as a constituent of Recent nodules from the South Pacific (ANDRUSHCHENKO & SKORNYAKOVA, 1969).

## Geochemistry

Several analyses of the black crusts and nodules associated with Jurassic red limestones have been carried out by various authors and these are summarised below (Table 1). It is apparent that no detailed quantitative data, apart from determinations of iron and manganese, has been produced; the analyses of SIGAL & TRUILLET (1966) are the most comprehensive. The disparity between the major-element composition must be due to a carbonate dilution factor as it is impossible to exclude some calcareous matter when analysing by standard geochemical methods. To overcome this, the present determinations have been performed using the electron-probe microanalyser.

Table 1. Previous analyses of Tethyan ferromanganese nodules.

| Authors | Chemistry of nodules or crusts | Age | Localities |
|---|---|---|---|
| LECHNER & PLÖCHINGER, 1956 | Mn 18.6%<br>Fe 25.2% | Jurassic | Aultausse/ Steiermark region, Austria |
| SCHWANDER, in WIEDENMAYER, 1963 | Mn, Fe – major components<br>Mg, Si, Ti – subsidiary<br>Be, B, Pb, Alkalis, Cu, Zr, Co, Ni, Sr, Cr – traces | Lower Jurassic | Saltrio/Tremona region, Italian-Swiss border |
| HOLLMANN, 1964 | Pyrolusite (1–2%)<br>Fe-minerals (3–6%)<br>Calcite (45–55%)<br>Illite (30–35%) | Middle Jurassic | Monte Baldo region, north Italy |
| SIGAL & TRUILLET, 1966 | Mn 6.20 11.80<br>Fe 18.70 15.65<br>Ti 0.64 0.44<br>Al 2.70 2.30<br>Mg 3.30 3.75<br>P 1.72 0.05<br>Ca 10.90 13.00 | Middle-Upper Jurassic | Taormina region, eastern Sicily |
| HALLAM, 1967 | MnO 3.29%<br>$Fe_2O_3$ 4.68% | Lower Jurassic | Lofer region, Austria |

Fossil ferromanganese nodules have been analysed from a variety of localities in western Sicily; the sample locations are shown in Fig. 1. Polished blocks were used for the determinations with 125-second scans across selected parts of the sample. The traverse distance, in all samples but one, was $375\mu$. Errors were minimised by using a composite-oxide standard for most of the analyses (comparable in composition to a nodule); but the results have been presented as weight percentages of the elements except for calcium which has only been determined semi-quantitatively, using a pure limestone standard. Only a selection of analyses are shown here; further electron-probe traces are contained in Jenkyns (1969).

With the graphs shown in Fig 14–21 the zero percentage has been calculated for the ferromanganiferous area and the background is higher here than for the calcareous phase; this accounts for the scan line falling below zero in the lime-rich part of the traverse.

Accuracy for the major elements (Fe, Mn) should lie in the range ± 5%. Errors increase as the amounts of trace-metal decrease and, for the minor elements, the uncertainty value is probably ± 20%. The detection limits, in per cent, of the various elements are set out below:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Al | 0.037 | Ca | 0.039 | Mn | 0.016 | Cu | 0.038 |
| Si | 0.027 | Ti | 0.011 | Fe | 0.023 | Zn | 0.034 |
| P | 0.012 | V | 0.012 | Co | 0.038 | Ba | 0.028 |
| $CaCO_3$ | 0.097 | Cr | 0.012 | Ni | 0.026 | | |

## Major elements

It is evident that the concretions show a tremendous variation in elemental composition, notwithstanding the disparity in carbonate content; and since the publication of JENKYNS (1967), several nodules with manganese higher than iron have been discovered (Fig. 14 and 15). Fig. 13 shows a microprobe analysis of a modern ferromanganese nodule from the central Pacific, and it is apparent that as far as the abundances of major (and minor) elements are concerned, many of the fossil concretions are comparable to this. Two nodules, those from Monte Bonifato (see JENKYNS, 1969) and Rocca Argenteria (Fig. 15) assay particularly high in manganese, are rather low in iron, and impoverished in trace elements. Modern equivalents of these have been recorded by NIINO (1955), GOLDBERG (1961), and MERO (1965, p. 207, 227–228); the nodules described by NIINO are in the Fuji volcanic zone and their formation may be due to manganese-rich springs (geothermal brines?) entering the ocean at this point. Alternatively, the formation of iron-poor manganese nodules may result from diagenetic addition of manganese (CHENEY & VREDENBURGH, 1968).

Two crusts have been analysed from Rocce Maranfusa, coming from different parts of the succession (Fig. 16 and 17), and understandably the Fe/Mn ratios are somewhat different. However, at Monte Inici two concretions coming from the same bed, and separated by only a few millimetres, have vastly different amounts of manganese present, although the iron content is comparable (Fig. 19 and 20). The iron-rich nodule is not dissimilar in composition to the Toarcian iron pisoliths that occur in parts of western Sicily (JENKYNS, 1970).

A possible modern parallel of this situation has been recorded by BONATTI & JOENSUU (1968) from the East Pacific Rise: they describe high-iron deposits in intimate association with manganese crusts, and postulate a local source for the differentially fractionated material. AHRENS, WILLIS & OOSTHUIZEN (1967) have also recorded marine limonitic nodules, which contain 0–1.5% manganese. BONATTI & JOENSUU assume rapid precipitation for the more iron-rich phases; and RONA, HOOD, MUSE & BUGLIO (1963) have shown in a laboratory study that, if manganese and iron are co-precipitated, the amount of manganese thrown down is inversely proportional to the rate of precipitation. GOLDBERG & ARRHENIUS (1958) found inshore limonitic nodules that had formed around metallic shell fragments, probably not more than fifty years old. For the samples from the East Pacific Rise, hydrothermal solutions of volcanic origin and leaching of basic lavas are suggested as source materials, and CRONAN & TOOMS (1967) also explained the presence of two morphologically and chemically different nodule populations as due to hydrothermal and volcanic agencies. Thus the close juxtaposition of the manganese-high and manganese-low concretions from Monte Inici may be important in understanding the genesis of the Jurassic ferromanganese nodules.

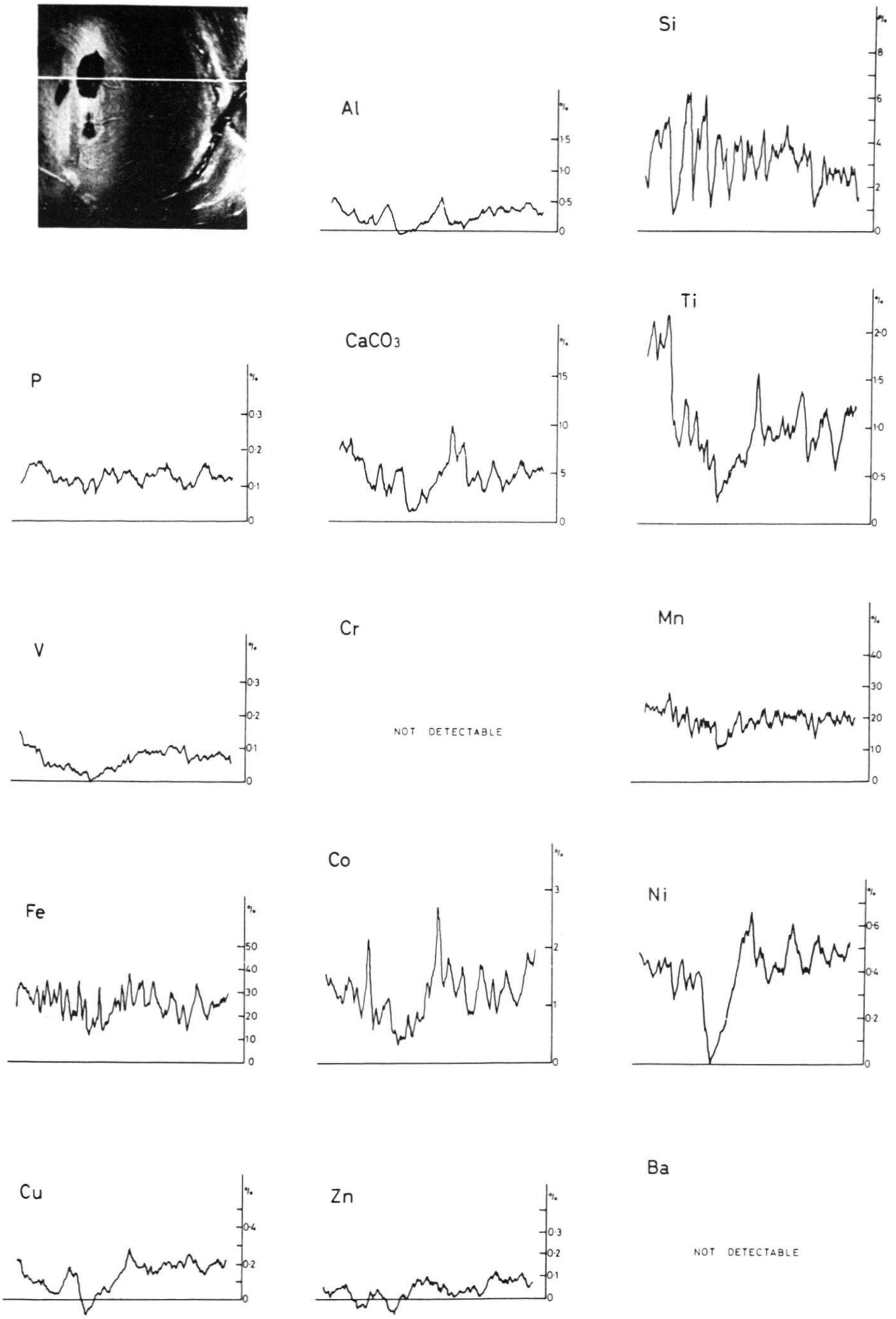


Fig. 13. Electron-probe microanalysis of Recent ferromanganese nodule from the central Pacific. Length of scan-line = 375 $\mu$.

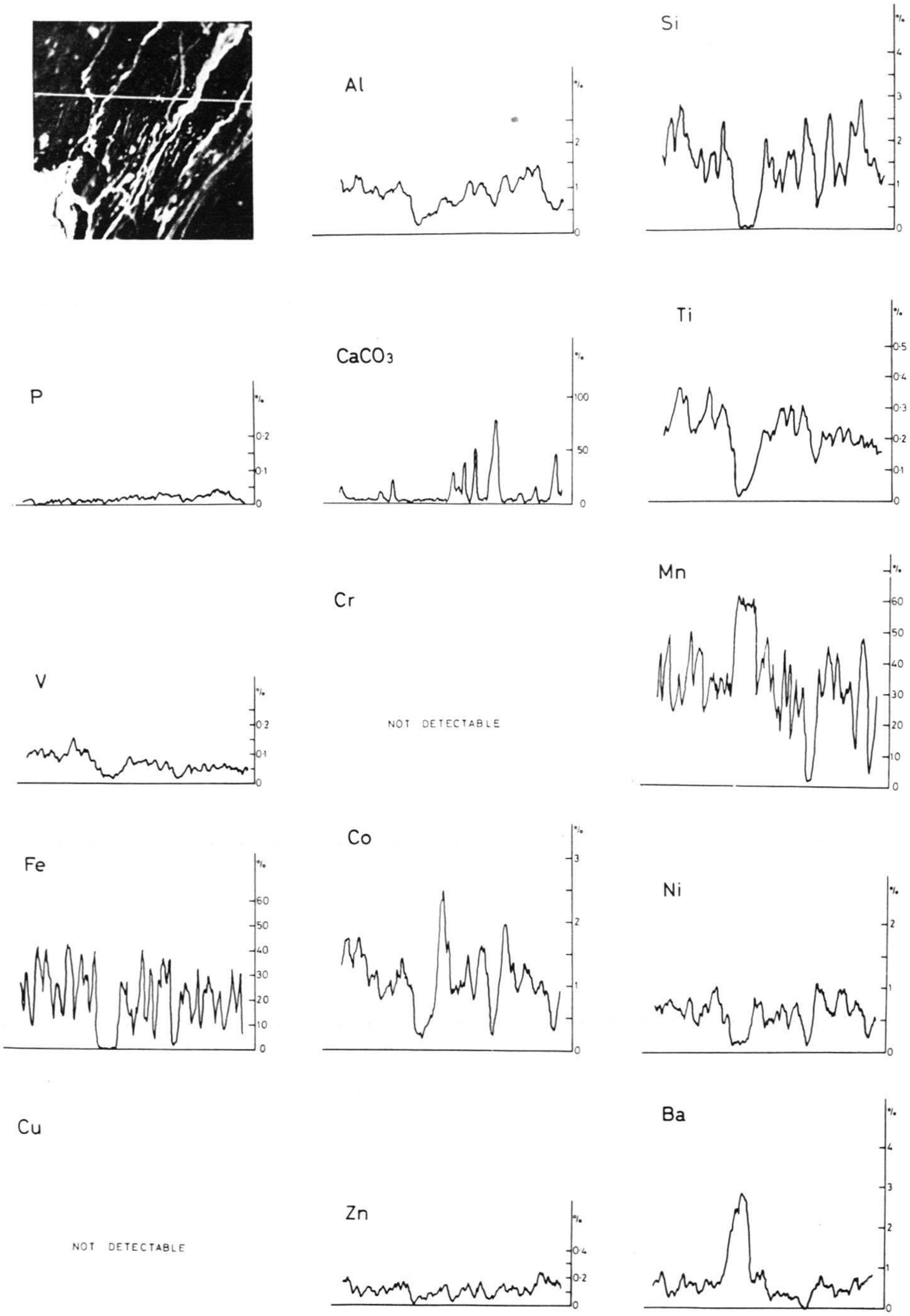


Fig. 14. Electron-probe microanalysis of ferromanganese crust from Monte Maranfusa, western Sicily. Length of scan-line = 375 $\mu$.

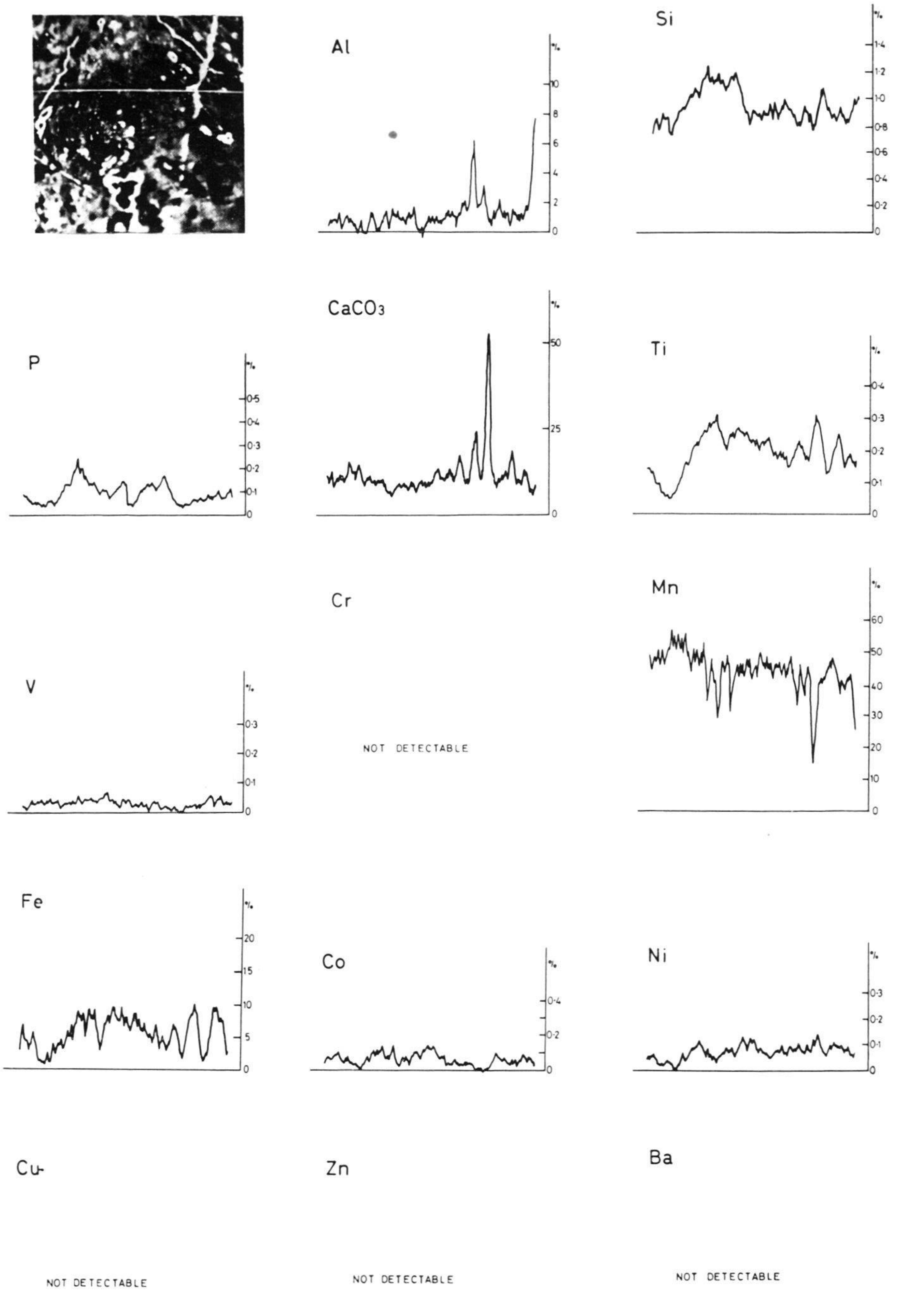


Fig. 15. Electron-probe microanalysis of ferromanganese nodule from Rocca Argenteria, western Sicily. Length of scan-line = 375 $\mu$.

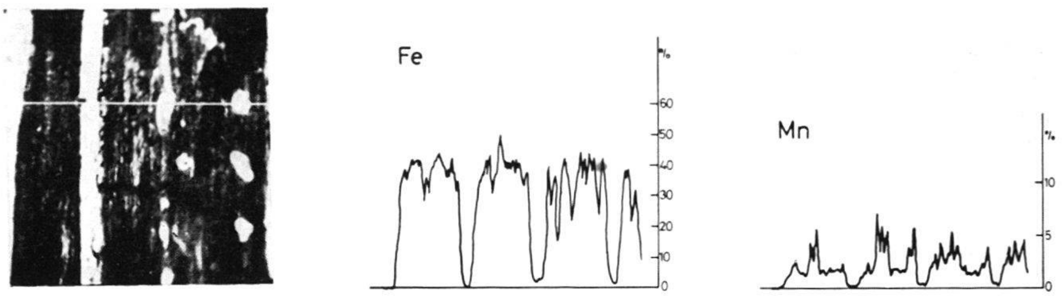


Fig. 16. Electron-probe microanalysis of ferromanganese crust (Fe and Mn only) from Rocce Maranfusa, western Sicily. Length of scan-line = 375 μ.

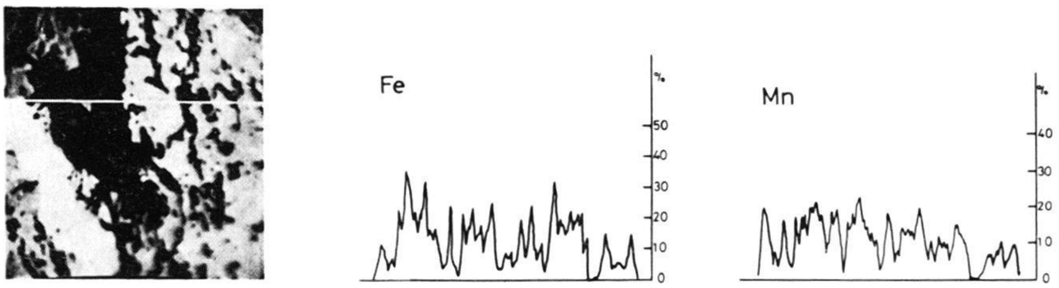


Fig. 17. Electron-probe microanalysis of ferromanganese crust (Fe and Mn only) from Rocce Maranfusa, western Sicily. This sample comes from a stratigraphically higher position than that analysed in Fig. 16. Length of scan-line = 375 μ.

Electron-scanning beam photographs of a thin ferromanganese-coated intraclast from Monte Inici are shown in Fig. 22. It is evident from these that manganese is essentially confined to the mineral crust and is very much enriched in certain bands where iron is correspondingly poor. Iron, on the other hand, is also present to considerable extent in the calcareous centre of the nodule, where it may be bound in clay minerals or as limonite in algal or fungal borings. A calcareous band is also present in the crust, presumably formed by trapping of local sediment when ferromanganese precipitation waned. The manganese- and calcite-rich bands both suggest that conditions during the formation of this concretion were subject to change: this may again be interpreted as due to intermittent local supply. In other crusts and nodules, the amounts of iron and manganese may also vary considerably across a traverse.

Many of the Sicilian Jurassic nodules show a relatively high iron content and this would seem atypical when compared with MERO's (1965) analyses of modern Pacific concretions, though not perhaps with those of samples from other oceans. This relatively high iron concentration could be primary or may on the other hand reflect the diagenetic mobility of manganese. MURRAY & IRVINE (1891), WANGERSKY (1963), LYNN & BONATTI (1965) and others have suggested that manganese can be remobilised upwards toward the sediment-water interface during early diagenesis, especially under reducing conditions. Thus, in this situation, any buried nodules would end up with a higher Fe/Mn ratio than their original one; LEPP (1963) has also pointed this out with reference to iron-manganese deposits. The limestones in

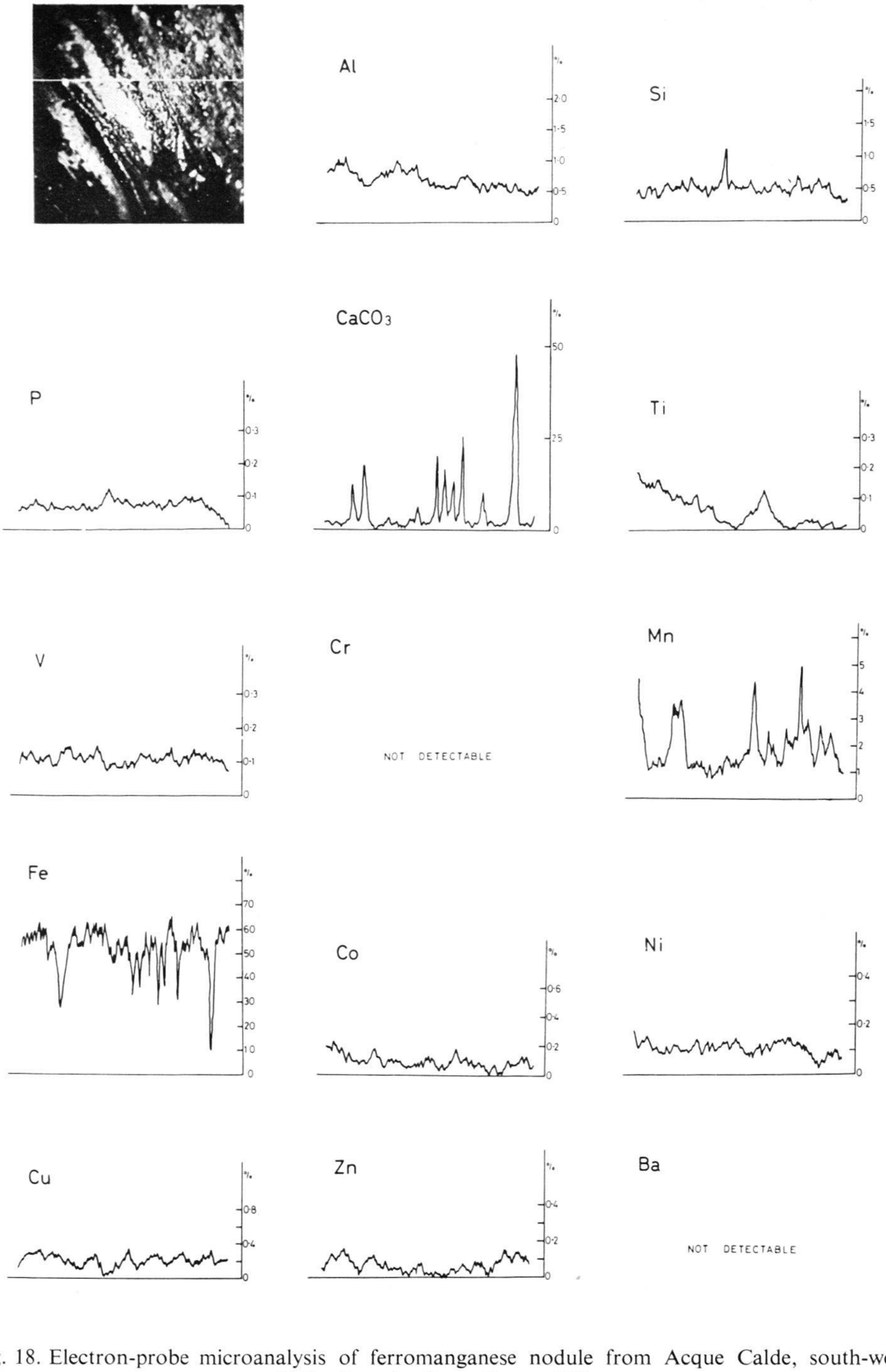


Fig. 18. Electron-probe microanalysis of ferromanganese nodule from Acque Calde, south-west Sicily. Length of scan-line = 375 $\mu$.

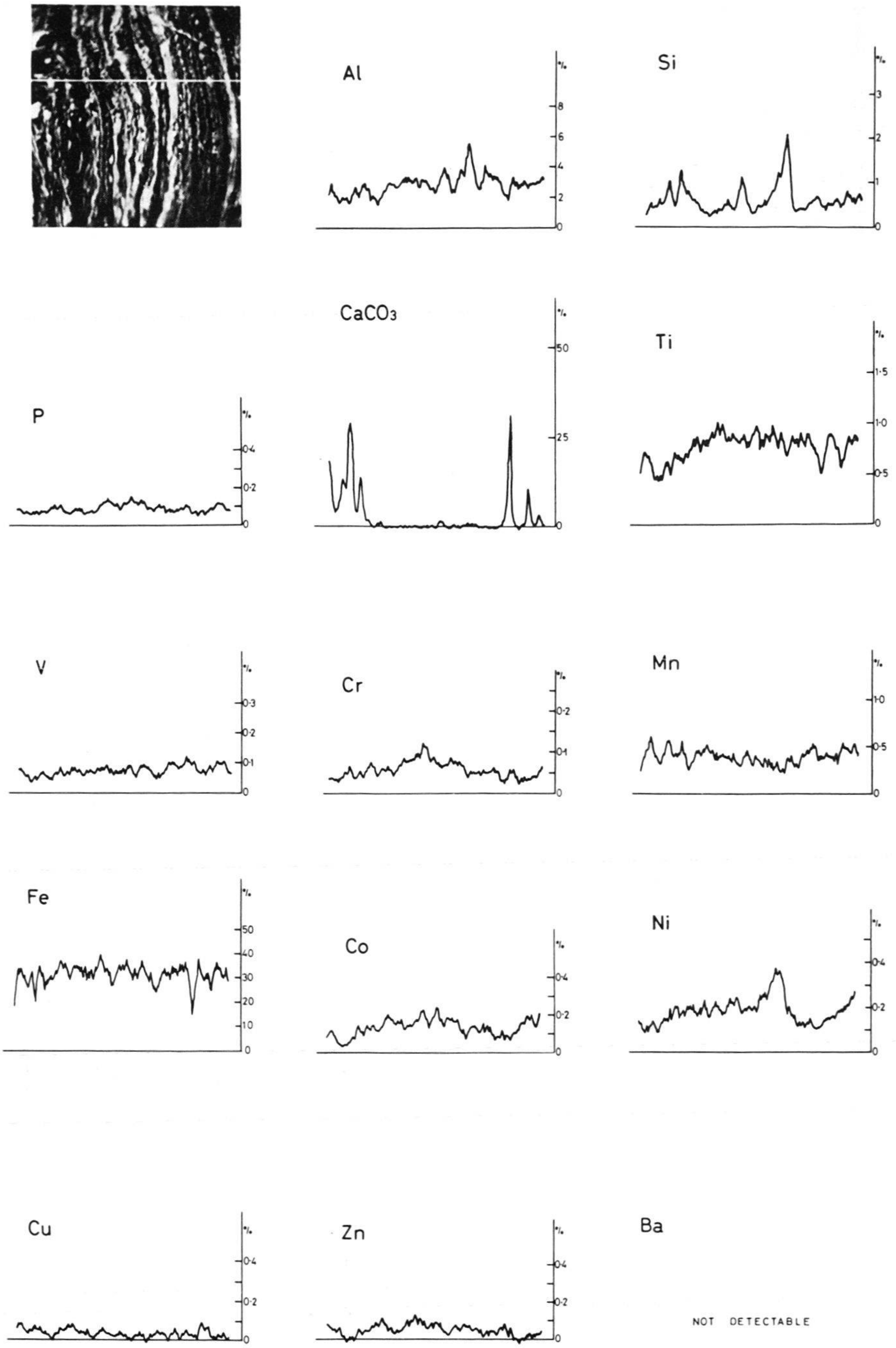


Fig. 19. Electron-probe microanalysis of high-iron nodule from Monte Inici, western Sicily. Length of scan-line = 375 $\mu$.

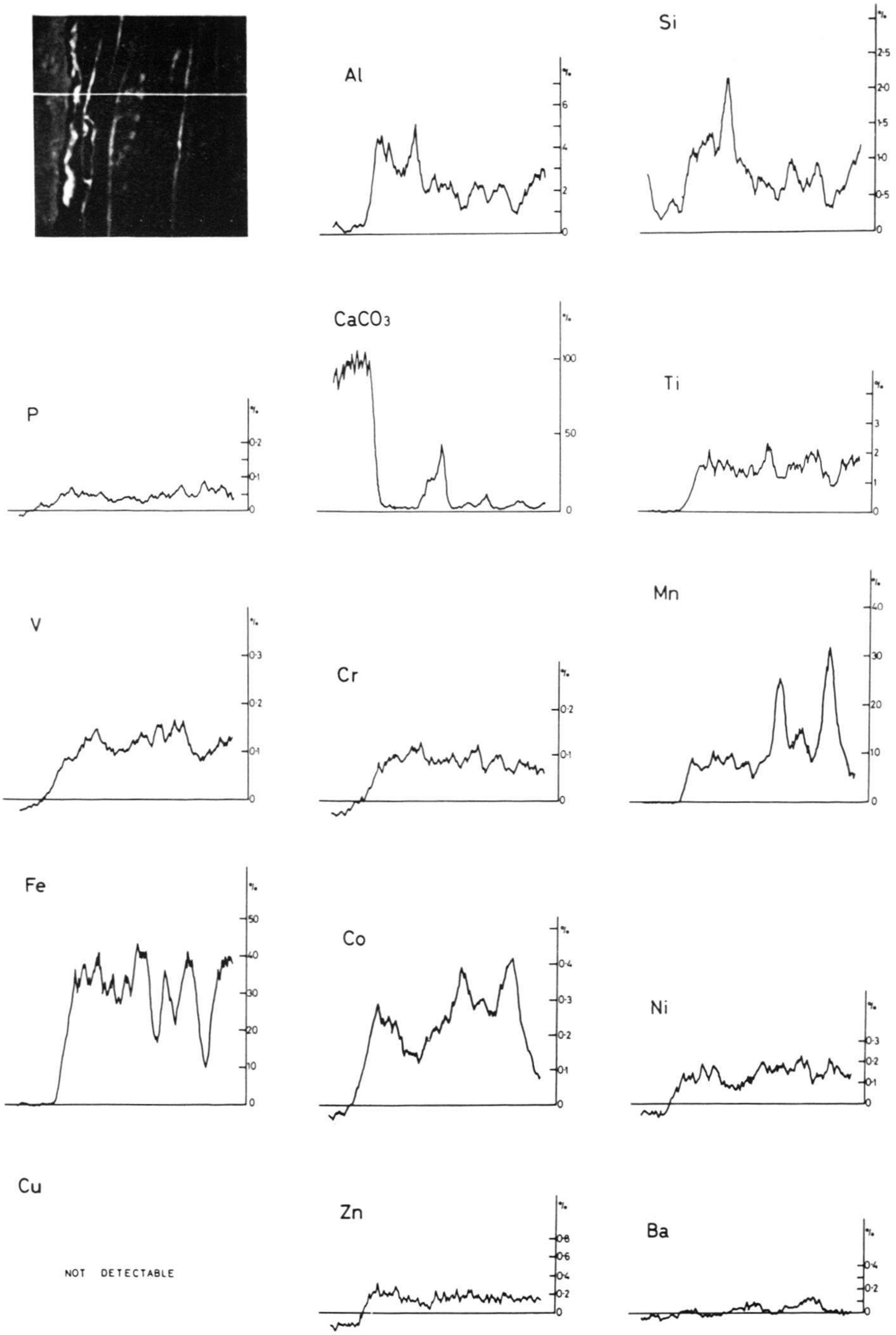


Fig. 20. Electron-probe microanalysis of ferromanganese-coated limestone intraclast from Monte Inici, western Sicily. Length of scan-line = 188 $\mu$.

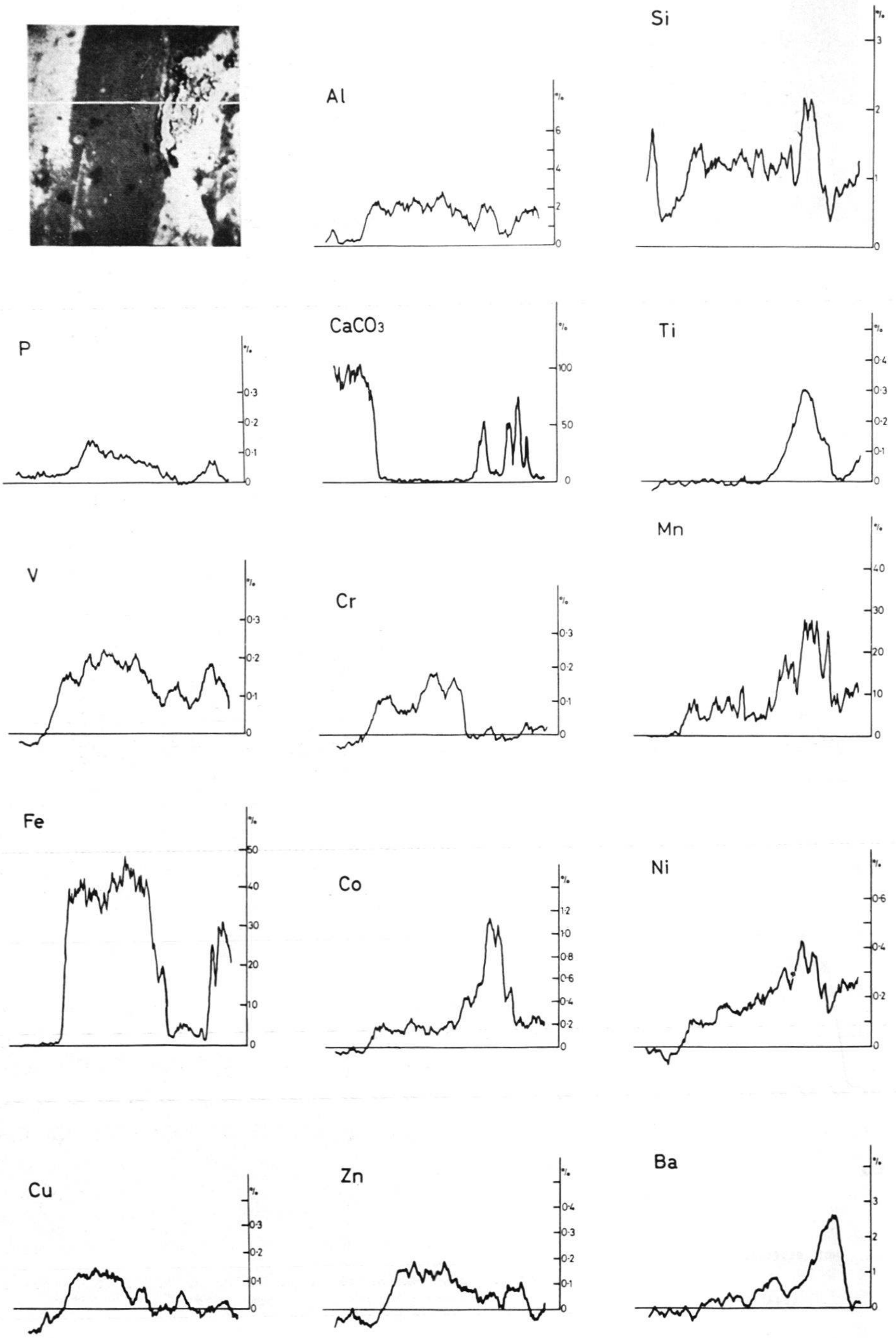


Fig. 21. Electron-probe microanalysis of ferromanganese crust from Monte Kumeta, western Sicily. Length of scan-line = 375 $\mu$.

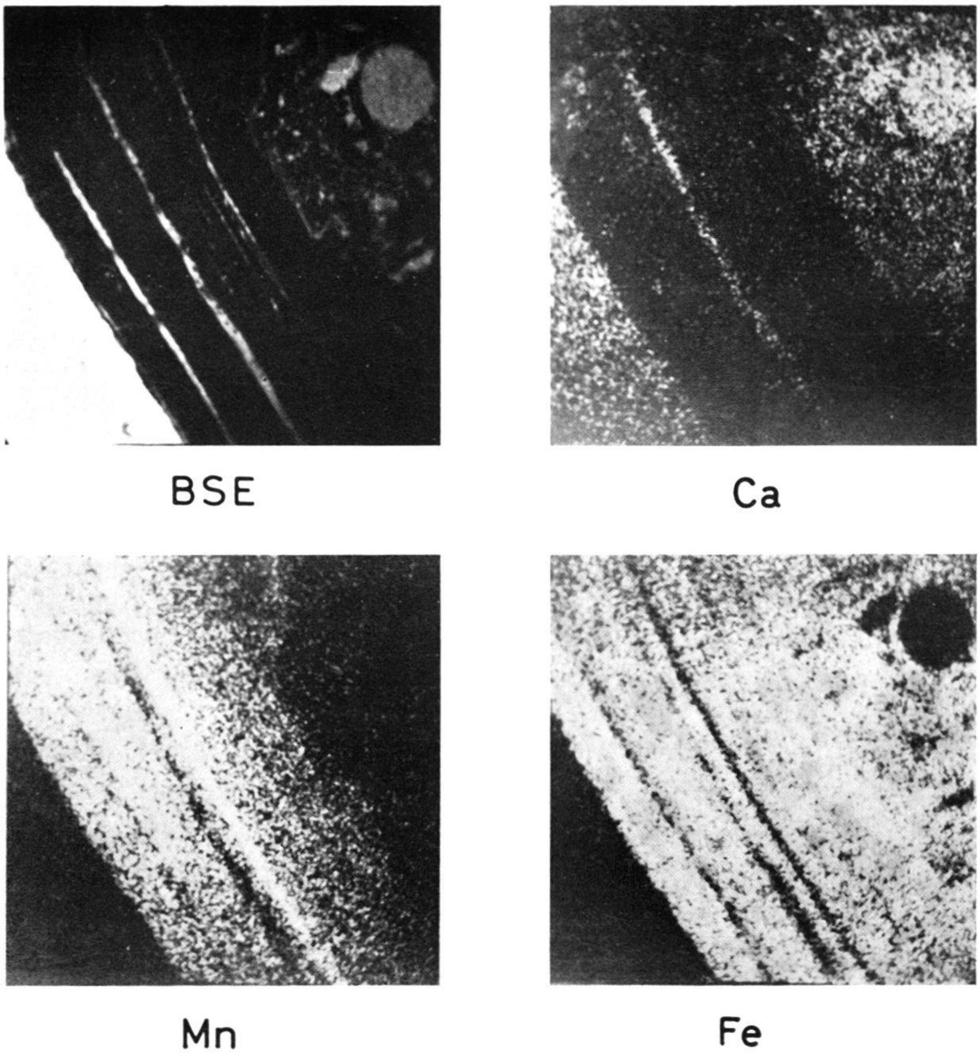


Fig. 22. Electron-scanning beam photographs of ferromanganese-coated intraclast from Monte Inici, western Sicily. Areas scanned = $375 \times 375\ \mu^2$. (Light portions of photograph indicate presence of element.)

which the nodules are found are generally red, which suggests that oxidising conditions persisted after deposition; but nevertheless bleached reduction zones, with pyrite, can be seen in some condensed sequences – though these may be of very late diagenetic origin. Nevertheless, dendrites occur commonly in the limestone around which the nodules are buried (Fig. 10) and this confirms that such migration of manganese can indeed take place. Some nodules from Rocca Argenteria are virtually hollow and perhaps this loss of material could be attributed to mobility of the constituents at some stage during diagenesis, as well as to the dehydration of goethite to haematite.

## Minor elements

The trace-metal composition of the modern nodule (Fig. 13) is, in general, comparable to the Sicilian examples, though some of these are more enriched than others (compare Fig. 14 and 21 with Fig. 15). Those samples that contain very high iron or very high manganese are usually relatively depleted in minor elements; and the same phenomenon is apparent in the Cretaceous nodules from Timor (AUDLEY-CHARLES, 1965). Barium and chromium, however, not detected by the microprobe in the modern nodule, are present in some of the Jurassic samples, occasionally in relatively high but local amounts (Fig. 14 and 21). Some of the modern nodules analysed by MERO (1965, p. 182) have high barium but chromium is very low since, according to ARRHENIUS & BONATTI (1965), this element cannot easily be removed from igneous rocks and hydrolysed. Where both barium and chromium occur in significant amounts in modern oceans is in the region of the East Pacific Rice (BOSTROM & PETERSON, 1966); here hydrothermal exhalations are assumed to reach the surface and chromium attains values up to 0.02%, barium up to 3.5%. The presence of these elements in some of the Jurassic nodules may thus also have a bearing on the interpretation of their genesis.

Cobalt, nickel, titanium and vanadium are detectable in all of the west Sicilian Jurassic samples; zinc and copper only in a few.

Using the direct-reading spectrometer some semi-quantitative determinations were carried out for elements not attempted on the probe: samples from Rocche San Felice, Monte Bonifato, Monte Inici, and Monte Kumeta were analysed. Of the elements sought Ag, Li, Sn, and W were not detected, while Pb, K, Zr, Cd, Sr, Mo, Bi, Be, Ga, and Ge were found. Of these, lead was the most abundant and could, in fact, be picked up by the probe; no detailed analyses were attempted, however, since the specimens were polished on a lead lap with the consequent likelihood of contamination.

## Inter-element relationships

Using microprobe techniques on modern nodules and crusts, inter-element relationships have been established by BURNS & FUERSTENAU (1966), CRONAN & TOOMS (1968), AUMENTO, LAWRENCE & PLANT (1968) and FRIEDRICH, ROSNER & DEMIRSOY (1969). From a study of their data it is evident that such phase relationships differ from sample to sample; and such a situation can be seen with the fossil nodules analysed here. The only association found by all these authors is a general covariance of nickel with manganese; yet in the Jurassic nodule analysed in Fig. 14 this relationship is not fully established. Generally, however, (see Fig. 21 for most obvious example) nickel does seem to be sorbed in the manganese-rich phase. Titanium is usually sorbed with iron (Fig. 14, 15, 20), a relationship found by BURNS FUERSTENAU (1966), but is sympathetic with manganese in Fig. 21. Cobalt is sympathetic with manganese in Fig. 20 and 21 (cf. AUMENTO, LAWRENCE & PLANT, 1968) and ambiguous with many of the others. Barium is spectacularly sorbed with manganese in Fig. 14 and 21. Fig. 21, showing the analysis of a crust from Monte Kumeta, gives by far the clearest display of inter-element relationships; apart from the elements previously referred to, zinc, copper, vanadium, chromium and possibly aluminium all appear to be sympathetic with iron, while silicon perhaps shows some covariance with manganese (cf. the data of CRONAN, 1969, on Recent nodules).

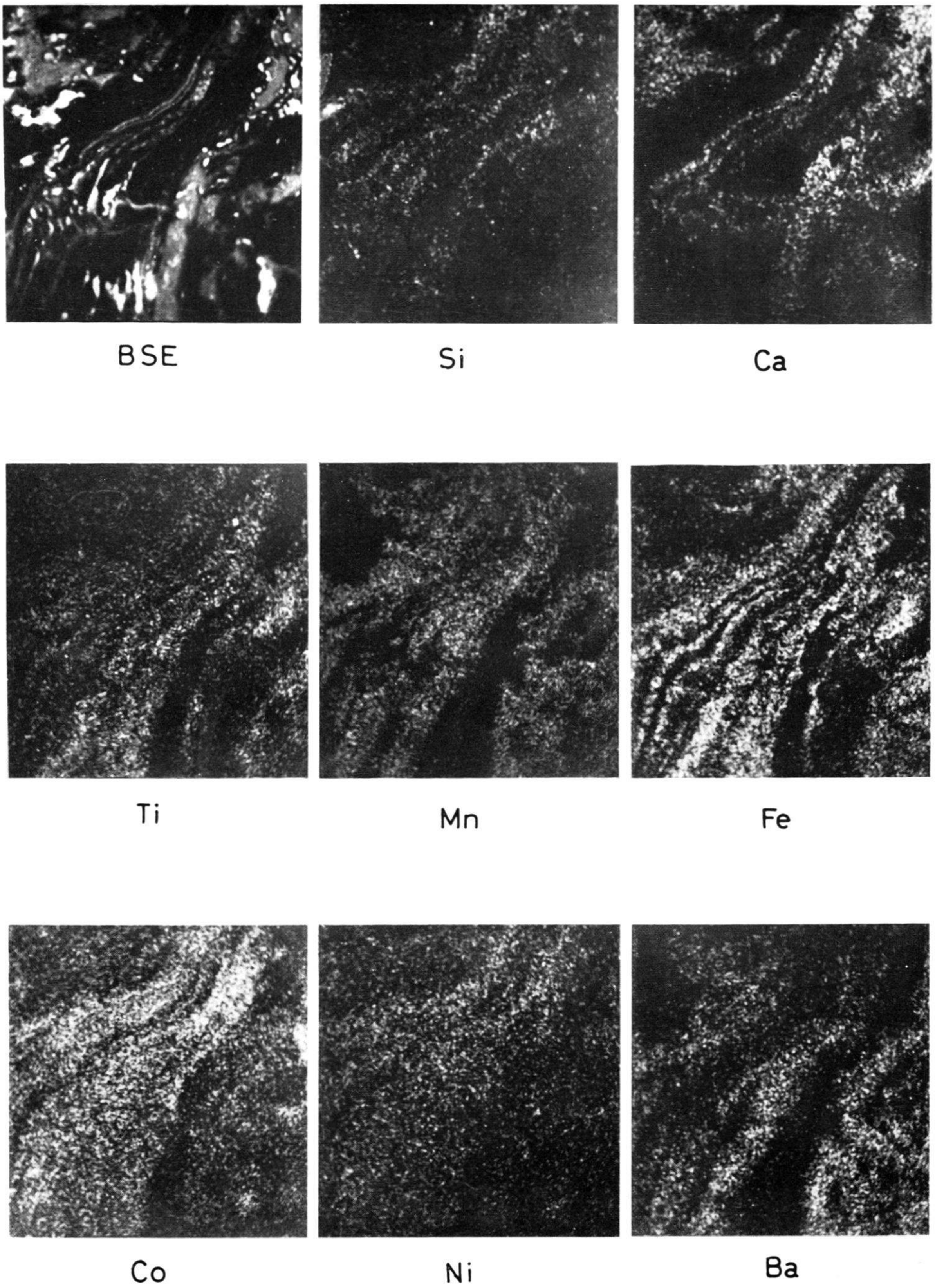


Fig. 23. Electron-scanning beam photographs of ferromanganese crust from Monte Maranfusa, western Sicily. Area scanned = $375 \times 375\ \mu^2$. (Light portions of photograph indicate presence of element.)

Electron-beam scanning photographs of a crust from Monte Maranfusa (same sample as Figure 14) are shown in Figure 23. These show that titanium is strongly sorbed with iron, and barium with manganese. Nickel and cobalt are more ambiguous. The ferromanganese phase is always antithetic to the calcite matrix.

## Distribution of ferromanganese crusts and nodules in the Jurassic of the Tethyan region

The red pelagic limestone that is characteristic of the Mediterranean Jurassic is known by various local names such as "Ammonitico Rosso" and "Adneter Kalk": this is a red nodular calcilutite. In its condensed facies, however, the limestone is never nodular – and it is only in these stratigraphically reduced horizons that ferromanganese deposits occur (see AUBOUIN, 1964, for data on the distribution of red limestones in time and space in the Tethyan region).

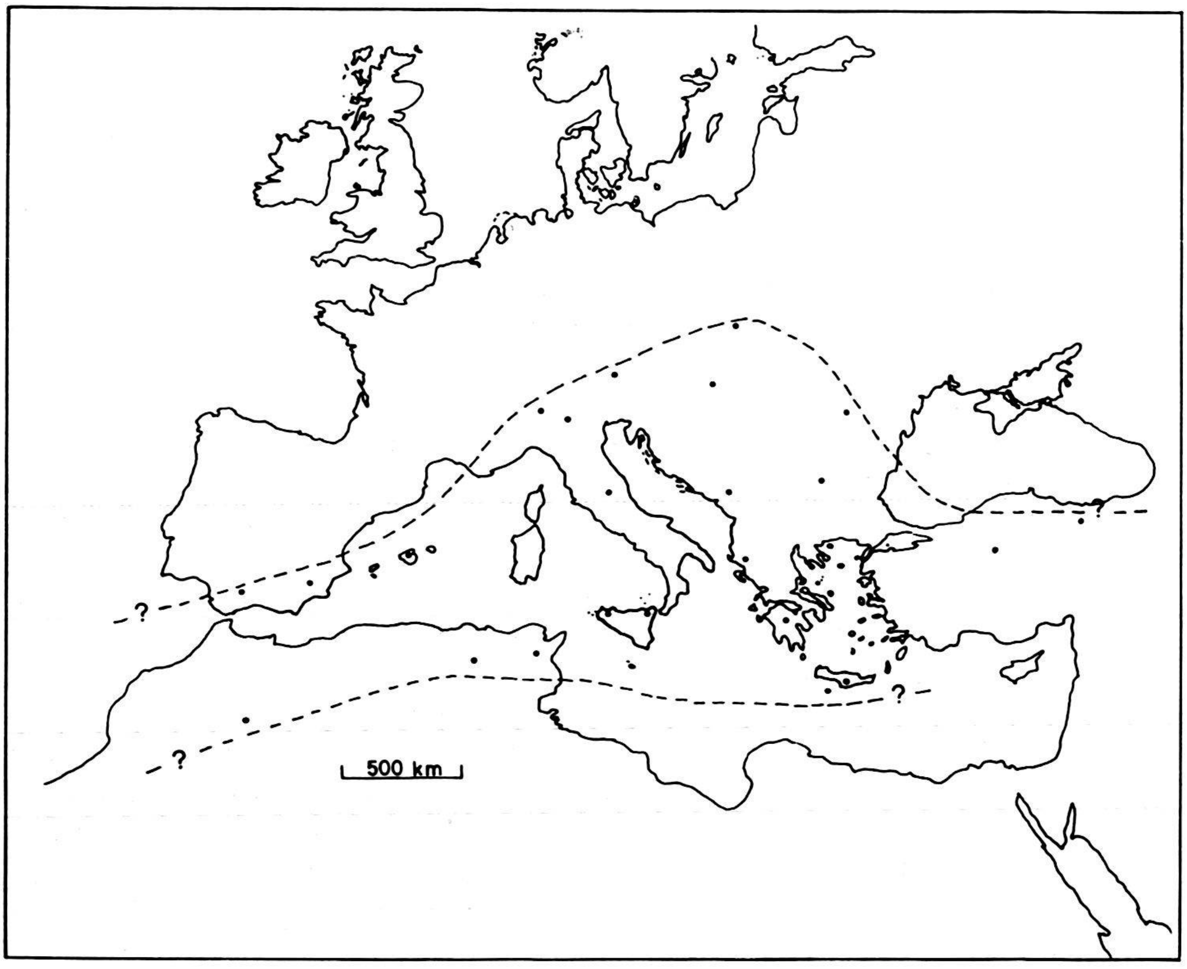


Fig. 24. Approximate present-day distribution of ferromanganese-enriched red limestone; generalised for the whole of the Jurassic .Data from AUBOUIN, 1964; AUBOUIN, CADET, RAMPNOUX, DUBAR & MARIE, 1964; AUBOUIN & NDOJAJ, 1964; AUBOUIN & DERCOURT, 1965; ARKELL, 1956; BERNOULLI, 1967; BREMER, 1966; CASTANY, 1956; COLOM & RANGHEARD, 1966; DU-DRESNAY, 1964; DURAND-DELGA, 1962; GECZY, 1961; GEYER, 1967; HALLAM, 1967; JENKYNS, 1967; SIGAL & TRUILLET, 1966; SZULCZEWSKI, 1965.

The approximate present-day limits of this red limestone zone, which can be taken as reflecting "oceanic" conditions (HALLAM, 1967), are shown in Fig. 24 and it is only in this area that Jurassic ferromanganese nodules occur. It must be stressed, however, that red limestones are not by any means the only facies found within this area as carbonate-platform and even continental deposits are developed in some places (ARKELL, 1956).

Occasionally ferromanganese enrichment may be found associated with hardgrounds in oolitic and pelletal deposits rather than the red biomicrites (e.g. STURANI, 1964, for the Venetian Alps; ACCORDI & BOSELLINI, 1965, for the Dolomites), though these localities still fall within the "oceanic" realm.

## Origin of "ferromanganese"

The origin of modern ferromanganese concretions is still in dispute; thus the genesis of the Jurassic nodules is also somewhat problematic. Two primary sources of manganese are postulated for modern iron-manganese accumulations: hydrothermal or volcanic effusions within the ocean basin, and continental run-off (MURRAY & RENARD, 1891, p. 372–378; ARRHENIUS, MERO & KORKISCH, 1964; ARRHENIUS & BONATTI, 1965; BONATTI & NAYUDU, 1965; MANHEIM, 1965). WANGERSKY & GORDON (1965) have stressed the importance of organic aggregates as carriers of manganese. Currently, the volcanic theory seems to be the most fashionable; certainly its importance in the genesis of oceanic nodules cannot be disputed.

Terrigenous clastics are lacking both in the ferromanganiferous condensed sequences of the west Sicilian Jurassic and in coeval basinal sediments; the clay content, mainly illite, could be typical of an oceanic environment (GRIFFIN, WINDOM & GOLDBERG, 1968), so any major land-mass was probably at some distance. Minor exposed areas may, however, have existed in Sardinia and over parts of eastern Sicily and Calabria (ARKELL, 1956) during some of the Jurassic, and river drainage may have supplied small amounts of iron and manganese to the Tethyan Ocean. Moreover, the Jurassic was a time of widespread ironstone formation, particularly in northern Europe (HALLAM, 1967), and also in a very minor way in North Africa (LUCAS, 1942). This iron is generally assumed to be derived from continental sources (e.g. TAYLOR, 1948; HALLAM, 1967) and, if this is so, one would also expect some manganese to be leached into the ocean. These epicontinental iron ores are not rich in manganese (e.g. TAYLOR, 1948; HEGEMANN & ALBRECHT, 1954; SCHELLMANN, 1969), so presumably this element must have become separated from iron and transported oceanwards in the manner outlined by KRAUSKOPF (1957). Thus some continental contribution is to be expected for the Jurassic ferromanganese nodules associated with Tethyan red limestones.

However, submarine volcanism has already been appealed to as an explanation of the high iron, barium and chromium contents of some of the west Sicilian ferromanganese concretions, and this source was the one that WENDT (1963) favoured as most likely for the origin of the mineral accumulations. Volcanic activity in the Middle Jurassic, particularly the Bajocian, of western Sicily is well documented (e.g. FABIANI, 1926; TREVISAN, 1937; SCHMIDT di FRIEDBERG, BARBIERI & GIANNINI, 1960; BROQUET,

CAIRE & MASCLE, 1966; CAFLISCH, 1966; MONTANARI, 1966). The extrusions, which occur in several different areas, are generally described as basaltic and are often considerably altered; they may be extensively limonitised, chloritised, and replaced by carbonate in a comparable manner to that described by MATTHEWS (1961), NAYUDU (1964) and BONATTI & NAYUDU (1965) when dealing with modern altered volcanics and their association with ferromanganese enrichment. Reworked fragments of the altered trachytic tuffs and lavas from the condensed sequence on Monte Bonifato (Fig. 25) match the descriptions of these authors very closely.

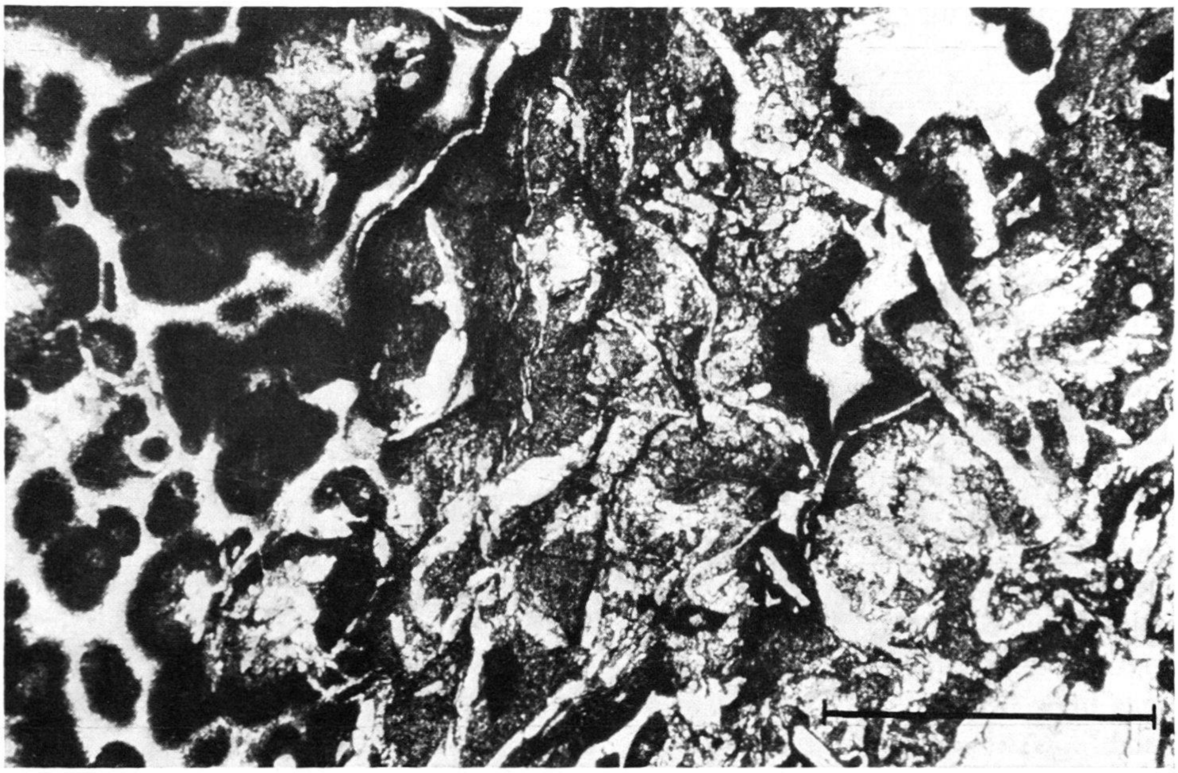

Fig. 25. Altered trachytic lava fragment from the ferromanganiferous horizon on Monte Bonifato, western Sicily. Note ferromanganese segregations; the matrix is largely replaced by calcite. Thin section. Scale bar = 1 mm.

Thus, for the Middle Jurassic ferromanganese crusts and nodules of western Sicily, volcanism was probably the most immediate source of material.

Although normal submarine volcanics are spatially related to ferromanganese deposits in western Sicily, and a similar relationship may perhaps be found in southern Spain (GEYER, 1965), elsewhere in the Tethyan region this association may not seem so obvious. However, some of the ophiolites (greenstones) which occur in parts of the Tethyan region may be of Jurassic age (AUBOUIN, 1965, p. 61; GRUNAU, 1965) and extrusion of this basic material on to the ocean floor would have supplied considerable quantities of iron and manganese to the sea water. Some of this appears to have been precipitated locally, since iron and manganese are often intimately associated with radiolarites and ophiolitic rocks – the so-called Steinmann Trinity (e.g. GEIGER, 1948, for Switzerland; TROMP, 1948, for Turkey; DEBENEDETTI, 1964, for Italy).

Further evidence of dated Jurassic Tethyan volcanicity is supplied by the bentonite that has been discovered in the Venetian Alps (BERNOULLI & PETERS, 1970).

Thus, generalising for the whole of the Jurassic Tethyan Ocean, primary source materials for the formation of ferromanganese crusts and nodules probably came from oceanic sources – submarine volcanism and exhalations – and from continental run-off.

## Environment of deposition: effect on chemical composition

The depositional environment of the Sicilian ferromanganese crusts and nodules has been outlined elsewhere (JENKYNS, 1967): they are considered to have formed on ancient limestone (non-volcanic) seamounts. These topographic highs probably reached to within a hundred or so metres of the surface, since the mineral concretions are often associated with algal stromatolites – and thus a depth limit must be imposed by the extent of the photic zone (see MCMASTER & CONNOVER, 1966, for maximum depth recorded for "live" algal-mat structures).

Attempts have been made to correlate mineralogy and elemental composition of Recent ferromanganese nodules with depth (e.g. BARNES, 1967; CRONAN & TOOMS, 1969), high cobalt, according to the former author, being indicative of relatively shallow-water environments. MERO (1965, p. 229–230), too, noted an association of cobalt-enriched nodules with topographic highs. CRONAN & TOOMS (1969) concluded that nickel and copper were positively correlated with depth, cobalt, vanadium, and barium negatively so. Many of the "shallow-water" nodules analysed by these last-named authors come from seamounts, but since Recent oceanic swells are generally volcanic, it is probable that at least some of the elemental composition of the concretions is governed by proximity to basaltic material.

Some of the west Sicilian Jurassic nodules contain high cobalt (e.g. Fig. 14) but most of them do not; so this element is probably unreliable as a depth indicator. The same also holds for barium. Nickel also shows a great disparity from nodule to nodule, although this element is generally not particularly enriched. All of the fossil nodules so far analysed are, however, relatively enriched in vanadium and relatively depleted in copper (cf. the analyses of MERO, 1965, p. 180–221; CRONAN & TOOMS, 1969) and this is in agreement with the data of the latter authors on Recent shallow-water nodules. CRONAN & TOOMS remark, in fact, that copper is particularly low in nodules from seamounts.

Nevertheless, local volcanic sources must have greatly affected the chemical composition of at least some of the west Sicilian concretions, and the scepticism of NICHOLLS (1967) and PRICE (1967) on the direct use of geochemistry as a depth indicator may well be justified.

## Conclusions

The Jurassic ferromanganese nodules from western Sicily are comparable in their shape, internal structure, mineralogy, and geochemistry to Recent oceanic iron-manganese concretions. The high-iron content of some of the fossil nodules, and the occasional presence of chromium and barium suggests that hydrothermal effusions may have strongly influenced the genesis of some of the mineral accumulations, and there is a spatial and temporal relationship with submarine volcanism. Elsewhere in the Tethyan Ocean, the ophiolites and other volcanics may have supplied iron and manganese to the sea water; however, the Jurassic was a time of widespread ironstone formation in epicontinental northern Europe and river drainage must have supplied some manganese to the ocean, whilst the iron was deposited nearer the shore.

Formation of the Tethyan ferromanganese crusts and nodules is thought to have taken place on non-volcanic seamounts whose tops probably reached to within some tens of metres of the surface; this shallow-water environment may have influenced their minor-element composition, particularly with respect to the abundances of copper and vanadium.

## Acknowledgments

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

I would also like to record my thanks to Professor P.C. Sylvester-Bradley for the facilities afforded in his depaıtment; and particularly to Dr. J.A. Dixon who undertook a daunting number of electron-probe microanalyses. Dr. J.D. Hudson read and criticized the manuscript and made many helpful suggestions.

I am also grateful to Dr. R. Burns and Dr. D.S. Cronan for supplying me with samples of Recent ferromanganese nodules; and to Dr. H.S. Torrens for introducing me to Sicilian geology.

## REFERENCES

ACCORDI, B. & BOSELLINI, A. (1967): *Lias*. In: P. LEONARDI and collaborators, *Le Dolomiti: Geologia dei Monti tra Isarco e Piave*. Trento: Consiglio Nazionale delle Ricerche, *1*, 357–359.

AHRENS, L.H., WILLIS, J.P. & OOSTHUIZEN, (1967): *Further observations on the composition of manganese nodules, with particular reference to some of the rarer elements*. Geochim. Cosmochim. Acta *31*, 2169–2180.

ALLEN, J.A. (1960): *Manganese deposition on the shells of living molluscs*. Nature, Lond. *185*, 336–337.

ANDRUSHCHENKO, P.F., SKORNYAKOVA, N.S. (1969): *Structure and mineral composition of iron-manganese nodules of the South Pacific Ocean*. (In Russian). Okeanologiia *9*, 282–294.

ARKELL, W.J. (1956): *Jurassic geology of the world*. Edinburgh: Oliver and Boyd, Ltd., 806 p.

ARRHENIUS, G. & 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. & KORKISCH, J. (1964): *Origin of oceanic manganese minerals*. Science, N.Y. *144*, 170–173.

AUBOUIN, J. (1964): *Réflexions sur le faciès «ammonitico rosso»*. Bull. Soc. géol. Fr. *6*, 475–501.

AUBOUIN, J. (1965): *Geosynclines*. Development in Geotectionics *1*. Amsterdam–London–New York: Elsevier, 335 p.

AUBOUIN, J., CADET, J.-P., RAMPNOUX, J.-P., DUBAR, G. & MARIE, P. (1964): *A propos de l'âge de la série ophiolitique dans les Dinarides yougoslaves: la coupe de Mihajlovici aux confins de la Serbie et du Monténégro (région de Plevlja, Yougoslavie)*. Bull. Soc. géol. Fr. *6*, 107–112.

AUBOUIN, J. & DERCOURT, J. (1965): *Sur la géologie de l'Egée: regard sur la Crète (Grèce)*. Bull. Soc. géol. Fr. *7*, 787–821.

AUBOUIN, J. & NDOJAJ, I. (1964): *Regard sur la géologie de l'Albanie et sa place dans la géologie des Dinarides*. Bull. Soc. géol. Fr. *6*, 593–625.

AUDLEY-CHARLES, M.G. (1965): *A geochemical study of Cretaceous ferromanganiferous sedimentary rocks from Timor*. Geochim. Cosmochim. Acta *29*, 1153–1173.

AUMENTO, F., LAWRENCE, D.E. & PLANT A.G. (1968): *The ferromanganese pavement on San Pablo Seamount*. Pap. geol. Surv. Can. *68–32*, 1–30.

BARNES, S.S. (1967): *Minor element composition of ferromanganese nodules*. Science, N.Y. *157*, p. 63.

BERNER, R.A. (1969): *Goethite stability and the origin of red beds*. Geochim. Cosmochim. Acta *33*, 267–273.

BERNOULLI, D. (1967): *Probleme der Sedimentation im Jura Westgriechenlands und des zentralen Apennin*. Verh. naturf. Ges. Basel *78*, 35–54.

BERNOULLI, D. & PETERS, Tj. (1970): *Traces of rhyolitic-trachytic volcanism in the Upper Jurassic of the Southern Alps*. Eclogae. Geol. Helv. *63*, 609–621.

BONATTI, E. & JOENSUU, O. (1966): *Deep-sea iron deposit from the South Pacific*. Science, N.Y. *154*, 634–645.

BONATTI, E. & NAYUDU, Y.R. (1965): *Origin of manganese nodules on the ocean floor*. Am. J. Sci. *263*, 17–39.

BOSTROM, K. & PETERSON, M.N.A. (1966): *Precipitates from hydrothermal exhalations on the East Pacific Rise*. Econ. Geol. *61*, 1258–1265.

BREMER, H. (1966): *Ammoniten aus dem unteren Bajocium und unteren Bathonium in der Umgebung von Ankara (Türkei)*. Neues Jb. Geol. Paläont. *125*, 155–169.

BROQUET, P., CAIRE, A. & MASCLE, G. (1966): *Structure et évolution de la Sicile occidentale (Madonies et Sicani)*. Bull. Soc. géol. Fr. *8*, 994–1013.

BUCHANAN, J.Y. (1891): *On the composition of oceanic and littoral manganese nodules*. Trans R. Soc. Edinb. *36*, 459–484.

BURNS, R.G. & FUERSTENAU, D.W. (1966): *Electron-probe determination of inter-element relationships in manganese nodules*. Am. Miner *51*, 895–902.

BUSER, W. & GRÜTTER, A. (1956): *Über die Natur der Manganknollen*. Schweiz. miner. petrog. Mitt. *36*, 49–62.

CAFLISCH, L. (1966): *La geologia dei Monti Palermo*. Mem. Riv. ital. Paleont. Stratigr. *12*, 108 p.

CASTANY, G. (1956): *Essai de synthèse géologique du territoire Tunisie–Sicile*. Ann. Mines Géol. *16*, 1–101.

CHENEY, E.S. & VREDENBURGH, L.D. (1968): *The role of iron sulphides in the diagenetic formation of iron-poor manganese nodules*. J. sediment. Petrol. *38*, 1363–1365.

COLOM, G. & RANGHEARD, Y. (1966): *Les couches à protoglobigérines de l'Oxfordien supérieur de l'Ile Ibiza et leurs équivalents à Majorque et dans le domaine subbétique*. Rev. Micropal. *9*, 29–36.

CRONAN, D.S. (1969): *Inter-element associates in some pelagic deposits*. Chem. Geol. *5*, 99–106.

CRONAN, D.S. & TOOMS, J.S. (1968): *A microscopic and electron probe investigation of manganese nodules from the northwest Indian Ocean*. Deep-Sea Res. *15*, 215–223.

CRONAN, D.S. & TOOMS, J.S. (1969): *The geochemistry of manganese nodules and associated pelagic deposits from the Pacific and Indian Oceans*. Deep-Sea Res. *16*, 335–359.

DEBENEDETTI, A. (1965): *Il complesso radiolariti-giacimenti di manganese-giacimenti piritoso-cupriferi-rocce a fuchsite, come rappresentante del Malm nella formazione dei Calcescisti. Osservazioni nelle Alpi Piemontesi e della Val d'Aosta*. Boll. Soc. geol. ital. *84*, (I), 131–163.

DU-DRESNAY, R. (1964): *Les discontinuités de sédimentation pendant le Jurassique, dans la partie orientale du domaine Atlasique Marocain, leurs conséquences stratigraphiques et leurs relations avec l'orogénèse Atlasique*. Colloque du Jurassique, Luxembourg, 899–912.

DURAND-DELGA, M. (1962): *Algerie*. In: R. FURON (Editor), Lexique Stratigraphique International, Afrique, *4*, Paris: Centre National de la Recherche Scientifique, 39–132.

FABIANI, R. (1926): *Scoperta di un apparato eruttivo del Giurese medio in Sicilia*. Boll. Ass. min. sicil. *2*, 3–12.

FABRICIUS, F.H. (1968): *Calcareous sea bottoms of the Raetian and Lower Jurassic Sea from the west part of the northern Calcareous Alps*. In: G. MÜLLER & G.M. FRIEDMAN (Editors), *Recent Developments in Carbonate Sedimentology in Central Europe*. Berlin–Heidelberg–New York: Springer, 240–249.

FISCHER, A.G. & GARRISON, R.E. (1967): *Carbonate lithification on the sea floor*. J. Geol. *78*, 488–496.

FRIEDRICH, G., ROSNER, B. & DEMIRSOY, S. (1969): *Erzmikroskopische und mikroanalytische Untersuchungen an Manganerzkonkretionen aus dem pazifischen Ozean.* Mineral. Deposita *4*, 298–307.

GARRISON, R.E. & FISCHER, A.G. (1969): *Deep-water limestones and radiolarites of the Alpine Jurassic.* In: G.M. FRIEDMAN (Editor), *Depositional Environments in Carbonate Rocks.* Soc. econ. Paleont. Miner. Spec. Publs *14*, 20-56.

GECZY, B. (1961): *Die jurassiche Schichtreihe des Tüzköves-Grabens von Bakonycserne.* Annls Inst. geol. publ. hung. *49*, 507–549.

GEIGER, Th. (1948): *Manganerze in den Radiolariten Graubündens.* Beitr. Geol. Schweiz. Geotechn. *27*, 1–89.

GEYER, O.F. (1967): *Zur faziellen Entwicklung des subbetischen Juras in Südspanien.* Geol. Rdsch. *56*, 973-992.

GOLDBERG, E.D. (1961): *Chemistry in the oceans.* In: M. SEARS (Editor), *Oceanography.* Publ. Am. Assoc. Advan. Sci. *67*, 583-597.

GOLDBERG, E.D. & ARRHENIUS, G. (1958): *Chemistry of Pacific pelagic sediments.* Geochim. Cosmochim. Acta *13*, 153–212.

GRANT, J.B. (1967): *Environmental controls underlying the morphology and composition of ferromanganese concretions of the southern oceans.* Geol. Soc. Am. Abs *1967*, p. 86.

GRIFFIN, J.J., WINDOM, H. & GOLDBERG, E.D. (1968): *The distribution of clay minerals in the World Ocean.* Deep-Sea Res. *15*, 433–459.

GRILL, E.V., MURRAY, J.W. & MACDONALD, R.D. (1968): *Todokorite in manganese nodules from a British Columbia Fjord.* Nature, Lond. *219*, 358–359.

GRUNAU, H.R. (1965): *Radiolarian cherts and associated rocks in space and time.* Eclogae. geol. Helv. *58*, 157-208.

GRUNWALD, R.E. (1964): *The mineralogy and origin of manganese concretions in the Oacoma Zone of the Pierre Shale near Chamberlain, South Dakota.* Proc. S. Dak. Acad. Sci. *43*, 193–196.

GULBRANDSEN, R.A. & REESER D.W. (1969): *An occurrence of Permian manganese nodules near Dillon, Montana.* Prof. Pap. U.S. geol. Surv. *650*-C, 49–57.

HALLAM, A. (1967): *Sedimentology and palaeogeographic significance of certain red limestones and associated beds in the Lias of the Alpine region.* Scott. J. Geol. *3*, 195–220.

HEGEMANN, F. & ALBRECHT, F. (1954): *Zur Geochemie oxydischer Eisenerze.* Chemie Erde *17*, 81–103.

HEIM, A. (1924): *Über submarine Denudation und chemische Sedimente.* Geol. Rdsch. *15*, 1–47.

HOLLMANN, R. (1964): *Subsolutions-Fragmente (Zur Biostratinomie der Ammonoidea im Malm des Monte Baldo/Norditalien).* Neues Jb. Geol. Paläont. Abh. *119*, 22–82.

HURLEY, R.J. (1966): *Geological studies of the West Indies.* In: W.H. POOLE (Editor), *Continental margins and island arcs.* Pap. geol. Surv. Can. *66–15*, 139–150.

JENKYNS, H.C. (1967): *Fossil manganese nodules from Sicily.* Nature, Lond. *216*, 673–674.

JENKYNS, H.C. (1969): *Sedimentology of the west Sicilian Jurassic.* Thesis, Univ. Leicester, 278 p.

JENKYNS, H.C. (1970): *Submarine volcanism and the Toarcian iron pisolites of western Sicily.* Eclogae Geol. Helv. *63*, 549–572.

JUKES-BROWNE, A.J. & HARRISON, J.B. (1892): *The geology of Barbados.* Part. 2. *The Oceanic Deposits.* Quart. Jl geol. Soc. Lond. *48*, 170–226.

JURGAN, H. (1967): *Genese und Fazies von Lias-Sedimenten in den Berchtesgadener Alpen.* Diss., Berlin, 122 p.

JURGAN, H. (1969): *Sedimentologie des Lias der Berchtesgadener Kalkalpen.* Geol. Rdsch. *58*, 464–501.

KOVÁCS, L. (1956): *Manganerzausscheidung in den jurassischen Ammonitenmeeren.* Mitt. Fak. Berg-Ing. Geo-Ing. Techn. Univ. Sopron *19*, 249–258.

KRAUSKOPF, K.B. (1957): *Separation of manganese from iron in sedimentary processes.* Geochim. Cosmochim. Acta *12*, 61–84.

LECHNER, K. & PLÖCHINGER, B. (1956): *Die Manganerzlagerstätten Österreichs.* In: J.G. REYNA (Editor), *Symposium sobre yacimientos de manganeso, 5,* Europa. 20th Int. Geol. Cong., 299–313.

LEPP, H. (1963): *The relation of iron and manganese in sedimentary iron formations.* Econ Geol. *58*, 515–526.

LUCAS, G. (1942): *Description géologique et pétrographique des Monts de Ghar Rouban et du Sidi el Abed (frontière algéro-marocaine).* Bull. Serv. Carte géol. Alger., 2$^{e}$ s., n°. *16*, 2 vols.

LYNN, D.C. & BONATTI, E. (1965): *Mobility of manganese in diagenesis of deep-sea sediments.* Mar. Geol. *3*, 457–474.

MANHEIM, F.T. (1965): *Manganese-iron accumulations in the shallow marine environment.* In: Symposium on Marine Geochemistry, Narragansett Mar. Lab., Occ. Publ. *3*, 217–276.

MATTHEWS, D.H. (1961): *Lavas from an abyssal hill on the floor of the North Atlantic Ocean.* Nature, Lond. *190*, 158–159.

MCFARLIN, P.F. (1967): *Aragonite vein fillings in marine manganese nodules.* J. sediment.Petrol. *37*, 68–72.

MCMASTER, R.L. & CONNOVER, J.T. (1966): *Recent algal stromatolites from the Canary Islands.* J. Geol. *74*, 674–652.

MERO, J.L. (1965): *The mineral resources of the sea.* Amsterdam–London–New York: Elsevier, 312 p.

MEYLAN, M. & GOODELL, H.G. (1967): *Mineralogy of manganese nodules from the Southern ocean.* Geol. Soc. Am. Abs. *1967*, p.149.

MOLENGRAAF, G.A.F. (1916): *On the occurrence of nodules of manganese in Mesozoic deep-sea deposits from Borneo, Timor, and Rotti, their significance and mode of formation.* Proc. Acad. Sci. Amst. *18*, 415–430.

MOLENGRAAF, G.A.F. (1922): *On manganese nodules in Mesozoic deep-sea deposits of Dutch Timor.* Proc. Acad. Sci. Amst. *23*, 997–1012.

MONTANARI, L. (1966): *Geologia dei monti di Trabia (Sicilia).* Riv. min. sicil. *17*, 1–41.

MURRAY, J. & IRVINE, R. (1894): *On the manganese oxides and manganese nodules in marine deposits.* Trans. R. Soc. Edinb. *37*, 721–742.

MURRAY, J. & RENARD, A.F. (1891): *Report on deep-sea deposits based on specimens collected during the voyage of H. M. S. "Challenger" in the years 1873–1876.* In: "Challenger" Reports. Edinburgh: H.M.S.O., 525 p.

NAYUDU, Y.R. (1964): *Palagonite tuffs (hyaloclastites) and the products of post-eruptive processes.* Bull. volcan. *27*, 391–410.

NIINO, H. (1955): *On a manganese nodule and* Petrochus *dredged form the banks near the Izu Islands, Japan.* Rec. Oceanogr. Wks. Japan *2*, 1–5.

NICHOLLS, G.D. (1967): *Trace elements in sediments; an assessment of their possible utility as depth indicators.* Mar. Geol. *5*, 539–555.

PETTERSSON, H. (1943): *Manganese nodules and the chronology of the ocean floor.* Medd. Oceanogr. Inst. Goteborg, Ser. B. *2*, 1–39.

PRATT, R.M. & MCFARLIN, P.F. (1966): *Manganese pavements on the Blake Plateau.* Science, N.Y. *151*, 1080–1082.

PRICE, N.B. (1967): *Some geochemical observations on manganese-iron oxide nodules from different depth environments.* Mar. Geol. *5*, 511–538.

RILEY, J.P. & SINHASENI, P. (1958): *Chemical composition of three manganese nodules from the Pacific Ocean.* J. mar. Res. *17*, 466–482.

RONA, E.D.W., HOOD, O.W., MUSE, L. & 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.

SCHMIDT DI FRIEDBURG, P., BARBIERI, F. & GIANINNI, G. (1960): *La geologia del gruppo montuoso delle Madonie (Sicilia centro-settentrionale).* Boll. Serv. geol. Ital. *81*, 73–140.

SIGAL, J. & TRUILLET, R. (1966): *Etude micropaléontologique et illustration des filons-couches granoclassés du Capo Sant'Andrea (Sicile).* Bull. Soc. géol. Fr. *8*, 986–993.

SMITH, R.E., GASSAWAY, J.D. & GILES, H.N. (1968): *Iron-manganese nodules from Nares abyssal plain: geochemistry and mineralogy.* Science, N.Y. *161*, 780–781.

SOKOLOW, N. (1901): *Die Manganerzlager in den tertiären Ablagerungen des Gouvernements Jekaterinislaw.* Mem. Comit. geol. St. Petersbourg (Trudy geol. Kom.) *18*, 61–82.

SOREM, R.K. (1967): *Manganese nodules: nature and significance of internal structure.* Econ. Geol. *62*, 141–147.

SOREM, R.K. & GUNN, D.W. (1967): *Mineralogy of manganese deposits, Olympic Peninsular, Washington.* Econ. Geol. *62*, 22–65.

STRAKOV, N.M. (1966): *Types of manganese accumulation in present-day basins: their significance in an understanding of manganese mineralisation.* Int. geol. Rev. *8*, 1172–1196.

STURANI, C. (1964): *La successione delle faune ad ammoniti nelle formazioni medio-giurassiche delle Prealpi Venete occidentali (Regione tra il Lago di Garda e la Valle del Brenta)*. Mem. Ist. geol. miner. Univ. Padova *24*, 1-63.

SZULCZEWSKI, M. (1965): *Observations sur la génèse des calcaires noduleux des Tatras*. Annls Soc. geol. Pol. *35*, 243-261.

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

TREVISAN, L. (1937): *Scoperta di basalti accompagnati da tufi fossiliferi dei Baiociano a Vicari (Palermo)*. Boll. Soc. Sci. nat. econ. Palermo *19*, 3-15.

TROMP, S.W. (1948): *Shallow-water origin of radiolarites in southern Turkey*. J. Geol. *56*, 492-494.

WANGERSKY, J.P. (1963): *Manganese in ecology*. In: V. SCHULTZ and A.W. KLEMENT, Jr. (Editors), Radioecology. New York: Rheinhold, 499-508.

WANGERSKY, J.P. & GORDON, D.C. (1965): *Particulate carbonate, organic carbon, and $Mn^{++}$ in the open ocean*. Limnol. Oceanogr. *10*, 544-550.

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

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

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

WENDT, J. (1970): *Stratigraphische Kondensation in triadischen und jurassischen Cephalopodenkalken der Tethys*. Neues Jb. Geol. Paläont. Mh. *1970*, 433-448.

WIEDENMAYER, F. (1963): *Obere Trias bis mittlerer Lias zwischen Saltrio und Tremona (Lombardische Alpen). Die Wechselbeziehungen zwischen Stratigraphie, Sedimentologie und syngenetischer Tektonik*. Eclogae Geol. Helv. *56*, 529-640.