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The geochemistry and palaeoenvironmental significance of iron pisoliths and ferromanganese crusts from the Jurassic of Mallorca, Spain

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ABSTRACT

The geochemistry of ferromanganese crusts and iron pisoliths from the Jurassic of Mallorca is investigated. The deposits are associated with Toarcian condensed sequences and hardgrounds which overlie Lower Lias platform limestones. Goethite is the principal mineral in the crusts and the pisoliths, which are both rich in iron; ramsdellite is the manganese phase in the ferromanganese crusts which contain 3–5% Mn. Inter-element relationships established by electron microprobe analysis show that P, V and perhaps Cr are sorbed with Fe, while Ni, Ti, Si and perhaps Ba and Co correlate positively with Mn.

Submarine hydrothermal exhalations were the likely source of much of the material, though continental run-off waters probably contributed elements towards the growth of the ferromanganese crusts. Composition-depth curves suggest a gradual deepening of the drowned margin, though appear to over-estimate the depth of formation of the deposits. Deposition occurred on a limestone seamount on subsiding continental crust during the early rifting phase which preceded the opening of the Ligurian Tethys.

RÉSUMÉ

On a étudié la géochimie des encroûtements ferrugineux-manganésifères et des nodules ferrugineux (pisolithes) du Jurassique de Majorque (Baléares). Les dépôts s'associent aux lacunes, aux couches successives condensées et aux couches durcies ("hard-grounds") qui recouvrent les calcaires de la plate-forme du Lias inférieur. Le composant minéral principal des encroûtements et des nodules, qui sont tous les deux enrichis en fer, s'avère la Goethite; dans les encroûtements, dont le contenu en Mn est de 3 à 5%, la phase manganésifère consiste en Ramsdellite. Les relations entre les composants, établies par les analyses d'«electron microprobe», sont les suivantes: le P, le V et peut-être le Cr sont liés au Fe; le Ni, le Ti, le Si et peut-être le Ba et le Co sont en corrélation positive avec le Mn.

La source d'une proportion importante de la matière étudiée s'avère probablement les exhalations hydrothermales sous-marines. Pourtant, les embouchements des eaux du plateau continental ont aussi de toute probabilité contribué quelques éléments à la croissance des encroûtements ferrugineux-manganésifères. Les courbes de composition contre profondeur semblent indiquer un approfondissement progressif de la marge noyeé, quoiqu'elles semblent surestimer la profondeur à laquelle ont été créés les dépôts. La deposition a eu lieu sur un «seamount» calcaire, ceci situé sur une croûte continentale affaissante, pendant la phase initiale de «rifting» qui a précédé l'ouverture de la Téthys ligure.

RESUMEN

La geoquímica de las costras de manganeso férrico y pisolitos ferruginosos del Jurásico de Mallorca ha sido investigada por primera vez. Los depósitos se asocian con secuencias condensadas y fondos endurecidos («hardgrounds») del Toarciense, que cubren a las piedras calizas de la plataforma con edad Liásica inferior. Goethite

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es el mineral principal en las costras y en los pisolitos, y tanto las costras como los pisolitos contienen hierro en abundancia; Ramsdellite es la fase manganesa en las costras de manganeso férrico que contienen 3–5% Mn. Los análisis llevados al cabo con «electron microprobe» establecen relaciones entre ciertos elementos y demuestran que P, V y tal vez Cr han sido absorbidos por Fe, mientras que Ni, Ti y Si y tal vez Ba y Co tienen una correlación positiva con Mn.

La mayor parte del material proviene probablemente de las exhalaciones submarinas hidrotermales y, tal vez, algunos elementos derivados de aguas continentales superficiales también contribuyeron al crecimiento de las costras de manganeso férrico. Las gráficas de composición contra profundidad sugieren que el margen submergido se profundizó gradualmente, aunque parecen sobre-estimar la profundidad de la formación de los depósitos. La deposición se realizó en un «seamount» de piedra caliza, que se encuentra en costra continental que se está hundiendo, y sucedió durante la fase temprana de «rifting» que precedió a la apertura del Tethys ligurio.

Introduction

The first discovery of marine ferromanganese deposits took place in 1868 during the course of the *Sofia* expedition to the Kara Sea east of Novaya Zemlya. However, since these findings were only published many years later (LINDSTRÖM 1884), it fell to the leaders of the *Challenger* expedition (1872–1876) to bring the widespread occurrence of ferromanganese nodules on the deep-sea floor to the attention of the Victorian scientific community.

Stimulated by this pioneering work, the study of modern ferromanganese deposits has continued apace, particularly since the Second World War, as the economic significance of the nodules, with their high concentrations of transition metals, has become apparent (MERO 1959). Nodules and encrustations are known from all the oceans, and their varying abundancies and compositions have been succinctly documented by CRONAN (1977, 1980).

"Fossil" ferromanganese deposits were first described in 1861 by GÜMBEL who was studying Lower Jurassic pelagic limestones from the Eastern Alps. Armed with knowledge of the *Challenger* expedition, geologists were soon recognising fossil equivalents of the *Challenger* samples around the world (e.g. GÜMBEL 1878; JUKES-BROWNE & HARRISON 1892, in Barbados; MOLENGRAAF 1916, 1922, in Timor; HEIM 1924, in Austria).

Renewed interest in these ancient ferromanganese deposits, perhaps as a result of the increased study of modern nodules, has resulted in numerous publications over the last three decades. In particular, many examples have been recorded from the Alpine mountain chains of central and eastern Europe, mostly from condensed Jurassic pelagic sequences. Specimens from Austria and Germany (Sonnwend Mountains and Berchtesgadener Alps) have been described by JURGAN (1967, 1969), WENDT (1969) and GERMANN (1971, 1972). JENKYNS (1967, 1970b) examined nodules and crusts from the Jurassic of western Sicily, while deposits from the Trento Zone, northern Italy were analysed by DRITTENBASS (1979). Manganese nodules from the Bakony Mountains in western Hungary have also been described (MINDSZENTY et al. 1986).

Further west, ferromanganese deposits have been studied from the Cretaceous/Palaeocene of the Briançonnais region by BOURBON (1971) and from the Montagne Noire (Devonian) by TUCKER (1973).

In comparison, fossil ferromanganese deposits from the Iberian realm are poorly documented. Stratigraphic gaps, condensed horizons and hardgrounds punctuate the Jurassic sequence, but though both GEYER (1967) and SEYFRIED (1980) illustrated "Limonitkrusten" from the Betic Cordillera of southern Spain, little work has been done on the geochemistry and significance of these mineralised deposits. In this study, the geochemistry of a ferromanganiferous hardground and associated iron pisoliths from the Jurassic of Mallorca, Spain, is described for the first time, and interpreted in terms of its paleoenvironmental significance.

Most of the mineralised Jurassic hardgrounds analysed in the literature are from terrains which originally formed part of the southern margin of the Ligurian Tethys and now constitute the Central Alps. The analyses presented here are the first from comparable deposits pertaining to the northern margin, Mallorca being situated to the northwest of the incipient ocean in the Jurassic.

Mallorca – setting and stratigraphy

Situated in the western Mediterranean off the east coast of Spain, Mallorca is the largest island of the Balearic archipelago. A wide plain across the centre of the island separates the mountains of the Sierra Norte from the hills of the Sierra de Levante. Major outcrops of Jurassic limestone are restricted to these upland areas, though minor inliers do occur as isolated hills in the central plain (Fig. 1).

The Jurassic stratigraphy of Mallorca closely parallels that of other Tethyan zones (Fig. 2). BERNOULLI & JENKYNS (1974) noted the widespread collapse and drowning of carbonate platforms during the Early Jurassic, with the subsequent deposition of pelagic and hemipelagic sediments. On Mallorca, the youngest platform deposits, commonly dolomitized, are probably Carixian (Lower Pliensbachian) in age. The Domerian (Upper Pliensbachian) is largely absent, though in some areas of the Sierra Norte the biomicrites and crinoidal calcarenites that succeed the platform may be of this age (ALVARO et al. 1984). Hardgrounds, locally mineralised, and referred to the Toarcian, are succeeded by Aalenian red, nodular limestones which effectively mark the start of sedimentation on the drowned margin.

The Toarcian hardground

General appearance

Liassic platform limestones and dolomites are abundantly exposed in the mountains of Mallorca. Due to the tectonic complexity of the highland areas, however, outcrops of the condensed sequences which overlie them are restricted, particularly in the Sierra Norte. These condensed deposits contain the mineralised hardgrounds which are the focus of this study.

Despite the paucity of well-preserved sections, a hardground of sorts is usually visible wherever the post-platform sediments are exposed. Only in certain parts of the northern Sierra de Levante does it appear that an indurated submarine surface did not develop. Brief descriptions of some of these outcrops are contained in FORNOS et al. (1984) and ALVARO et al. (1984); the locations of informative sections are shown in Figure 1.

Generally, the hardground manifests itself as an eroded, corroded and iron-stained surface above or within crinoidal calcarenites. Clasts of limestone and fragments of

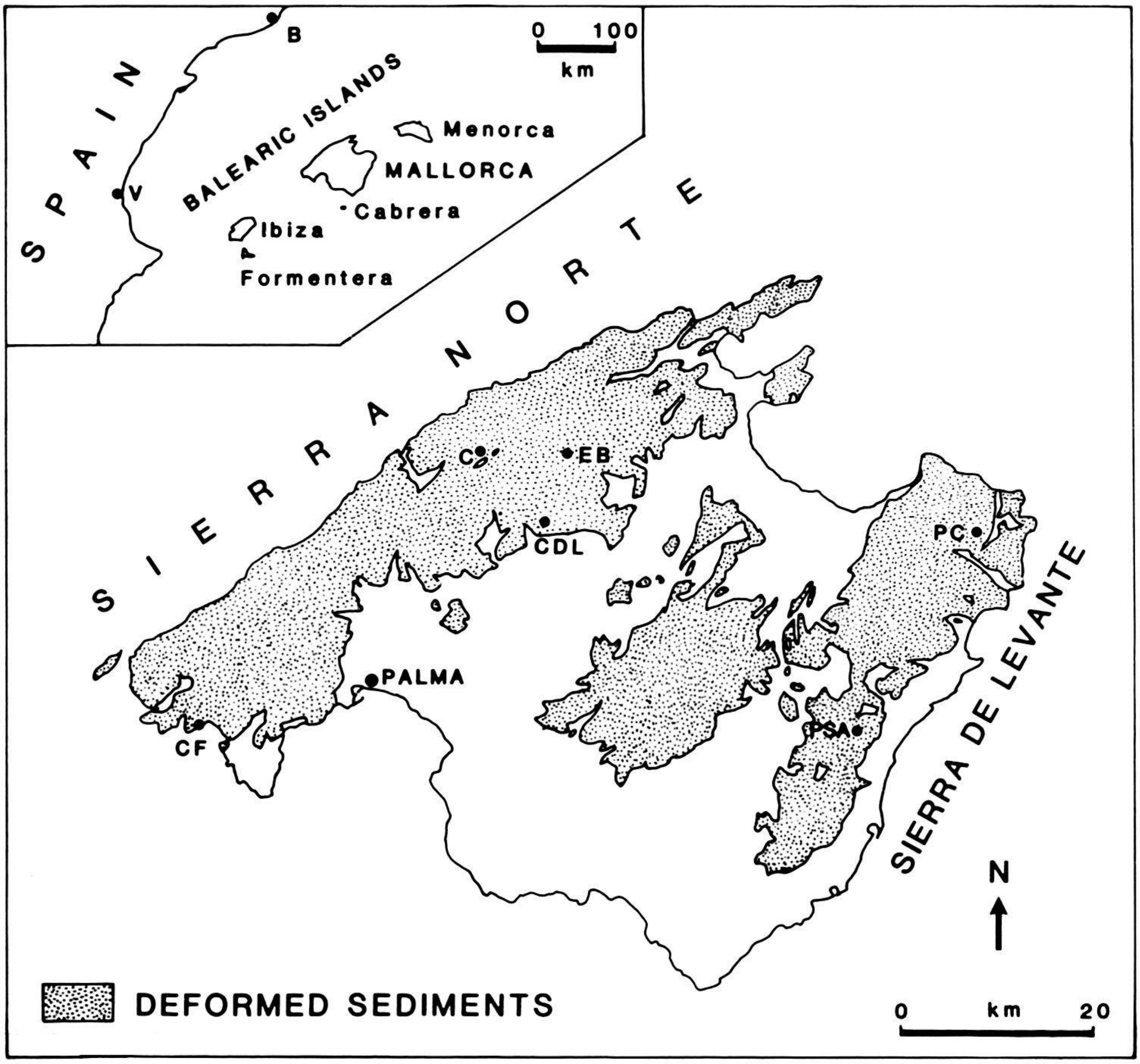

Fig. 1. Mallorca – morphology and geology. Stipple represents sequences deformed during the Miocene orogeny, including Jurassic outcrops. Post-tectonic deposits surround and overstep the older sedimentary rocks. Localities mentioned in the text: CDL = Cantera de Lloseta; CF = Cala Fornells, PC = Puig Cutri; C = Cuber; EB = Es Barraca; PSA = Puig Son Amoixa. Inset: Mallorca and the other Balearic Islands in the western Mediterranean.

ammonites are usually coated with thin pellicles of goethite (e.g. at Son Amoixa, Cuber and Es Barraca). At Son Amoixa, glauconite is a major constituent of the crinoidal sands, while the section at Puig Cutri is characterised by coatings of haematite up to 10 mm thick around intraclasts and ammonites.

The black ferromanganese deposits which are the subject of this study are exposed at only two localities. At Cala Fornells a thin black crust containing abundant encrusting foraminifera overlies red and grey micritic limestones with small iron pisoliths, but pervasive faulting has severely disrupted the outcrop and the facies relationships are not clear. At the Cantera de Lloseta, however, the hardground is spectacularly exposed. The bulk of the samples analysed are from this section which will be described in more detail below.

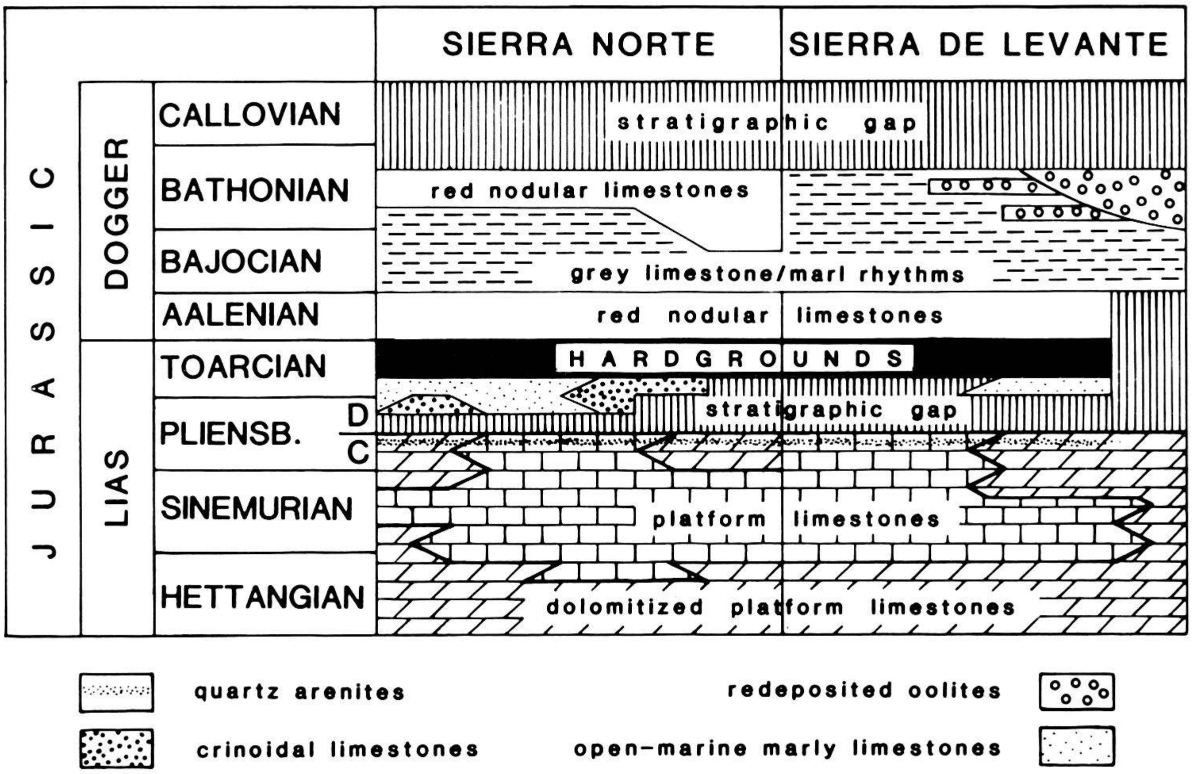

Fig. 2. General stratigraphic scheme for Lower and Middle Jurassic of Mallorca. Based on ALVARO et al. (1984), ARBONA et al. (1984/5) and the author's own work.

Palaeontology

Ammonites recovered from the hardgrounds have allowed the age of the deposits to be determined with some accuracy. At Puig Cutri the fauna includes *Pleydellia ?mactra* (BUCKMAN), *Pleurolytoceras hircinum* (SCHLOTHEIM), *Polyplectus discoides* (ZIETEN), *Hammatoceras insigne* (ZIETEN), *Hammatoceras* sp., *?Grammoceras* sp., *Harpoceras exaratum* (YOUNG & BIRD), *Harpoceras* sp. and *Partischeras* sp., spanning the *bifrons* to *levesquei* zones of the Toarcian. The specimens collected from the Cantera de Lloseta (*Catacoeloceras ?confectum* (BUCKMAN), *Hammatoceras* sp., *Harpoceras falcifer* (SOWERBY), *Phylloceras* sp. and ?*Dumortieria* sp.) range from the *falciferum* zone to the *levesquei* zone. Though forms specific to the *variabilis* zone have not been recorded at either locality, the bulk of the Toarcian is represented in these sections. Since the deposits pertaining to the hardgrounds total rather less than 25 cm in both sections, it is clear that these sequences are extremely condensed.

Cantera de Lloseta

The best exposures of the Toarcian hardground occur in a large quarry (cantera) near the small town of Lloseta at the foot of the Sierra Norte. Again the exposures are complex, but the facies relationships are reasonably clear, allowing the recognition of a precise sequence of events in the genesis of the hardground (Fig. 3).

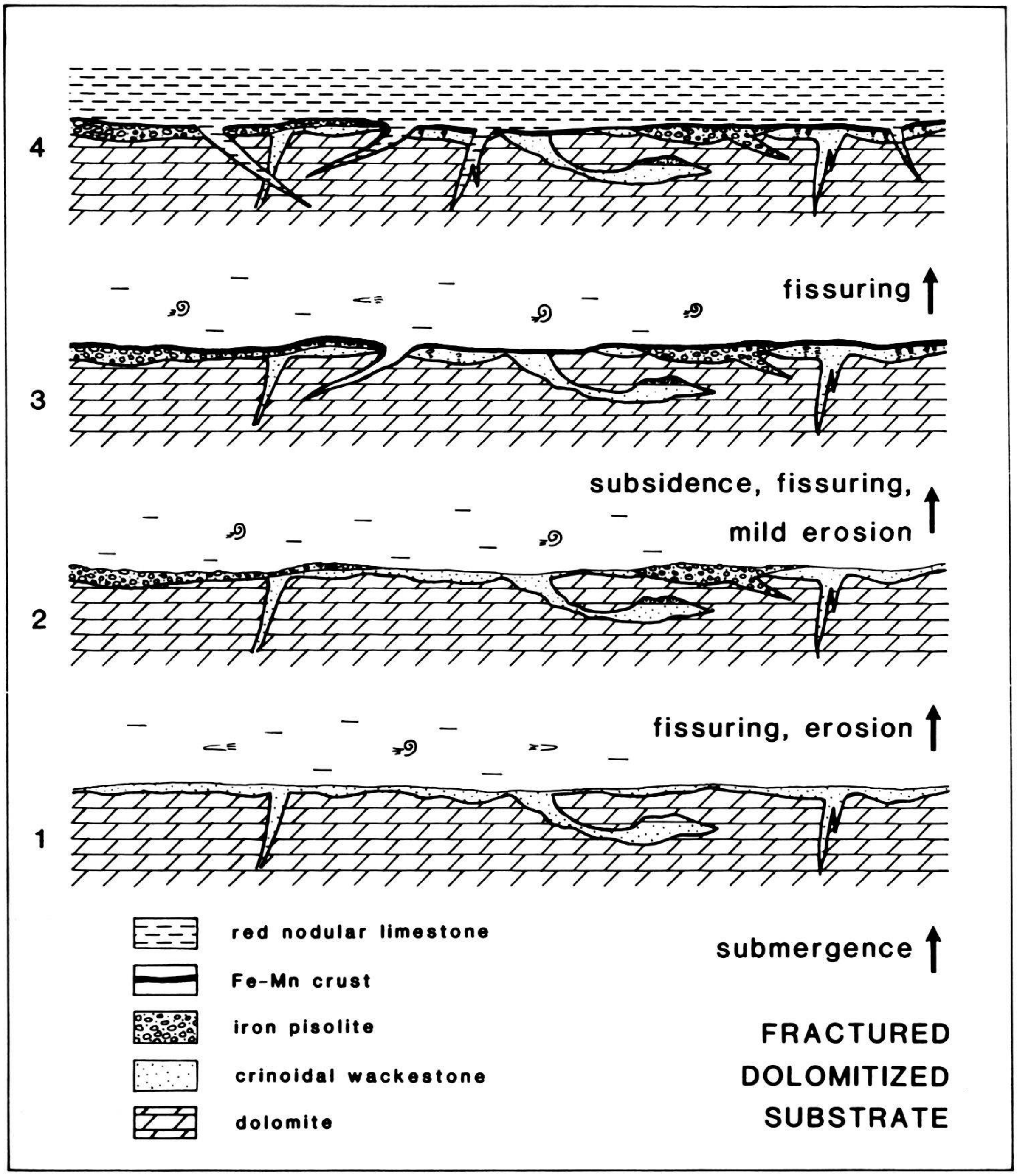

Fig. 3. Genesis of the Toarcian hardground exposed in the Cantera de Lloseta. Submergence of fractured dolomitic substrate followed by (1) deposition of thin veneer of bioclastic limestone. Erosion and fissuring preceded (2) the formation of iron pisoliths with locally-derived cores. (3) Precipitation of the Fe-Mn crust and growth of "pseudo-stromatolitic" structures followed by (4) deposition of red nodular limestone ("Ammonitico Rosso").

Substrate

The oldest formations consist of cryptalgal laminites and grainstones deposited in intertidal and subtidal environments. These carbonate-platform sequences are overlain by dolomicrites, but the intervening units have been cut out by faulting. The top surface of the dolomites is very uneven; small lithophage borings are common (Fig. 4a, b), and the dolomites are cut by neptunian fissures several centimetres deep and of considerable lateral extent (Fig. 5). The latter are filled with pink biomicrites rich in ammonites and other molluscs, small brachiopods and *Bositra*. The varied microfauna includes calcitized radiolarians and abundant foraminifera (e.g. *Involutina*, *Vidalina* and *Glomospirella*). Geopetal structures are common, with sparry calcite occluding cavities only partly filled with lime mud.

"Stromatolitic growth structures"

Overlying the dolomites in some areas is a thin layer (1–2 cm) of red bioclastic limestone with abundant bivalves, gastropods, crinoid fragments and indeterminate foraminifera. Within this layer small "growth" structures can be seen which display stomatolite-like forms, the shapes being picked out by mineral segregations (Fig. 4a, b). Similar structures have been recorded from both modern and ancient ferromanganese deposits by many workers, but their origin remains controversial. WENDT (1969) cited the presence of encrusting foraminifera between columnar structures in Jurassic ferromanganese deposits from the Sonnwend Mountains of Austria as evidence of their primary nature. In addition, MONTY (1973) suggested that similar "growths" in some recent nodules were stromatolites. By contrast, a diagenetic origin has been proposed by CRONAN & TOOMS (1968), JENKYNS (1970a) and TUCKER (1973) for some structures of this kind.

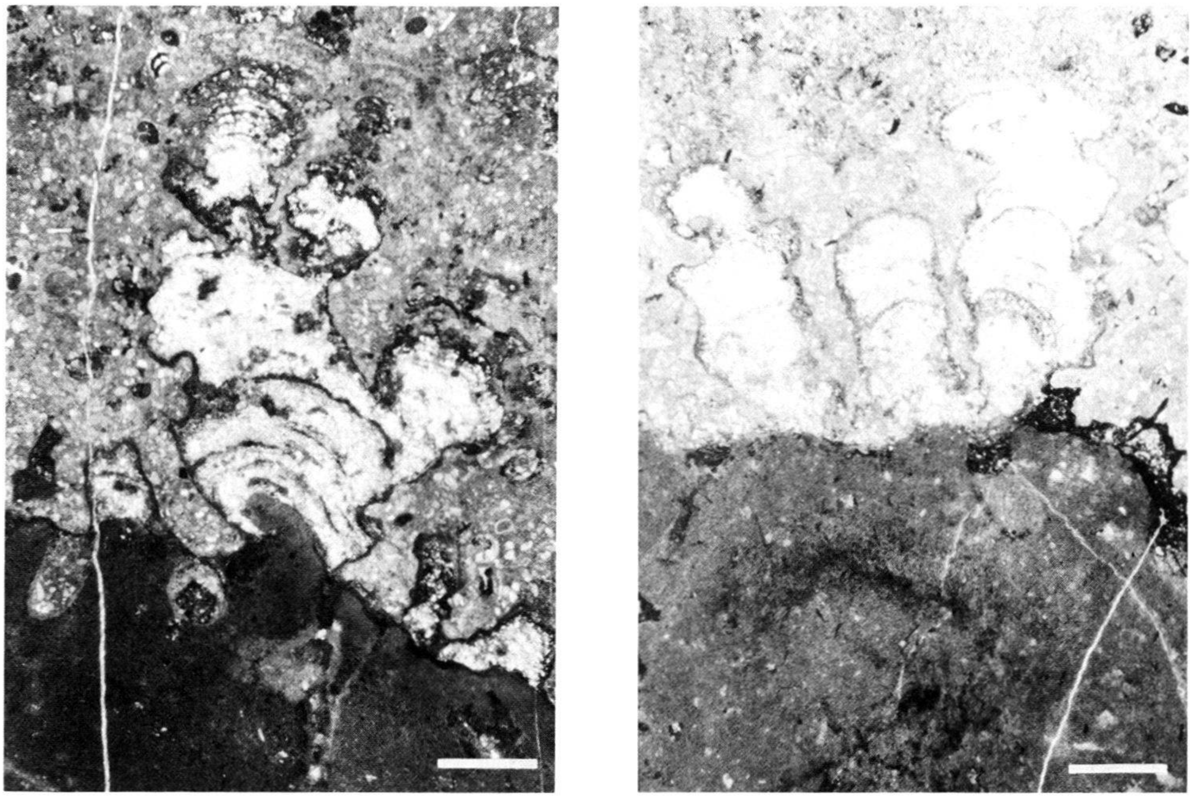

Fig. 4a and b. "Growth" structures in the bioclastic limestone overlying the dolomicrite substrate. Thin-section photomicrographs, Cantera de Lloseta. See text for discussion. Small lithophage borings are visible in the substrate. Scale bars = 1.0 mm.

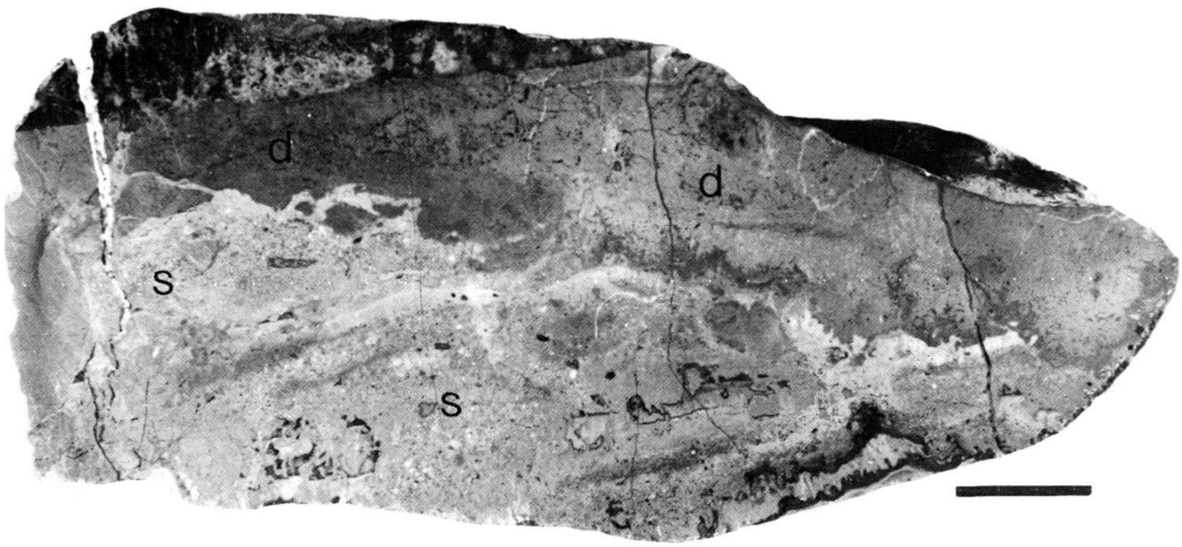

Fig. 5. Polished hand specimen of dolomicrite substrate, Cantera de Lloseta. A thin layer (1 cm) of bioclastic limestone overlies the substrate (d), which is cut by limestone-filled fissures (s). Scale bar = 2.0 cm.

The structures seen in the Mallorcan samples do not appear to be primary, but instead reflect the migration of a micro-diagenetic front through the bioclastic wackestone from the dolomites. The successive positions of the front are recorded by precipitates of ferromanganese material within the unaltered limestone, but in the more proximal parts of the structures (closest to the dolomite-limestone contact) the micritic matrix of the wackestone has been neomorphosed to a patchy clear spar. In all cases the "growths" stop a few millimetres below the black crust which overlies the limestone, suggesting that this was an early diagenetic process. Moreover, it indicates that this process did not contribute to the growth of the ferromanganese crust. The migration of iron- and manganese-rich fluids from the dolomite into the overlying limestone would have been halted by contact with highly oxidising waters in the upper parts of the lithified sediments which would have caused precipitation of the oxides below the growing ferromanganese crust.

The cause of the remobilization is unclear. Presumably the oxidising potential (Eh) of the pore fluids in the dolomites was low enough to permit the existence of divalent iron and manganese ions, a condition which could have been caused by the oxidation of buried organic matter.

Iron pisoliths

Other sections in the quarry show hollows and fissures in the irregular dolomite surface filled with iron pisoliths set in a red bioclastic wackestone matrix rich in echinoderm debris, mollusc fragments and foraminifera (Fig. 6, 7, 8). The cores of these coated grains are of local derivation; clasts of dolomicrite and bioclastic wackestone are most common, but eroded and corroded ammonites are also coated with layers of goethite.

Fig. 6. Lens of iron pisolite with black oxide crust coating the lower surface, which was the roof of a neptunian sill, and the upper surface. Cantera de Lloseta. Hammer shaft is 30 cm long.

The clasts range from 5 to 60 mm in diameter, though the larger pisoliths tend to have a more discoid shape than the smaller, more spherical samples. Many of the clasts are deeply impregnated with iron oxides. This is thought to be due to the action of boring algae or fungi – borings and tubules a few microns in diameter are noticeable in some of the clasts (Fig. 9). These are filled with iron oxides, but are restricted to the clasts, the goethite coatings being unaffected by this "limonitisation" process and presumably deposited after its completion. JENKYNS (1970a) illustrated similar structures in Toarcian iron pisoliths from Sicily and equated the "limonitisation" with the micritisation described by BATHURST (1966). Photosynthetic algae are often held responsible for micritisation, suggesting that the process is limited to regions within the photic zone. However, FRIEDMAN et al. (1971) and AMEZIANE-COMINARDI & ROUX (1987) have shown that a variety of other organisms (e.g. bacteria and fungi), which are not light-dependent, can bore into carbonate grains. BROMLEY (1965) listed the criteria for distinguishing algal and fungal bores and demonstrated that structures produced by the activity of endolithic algae, when compared with their fungal equivalents, generally have larger and more variable diameters and an irregular pattern of branching. In addition, BATHURST (1966) stated that most algal bores have diameters of 6–15 μm, while those produced by fungi are only 1–2 μm thick. The structures visible in Figure 9 have diameters of 5–25 μm, suggesting an algal derivation. Combinations of algal and fungal bores, which resemble those in Figure 9, were illustrated by GATRALL & GOLUBIĆ (1970, Plate 1), but they also showed the similarity of many algal and fungal

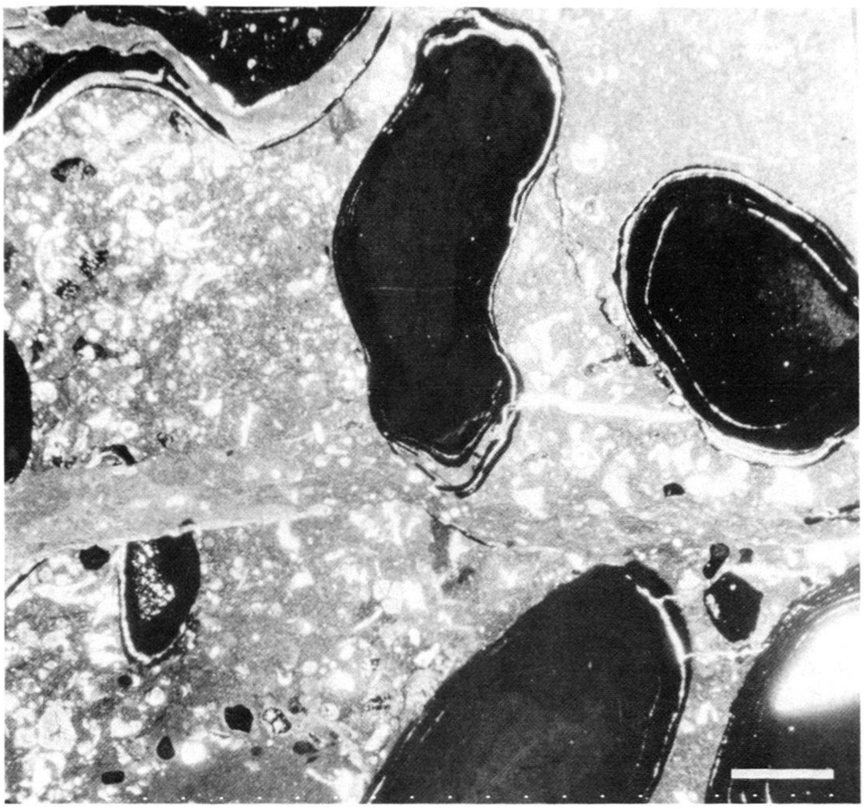

Fig. 7. Small iron pisoliths set in crinoid-mollusc-foram wackestone. The pisolith cores are dolomicritic. Thin-section photomicrograph, Cantera de Lloseta. Scale bar = 1.0 mm.

Fig. 8. Polished hand specimen from the Cantera de Lloseta showing large iron pisolith (5.0 × 3.0 cm) with a smaller, older pisolith at its core, indicating repeated phases of deposition, lithification, erosion and reworking. Scale bar = 2.0 cm.

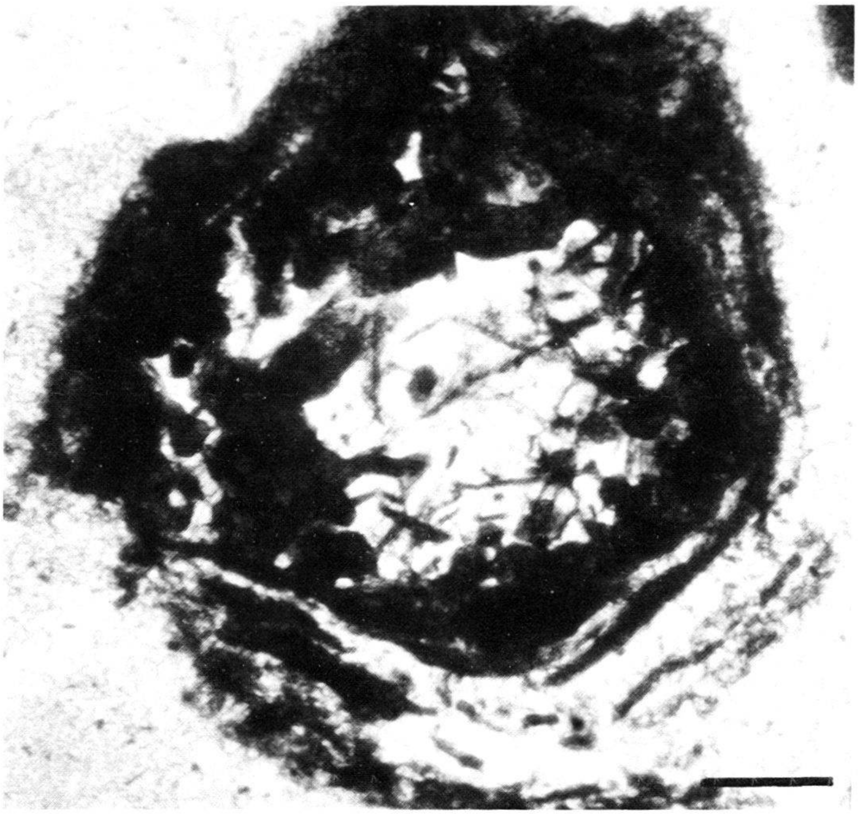

Fig. 9. Small pisolith showing boring structures (5–25 μm diameter) in skeletal calcite grain. Thin-section photomicrograph, Cantera de Lloseta. Scale bar = 50 μm.

bores. Consequently, it is not possible to state definitively that the "limonitisation" occurred in shallow waters within the photic zone.

The brown goethite coatings are up to 1 cm thick around the larger clasts and comprise individual laminae of 10–100 μm (Fig. 7, 8, 10). Radial and tangential calcite veins accentuate the pattern of concentric laminae. It is likely that post-depositional dewatering and shrinkage created the cavities which were subsequently filled with calcite, though some of the concentric veins may be of primary origin. Encrusting foraminifera (cf. *Tolypammina*) and serpulid worm tubes are common in the brown coatings, particulary on concave surfaces.

Ferromanganese crust

Further fissuring and mild erosion preceded the deposition of the black ferromanganese crust which mantles the whole hardground, lining cavities and evenly coating the irregular substrate resulting in a botryoidal appearance (Fig. 6, 8, 10). The crust is up to 2 cm thick in places and consists of innumerable fine lamellae, each a few microns across. Thin layers of brown goethitic material similar to that coating the pisoliths are common; their discontinuous nature indicates that periods of mild erosion punctuated the slow accretion of the ferromanganese crust. Tiny encrusting foraminifera are abundant (Fig. 10), raising the question of their rôle in the precipitation of ferromanganese material from seawater.

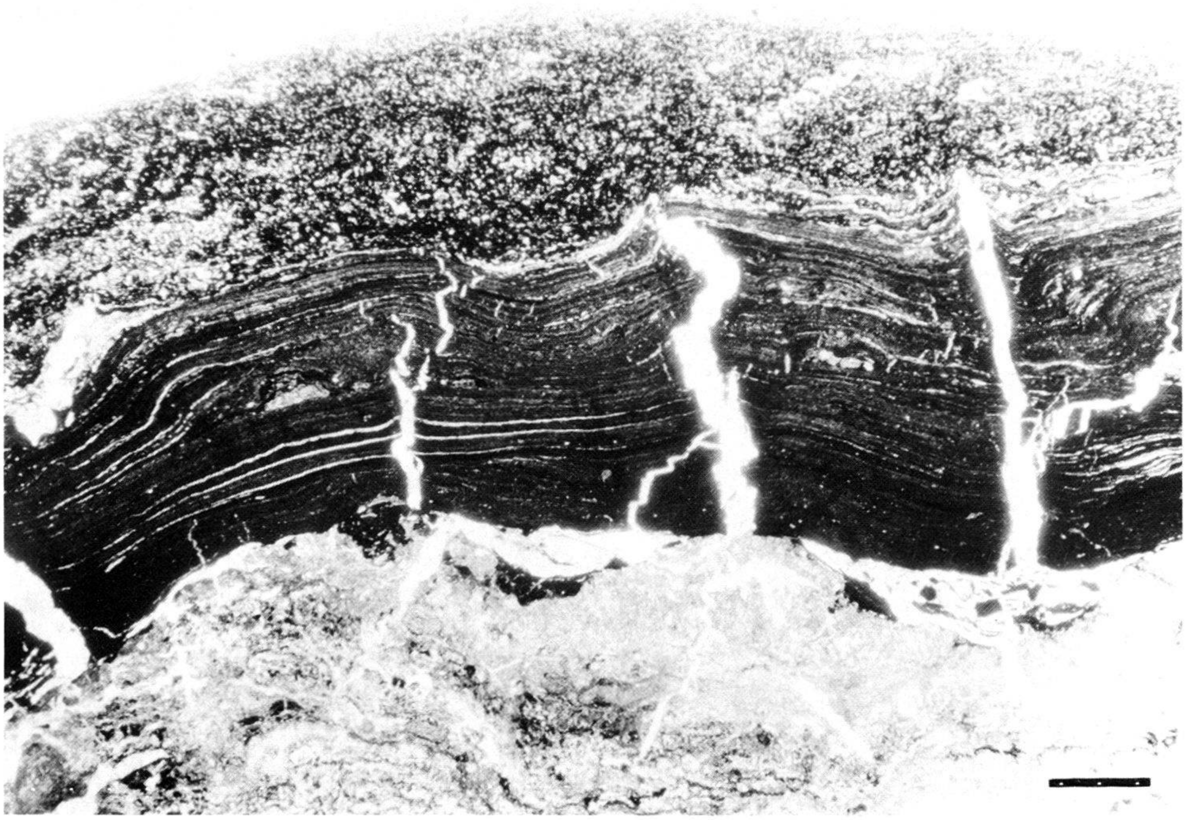

Fig. 10. Black oxide crust, containing abundant foraminiferal remains, overlying finely laminated pisolith coating. Thin-section photomicrograph, Cantera de Lloseta. Scale bar = 1.0 mm.

Thin calcite veins accentuate the lamellar structure but are probably of secondary origin. An earlier set of veins cutting across the crust shows the extent of post-depositional compaction, with structures resembling ptygmatic folds visible in thin section.

The crust is overlain by red, nodular, marly limestones ("Ammonitico Rosso") which also fill neptunian dykes and sills generated during another phase of fissuring.

Geochemistry

Method

Chemical analyses of the black crusts and pisolith coatings were performed on carbon-coated polished thin sections of samples from the Cantera de Lloseta using a Cambridge Instruments Microscan 9 electron probe microanalyser. The standard on-line ZAF correction programme of Sweatman & Long (1969) was applied to all the data. Theoretical detection limits (in weight percentages of the elements) for the various elements were calculated and are set out below.

Al 0.027	Si 0.033	P 0.010	Ca 0.023	Ti 0.018
V 0.022	Cr 0.036	Mn 0.056	Fe 0.073	Co 0.024
Ni 0.052	Cu 0.071	Zn 0.094	Ba 0.037	Pb 0.032

Step scans were built up by analysing between forty and sixty points along short traverses. In this way the inter-element relationships can be most easily seen. A selection of the results is shown graphically in Figures 11–14. Average compositions of the pisolith coatings and the black crusts, calculated from the individual point data, are given in Table 1, which also includes a number of analyses performed on samples from other outcrops of the Toarcian hardground. Since the deposits comprise a complex, fine-grained mixture of minerals (oxides,

Table 1: *Average compositions (expressed as weight percentages of the elements) of black ferromanganese crusts (CDL 7–CF 4), brown pisolith coatings (CDL 7–CDL 13ii) and other iron-stained clasts and pisoliths (PC 1–PC S) from Toarcian hardgrounds on Mallorca.*
Localities: CDL = Cantera de Lloseta; CF = Cala Fornells; PC = Puig Cutri; C = Cuber; EB = Es Barraca; PSA = Puig Son Amoixa.
Theoretical detection limits for the various elements and the number of points used in the calculation of the "averages" are shown.

	BLACK CRUSTS					IRON PISOLITHS				OTHERS						
Sample	CDL 7	CDL 8	CDL14	CDL13ii	CF 4	CDL 7	CDL 8	CDL14	CDL13ii	PC 1	C Ai	EB 3	C H3	PSA	PC S	Detection
Element																limit
Al	1.37	1.76	2.33	2.68	2.52	2.42	2.09	2.32	2.27	1.48	0.33	1.17	1.13	1.39	0.91	0.027
Si	1.21	2.62	1.85	3.28	2.49	1.94	1.19	1.05	1.00	3.38	1.01	2.68	1.33	2.24	2.93	0.033
P	0.13	0.11	0.39	0.31	0.13	0.27	0.24	0.43	0.33	1.32	0.09	0.29	0.31	2.24	0.77	0.010
Ca	12.17	13.12	8.28	1.28	6.58	8.87	8.96	3.09	6.80	18.92	5.59	5.05	24.23	31.49	27.42	0.023
Ti	0.49	0.51	0.64	2.03	1.00	0.31	0.29	0.40	0.62	0.10	0.01	0.18	0.19	0.06	0.30	0.018
V	0.05	0.07	0.06	0.19	0.07	0.08	0.12	0.10	0.14	0.07	0.05	0.12	0.07	0.04	0.17	0.022
Cr	0.01	0.01	--	0.01	0.01	0.01	0.04	0.03	0.03	0.01	0.02	0.03	0.05	0.02	0.02	0.036
Mn	3.08	4.07	5.28	2.00	3.83	0.50	0.27	0.19	0.15	0.04	--	0.07	0.03	0.06	0.05	0.056
Fe	28.81	25.24	40.33	41.43	28.73	37.90	40.49	52.90	42.18	25.02	49.00	47.80	21.17	10.06	14.31	0.073
Co	0.08	0.09	0.17	0.10	0.11	0.07	0.11	0.14	0.08	0.08	0.13	0.02	0.01	--	--	0.024
Ni	0.13	0.17	0.19	0.15	0.12	0.04	0.05	0.03	0.05	0.01	0.02	0.04	0.02	0.02	0.02	0.052
Cu	0.02	0.03	0.04	0.05	0.01	0.01	0.02	0.04	0.02	0.01	0.01	0.01	--	--	0.01	0.071
Zn	0.02	0.02	0.05	0.06	0.02	0.03	0.04	0.02	0.04	--	0.14	0.06	0.05	0.02	0.01	0.094
Ba	0.11	0.10	0.16	0.32	0.16	0.08	1.17	0.09	Q.11	0.06	0.04	0.04	0.03	0.02	0.05	0.037
Pb	0.02	0.01	0.04	0.05	0.01	0.03	0.03	0.02	0.02	0.01	0.02	0.01	0.02	--	0.01	0.032
Points	29	13	22	28	51	8	25	34	25	5	5	5	5	5	16	

oxyhydroxides, carbonates and, perhaps, a clay mineral – see p. 403–404), it was not possible to analyse individual mineral phases. Consequently, the average compositions quoted in Table 1 represent "bulk" analyses. Clearly, the individual data points show a wide scatter (as can be seen in Figures 11–14), due to the inhomogeneity of the deposits on a fine scale. Due to the complex mineralogy of the samples, the difficulty of knowing into which minerals (and where in those minerals) the trace elements have substituted, and the consequent uncertainty regarding the oxidation states of some of the elements, the results are expressed as *weight percentages of the elements* throughout this paper. Sums are not given, since they would be meaningless in the absence of analyses of elements such as potassium, sodium, magnesium and sulphur.

A comparison of the theoretical detection limits quoted above with the average compositions given in Table 1 shows that, for most of the elements, their contents are well above the detection limits. For nickel, the measured contents in the black crusts are statistically valid, but are rather too low in the pisolith coatings to be quoted with confidence. Similarly, the data for the chromium and lead contents should be treated with caution. The analyses of copper and zinc are worthless, and are included here for the sake of completeness – the contents of these elements have traditionally been measured in the analysis of ferromanganese deposits.

Results

Ferromanganese crusts

The step scans show that there are considerable compositional variations across the black ferromanganese crusts. However, the results are fairly uniform when the dilutant

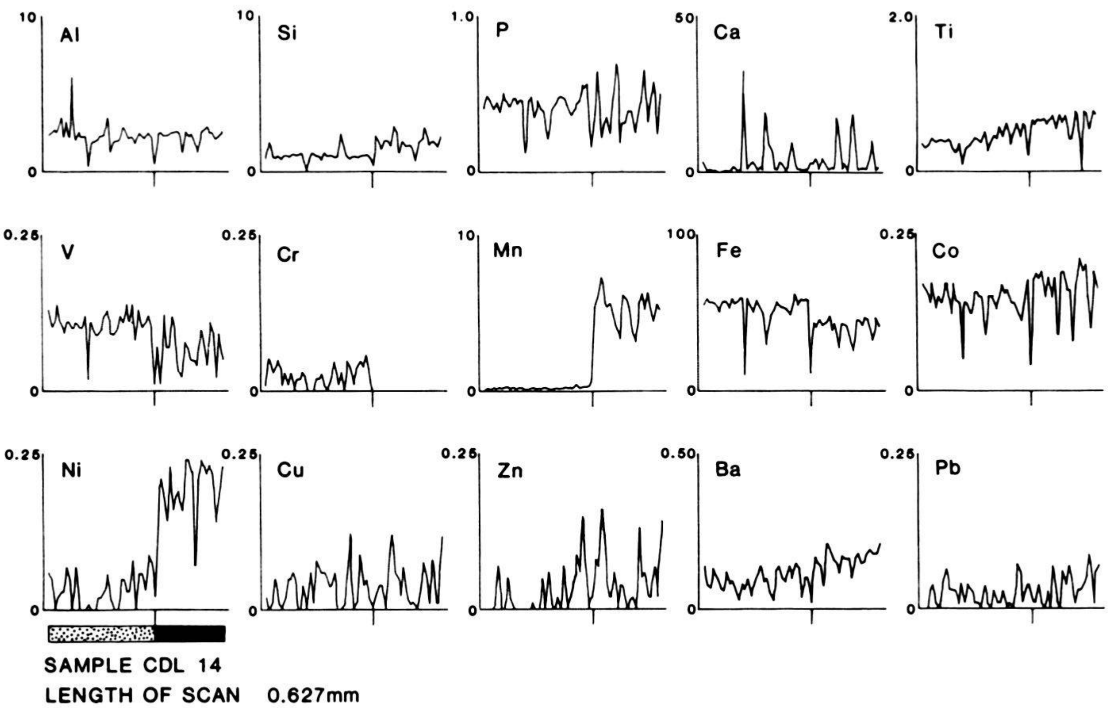

Fig. 11. Electron microprobe analysis of pisolith coating (stippled) and black crust (black) from the Cantera de Lloseta (Sample CDL 14) based on individual analyses of 57 points. Compositions expressed as weight percentages of the elements.

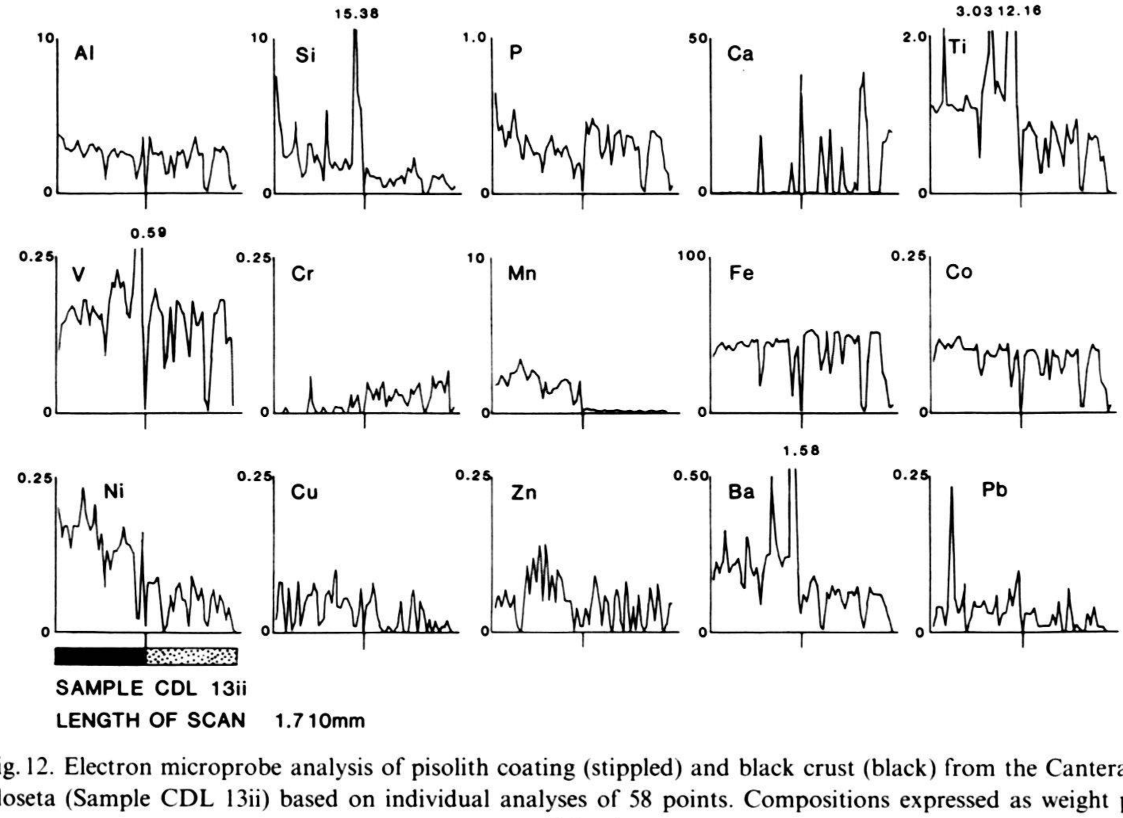

Fig. 12. Electron microprobe analysis of pisolith coating (stippled) and black crust (black) from the Cantera de Lloseta (Sample CDL 13ii) based on individual analyses of 58 points. Compositions expressed as weight percentages of the elements.

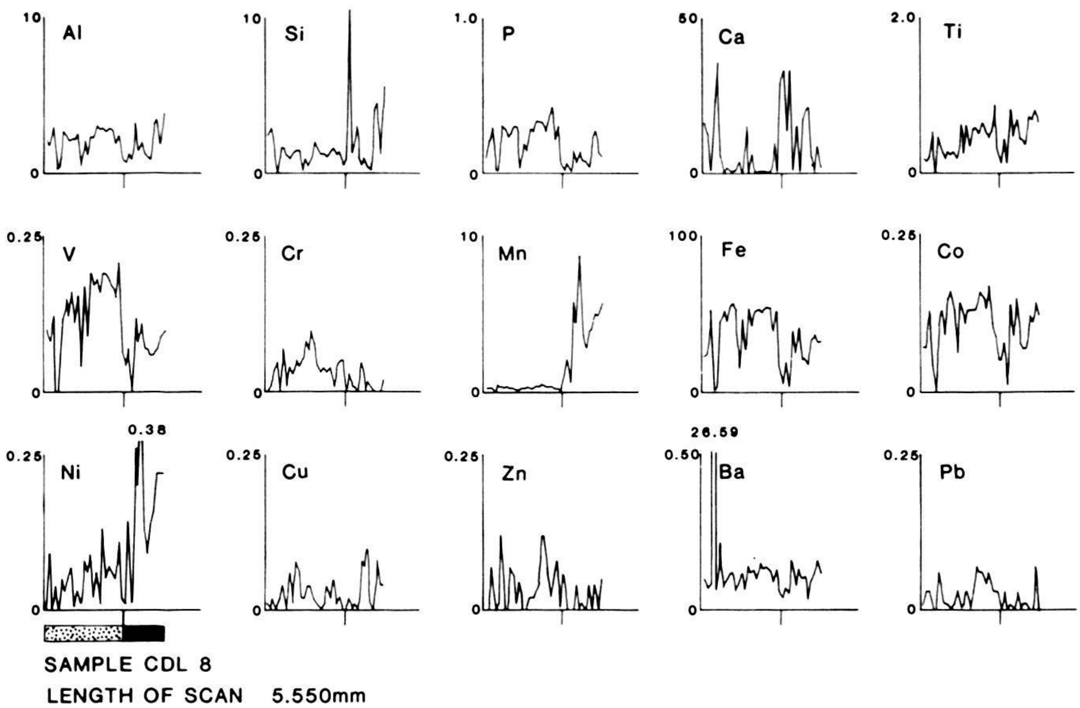

Fig. 13. Electron microprobe analysis of pisolith coating (stippled) and black crust (black) from the Cantera de Lloseta (Sample CDL 8) based on individual analyses of 38 points. Compositions expressed as weight percentages of the elements.

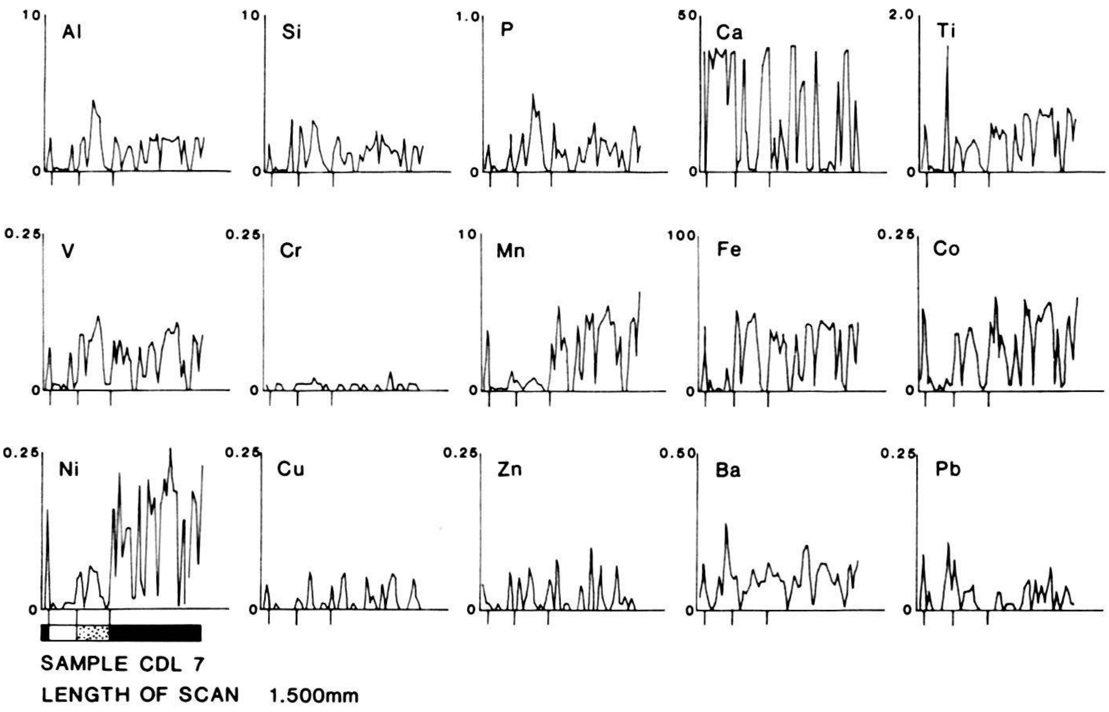

Fig. 14. Electron microprobe analysis of black crust containing calcite (clear) and brown iron-rich (stippled) laminae from the Cantera de Lloseta (Sample CDL 7) based on individual analyses of 51 points. Compositions expressed as weight percentages of the elements.

effect of calcite is taken into account, though the levels of manganese, vanadium, barium and titanium are rather anomalous in sample CDL 13ii (Fig. 12).

Manganese concentrations are low (around 4%) when compared with the average value (16%) for modern ferromanganese deposits from the World Ocean (CRONAN 1976). Similarly, silicon, cobalt, copper, nickel and lead are rather depleted. However, the values for copper and lead are below the theoretical detection limits, and the strict accuracy of these results is questionable. Only calcium (largely in the form of calcite) and, in particular, iron show a strong enrichment by comparison with the global average.

The Mallorcan deposits formed on a young continental margin undergoing active rifting during the early stages of the formation of the Ligurian Tethys. Hence, they should be directly comparable to ferromanganese nodules and crusts forming on modern marginal seamounts and banks. CRONAN (1977) gives the typical compositions of these deposits (in weight percentages of the elements) as:

Mn 15.65% Fe 19.32% Co 0.419% Ni 0.296% Cu 0.078%

Again the Mallorcan samples are comparatively depleted in manganese, cobalt, copper and nickel, and enriched in iron.

The chemistry of Jurassic Tethyan nodules is immensely varied. DRITTENBASS (1979, Table 3) listed a large number of analyses, mostly from the Jurassic of Europe, which show the wide range of compositions seen in crusts and nodules. When compared with these, the Mallorcan crusts have fairly typical compositions, though are generally depleted in calcium, a function perhaps of the choice of analysis points for this study. Given their low calcium contents, the level of manganese is rather low, while titanium is moderately enriched. Most noticeably, the iron contents are extremely high.

Iron pisoliths

Analyses of the pisolith coatings are contained in Figures 11, 12 and 13; Figure 14 includes analyses of a brown band in the black ferromanganese crust. The average compositions calculated from these scans (shown in Table 1) again show only modest variation. The iron contents are high (40–50%), in direct contrast to the very low levels of manganese (0.2–0.5%).

The most comparable analyses in the literature are those of JENKYNS (1970a) who described iron pisoliths from the Toarcian of western Sicily; the contents of iron, aluminium, vanadium, titanium and silicon correspond closely. Chromium, manganese, cobalt, nickel, copper and zinc are all relatively depleted in the Mallorcan samples which, by contrast, are enriched in phosporus and barium.

Inter-element relationships

Apart from the obvious antithetic relationship of calcium/calcite with the ferromanganese phase, a number of other relationships are shown in Figures 11–14. Most striking is the covariation of nickel with manganese. Similar relationships with manganese are displayed by titanium, silicon and barium, though these are not always developed. Phosphorus, vanadium and perhaps chromium are generally sorbed with iron (see in particular Figure 11/sample CDL 14), but again these relationships can vary, and in the case of chromium, the very low levels of this element cast doubt on the accuracy of the data. The behaviour of cobalt is most difficult to interpret. Cobalt is clearly linked with iron in Figure 13/sample CDL 8, but in several of the other graphs it correlates positively with manganese.

The inconsistency of inter-element relationships in fossil deposits is clear when the findings of other workers are examined. JENKYNS (1970b) illustrated a general association of nickel, barium and occasionally cobalt with manganese, and titanium with iron (but see his Figure 21) in Jurassic nodules from Sicily. GERMANN (1971) pointed out the covariance of nickel and cobalt with manganese in ferromanganese deposits from the northern Calcareous Alps. Titanium, cobalt, chromium and lead correlate positively with iron in nodules from the Jurassic of the Trento Zone, northern Italy (DRITTENBASS 1979), but since manganese also shows this relationship it is difficult to interpret these results.

With regard to the geochemistry of modern ferromanganese deposits, the most widely reported relationships are those of nickel and copper with manganese (GOLDBERG 1954, CRONAN 1969). GLASBY et al. (1974), CRONAN (1975), MOORBY (1978) and AHMAD & HUSAIN (1987) have confirmed these observations and also show zinc to correlate positively with manganese. The sympathetic behaviour of titanium and cobalt towards iron has been described by GOLDBERG (1954), GLASBY et al. (1974), MOORBY (1978) and AHMAD & HUSAIN (1987). BURNS & FUERSTENAU (1966) and CRONAN (1969) confirmed the iron-titanium link, but CRONAN (1969) found no correlation between iron and cobalt. Indeed, CRONAN (1975) and AUMENTO et al. (1968) have suggested that cobalt is in fact sorbed with manganese.

This considerable variation in inter-element relationships in both modern and ancient ferromanganese deposits strongly suggests that the growth of crusts and nodules is controlled by many competing processes.

Mineralogy

Data from the electron microprobe analyser show that regions with anomalous chemistries can be identified within the black ferromanganese crusts. A single point from sample CDL 8 (Fig. 13) gave a barium content of 26.59%, while high titanium values (12.16% and 10.96%) were recorded from sample CDL 13ii (Fig. 12). An analysis from sample CF 4, produced during a preliminary survey of the crusts, yielded a manganese content of 22.01%.

X-ray diffraction analyses were conducted to determine the dominant mineralogies of the black ferromanganese crusts and the brown pisolith coatings, and also to try and identify phases which might have caused the anomalies mentioned. Given the X-ray-amorphous nature of many ferromanganese deposits (e.g. SMITH et al. 1968), samples were only lightly ground by hand before analysis.

The dominant mineral in the brown pisolith coatings is goethite ($< 70\%$), with calcite a major accessory (up to 30%). The black ferromanganese deposits also contain goethite and calcite, along with ramsdellite ($< 10\%$), an orthorhombic form of manganese dioxide.The aluminium and silicon contents of the deposits suggest that an alumino-silicate, possibly a clay mineral, may also be present.

Todorokite, birnessite, nsutite and δMnO_2 are the most common manganese minerals in ferromanganese deposits. Ramsdellite is among the less common phases reported by BURNS & BURNS (1977). CRONAN (1980) notes that deposits, usually encrustations, from highly oxidising environments (e.g. seamounts) which are swept clear of sediments by strong bottom currents usually contain δMnO_2, the most highly oxidised of the common minerals. Goethite has been widely reported as the main iron phase in modern and ancient ferromangenese nodules and crusts (e.g. BUSER 1959, ARRHENIUS 1967, JENKYNS 1970b, GERMANN 1971, GLASBY 1972).

The microprobe analyses show that the concentrations of several of the minor elements are higher in the black ferromanganese crusts. To try to confirm the association of these elements with ramsdellite, carbon-coated fragments of the crusts were examined using a scanning electron microscope fitted with an energy dispersive X-ray spectrometer. However, despite an exhaustive search, a separate manganese phase could not be discerned, the element always being associated with goethite. In addition, the comparatively low concentrations of the minor elements prevented identification of a host mineral.

Discussion

The sedimentological data presented so far allow certain conclusions to be drawn about the general environment in which the iron pisoliths and ferromanganese crusts were produced (Fig. 3). In order for such obviously high, primary concentrations of iron to occur, essentially non-depositional conditions must have prevailed. In the Cantera de Lloseta, the fissured and bored hardground, produced by the action of currents, eroding organisms and the tectonically induced fracturing of lithified sediments, became the site for the accumulation of a remanié bed of iron pisoliths which filled hollows and cracks in the submarine surface. A period of mild erosion preceded the deposition of the ferromanganese crust whose fairly uniform and continuous nature suggests that erosion was minimal during the period of its formation (c.f. FÜRSICH 1979). The sedimentological characteristics, the associated pelagic fauna, and the general tectonic setting suggest that the ferromanganese deposits formed on a limestone seamount.

Within this general environment a large number of factors interacted to control the composition of the pisoliths and the ferromanganese crusts. Assessing the effects of the competing factors by examining the mineralogical and geochemical data should allow a more precise reconstruction of the palaeoenvironment.

Diagenetic factors

Before examining the data more closely, it is necessary to consider the effect of post-depositional diagenesis, which could have caused considerable changes in the composition of the ferromanganese material. The presence of goethite in both the pisoliths and the crusts suggests that the deposits have been little altered, since BERNER (1969) has shown that goethite is unstable relative to haematite in almost all geological conditions. Similarly, there is no evidence for the large-scale migration of manganese out of the deposits. Manganese is very mobile in even mildly reducing conditions, but there are no equivalents of the hollow nodules and dendrites recorded from the Jurassic limestones of western Sicily by JENKYNS (1970b). It is also clear that the temperature of the deposits has not been drastically raised, as this would have caused the inversion of the manganese phase ramsdellite; above 300 °C this orthorhombic form of manganese dioxide converts to pyrolusite. Consequently, it appears that the original chemistry and mineralogy of the deposits have been preserved relatively unchanged.

Element sources

Two main sources of iron and manganese have been suggested for marine ferromanganese deposits:

Diagenetic remobilization from the sediment column
Direct precipitation from seawater – i.e. a hydrogenous origin

Diagenetic remobilization

A number of lines of evidence suggest that the diagenetic remobilization hypothesis (LYNN & BONNATTI 1965) can be discarded for the Mallorcan samples. The sediments directly below (and above) the mineralised hardground are pink to red micritic limestones and dolomites. There is little evidence for the establishment of reducing conditions over the long period that would have been neccessary for iron and manganese to migrate back to the sediment-water interface. It has already been shown that the very limited remobilization that did occur did not contribute to the growth of the crust in the Cantera de Lloseta.

A number of authors (e.g. GLASBY & THIJSSEN 1982, USUI 1983/4, USUI et al. 1987) have noted that nodules at the sediment surface have different compositions and textures depending on the supply of elements. If seawater is the dominant source, nodules tend to be smooth-surfaced, rich in iron, low in manganese and with δMnO_2 the main manganese phase. Conversely, when the dominant element supply is from the sediments, nodules have a rough surface and high manganese contents, the manganese being present as todorokite ("10 Å manganite"). Indeed, CRONAN (1978) and LEMAÎTRE et al. (1984) have described nodules which show distinct textural and chemical differences on opposed surfaces. The ferromanganese crust on Mallorca has a very smooth surface, is iron-rich and contains ramsdellite, a polymorph of manganese dioxide, suggesting that supply from seawater was dominant.

Hydrogenous origin

Iron and manganese are supplied to the marine environment by volcanic/hydrothermal activity and continental run-off. The very high levels of iron in both the pisoliths and the crusts, and the low manganese/iron ratios suggest a local source for the elements. In moderately oxidising conditions ferrous iron is oxidized to ferric iron which is highly insoluble and will rapidly precipitate. In contrast, manganese will only precipitate if oxidized up to the tetravalent state, a step which requires a high oxidizing potential (KRAUSKOPF 1957). Consequently, with increasing distance from the source, the manganese/iron ratio will rise.

Volcanic/hydrothermal activity

Evidence for volcanic activity in the Tethyan realm during the Toarcian is widespread, and led JENKYNS (1970a, b) to conclude that the iron pisolites and ferromanganese deposits of western Sicily were largely composed of material derived from volcanic sources. Indeed, he illustrated fragments of lavas at the cores of some of the pisoliths (JENKYNS 1970a). Further west, volcanic activity in the late Lias has been described from the Iberian Cordillera (GOMÉZ 1979) and the Betic Cordillera (see GARCÍA-HERNANDEZ et al. 1980).

ARRHENIUS et al. (1964) have suggested that a manganese/cobalt ratio of less than 300 in ferromanganese deposits is indicative of a volcanic source; the value is considerably less than this in all the Mallorcan samples (average value = 34 in black crusts, 3.2 in pisolith coatings). The presence of barium and chromium could also be taken as evidence of a volcanic supply of elements; BOSTROM & PETERSON (1966) recorded abnormal concentrations of these elements in ridge sediments from the East Pacific Rise. Hydrothermal fluids venting from the Galápagos Rift also contain a significant quantity of barium (CORLISS et al. 1979). Chromium, however, is thought to be of detrital origin in pelagic sediments and manganese nodules from the equatorial and southwest Pacific (GLASBY et al. 1987).

Modern ferromanganese deposits can be classified by their position on the ternary Mn/Fe/(Co + Ni + Cu) × 10 plot of BONATTI et al. (1972). Although the concentrations of copper in the Mallorcan deposits are rather below the theoretical detection limits of the microprobe, the extreme iron enrichment of the samples ensures that the inaccuracies in the copper data are insignificant. When the Mn/Fe/(Co + Ni + Cu)

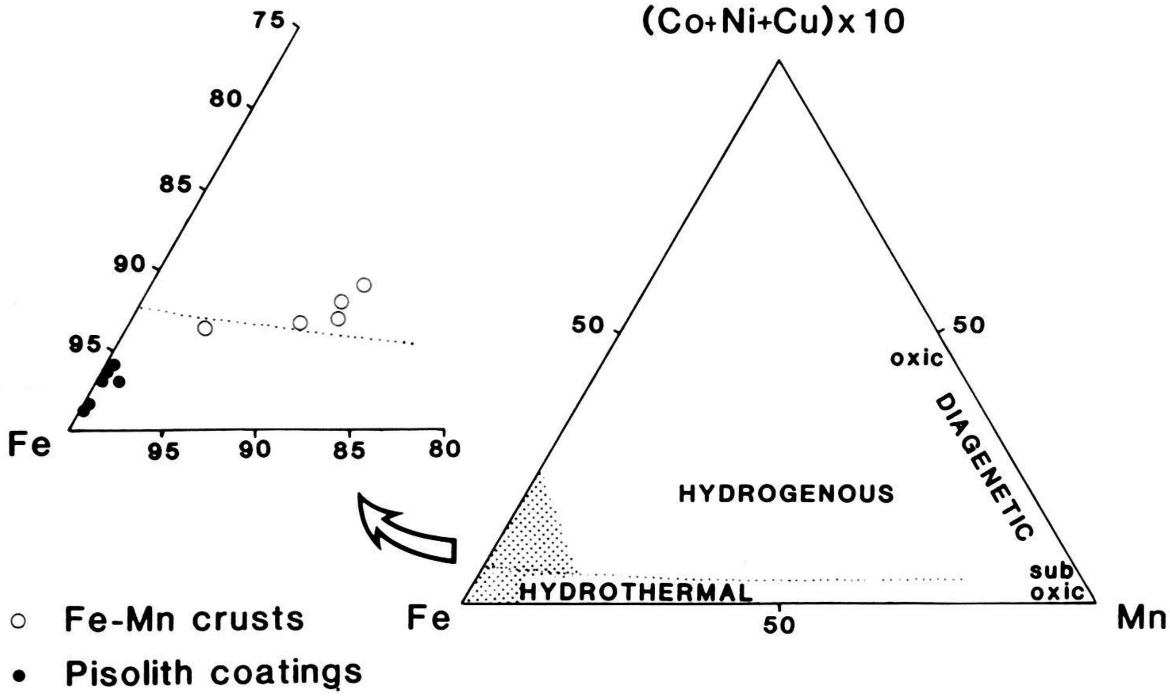

Fig. 15. Triangular Fe/Mn/(Co + Ni + Cu) × 10 plot of BONATTI et al. (1972). Fields from DYMOND et al. (1984) and SUGISAKI et al. (1987). Data on ferromanganese crusts from the Cantera de Lloseta and Cala Fornells; pisolith coatings from the Cantera de Lloseta, Es Barraca and Cuber.

× 10 ratios are recalculated for any copper content between 0% and 0.071% (the theoretical detection limit), the plots of the data on the ternary diagram are not shifted significantly. Hence, it is reasonable to use this diagram to classify the deposits. The ferromanganese crusts on Mallorca plot on the hydrogenous/hydrothermal boundary, while the iron pisoliths plot close to the iron apex within the hydrothermal field (Fig. 15). This supports the contention that volcanic/hydrothermal activity was crucial to the formation of the deposits.

Continental run-off

While a volcanic source seems feasible, the absence of more directly observable evidence (e.g. lava flows, volcanic clasts, tuffs, etc.) in the Balearics perhaps indicates that continental run-off waters may also have been a significant source of elements, as is suggested by Figure 15. During the late Lias, exposed terrains surrounded the Balearic area (Fig. 16 and see the palaeogeographic reconstructions of DERCOURT et al. 1986), and the topmost parts of the Liassic carbonate platform are characterised by a

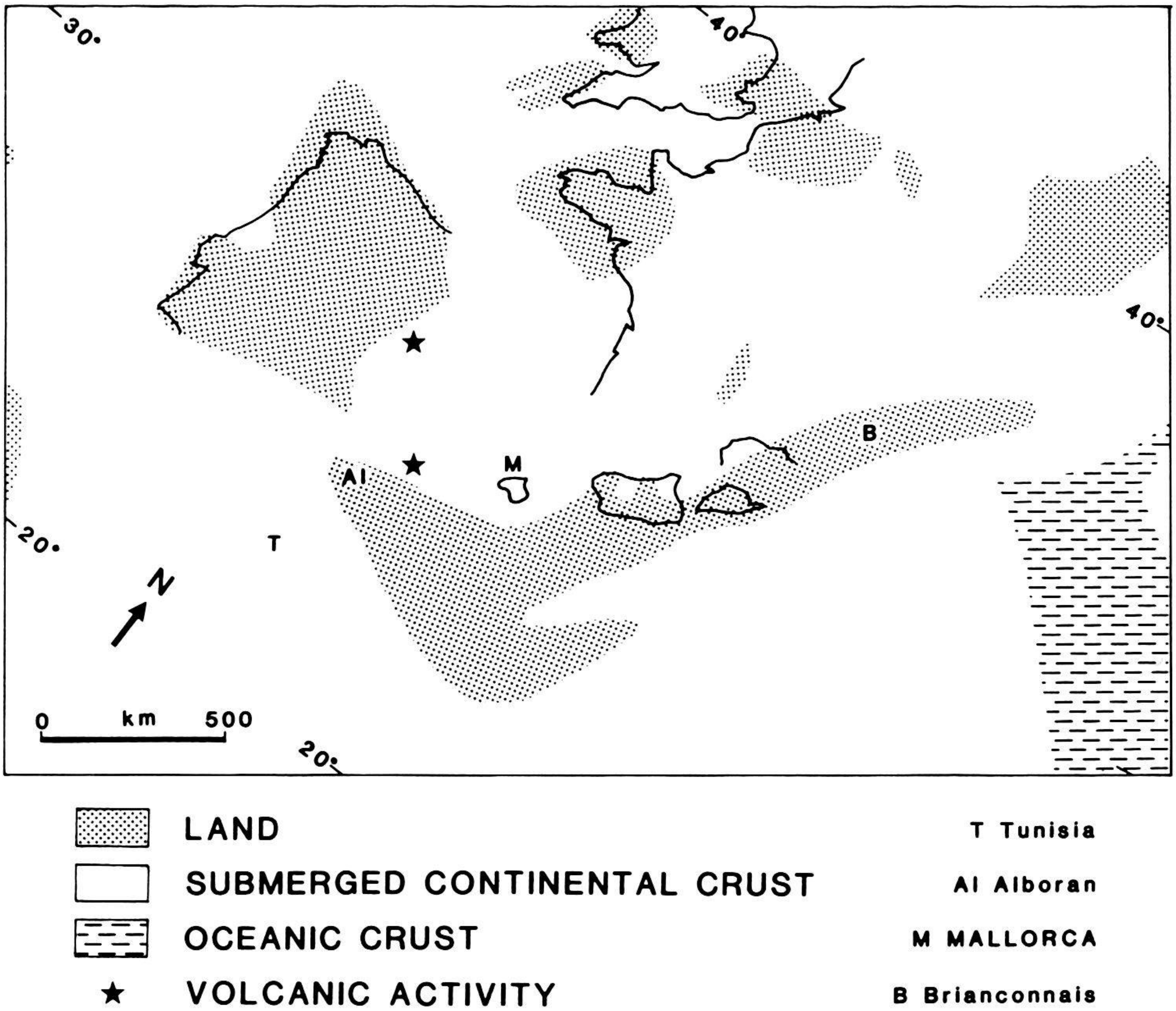

Fig. 16. Paleography of the western Tethys in the Late Lias (from DERCOURT et al. 1986), showing sites of Toarcian volcanism and emergent areas.

major influx of siliciclastic debris, dated as Pliensbachian by ARBONA et al. (1984/5) on the neighbouring island of Cabrera. Since HALLAM (1985) shows the Iberian area to have been on the margins of the humid zone in his palaeoclimatic reconstruction for the Early Jurassic, it seems certain that the presence of exposed land areas near Mallorca had a considerable influence on the composition of the ferromanganese deposits.

It seems likely, therefore, that volcanic/hydrothermal and, perhaps, continental sources of material were important during the formation of the Mallorcan iron pisoliths and ferromanganese crusts. This conclusion is supported by comparing the geochemical data with that given by TOTH (1980) in his study of crusts rich in iron and manganese from the Recent. An extreme range of iron/manganese ratios is shown by crusts from areas of submarine hydrothermal activity, the more iron-rich members having similar compositions to those of the Mallorcan pisoliths. The black crusts from Mallorca compositionally resemble the iron-rich ferromanganese crusts of TOTH (1980), which he interprets as having been formed by the flocculation of colloidal iron and manganese oxides and oxyhydroxides and the precipitation of ionic species still in solution. These substances, largely derived from hydrothermal effusions, were advected away from the immediate source area by bottom currents. The longer residence time of the colloids in the water column allowed chemical scavenging, from the seawater, of trace elements which were themselves ultimately derived from continental run-off waters or hydrothermal solutions.

Hydrothermal effusions themselves show widely varying compositions, though an iron/manganese ratio of 3:1 is most common (EDMOND et al. 1982). More significantly, hydrothermally-derived material suspended over active centres is extremely rich in iron (BOLGER et al. 1978), having iron/manganese ratios of 9.5 to 125 at depths of 2000 m or less. Clearly, deposits which accreted from material of this nature would be highly enriched in iron.

Local variations

The compositional differences between the pisoliths and the ferromanganese crusts can be attributed to several factors. A reduction in volcanic/hydrothermal activity would have cut the supply of iron to the marine environment, while a slight increase in the oxidising potential of the seawater would have caused more iron to precipitate closer to the source(s). In either case, the depositional rate on Mallorca would have been reduced, allowing more time for the concentration and precipitation of manganese, particularly if the oxidising potential had increased.

Local changes in the oxidising potential are possibly recorded in the ferromanganese encrustations. It was noted earlier that some results from sample CDL 13ii (Fig. 12) are anomalous when compared with the other data from the black crusts. Vanadium, barium and titanium are all rather enriched on average, while the manganese content (around 2%) is only half that of the other samples. Examination of the traces shows that, in the case of the enriched elements, the discrepancies can be accounted for by the presence of large local deviations from the background levels. For manganese, however, an alternative explanation is necessary. Significantly, the black coating analysed comes from inside a fissure in the hardground i.e. deposition took place not at the main surface-seawater interface, but in a restricted cavity. Perhaps conditions of slightly lower Eh were established in this local microenvironment, resulting in a slower rate of manganese dioxide precipitation than at the fully exposed surface.

Minor elements

The microprobe data show that the Mallorcan ferromanganese deposits are depleted in copper, cobalt and nickel when compared with most modern nodules (CRONAN 1976). The levels of zinc and lead are also rather low. This applies, in fact, to most of the Tethyan deposits described in the literature, and can be explained in terms of their depositional milieu. Whereas most modern ferromanganese deposits are found far from land in the deep oceans, the Tethyan samples grew on the subsiding continental crust which, during the Jurassic, separated the European and African landmasses from the incipient Ligurian Tethys. These exposed areas and the newly forming oceanic crust acted as sources of iron, diluting the concentrations of other elements.

This reasoning explains too the depleted nature of the Mallorcan deposits when compared with modern examples from mature continental margins. Again the cobalt, copper, nickel and manganese contents are very low, while the iron content is extremely high.

The contrasting abundances of silicon and calcium/calcite in modern and Tethyan deposits are also due to the different depositional environments. The bulk of modern manganese nodules and crusts are from the deep sea, below the calcite compensation depth (CCD). As a result, the calcium/calcite content is low, and the silicon content high. The reverse is true for most Tethyan equivalents, deposited in relatively shallow waters above the CCD.

Inter-element relationships

The rather variable inter-element relationships reported by many workers on ferromanganese crusts and nodules are reflected in the results from the Mallorcan deposits. The correlation of titanium with manganese is the most surprising, given the widely acknowledged covariance of titanium and iron, particularly in modern examples (e.g. GOLDBERG 1954, BURNS & FUERSTENAU 1966, CRONAN 1969, GLASBY et al. 1974, MOORBY 1978, AHMAD & HUSAIN 1987). In this case it is likely that the higher concentrations of titanium in the manganese-bearing crusts resulted from the different rates of deposition of the iron pisoliths and the ferromanganese crusts. A mineralogical control seems unlikely, goethite being the dominant mineral in both deposits, but the slower rate of accretion of the crusts would have allowed more time for chemical scavenging by the ferromanganese material for transition metals and other elements.

Composition-depth relationships

CRONAN & TOOMS (1969) used manganese nodules from the Pacific and Indian Oceans to show a relationship between their depth of deposition and their chemical composition. Using their data, GERMANN (1971) constructed a series of composition/

depth curves based on the ratios of nickel, copper, cobalt and lead (Ni/Co, Ni/Pb, Cu/Co, Cu/Pb vs. depth) in order to take into account the very different chemistries of Tethyan and modern deposits. From these he concluded that the Jurassic ferromanganese deposits of the northern Calcareous Alps formed on a marginal seamount similar to the Blake Plateau.

Unfortunately, the analysed levels of copper and lead in the Mallorcan samples are too low for any statistical validity to be attached to results generated by their use. The Ni/Co ratios, however, suggest that the black ferromanganese deposits accreted between 3400 m and 3800 m below sea level, while the iron pisoliths were deposited in rather shallower waters. It is impossible to accurately quantify this depth, given the low nickel contents of the pisoliths.

Whether any significance can be attached to these results is debatable, given the huge differences between the Mallorcan deposits and modern manganese nodules. The presence of ?algal borings in some of the pisolith cores suggests that the hardground was within the photic zone during the early stages of its formation (Fig. 9). Perhaps the absence of these structures from the pisolith coatings indicates that subsidence had taken the hardground below the photic zone by that stage. The depth/composition curves support the hypothesis of gradual subsidence during the growth of the hardground, but it is hard to envisage the collapse of the Mallorcan platform from sea level in the early Pliensbachian to over 3 km below sea level by the end of the Toarcian.

Other hardgrounds

So far the discussion has centered almost exclusively on the deposits exposed in the quarry at Lloseta, since this is the only locality, with the exception of the small outcrop at Cala Fornells, where a black ferromanganese crust has developed. Other exposures in the Sierra Norte and in the southern Sierra de Levante lack this feature, though brown coated pisoliths and iron-stained intraclasts are common. A possible explanation for this lies in the fact that, in contrast to the hardgrounds at Cala Fornells and the Cantera de Lloseta, which developed above lithified micritic limestones and dolomites, the other "hardgrounds" actually developed on crinoidal calcarenites. It is likely that these low density sands would be kept mobile for long periods, their abrasive action being sufficient to destroy any incipient crust growth. Pisolith coatings and stained clasts from these hardgrounds have similar compositions to the iron pisoliths from the Cantera de Lloseta, though have rather high calcium/calcite contents.

In the northern Sierra de Levante diagenetic factors have been crucial in determining the composition of the mineralised hardground. In the extremely condensed section at Puig Cutri, the crust is dominated by haematite which contains only traces of manganese and the other minor elements. However, the platform limestomes only a few metres below the hardground, and the redeposited oolitic limestones which characterise the subsequent Middle Jurassic sequence both show evidence of late burial dolomitization. The elevated temperatures and the through flow of dolomitizing fluids would probably have been sufficient to disperse any manganese in the hardground, and to have converted original goethite to haematite (Berner 1969).

Conclusions

Lower Lias platform limestones and dolomites of Mallorca are overlain in some areas by iron pisoliths and ferromanganese crusts pertaining to a Toarcian hardground. The pisolith cores are of local derivation and show boring structures which suggest that the hardground lay within the photic zone during the early stages of its formation. The chemical composition of the pisolith coatings suggests that submarine volcanic/hydrothermal activity was the main source of elements.

Further collapse of the drowning margin, a reduction in volcanic activity, and perhaps a change in redox conditions resulted in the accretion of iron-rich ferromanganese crusts. Continental run-off waters and hydrothermal effusions were probably responsible for supplying elements to the growing crust.

Element-depth relationships appear to over-estimate the depth of formation of the deposits. The extremely condensed nature of the hardground deposits and the palaeogeography of the western Tethys during the Upper Lias suggest that deposition took place on a subsiding limestone seamount surrounded by exposed terrains, during the early rifting phase preceding the opening of the Ligurian Tethys.

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