Diagenesis of ferriferous phases in the Northampton ironstone in the Cowthick quarry near Corby (England)

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Abstract – Berthierine, siderite and pyrite are the major ferriferous phases in the Northampton ironstone (NIS). Mineralogical and chemical data suggest a formation of these phases in a diagenetic marine environment changing from post-oxic to sulphidic conditions. Berthierine was formed first when the Fe^{2+} activity in the diagenetic system increased. Later, this phase was partially replaced by siderite and/or pyrite. A second stage of the diagenetic development in the NIS with increasing CO_2 partial pressure (P_{CO_2}) is documented by siderite. The isotopic composition ($\delta^{18}O$ mean value: $-1.7\%_0$ PDB; $\delta^{13}C$ mean value: $-8.6\%_0$ PDB) points to siderite precipitation from a marine porewater environment with a microbial CO_2 source. The shift from post-oxic to sulphidic conditions is indicated by the occurrence of pyrite and can be considered as a final stage. The diagenetic processes in the marine environment and the formation of the ferriferous phases were stopped by the influx of brackish or fresh water when the Midland Shelf turned estuarine.

1. Introduction

Oolitic ironstones are widespread in early Middle Jurassic deposits in Great Britain. The most prominent is the Northampton ironstone (NIS) in the eastern Midlands. The NIS is a minette-type ore of Aalenian age and has been particularly well studied since it was of considerable economic importance (see Hollingworth & Taylor, 1951). Taylor and co-workers have extensively described the geology of the NIS compiling stratigraphic, petrographic, chemical and structural data (Hollingworth & Taylor, 1946; Taylor, 1949, 1950). Furthermore the NIS has been studied under palaeogeographic aspects such as tectonic uplift and sea level changes (Hallam & Sellwood, 1976; Hallam & Bradshaw, 1979).

Data about the chemical conditions within the sedimentary environment during the formation of the NIS are rather scarce. Curtis & Spears (1968) presented theoretical chemical aspects of the formation of ferriferous phases in ironstones. Based on mineral equilibrium diagrams they suggested that anion activity (HS^- and HCO_3^-) is the most important control for the diagenetic development of oolitic ironstones. Berner (1981) proposed a geochemical classification of sedimentary environments based on observations of Recent sediments. In this classification, which also considered microbial activity, the concentrations of dissolved oxygen and sulphur were used as variables to describe the formation of ferriferous phases. Furthermore, Maynard (1982) demonstrated that this classification can be expanded to ancient sedimentary environments.

The aim of this study is to present chemical and mineralogical data in order to deduce chemical conditions within the sedimentary environment during the formation of the NIS.

2. Geological background

2.a. Palaeogeographic situation of the NIS

Palaeogeographic reconstructions of Phanerozoic sequences reveal that oolitic ironstones were mainly accumulated on shallow shelves around dispersive cratonic blocks during episodes with mild maritime climate (Van Houten & Purucker, 1984). In such a framework, lateritic weathering processes on the cratons can be considered as the iron source. Ferriferous residual products released during these weathering processes could be transported from the land to the sea and subsequently accumulated along embayed coastlines (Van Houten & Purucker, 1984). The above schematic scenario has also been considered in context with the formation of the NIS in the eastern Midlands (Hallam & Bradshaw, 1979). During the latest Lias and early Middle Jurassic times the Midlands were part of a widespread shallow shelf at the northern margin of the London–Brabant Massif (Fig. 1). On this shallow shelf a sandy regressive facies, the Northampton Sand Formation, was formed during early Aalenian time. This formation, containing a sparse marine fauna dominated by bivalves (Sellwood, 1978), rests disconformably on top of lower Toarcian (Lias) clays and shows discontinuities partially caused by erosion (Taylor, 1949). The NIS is part of the Northampton Sand Formation and is particularly well developed near Corby (See Fig. 1) and in the Kettering district (Hollingworth & Taylor,

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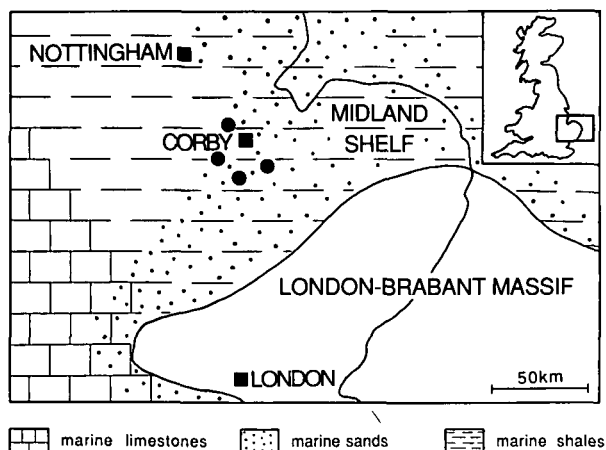marine limestones   marine sands   marine shales

Figure 1. Schematic reconstruction of the early Middle Jurassic palaeogeography of eastern England (after Ziegler, 1982) with the Northampton ironstone near Corby (black dots).

1946). Hallam & Bradshaw (1979) suggested that the NIS was accumulated in a sink within the widespread shelf since the thickness of oolitic deposits is similar to that of their lateral sandy equivalents.

2.b. The Cowthick quarry

The Cowthick quarry near Corby (National Grid Ref. SP925875) is one of the few localities where the NIS is accessible. The stratigraphic section in this disused pit (Fig. 2) shows a shallowing-upward cycle from fully marine to estuarine deposits. Such a sequence is characteristic for the Lias/Middle Jurassic boundary in the eastern Midlands (Anderton et al. 1983). The stratigraphic section begins with Upper Lias clays. Discontinuities containing phosphatic nodules occur on top of the clay beds. These discontinuities are overlain by a silty sandstone which forms the lowest part of the Northampton Sand Formation. The following upper beds are minette-type ores referred to as the NIS. The NIS can be subdivided macroscopically into two parts. The lower one is intensely green, poor in calcite and not very consolidated whereas the upper one is grey-green, compact and partially cross-bedded and with coquina layers. The NIS is capped by silty clays of the Grantham Formation. This clay contains roots and lignites and marks the base of the Estuarine Series (Kent, 1975).

3. Methods

The NIS was studied in the above-described section of the Cowthick quarry (see Fig. 2). The samples were first examined with polarized microscopy. The thin sections were stained with alizarin-red to distinguish the carbonate phases calcite ($CaCO_3$) and siderite ($FeCO_3$). The mineralogical bulk composition was analysed by X-ray powder diffractometry using CuK_α radiation (XRD type: Seifert with PSD) and a Guinier-IV camera with FeK_α radiation.

clay   oolitic ironstones:
phosphatic pebbles   berthierinic - sideritic
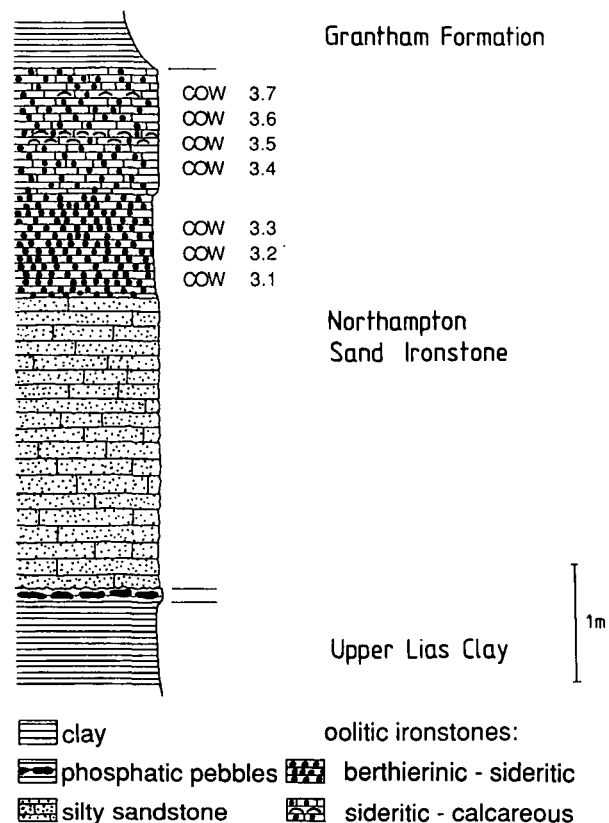silty sandstone   sideritic - calcareous

Figure 2. Stratigraphic section of the Northampton Sand Formation in the Cowthick quarry near Corby.

The chemical composition of the major ferriferous mineralogical phases berthierine and siderite was determined by electron microprobe analysis (EMA type: SEMQ ARL). The data were then ZAF corrected (by the method of J. Sommerauer, unpublished report, ETH Zürich, 1981). For the EMA investigations the samples were prepared as polished sections and coated with carbon. In addition bulk samples (COW 3.3 and COW 3.4) were analysed at room temperature by electron spin resonance spectroscopy (ESR).

For the stable isotope analyses of siderite the samples were heated to 400 °C in vacuum for 1 h to remove the organic matter. Then the samples were reacted under vacuum with 100 % phosphoric acid in order to release CO_2 from the carbonate (McCrea, 1950). The slow reaction of siderite at 25 °C was used to separate the CO_2 from calcite and siderite in single samples (cf. Rosenbaum & Sheppard, 1986). The CO_2 of the siderite was extracted in 8 h at a temperature of 60 °C and analysed with a Micromass 903 mass spectrometer. The temperature correction to PDB-standard at 25 °C was made according to the method of Bahrig (1989). This correction is in good agreement with that published by Carothers, Adami & Rosenbauer (1988).

4. Results

4.a. Petrographic observations

The macroscopic division of the NIS in the Cowthick quarry is also reflected in thin sections. Samples from
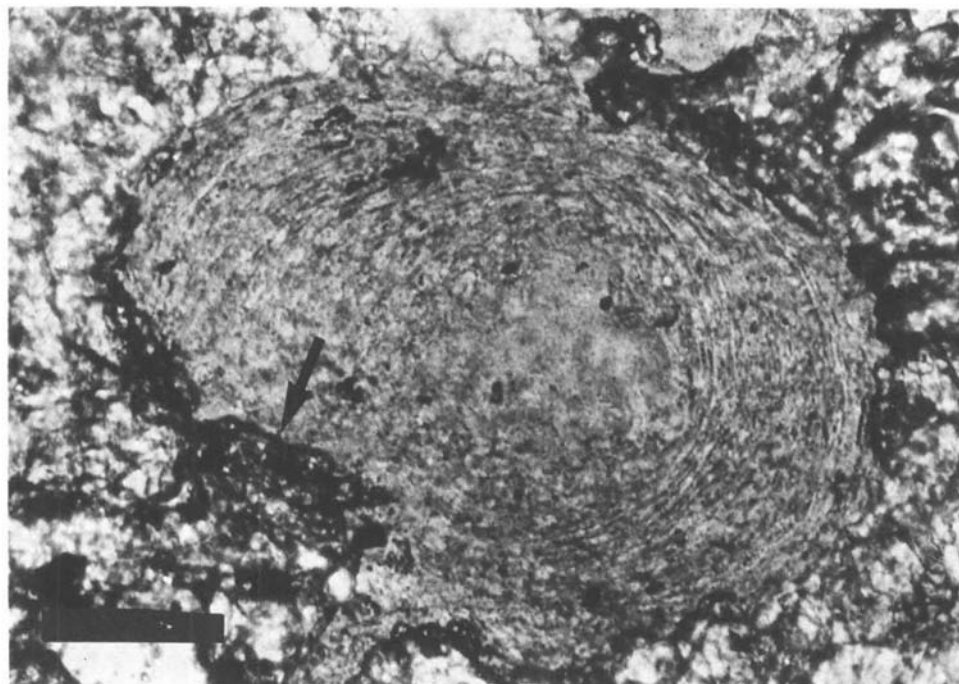
Figure 3. Berthierinic ooid in a sideritic matrix, partially replaced by granular siderite (arrowed). Scale bar = 0.3 mm.
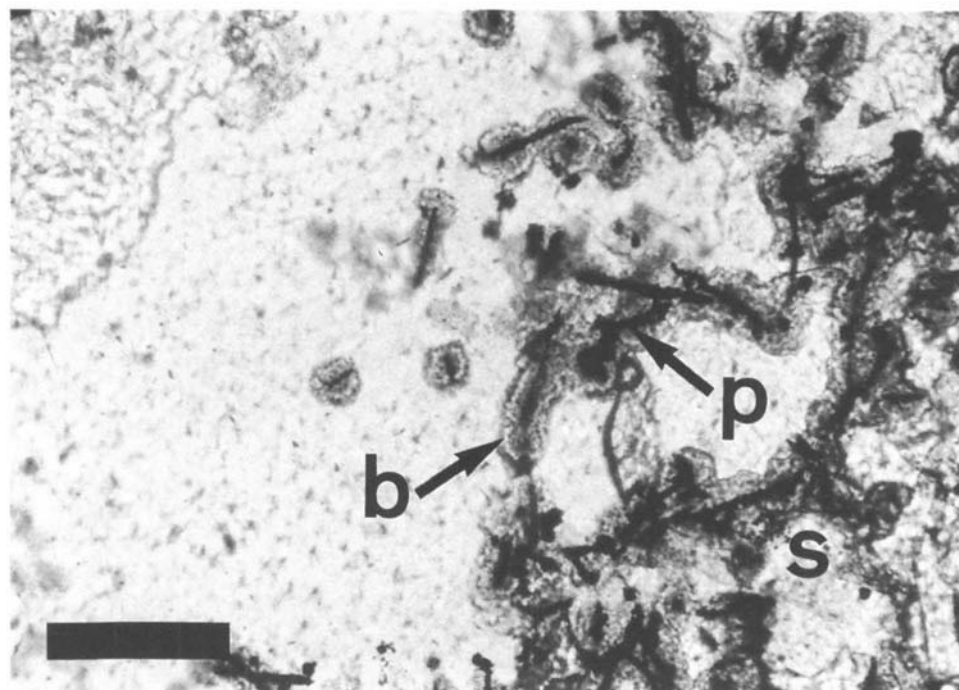

Figure 4. Traces of microbial borings: the centre of the ramified structure is filled with pyrite (p); the outer crusts are composed of berthierine (b) and occasionally siderite (s). Scale bar = 0.1 mm.

the lower part of the NIS show an oolitic ironstone with berthierinic ooids in a berthierinic-sideritic matrix. In the samples from the upper part, the berthierinic ooids are contained in a calcareous-sideritic matrix. There, the presence of broken ooids, iron oolitic clasts and a high proportion of shell debris suggest a depositional environment with episodic reworking. This does not exclude the possibility that part of the ooid deposit was transported into the depositional environment rather than having been formed *in situ*.

The ferriferous phases berthierine, siderite and pyrite can be distinguished in thin sections. Berthierine is the only phase which forms ooids (Fig. 3). It can also be an important part of the matrix. Sometimes it fills microbial borings together with the other two ferriferous minerals (Fig. 4). Siderite can appear as granular or sparry type. The granular type consists of
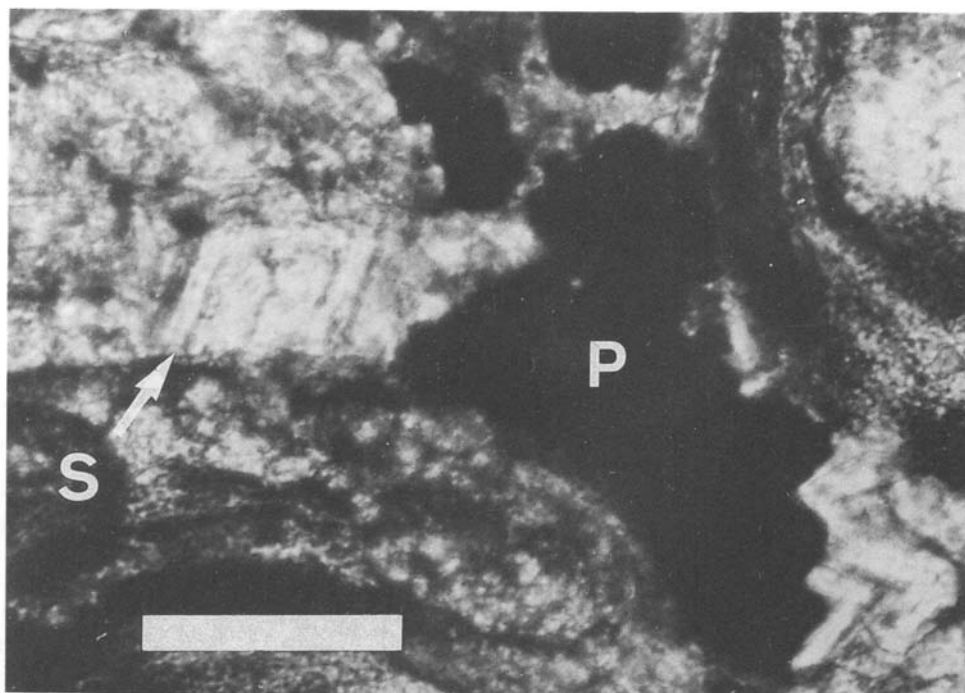
Figure 5. Idiomorphic pyrite (p) within pore spaces between berthierinic ooids. Euhedral siderite crystal on the edge of a berthierinic ooid (s). Scale bar = 0.15 mm.

xenomorphic crystals (10–20 μm size range) which appear together with berthierine in the matrix, on the margin of ooids as well as in traces of microbial borings (Figs 3, 4). This type is characteristic for the lower part of the oolitic iron ore where it often replaces calcite and berthierine in the matrix. The sparry siderite type forms crystals (20–60 μm size range) which can replace berthierinic ooids, as well as berthierine and calcite of the matrix. Idiomorphic crystals often show a zoning which points to a multiphase growth process (Figs 3, 5). The sparry type is limited mainly to the upper part of the NIS. Pyrite is a subordinate phase but occurs in all samples analysed. Furthermore pyrite is distributed unevenly and can form aggregates (20–400 μm size range) consisting of cubic or polyhedral crystals (1–10 μm size range). Such crystals can appear on the margin of ooids, within pore spaces, and between particles and cements (Fig. 5). In addition pyrite can also appear in microbial borings (Fig. 4).

The distribution and interrelation of these three principle ferriferous phases suggest that berthierine was formed first since siderite and pyrite can replace it. From the petrographic observations no clear sequence of the siderite and pyrite formation can be deduced. Idiomorphic pyrite crystals often seem to have replaced siderite partially (Fig. 5), suggesting a siderite formation prior to pyrite.

4.b. Mineralogy and geochemistry of the ferriferous phases

4.b.1. Chemical composition of berthierine and siderite

Berthierine (7Å trioctahedral serpentine) and siderite ($FeCO_3$) were detected by XRD in all samples.
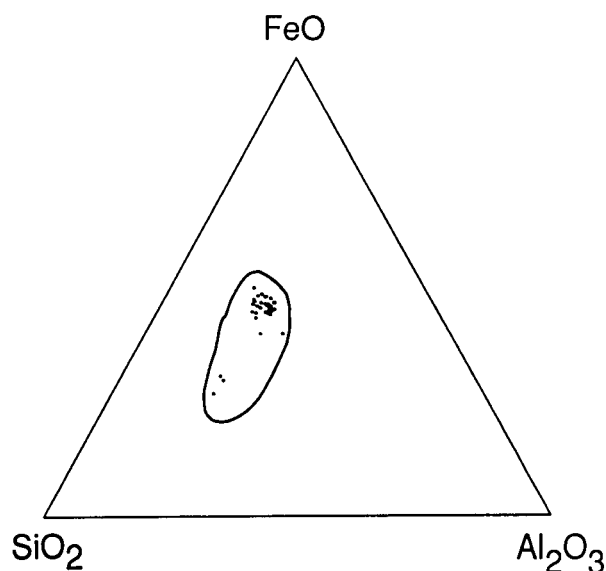

Figure 6. Electron microprobe analyses of individual berthierinic ooids. The concentration of the three principal elements Fe, Si, Al is determined from their oxide form of a total analysis.

Berthierine, determined by the characteristic (001), (002) and (201) lines, reveals a monoclinic structure very similar to that published by Brindley & Youell (1953).

Berthierine is reported as a mineral with variable chemical composition (see Brindley, 1982). Electron microprobe measurements of berthierinic ooids show slight variation of the main chemical components Fe, Si and Al (Fig. 6). This finding is in good agreement with EMA data comparing nuclei and cortices of single berthierinic ooids (Maynard, 1986) as well as element distribution images of berthierinic ooids

Table 1. Chemical composition of berthierine from the NIS

	Berthierinic ooids		Berthierinic clay[1]	Berthierinic oolith[2]
	COW 3.3	COW 3.5		
SiO_2	24.94	25.31	24.9	27.8
Al_2O_3	12.76	14.55	14.9	17.4
FeO*	37.67	35.97	22.4	—
$FeO + Fe_2O_3$	—	—	—	33.9
MgO	2.32	1.72	2.31	1.8
CaO	0.08	0	0	0
K_2O	0.22	0.4	n.d.	n.d.
Cr_2O_3	0.14	0.11	n.d.	0.1
TiO_2	0.06	n.d.	0.7	
Total (wt %)	77.98	78.89	64.5	82.0

* All Fe reported as FeO; n.d. = not detected. (1) Maynard (1986): sample from Corby, Northamptonshire. (2) Taylor (1949): sample from Irthlingborough Mine, P_2O_5 0.5 wt %; V_2O_3 0.3 wt % and H_2O 6.4 wt % not included.

FeO
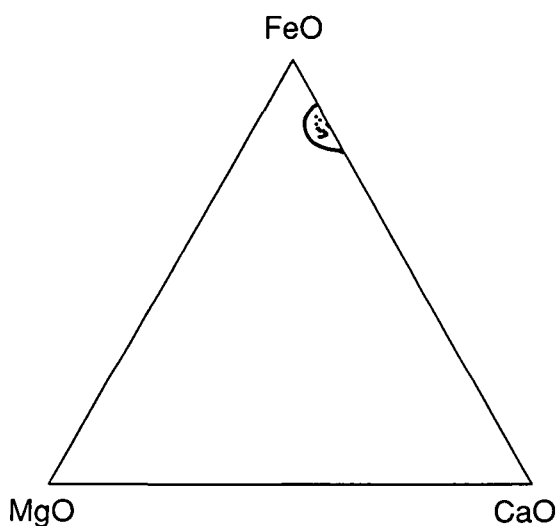

MgO   CaO

Figure 7. Electron microprobe analyses of siderite. The concentration of the main components Fe, Ca, Mg is determined from their oxide form of a total analysis.

(Gehring, 1985) from the NIS. The average main oxide components in the ooids from the Cowthick quarry are 36 wt % FeO, 26 wt % SiO_2 and 14 wt % Al_2O_3 (Fig. 6). These chemical data are consistent with those from other localities in the NIS (see Table 1). Berthierine from localities outside the NIS is generally richer in Al (see Brindley, 1982). Apart from the main elements (Fe, Si, Al), Mg is the most prominent chemical component in the ooids. Its concentrations varies between 1.5 and 2.5 wt %. Mg can be considered as part of the berthierine structure (Brindley, 1982). Furthermore K, Cr, Ti, Ca, Na and Mn appear in small proportions (total > 1 wt %) in all ooids measured. The potassium content of the samples is mostly below 0.5 wt %. A potassium content higher than 0.5 wt % in the berthierinic ooids can probably be explained by the occurrence of a transitional mineralogical phase between berthierine and glauconite (see Thompson & Hower, 1975). The possibility of the presence of glauconite in berthierinic ooids was described by Taylor (1949). Cr occurs in all

samples, with an average content of 0.1 wt %. Cr can be an important element in laterites (e.g. Ogura, Murata & Iwai, 1987) and can coprecipitate with ferric iron in oxide form (Gehring & Karthein, 1989). Therefore it seems likely that Cr was transported together with Fe from the iron source to the depositional environment. The remaining elements (Ti, Ca, Na, Mn) are part of unspecified impurities within the berthierinic ooids.

EMA of euhedral siderite (Fig. 5) and siderite which replaces berthierinic ooids (Fig. 3), show that its chemical composition is rather uniform (Fig. 7). The average composition is 28.5 wt % FeO, 9 wt % CaO and 1.5 wt % MgO. The CaO/MgO ratio is about 6. It follows that Fe of the siderite was substituted mainly by Ca but also by Mg. A comparison of chemical data of siderites isolated from bulk samples of the NIS shows the same degree of Fe substitution but a CaO/MgO ratio of near 1 (Taylor, 1949). This suggests that the siderite in the NIS from the Cowthick quarry is rather poor in Mg.

4.b.2. Electron spin resonance spectroscopy

The ESR spectra of the bulk samples COW 3.3 and COW 3.4 at room temperature reveal a similar lineshape. A very broad signal occurs in all samples as background (Fig. 8). This signal is probably caused by a small amount of ferric oxides which can often be found as impurities in the NIS samples. Furthermore, the ESR spectra show a characteristic hyperfine split Mn^{2+} and Fe^{3+} signal with a g-value of 4.3 (Fig. 8). The occurrence of Mn^{2+} and Fe^{3+} in the bulk samples suggest that these cations are located within a foreign structure (Meads & Malden, 1975). The only candidate in the NIS to incorporate cations is the berthierine with its trioctahedral serpentine structure (cf. Brindley, 1982). Another possibility, that free Mn^{2+} is associated with a carbonate phase, can be excluded since Wersin et al. (1989) show that Mn^{2+} will bind when incorporated in siderite.
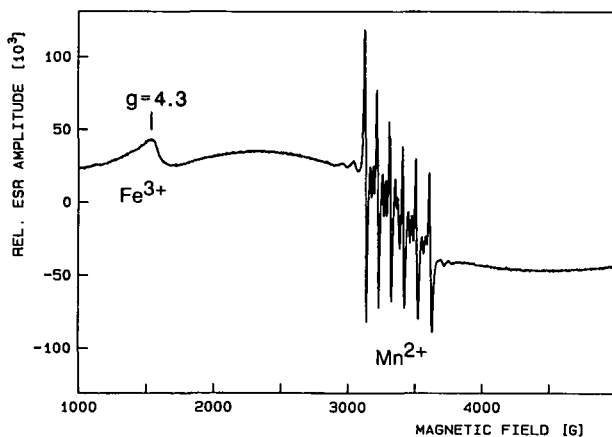
Figure 8. ESR spectra of a NIS bulk sample (COW 3.3) at room temperature.

4.b.3. Stable isotope analysis of siderite

Stable isotope analysis of siderite from bulk samples shows that their isotopic composition does not vary significantly within the NIS. The $\delta^{13}C$ values lie between $-5.8\%_0$ and $-12.5\%_0$ PDB and the $\delta^{18}O$ values are between $+0.3\%_0$ and $-3.9\%_0$ PDB (see Table 2). The $\delta^{18}O$ data (mean value -1.7% PDB) indicate siderite precipitation in a marine environment (Hoefs, 1980). Isotopic data obtained from calcite cements in submarine hardgrounds within the slightly younger Lincolnshire Limestone (Bajocian) in the Cowthick quarry show similar $\delta^{18}O$ values (Ashton & Marshall, 1980). This supports the idea that the NIS siderite precipitated from a marine porewater environment. The $\delta^{13}C$ data (mean value $-8.6\%_0$ PDB) point to a siderite precipitation from a solution slightly depleted in ^{13}C. This indicates a diagenetic environment with an organic CO_2 source for the siderite formation (Gautier, 1982). In summary, the $\delta^{18}O$ and $\delta^{13}C$ composition of the siderite reveals a diagenetic marine porewater environment during the development of the NIS.

Table 2. Stable isotope analysis of siderite from the NIS

Samples	$\delta^{13}C$ (‰ PDB)	$\delta^{18}O$ (‰ PDB)
COW		
3.1	−6.11	−3.89
3.1.1	−6.14	−3.42
3.2	−5.78	−1.17
3.2.1	−8.23	−1.99
3.3	−8.10	−3.37
3.3.1	−12.10	−1.07
3.4	−7.98	−2.30
3.4.1	−7.29	−2.29
3.4.2	−9.13	−3.00
3.5	−12.13	−1.37
3.51	−12.51	−0.85
3.6	−8.53	−1.02
3.6.1	−6.37	+0.35
3.7	−10.72	+0.13
3.7.1	−8.10	+0.25

5. Discussion

In a geological framework, the NIS can be considered as an iron ore in which iron released due to lateritic weathering on the London–Brabant Massif was accumulated within the Midland shelf. Based on petrographic, mineralogical as well as chemical data of the major three ferriferous phases accumulated in the NIS, a reconstruction of the diagenesis can be proposed. Berthierine, siderite and pyrite were formed in a diagenetic environment under reducing, marine conditions with an at least initially high activity of Fe^{2+}. According to the classification scheme proposed by Berner (1981), the formation of the ferriferous phases in the NIS can occur under post-oxic or sulphidic conditions. During diagenesis post-oxic conditions result from microbial oxidation of organic matter to CO_2 by dissolved O_2. Such a process generally indicates an early diagenetic stage. A subsequent sulphidic environment can build up when microbial activity tends to deplete the system of O_2 and creates sulphate-reducing conditions. Studies in recent environments demonstrate that changes from oxic to post-oxic and sulphidic conditions are very dynamic process (e.g. Boesen & Postma, 1988). Investigations of the ancient environment give only information on distinct stages of chemical balance within the diagenetic system. Therefore dynamic processes can be considered only very schematically.

However, according to Maynard (1982) the isotopic data of siderite in the NIS are characteristic for a post-oxic environment. Furthermore, traces of microbial activity and the occurrence of pyrite are indicative that the NIS reached sulphidic conditions during diagenesis (Fig. 4 and 5).

Petrographic observations suggest that berthierine was formed prior to siderite during diagenesis in the NIS. Experiments by Bhattacharyya (1983) demonstrate that berthierine can be formed by transformation processes under reducing conditions whereby a kaolinite precursor accumulates Fe and releases Al and Si. Therefore, this ferriferous phase is considered to have been formed when the reducing conditions led to increase the Fe^{2+} activity within the diagenetic environment. ESR data suggest that berthierine incorporated Mn^{2+} in its structure. Mn^{4+} oxide reduction to Mn^{2+} points to early redox processes within diagenetic systems (cf. Stumm & Morgan, 1981, p. 460). Data from Puget Sound cores demonstrated that the Mn^{2+} maximum concentration occurs close to the sediment/water interface above the zone with a Fe^{2+} maximum (Peterson & Carpenter, 1986). This supports the assumption of an early diagenetic berthierine formation.

Siderite in the NIS is considered to indicate a further stage of the diagenesis. Siderite-forming conditions are generally characterized by a high Fe^{2+} activity and high partial pressure of CO_2 (P_{CO_2}) (e.g.

Stumm & Morgan, 1981, p. 265). It seems very likely that berthierine formation did not substantially decrease the Fe^{2+} activity. The increase of the P_{CO_2} can be explained by continuing microbial decay of organic matter during the diagenesis. The forming of such conditions seems to be a dynamic process since siderite often shows zoned crystals (Fig. 5). As the isotopic composition reveals siderite precipitation from a marine porewater environment, it is very likely that this process was completed before the estuarine Grantham Formation was deposited.

Pyrite formation in the NIS indicates the continuation of the diagenesis to sulphate-reducing conditions. Berner (1983) pointed out that a shift to sulphidic conditions occurs in a diagenetic environment when the oxygen is consumed by aerobes and subsequent bacterial activity increases the sulphate reduction rate. However, the small quantity of pyrite in the NIS indicates conditions not favourable for an extended sulphide formation. Since sulphate is not scarce in marine environments, the concentration of reactive ferrous compounds and/or organic matter can be a limiting factor in pyrite formation (e.g. Berner, 1983). On the other hand, pyrite precipitation may be inhibited by the influx of brackish or fresh water and subsequent increase of the redox potential within the diagenetic environment. This possibility seems very likely since the NIS is capped by estuarine sediments, containing lignites and roots. Non-marine diagenetic processes are not indicated in the NIS at the Cowthick quarry. Therefore it is postulated that the diagenesis of the NIS was completed when the Midland Shelf turned estuarine.

6. Conclusions

The mineralogical and chemical investigations of the ferriferous phases in the NIS at the Cowthick quarry lead to the following conclusions:

(1) The formation of berthierine, siderite and pyrite took place in a marine diagenetic environment containing high Fe^{2+} activity which changed from post-oxic to sulphidic conditions.

(2) Berthierine was formed first and indicates the initiation of diagenesis of the ferriferous phases in the NIS.

(3) Continuing microbial activity lead to an increase in the P_{CO_2} in the diagenetic environment and subsequent precipitation of siderite.

(4) The occurrence of pyrite indicates sulphidic conditions and the final stage of diagenesis in the NIS.

(5) The cessation of ferriferous phase formation is explained by influx of brackish or fresh water into the diagenetic environment. Therefore it is postulated that diagenesis was completed when the Midland Shelf turned estuarine.

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