diffuses more effectively than ^{37}Cl towards the cathode end of the tube. In a groundwater analogue of counter-current electromigration, the electrostatic force may be provided by charged clay mineral surfaces and streaming potential produced by forced convection of water. The convective movement is induced by natural hydraulic and osmotic pressure gradients. Although discussions of fractionation mechanisms based on our results are speculative, experiments and the construction of theoretical models designed to clarify the nature of possible mechanisms are underway.

We thank the following for providing samples for study: W. Kaiser, Texas Bureau of Economic Geology; A. Truesdell, US Geological Survey, Menlo Park, California; T. Casadevall, US Geological Survey, Vancouver, Washington; J. Fabryka-Martin, University of Arizona. This work was supported in part by US Nuclear Regulatory Commission contract NRC-04-78-272.

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Suboxic diagenesis in banded iron formations

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Anomalous isotopic composition has been reported for the carbon in carbonate minerals of banded iron formations. Well studied examples show an enrichment in the light isotope of carbon, ^{12}C. This enrichment presumably reflects unusual circumstances in the deposition of these sedimentary rocks. It is suggested here that the isotopically-light carbonate results from early diagenetic oxidation by bacteria of substantial amounts of isotopically light organic carbon. The electron acceptor that permits oxidation in the absence of free oxygen is presumed to be iron(III) which may have been significantly more abundant in the initial chemical precipitate than in the post-diagenetic sedimentary rock.

Banded iron formations are chemical sediments, formed by precipitation of dissolved species from solution[1]. They are composed principally of cryptocrystalline or crystalline quartz, iron oxides (haematite and magnetite), iron silicates (greenalite and related minerals) and iron carbonates (siderite and ankerite)[2]. Banded iron formations are major sources of iron ore. Essentially all of them were deposited before $\sim 1.7 \times 10^9$ yr ago[3], an observation that has been interpreted to reflect a transition at about this time from a hydrosphere devoid of oxygen to a hydrosphere rich in oxygen[4,5]. Because oxidized iron(III) is almost insoluble in all but very acid solutions, the transport of iron in solution and its subsequent chemical precipitation in banded iron formations must have occurred in anoxic waters. The extensive area of some banded iron formations and substantial rates of accumulation of iron and silica seem to imply deposition in basins that were open to the ocean[6–9].

The isotopic composition of the carbonate minerals in banded iron formations has been studied most thoroughly in formations of the Hamersley Basin of Western Australia[9,10]. These undeformed sedimentary rocks have been subjected to only low-grade metamorphism[11]; they date from $\sim 2.5 \times 10^9$ yr ago[12] and appear to have been deposited on a submarine platform or bank protruding into or marginal to an ocean[9]. Carbonate minerals are fairly abundant, typically making up between one-tenth and one-half of the rock[10,13]. Becker and Clayton[14] studied the isotopic composition of the carbonate minerals in the Dales Gorge Member of the Brockman iron formation and reported an enrichment in the light isotope of carbon. Expressed as the departure of the ratio of carbon isotopes from the ratio in a standard carbonate, this departure amounted to an average of $\sim 10\permil$, expressed as $\delta^{13}C = -10\permil$. This finding has been confirmed and extended by Baur et al.[10], who studied the underlying Marra Mamba and Mt Sylvia formations as well as the Dales Gorge Member of the Brockman iron formation. These authors found variable isotopic compositions, but in all cases the carbonate minerals were strongly enriched in the light isotope of carbon. Similar results for banded iron formations in North America have been reported[15,16].

Little isotopic fractionation with respect to dissolved carbonate results from the precipitation of carbonate minerals including the iron carbonates, siderite and ankerite[17], so most marine carbonates have isotopic compositions close to the standard, $\delta^{13}C \sim 0\permil$. Indeed, isotope measurements on marine carbonate rocks of different ages are used to infer the history of the carbon isotopic composition of seawater. Such studies have revealed only minor variation of seawater carbon from a value near $\delta^{13}C = 0\permil$ since at least 3.5×10^9 yr ago[18–20]. There is no reason to suppose that the isotopic composition of the ocean was any different at the time of deposition of the banded iron formations of the Hamersley Basin. Indeed, the Wittenoom Dolomite[10,14], a non-iron formation carbonate rock immediately overlying the Marra Mamba iron formation, has a carbon isotopic composition of $\delta^{13}C = 0.36\permil$ very close to the marine carbonate standard. It does seem likely, therefore, that the carbonate minerals in the iron formations were deposited with isotopic compositions different from that of the seawater from which these minerals were ultimately derived.

Isotopically-light marine carbonate in Phanerozoic sedimentary rocks would generally be attributed to the oxidation of reduced organic carbon during early diagenesis[21]. Reduced organic carbon is strongly enriched in the light isotope, $\delta^{13}C = -25\permil$ or lower[22,23]. Diagenetic oxidation of organic carbon in young sediments can dilute the seawater carbonate dissolved in the pore waters of the sediments, yielding isotopically light dissolved carbonate[24]. The carbonate minerals that equilibrate with these pore waters can also be isotopically light. Data on isotopically light marine carbonates of Mesozoic age, presumably produced in this way, have been presented by Irwin et al.[21]. Could this process not also have been responsible for the isotopically light carbonates in banded iron formations, a possibility suggested by Baur et al.[10]?

The problem with this mechanism is to identify the electron acceptor that made possible the oxidation of organic carbon in iron formations. The assemblage of minerals in these formations provides clear evidence for a very low oxygen fugacity in the pore waters of the sediment[2]. This conclusion is not contradicted by the presence of some iron(III), which is stable even at low oxygen fugacities. So the electron acceptor was not oxygen. There is also no reason to suppose that dissolved nitrate was abundant on the anoxic Earth[25]. But the oxidation process evidently did not involve the reduction of dissolved sulphate to sulphide, because sulphide minerals are not abundant in the iron formations of the Hamersley Basin[3]. Data[26] on the Dales Gorge Member of the Brockman iron formation reveal maximum concentrations of ~ 0.3 wt% and average concentrations much lower. Iron sulphides are relatively insoluble, and any sulphide produced in the sediments by diagenesis would have been precipitated by reaction with the abundant dissolved iron[27,28]. The apparently minor role of sulphate reduction may have been a consequence of low sulphate concentrations in the
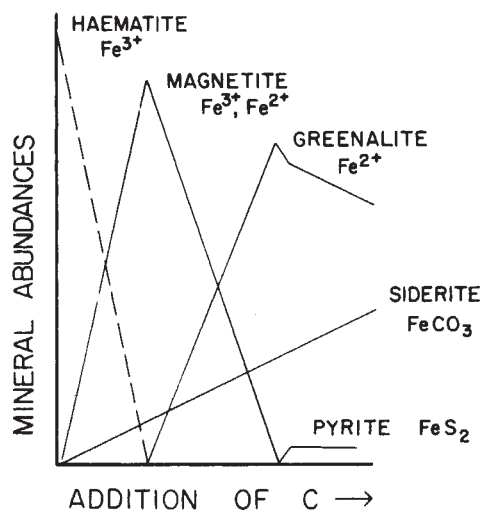
Fig. 1 Suboxic diagenesis of increasing amounts of reduced organic carbon causes the progressive reduction of iron(III) to iron(II). The result is that haematite is replaced by magnetite which is in turn replaced by greenalite and related silicate minerals that contain little or no iron(III). Sulphate reduction and the precipitation of pyrite do not commence until all iron(III) has been reduced. The carbonate produced by diagenetic oxidation of organic carbon precipitates as iron carbonate minerals, siderite and ankerite. The oxide, silicate, and sulphide facies of banded iron formations may reflect increasing amounts of organic carbon in the original sediments.

Archaean and early Proterozoic ocean[29–31]. In recent sediments, when sulphate is exhausted, further diagenetic oxidation of organic matter uses organic matter as the electron acceptor. The metabolic processes are fermentation and methanogenesis. Methanogenesis, however, produces isotopically very light methane and isotopically heavy carbonate[24]. This process could not, therefore, be the source of the isotopically-light carbonates in the banded iron formations. (For a contrary opinion see ref. 10.)

It has recently become clear, however, that iron(III) can serve as electron acceptor in the early diagenetic, bacterial oxidation of organic carbon (see refs 28, 32–34). There is good evidence that particulate iron(III) is reduced to dissolved iron(II) during the anaerobic oxidation by bacteria of reduced organic carbon. The reduction of iron occurs after dissolved oxygen and nitrate have been exhausted and after the reduction of oxidized manganese, but before the reduction of sulphate[32]. Banded iron formations are, of course, rich in iron. Iron(III) could well have been the electron acceptor that permitted diagenetic oxidation of isotopically-light organic carbon by bacteria to produce the isotopically-light carbonate minerals in iron formations[10,15]. A stoichiometrically equivalent reaction was proposed by Perry et al. as an abiological, metamorphic process.

The initial oxidation of dissolved iron(II) to particulate iron(III) would have occurred in the water column, possibly near the surface. There are several oxidation processes that would not have required significant concentrations of free oxygen. Abiotic photochemical oxidation has been suggested and investigated experimentally[35,36]. Iron(II) may have served as electron donor in a metabolic process of bacterial photosynthesis[37]. Alternatively, the electron donor for biological photosynthesis may have been water, with the oxygen produced in the process consumed immediately by reaction with excess dissolved iron[4].

Consider an iron formation that contains 5 wt% of CO_2 in the form of carbonate minerals[26]. Suppose that this carbon has an isotopic composition of $\delta^{13}C = -10‰$, which represents a mixture of equal parts of oceanic carbonate with $\delta^{13}C = 0‰$ and diagenetic carbonate produced by the oxidation of organic matter with $\delta^{13}C = -20‰$. The oxidation of 0.7 g of organic carbon per 100 g of rock is required. This would not represent an

unreasonably large concentration of organic carbon in the initial sediment.

Oxidation of this carbon according to the stoichiometric relationship

$$C + 2\,Fe_2O_3 \rightarrow CO_2 + 4\,FeO$$
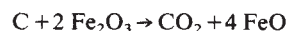
would produce 16 g of FeO per 100 g of rock. Iron formations, including those of the Hamersley Basin, typically contain from 20 to 25 wt% of FeO by weight[3]. The proposed role for early diagenetic oxidation of reduced organic carbon by iron(III) is therefore not contradicted by data on the iron(II) content of banded iron formations.

On the other hand, if 0.7 g of organic carbon were oxidized according to the stoichiometric relationship

$$2C + H_2SO_4 \rightarrow 2CO_2 + H_2S$$
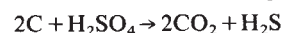
the yield would be 0.9 g S per 100 g of rock. The average sulphide concentration of banded iron formations, including those of the Hamersley Basin, is substantially less than this[3,26].

What are the implications of an early diagenetic source for much of the carbonate in banded iron formations, a source involving the oxidation of reduced organic carbon and the reduction of oxidized iron(III)? First, because this early diagenetic process is a consequence of the metabolic activities of bacteria, the isotopically light carbonate in banded iron formations may be evidence for the presence of bacteria in the sediments that became banded iron formations[38]. Microfossils have not yet been discovered in the banded iron formations of the Hamersley Basin[38]. The calculations presented above suggest that a large fraction of the total iron(II) in these formations may have been reduced by bacteria during early diagenesis. The initial deposits, in this view, contained iron largely in the iron(III) form together with reduced organic carbon in an amount that was stoichiometrically comparable. The preserved ratio of iron(III) to total iron in these sediments is therefore not primary, but is a product of early diagenesis. Also, the generally low concentration of organic carbon in banded iron formations[3] is explained as a consequence of the early diagenetic oxidation of an initially much larger amount of carbon by the oxidized iron of the formations themselves. Finally, the oxide, silicate, and sulphide facies of iron formations[2,39] may reflect a response of the sedimentary system to the early diagenetic alteration of progressively larger amounts of reduced organic carbon (Fig. 1). The oxide facies contains both iron(II) and (III), the silicate facies contains principally the iron(II) form, and the sulphide facies contains iron(II) and sulphide that is presumably the product of bacterial sulphate reduction.

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33,000-yr old chert mining site and related *Homo* in the Egyptian Nile Valley

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The Nazlet Khater 4 site (Nile Valley, Upper Egypt) is located on one of the small wadi-interfluves in the lower desert near the steep cliffs bordering the western Nile Valley edge (Fig. 1). We have previously reported[1] the excavation of an early Upper Palaeolithic blade industry at this site, although blade industries in the Nile Valley had only been known[2] to occur since 18,000 yr ago. The 1982 excavation reported here confirms that Nazlet Khater 4 is a chert mining site with a complex extraction strategy, going back 33,000 yr. A nearby grave contained a skeleton of a man in the extended position. We show that the cranial morphology is anatomically modern with archaic characteristics such as a very robust mandible. There is evidence that the skeleton has a similar age to that of the mining site.

The 1982 excavation enabled us to distinguish three sedimentary units: (1) the substratum of the site or the pre-Upper Palaeolithic natural deposits, (2) Upper Palaeolithic diggings in the substratum and their related infills, and (3) later deposits on the site.

The basement of the site consists of greenish silts and fine sands covered by a 1.5-m thick Nile channel deposit, composed of channel lag deposits of well-rounded Nile gravels and chert cobbles and of brown granuliferous silts, covered by a wadi deposit of local limestone gravels (Fig. 2).

Three Upper Palaeolithic digging activities can be distinguished (Figs 1, 2). (1) A trench, 9 × 2 m, with a depth of 1.5 m had been opened at the northern edge of the Nile deposit, just beyond the covering wadi deposit. All the Nile deposits had been removed from this trench which represents ~15 m³ of ground. (2) Vertical shafts, dug down to the channel lag gravel, had sometimes been enlarged at their base to form bell pits. (3) From the walls of the trench or from the bell pits, the channel lag gravels had been extracted from the substratum for several metres, creating short galleries.

The deposits in the trench and in the bell pits consist of two lithological units: gravels at the base, covered by yellow fine aeolian sand. The gravel unit is a purely gravitational deposit, composed mainly of Nile pebbles, mixed with coarse sands, silts, local limestones, Upper Palaeolithic artefacts, and a fragment of gazelle horn core. Several hearths *in situ* with an abundance of charcoal were observed. This gravel unit is heavily encrusted by a 10-cm thick calcrete on its surface. The top of this unit forms a depression and represents an occupation floor with a large hearth.

The overlying infilling of loose aeolian sands completely hides all Upper Palaeolithic diggings. In the trench, three very slightly encrusted layers with gravels and derived artefacts are intercalated[1]. During the formation of this unit, important deflation and sand accumulation, not found in the gravel layers, took place. The presence of an *in situ* hearth in this sand unit indicates that the site was occupied during this stage. The post-occupation evolution of the site consists of the formation of a salt crust with desiccation wedges and in the flattening out and re-installation of the overall perfect gently eastward dipping slope.

We have currently nine ^{14}C dates at our disposal (Fig. 2). Samples GrN-11297, GrN-11300, Lv-1139D, GrN-11301 and GrN-11299 are from different hearths; samples Lv-1142D, Lv-1141D, Lv-1140 and GrN-11296 are from dispersed charcoal. All dates, ranging from 35,100 to 30,360 yr BP, confirm the great age of the mining site. Statistical tests on different combinations of these samples indicate that they do not belong to the same population (significance level better than 99%), so that it is inappropriate to calculate a mean age for the site. It seems justifiable, however, to classify the ^{14}C dates from the trench according to their lithological positions. The weighted average for the three samples in the gravel unit is 33,470 ± 360 yr BP, and for the three samples in the sand unit, 31,980 ± 650 yr BP. As their significance level is 5%, we suggest that the mining activities were spread over a period of time which can be determined by ^{14}C dating.

Large quantities of lithic artefacts were recovered. The raw materials are the chert cobbles from the Nile channel lag deposits. Flat elongated chert cobbles were chosen. Flaking of short but regular blades was performed by direct blows with a soft hammer. The butts are flat or punctiform, the bulbs are thin; the Levallois technique was not used.

Tools are rare and are made from flakes or blades by flat retouching, sometimes bifacial, or by oblique retouching. Denticulates are the best represented tools although some burins and end-scrapers are present. Some bifacial axes have been collected; these are flat, made from flakes or blocks, with concave sides and a convex cutting edge (Fig. 3a, b).

The Upper Palaeolithic trenches in the substratum were clearly intended for the extraction of chert cobbles which were subsequently used for flaking. The method of exploitation consisted of undercutting the brown granuliferous silts so that the chert cobbles could be extracted, leaving galleries. This technique mainly took place from the trench. The trench was probably the result of an earlier 'trenching exploitation'[3] of the cobble-bearing layer. On the other hand, the trench may have been the result of cleaning after merging different bell pits. It was during the search for the chert cobble-bearing layer, that the bell pits were dug.

The rubble from the trench was dumped on the northeastern edge of the site probably where the chert cobble layer was naturally exposed. We believe that this natural exposure was the reason why the exploitation started.

Such extractions of mineral substances can be considered as real mining[3]. That this was not continuous mining can be deduced from the fact that prehistoric man was not always sure where to start his digging activities: a shaft was lowered into the rubble from earlier extractions and a search for exploitable chert was carried out in the neighbourhood of the site, such as the site of Nazlet Khater 1, where we excavated a similar bell pit filled with aeolian sand and containing charcoal dated at 31,600$^{+3,600}_{-2,500}$ yr BP (GrN-11298). Mining probably only took place when Upper Palaeolithic man came near Nazlet Khater, where he knew fresh chert to be available.

During the 1980 season a narrow (0.2–0.4 m) grave (1.6 m length and 0.6 m deep) was found on the summit of the boulder hill (Fig. 1). Within the grave was a corpse, lying at full length on its back, with the arms stretched along the body. The covering consisted of several boulders, some more than 0.4 m in diameter. The interstices were filled with loose aeolian sand. A tool was laid on the bottom of the grave, at the right of and next to the