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MODELAÇÃO DE SISTEMAS GEOLOGICOS

Homenagem ao Professor Doutor Manuel Maria Godinho

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On Proterozoic ecosystems and the carbon isotopic composition of carbonates associated with Banded Iron Formations

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Abstract

A compilation of over 400 carbon isotope analyses of carbonates associated with Banded Iron Formations (BIF) reveals a strong major mode at $\delta^{13}\text{C} \sim -7\text{‰}$ (VPDB), a second major mode at $\delta^{13}\text{C} \sim -10\text{‰}$, and a minor mode at $\delta^{13}\text{C} \sim -1\text{‰}$. The minor mode is readily attributed to contemporaneous marine bicarbonate, perhaps slightly modified by mixing with carbon of lower $\delta^{13}\text{C}$ (i.e. $< 0\text{‰}$). We compared the two major modes with literature examples of the structure of histograms of $\delta^{13}\text{C}$ of secondary carbonate cements from Phanerozoic sandstones which are hydrocarbon reservoirs. The processes and mechanisms responsible for the predominant modes in the sandstone cements $\delta^{13}\text{C}$ are thought to be reasonably well understood. Whereas the BIF-mode at $\delta^{13}\text{C} \sim -10\text{‰}$ corresponds to the most salient mode in the Jurassic cements (also $\delta^{13}\text{C} \sim -10\text{‰}$) and is accordingly ascribed to deep burial (thermal) remineralisation of organic matter, the BIF-mode at $\delta^{13}\text{C} \sim -7\text{‰}$ is not prominent in the sandstone cement compilations. We suggest it is attributable to a hydrothermal source. We conclude that the BIF-carbonate data can be explained without invoking a significant carbon source from biogenic processing of organic matter during shallow burial. We note that the absence of such microbial recycling of organic matter would preclude significant accumulation of biogenic CH_4 in the sediments until a vibrant community of appropriate obligate anaerobes became established in the subsurface.

Introduction

Banded Iron Formations (BIF) are sedimentary rocks deposited mainly in the interval ~ 3.6 to ~ 2 billion years age (Trendall, 2002; Simonson, 2003;

Clout and Simonson, 2005; Klein, 2005 and Beukes and Gutzmer, 2008 for reviews) in which components rich in iron alternate with others rich in silica; carbonates can be associated with both. BIF have long attracted the attention of earth scientists because of their intriguing episodicity in the geological record (James, 1983); because *inter alia* they have been considered to offer insight into palaeoenvironmental conditions during earlier phases of planetary development (e.g. Cloud, 1983, as a thoughtful example) and because of their economic significance as major sources of iron ores (Dalstra and Flis, 2008). Iron Formations are conventionally classified into three groups *viz* Lake Superior, Algoma and Rapitan (see Beukes and Gutzmer, 2008 for a recent discussion).

Important advances in our understanding of the sedimentology, architecture and depositional environment of BIF have recently been achieved through: critical syntheses; new approaches including sequence stratigraphy; recognition of the diverse range of microbial processes which could contribute to iron oxide precipitation; and application of new geochemical and isotopic methods (mass-independent S isotope fractionations, iron isotope ratios, etc). – see e.g. Beukes and Gutzmer, 2008; Simonson, 1985 and 2003; Konhauser *et al.*, 2005. An exhalative hydrothermal source seems likely for the iron (Gross, 1980; Simonson, 1985) and also for the Rare Earth Elements, especially Nd (Beukes *et al.*, 1990; Beukes and Klein, 2008). Raiswell (2006) has recently provided a critical evaluation and quantitative estimate of the potential of diagenetic recycling to contribute iron to BIF; he concluded that this mechanism is unlikely to provide a major iron source, albeit the diagenetic flux can be amplified by special factors such as an enhanced ratio of the area of source to sink.

Very recent ideas which have not, as yet, achieved acceptance and which will likely be the focus of much discussion, include biological iron oxidation (Konhauser *et al.*, 2007, and discussion therein), and cycling between microbially-mediated iron mineral deposition and abiotic silica mineral precipitation (thereby accounting for the alternating mineral assemblages) by natural ambient temperature fluctuations in the water column (Posth *et al.*, 2008).

Notwithstanding all this significant progress, consensus has yet to be achieved on certain issues, including interpretation of the carbon isotopic composition of BIF-associated carbonates. We recently hypothesised (Fallick *et al.*, 2008) that the pre-2000 Ma biosphere had a general mode of operation which differed from the modern one in that remineralisation of organic matter was predominantly in the anoxic water column and sediment-

water interface, and rarely within sediments. The bases for the proposal were the relative paucity of sedimentary concretions in the geological record prior to c. 2000 Ma, and the observation that – for the older rocks – diagenetic carbonates usually resemble contemporaneous sedimentary carbonates in having $\delta^{13}\text{C} \sim 0 \pm 3\text{‰}$ (VPDB). We explicitly recognised that within this context BIF-associated carbonates were anomalous in frequently displaying low $\delta^{13}\text{C}$ values.

The oxygen isotopic composition of quartz and iron oxides from banded iron-formations was reviewed by Müller *et al.* (1986), mainly from the perspective of metamorphic re-equilibration. Whilst noting the complexity introduced in polymetamorphic instances, they pointed to a broad agreement between temperatures of metamorphism deduced from petrological constraints and those calculated from oxygen isotope distributions. What then of low $\delta^{13}\text{C}$ carbonates associated with BIF being a consequence of metamorphic resetting via late stage organic matter oxidation by ferric oxides? Whilst this view has been suggested by Perry *et al.* (1985), it was discounted by Baur *et al.* (1985) and had previously been rejected by Becker and Clayton (1972), on the grounds of internal consistency with low organic matter concentrations, observations of occurrence of ferrous and ferric iron minerals, and preservation of small scale isotopic inhomogeneity in vertical sections.

The purpose of the present paper is firstly to expand a little on the previously proposed organic matter (OM) recycling hypothesis (Fallick *et al.* 2008), and secondly to look in greater detail at $\delta^{13}\text{C}$ of BIF-associated carbonates based on already published data. The objective here is to contribute to the debate over the extent to which these low $\delta^{13}\text{C}$ values document substantial remineralisation of organic matter, as opposed to for example a significant component of low $\delta^{13}\text{C}$ from a hydrothermal exhalative source. Our approach is to compare the frequency distribution of compiled BIF-associated carbonate $\delta^{13}\text{C}$ values with those of other published databases, together with theoretical considerations, taken as representing relatively pure end-member cases (deep-seated “hydrothermal” carbon, carbon derived from remineralised organic matter by a variety of mechanisms, etc).

Development of the Proterozoic Ecosystems Hypothesis

An implication of the hypothesis, not examined in Fallick *et al.* (2008), concerns generation of methane within the sediment column. In the absence of a sedimentary community of fermenting organisms, it seems unlikely that

there would be significant generation therein of biogenic CH₄, and consequently no opportunity to build up sizeable concentrations of methane-hydrate clathrate until thermogenic methane production commences. The opportunity for sedimentary biogenic methane accumulation arises (perhaps for the first time?) when fermentative recycling of buried organic matter is enabled by a vibrant and active community of appropriate organisms in the sediment: see Table 1 for a summary of some relevant key events, not necessarily in strict temporal sequence.

Table 1. Aspects of Palaeoproterozoic

APPROXIMATE TIME (Ga)	OBSERVATIONS AND SPECULATIONS
~2.5	
~2.4	Global Rifting. ¹ Development of oxygenic photosynthesis. ² Onset of Huronian glaciation. ³
~2.3	Water column OM recycling falters. ⁴ Water column not conducive to obligate anaerobes. ⁴ ?Start of L-J isotope excursion.
~2.2	Accumulation of sedimentary CH ₄ . ⁵ Development of deep water basins. ⁶
~2.1	Vibrant subsurface biosphere allows efficient OM recycling in sediments. ⁴ Sedimentary concretions abundant. ⁴ End of L-J isotope excursion. ⁷
~2.0	

Notes: Most timings are not well-constrained and so neither is the sequence implied in the Table.

References are: 1. Heaman 1997; Vogel *et al.* 1998. 2. Kirschvink 2005; Kopp *et al.* 2005. 3. Young *et al.* 2001; Hannah *et al.* 2004; Melezhik 2006; 4. Fallick *et al.* 2008. 5. This work. 6. Bekker and Eriksson 2003; Wanke and Melezhik 2005. 7. Karhu and Holland 1996; Melezhik *et al.* 2007.

The modern analogue suggests that the CO₂ produced during methanogenesis would usually (but not always) be lost to the overlying water column, resulting in a local CO₂ source with high δ¹³C. By contrast,

the carbon remaining sequestered in the sediment comprises that fraction of the organic matter not recycled and low $\delta^{13}\text{C}$ carbon in carbonate cements, plus the retained methane with $\delta^{13}\text{C} \sim -50\text{‰}$. Recall that we expect the flux of organic carbon into the sediment to be high because of relatively inefficient processing in the newly oxic water column as aerobic recyclers become established. Note, too, that retention of low $\delta^{13}\text{C}$ carbon as methane decreases the amount of reduced carbon (and so *ceteris paribus* the fraction of carbon sequestered that is reduced) necessary to achieve a given increase in marine carbonate $\delta^{13}\text{C}$, *i.e.* sequestered low $\delta^{13}\text{C}$ methane makes around twice the contribution (per atom of carbon) to isotope balance as does the burial of organic matter of primary production at -25‰ . At the present day the size of the methane clathrate-hydrate carbon reservoir is intermediate between the atmospheric reservoir of carbon dioxide and the reservoir of carbon in fossil fuels.

An interesting corollary is that the carbon stored as methane clathrate-hydrate will be expected to be recycled to the ocean/atmosphere as the environments of storage (outer continental margins) are destroyed. Given that the overall picture is one of supercontinent breakup and dispersal of the fragments by early plate-tectonic processes, the appropriate timescale is that of a tectonic cycle and the process is expected to be secular and episodic rather than catastrophic. The implication being examined here thus predicts a slow decline in marine carbonate $\delta^{13}\text{C}$ from the peak value of the Lomagundi-Jatulian isotope excursion, possibly accompanied by shorter-term internal structure of non-monotonic variation in $\delta^{13}\text{C}$, over a time scale of several tens of millions of years. The sedimentary record will contain low $\delta^{13}\text{C}$ diagenetic carbonates and only indirect evidence (e.g. collapse structures?) of the reduced carbon originally buried as methane clathrate-hydrate, and the “Paradox” of Melezhik and Fallick (1996) is somewhat alleviated – see also Shields (1997) and Melezhik and Fallick (1997).

The implication being considered here has a certain explanatory power, but a rather modest potential for testable predictions (at least in our hands). In mitigation, we note that this is an endemic feature of hypotheses related to methane storage and release. One prediction which can be made is that the set of circumstances envisaged should on occasion result in secondary carbonates (e.g. as cements or even parts of nodules) with carbon derived from the high- $\delta^{13}\text{C}$ CO_2 usually lost from the sediments. If an analogy with Phanerozoic cements is of any merit, this might be observed in the order of 1% of occurrences (see data presented in Figure 4 of Macaulay *et al.* 2000, amended here as Figure 2). In contrast to the weak predictive power of the methane implication of the new anoxic biosphere hypothesis,

there is *strong* predictive power in the hypothesis itself: the low-abundance carbonate nodules and diagenetic cements preceding the Lomagundi-Jatulian $\delta^{13}\text{C}$ excursion should normally have $\delta^{13}\text{C}$ which does not reflect microbial processing of organic matter within the shallow sediment. As was demonstrated in Fallick *et al.* (2008), this test was passed for the analysed samples outwith BIF– associations. Thus, we must turn our attention to the exceptions and reconsider BIF-associated low $\delta^{13}\text{C}$ carbonates as a potential counterexample.

BIF-associated carbonates

Methodological considerations

It is entirely conceivable that different BIF have associated carbonates of different modes of genesis, e.g. bedded carbonates in the same stratigraphic sequence; primary and/or secondary carbonates directly within a BIF package; nodular carbonates etc. Whilst it is clear that in any particular case the carbonate formation mechanism should be approached by careful, comprehensive field, petrographical and geochemical study of the rocks themselves, we here offer a different approach and investigate critically its efficacy in offering elucidation of the process(es) influencing sources of carbon, and carbonate precipitation.

The approach involves compiling the carbon isotope data from a multitude of individual studies and seeing whether distinct patterns emerge from the statistically large database. We recognise that there are potential problems with this approach (see below), which is essentially a form of statistical inference (Till, 1974 p48 *et seq.*), but it has a long and reasonably honourable history in geochemistry.

Amongst the potential problems recognised are:

(1) Sampling biases are a perennial problem, rarely conducive to solution. The collection of samples included in the compilation used here is unlikely to have been either random or comprehensively systematic, and as Till (1974, p48) has noted “... the usefulness of a statistical result depends on the care taken in designing the sampling procedures”. Where sampling bias has been circumvented – e.g. in the sulphur isotope anatomy of a world-class base metal ore deposit through $\delta^{34}\text{S}$ measurement of ore concentrates – the frequency distribution of isotopic composition proved to be quite different from that generated by intensive investigation of hand

specimens, albeit the genetic model remained basically the same (compare Anderson *et al.* 1998 with Fallick *et al.* 2001).

(2) Spurious patterns may emerge from a compilation which includes different categories of sample, e.g. diagenetic carbonates associated with organic-matter fermentation reactions often have high $\delta^{13}\text{C}$ and would overlap with primary sedimentary carbonates of the Lomagundi-Jatulian (c. 2200Ma) carbon isotope excursion. And overall trends may mask the characteristics – possibly unique – of specific individual studies.

(3) It may be tempting to classify sample groupings according to their isotopic composition (*i.e.* modes in the frequency distribution) without a robust theoretical understanding of the isotope fractionation mechanisms which produced the actual values e.g. uncritical assignment of diamonds of low ($\sim -25\text{‰}$) $\delta^{13}\text{C}$ to an origin from subducted organic carbon. Put differently, one must strive to avoid issues of circularity.

Accepting these (and other) deficiencies, we nevertheless recognise that examination of the internal structure of compilations has proven informative under favourable circumstances.

The BIF Associated Carbonate $\delta^{13}\text{C}$ Database

The database of $\delta^{13}\text{C}$ for BIF-associated carbonates used in this study has been compiled from published sources by VM at the Norwegian Geological Survey, from whom it is available; aspects of it were included in Figure 1 of Fallick *et al.* (2008) and references are given in the caption to that Figure. It consists of 440 entries, 209 of which pertain to the Dales Gorge Member of the Brockman Iron Formation, a component of the Hamersley Group on the Pilbara craton of Western Australia. Data for four other Formations comprise more than 30 samples each, viz. Krivoj Rog from the Ukrainian Shield (n=66), the Transvaal Supergroup of South Africa (n = 50), the Biwabik Iron Formation of the Mesabi Range in the Lake Superior region (n = 32), and the Hamersley Group Marra Mamba Iron Formation; the Mt Sylvania Formation, also of the Hamersley Group, is represented by 29 samples.

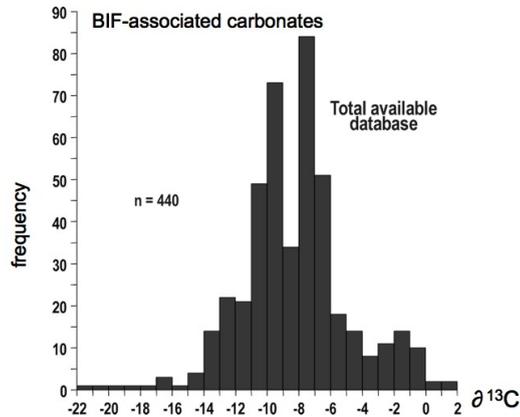


Figure 1. Histogram of carbonate $\delta^{13}\text{C}$ for 440 published analyses of BIF-associated carbonates. Note the major mode at around -7‰, another strong mode at around -10‰ and a minor mode at around -1‰.

The frequency distribution of the total available $\delta^{13}\text{C}$ database is shown in Figure 1. A 1‰ bin size has been selected as this will comfortably cover analytical errors, interlaboratory differences and intercalibration issues, whilst not being particularly sensitive to major geological processes. It is immediately apparent that the histogram is complex, with major modes centred on -7‰ and -10‰ (these are separated by a clear minimum), and a weaker but plausible mode at about -1‰. This overall structure, with prominent nodes at -7 and -10‰ can be clearly seen also in the restricted distributions for the individual BIF of the Dales Gorge Member, Krivoj Rog, Marra Mamba and Transvaal Supergroup (located at present on three different continents). The range extends continuously from +2 to -22‰, so there is skew to low $\delta^{13}\text{C}$ values. Whilst it is well-known that a batch or Rayleigh fractionation process operating on a closed pool generates a unimodal, but strongly asymmetric or skewed frequency distribution of isotope ratios (see e.g. Schwarcz and Burnie, 1973 for an apposite review), such a mechanism is unlikely to be of strong explanatory value here. This is because skew to low $\delta^{13}\text{C}$ would demand a fractionation process favouring the heavy rather than the light isotope (*i.e.* ^{13}C rather than ^{12}C): this would be a most unusual fractionation process indeed!

A Priori Expectations

(1) *Hydrothermal carbon*

Mantle (or deep-seated) carbon is normally characterised as having $\delta^{13}\text{C}$ around -5 to -7‰ (e.g. Taylor, 1986; Matthey, 1987), although this is certainly an oversimplification (see Deines, 1992 and discussion in Melezhik *et al.*, 2005). The isotopic composition of hydrothermal CO_2 will then be determined by the $\delta^{13}\text{C}$ of this source carbon, the ratio of CO_2 to CH_4 plus higher hydrocarbons in the exhalative system, and the temperatures at which carbon isotope exchange between oxidised and reduced carbon attain closure.

(2) *Normal marine dissolved inorganic carbon*

There is a general consensus, without sustained challenge, that the $\delta^{13}\text{C}$ of dissolved inorganic carbon in the open ocean (as opposed to environments of BIF-deposition) in the early Proterozoic was close to 0‰. This view has been advanced *inter alia* by Becker and Clayton (1972), Belevtsev *et al.* (1983), Baur *et al.* (1985) and Fischer *et al.* (2009).

(3) *Oxidised organic carbon*

The isotopic composition of carbonate resulting from the diagenetic remineralisation of organic matter will be determined by the original isotopic composition of the organic material and any isotopic fractionation involved in the remineralisation process; the latter depends intimately on the specific pathway (e.g. fermentation, thermal decarboxylation etc), see Irwin *et al.* (1977).

To estimate the starting isotopic composition of organic matter prior to degradational production of oxidised carbon for possible incorporation into carbonate, we conservatively suggest a value of around -25‰. For 33 organic matter $\delta^{13}\text{C}$ values reported for the Transvaal Supergroup, of South Africa by Beukes and Gutzmer (1990), the mean ($-25.7 \pm 2.1\text{‰}$) and mode (about -25‰) are similar, and also comparable to an average of $-26.1 \pm 1.2\text{‰}$ reported by Beukes *et al.* (1990) for oxide-rich BIF, also from the Transvaal Supergroup, though note that organic matter in other associations is notably isotopically lighter. Lower values (predominantly between -30 and -35‰) were reported by Fischer *et al.* (2009), and also by Baur *et al.* (1985) for the Marra Mamba Iron Formation, whereas a mean of $-18.6 \pm$

3.7‰ for the prehnite-pumpellyite grade Bruno's Band, and $-25.9 \pm 2.0\%$ and $-21.4 \pm 0.4\%$ for macrobands in the Dales Gorge Member were reported by the latter authors in their study of the Hamersley Group of Western Australia.

The different carbon isotope fractionations between original organic matter at -25% and the product CO_2 or bicarbonate are revealed in the range of $\delta^{13}\text{C}$ in secondary carbonates (albeit potentially modified by mixing with oxidised carbon from other sources). Our analogy for this will be the large database of $\delta^{13}\text{C}$ values of carbonate cements from sandstone oil reservoirs in the northern North Sea. Whilst we appreciate that a database closer in age to BIF deposition would be preferable, the exigencies of research funding dictate what is available and has an acceptable integrity. Interestingly, from our current perspective, there are two different categories of reservoir. Firstly, Jurassic sandstones received carbon predominantly during **late diagenesis** as hydrocarbons were generated during thermal maturation of adjacent organic-rich mudrocks (Macaulay *et al.* 1998). Free oxygen is not thought to have been available. Secondly, Tertiary sandstones, submarine fan deposits and marine sheet sandstones, were charged with oil in the Oligocene and ingress of meteoric water allowed fermentative and oxidative processes to occur during **early burial** (Macaulay *et al.* 2000). Note that the hydrocarbon source rocks for both Jurassic and Tertiary reservoirs are the Kimmeridge Clay Formation, perhaps with a contribution from coals in the Brent Group (Espitalié *et al.* 1991 and references therein).

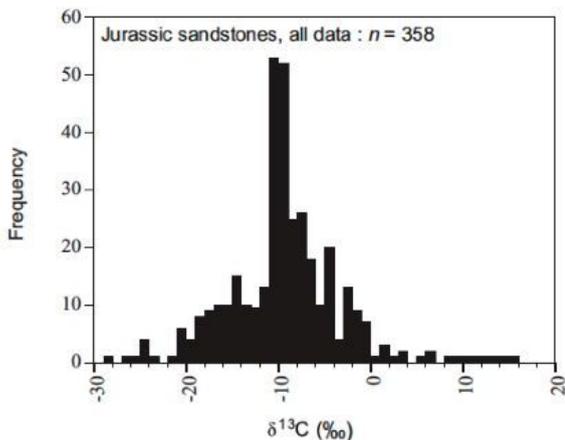


Figure 2. Histogram of $\delta^{13}\text{C}$ of carbonate cements for 358 analyses compiled by Macaulay *et al* (1998) from 13 Jurassic sandstone reservoirs in the North Sea. Note the very strong mode at around -10% .

The isotopic composition of on shore Kimmeridge Clay kerogen has been reported as -21‰ with extractable bitumen at -23.5‰ (Andresen *et al.* 1994). Clayton and Bjorøy (1994) reported $\delta^{13}\text{C}$ for four North Sea oils which defined a maturity sequence (from early generation through to early stages of gas cracking) giving -29.8, -28.9, -28.6 and -28.5‰. They also noted oil generation results in a small increase (around 1‰) in $\delta^{13}\text{C}$ and that source facies variations usually lead to an increase in $\delta^{13}\text{C}$ where the source is terrestrially influenced. Ness Formation coal measured by Andresen *et al.* (1994) had $\delta^{13}\text{C}$ of -26.4‰.

Macaulay *et al.* (1998) compiled 358 isotopic analyses of diagenetic cements in Jurassic reservoir sandstones from 13 oilfields. Whilst $\delta^{13}\text{C}$ ranges widely (+15.8 to -28.8‰, see Figure 2) there is a very strong mode at around -10‰, with approximately 40% of the data between -9 and -11‰. The few fermentation-related high $\delta^{13}\text{C}$ values were from cements (mainly ankerite and siderite) in Middle Jurassic deltaic sandstones.

For the Tertiary sandstones susceptible to meteoric water flushing during early burial, Macaulay *et al.* (2000) compiled 178 isotopic analyses with $\delta^{13}\text{C}$ spanning +18‰ to -30‰ (see Figure 3).

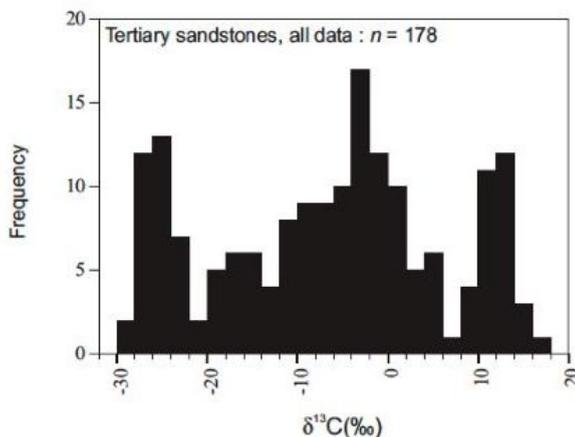


Figure 3. Histogram of $\delta^{13}\text{C}$ of carbonate cements for 178 analyses compiled by Macaulay *et al.* (2000) for Tertiary sandstones in the North Sea. Note the trimodal distribution with peaks around -26‰, -3‰ and +12‰.

By contrast to the Jurassic reservoir data, the histogram is trimodal with strong peaks around -26‰ (cements associated with oxidative oil biodegradation), -3‰ (attributed to mixed sources strongly influenced by marine bicarbonate), and +12‰ (bacterial fermentation reactions, see also Dimitrakopoulos and Muehlenbachs, 1987).

Discussion

The strongest mode (centred on $\delta^{13}\text{C}$ of -7‰) for the BIF-associated carbonates in Figure 1 is not prominent in either compilation of North Sea data (Figures 2 and 3). We suggest it is more plausibly attributed to a hydrothermal exhalative source. Thus ~ 50% of the data compiled in Figure 1 can be accounted for without invoking organic matter as a carbon source. The clearly separate mode at -10‰, by analogy with the data of Figure 2, is likely derived from deep burial (thermal) organic matter recycling, as are lower $\delta^{13}\text{C}$ values. The minor mode close to -1‰ is likely strongly influenced by open seawater bicarbonate, free of hydrothermal influence.

We propose therefore that the salient features of the distribution of $\delta^{13}\text{C}$ amongst BIF-associated carbonates – including the prominent low- $\delta^{13}\text{C}$ modes – can be explained without invoking biologically-induced shallow burial recycling of organic matter. In this sense, such BIF-associated carbonates do not provide a counter argument to the Palaeoproterozoic biosphere hypothesis advanced by Fallick *et al.* 2008. The conclusion that the predominance of low $\delta^{13}\text{C}$ values for Archaean-Palaeoproterozoic BIF-associated carbonates is highly influenced by a carbon source associated with exhalative processes, with remineralisation of organic carbon also a significant process, is not new but deserves emphasis. Re-examination of the exhalative origin for the large-scale BIF of early Proterozoic age was advocated by Simonson (1985), and Beukes *et al.* (1990 p.664) explicitly noted that: “Depletion of ^{13}C , therefore, may derive not from degradation of organic matter but from hydrothermal activity...”. Instructively, the statistically highly significant negative correlation between carbonate $\delta^{13}\text{C}$ and magnetite (ferric) iron, reported in the painstaking study of Baur *et al.* (1985) for the Hamersley Marra Mamba Formation, pertain to a suite of ankerite microbands for which mean $\delta^{13}\text{C} = -9.9 \pm 2.9$ ‰ (data in their Table 2). A biological origin was attributed, and our interpretation of deep-burial diagenesis concurs. By contrast, a separate sample suite of Marra Mamba carbonates reported in their Table 1 with mean $\delta^{13}\text{C} = -7.35 \pm 0.06$ ‰ would correspond nicely with our postulated hydrothermal source, and the tight cluster is consistent with a strongly predominant single source for carbon.

So, to conclude, why are BIF-associated carbonates distinctive, in the sense of Fallick *et al.* (2008)? The answer, at least in part, may be that the ready availability of (frequently hydrothermal) bicarbonate and cations, including iron, resulted in relatively rapid precipitation. This often occurred before mixing with other sources of bicarbonate compromised the tell-tale isotopic signature. The argument applies to hydrothermal carbonate as well

as that produced by deep-burial remineralisation of organic matter. Such opportunity was not so prevalent distal from the hydrothermally-influenced water bodies. To adapt Cloud's (1988) memorable terminology, the perhaps fecund (cf. Emerson and Moyer 2002) BIF-environments were, in a certain sense, 'oases in space'. Clearly, such a scenario, whilst illuminating, allows for much local variation – both in space and time.

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