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RAPID COMMUNICATION

Carbon isotope stratigraphy of the upper Telychian and lower Sheinwoodian (Llandovery–Wenlock, Silurian) of the Banwy River section, Wales

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Abstract

$\delta^{13}C_{org}$ and TOC data are presented from the upper *spiralis* Biozone (Telychian, Llandovery, Silurian) through to the upper Sheinwoodian (Wenlock, Silurian) of the Banwy River section, Wales. In laminated hemipelagites from the Telychian, $\delta^{13}C_{org}$ values rise through the upper *lapworthi* Biozone to a maximum in the lower *insectus* Biozone after which they decline slightly. The most conspicuous feature of the $\delta^{13}C_{org}$ curve is the prolonged positive excursion in the Sheinwoodian, commencing in the upper *murchisoni* Biozone and ending in strata yielding *Monograptus flexilis*. This Sheinwoodian positive $\delta^{13}C$ excursion in the Banwy River section correlates precisely with that recognized in the East Baltic. The interval with the highest $\delta^{13}C_{org}$ values also records the highest TOC values, suggesting that for the Sheinwoodian at least, burial of carbon may have contributed to the positive $\delta^{13}C$ excursion. Bioturbated strata yield very low TOC values; whether the $\delta^{13}C_{org}$ values from these beds reflect a primary signal or the result of biostratinomic or diagenetic modification is uncertain.

Keywords: carbon isotope, Silurian, Telychian, Sheinwoodian, Llandovery, Wenlock.

1. Introduction

The Banwy River section in eastern mid-Wales has been the subject of detailed biostratigraphical studies on its graptolites (Loydell & Cave 1996; see for locality map) and chitinozoans (Mullins & Loydell 2001). It is unique in Great Britain in exposing a continuous section through all of the upper Telychian and lower Sheinwoodian graptolite biozones. Because of the generally excellent biostratigraphical control, it is an ideal section upon which to undertake carbon isotope studies.

The present paper discusses the $\delta^{13}C_{org}$ record from the upper *spiralis* Biozone (Telychian) through to the top of the section, in the upper Sheinwoodian. Comparison is made with carbon isotope curves from the East Baltic that also have excellent graptolite biostratigraphical control.

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2. Methods, including new graptolite records from the section

The analysed samples from the upper *spiralis* Biozone through to lowermost *riccartonensis* Biozone were collected as part of Loydell & Cave's (1996) field work. The higher samples (above C+30; C = a conspicuous nodular horizon in the river bank, used as a marker bed) were collected in June 2006 by DKL at stratigraphical intervals of 1 m. For consistency, this study focuses on analyses of laminated hemipelagites (Fig. 1a). These occur interbedded with bioturbated strata within the Tarannon Shales Formation and Banwy Burrowed Member of the Nant-ysgollon Shales Formation; above the Banwy Burrowed Member the remainder of the Nant-ysgollon Shales Formation is dominated by laminated hemipelagites; bioturbated strata occur only within the upper *centrifugus* and middle and upper *murchisoni* biozones. Three bioturbated horizons (Fig. 1b–c) have been analysed by us; these are plotted separately (open circles in Figs 2–3) and are discussed in Section 5.b. Strong thermal alteration is indicated by the dark brown colour of acritarchs extracted from the section (Mullins & Loydell 2001). The higher part of the Banwy River section is characterized by strata that generally fracture at a variety of angles, but rarely parallel to bedding. This makes collection of identifiable graptolites difficult and very time-consuming. *Monograptus riccartonensis* Lapworth was found at C+47 m indicating that the *riccartonensis* Biozone must continue up to at least this level. Above this, identifiable graptolites were encountered at two levels only: at C+59 m, where the presence of *Cyrtograptus rigidus* indicates a level above the *riccartonensis* Biozone, and at the top of the section where a diverse assemblage including *Monograptus flexilis* Elles occurs (as recorded by Loydell & Cave 1996).

In total 45 samples were analysed for organic carbon isotopes and TOC. Hand specimens were cut and rock powder was prepared from a few grams of fresh sample. A few milligrams of rock powder were taken for total organic carbon (TOC) and total organic carbon isotope analyses. Before analyses, rock powders were decarbonatized with 10 % HCl at 40 °C for several hours, then washed and dried. About 20 mg of rock powder were used for TOC and about 10 mg for isotope analyses. Samples were combusted in a Fisons 1108 elemental analyser coupled on-line to a Finnigan Mat 251 mass spectrometer via a ConFlo interface.

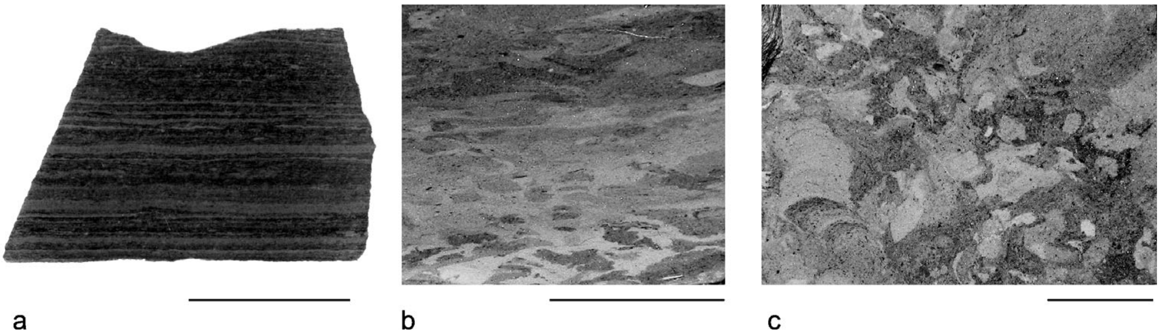

Figure 1. Polished lithological specimens of (a) laminated hemipelagite from the Nant-ysgollon Shales Formation (Bed C+4 m); (b, c) bioturbated mudstone from the Banwy Burrowed Member (Bed X+8.5 m); (a) and (b) were cut perpendicular to bedding, (c) parallel to bedding. Scale bars represent 10 mm.

As reference material, NBS 22 (Gulf oil, with $\delta^{13}C$ value -29.75 ‰) and acetanilid (Analytical Microanalysis, UK) were measured. Accuracy and precision were controlled by replicate measurements of laboratory standards and were better than ± 0.1 ‰ (1σ) for total carbon isotope analyses and better than ± 0.02 % (1σ) for total organic carbon content.

3. The Banwy river section $\delta^{13}C_{org}$ and TOC records

Figure 2 summarizes the results of the $\delta^{13}C_{org}$ and TOC analyses of the Banwy samples. The results from laminated hemipelagites and from bioturbated strata are plotted and discussed separately.

3.a. The $\delta^{13}C_{org}$ record from laminated hemipelagites

The upper *spiralis* and lower *lapworthi* biozones are characterized by very low $\delta^{13}C_{org}$ values, in the range -30.24 ‰ to -29.58 ‰, with the lowest value in the lower *lapworthi* Biozone. This is followed by a sharp rise in values through the upper *lapworthi* Biozone, a high of -28.56 ‰ occurring in the lower *insectus* Biozone. Following a slight fall to -28.95 ‰ in the middle *insectus* Biozone, with one exception (in the middle *centrifugus* Biozone), the next ten values fall within a narrow range of values (-29.21 ‰ to -28.71 ‰), through to the lower *murchisoni* Biozone. A significant rise in the upper *murchisoni* Biozone culminates in the highest value recorded in the section (-26.86 ‰) in the highest sample from this biozone. A decline to values which are still higher than most of those of the middle *insectus* to lower *murchisoni* Biozone interval characterizes the *firmus* Biozone. The transition into the *riccartonensis* Biozone marks the beginning of a considerable thickness (48 m) of section with high $\delta^{13}C_{org}$ values, mostly above -28.00 ‰ (range -27.23 ‰ to -28.22 ‰). The highest part of the section, which yields *Monograptus flexilis* Elles, records a sharp decline in $\delta^{13}C_{org}$ values.

3.b. Total organic carbon (TOC) and its relationship to $\delta^{13}C_{org}$

The lowest TOC values (0.05–0.12 %) occur in the *lapworthi* Biozone. All three samples were from bioturbated levels and are shown as open circles on Figures 2 and 3. With the exception of a single high (relative to other samples) TOC value in the *lapworthi* Biozone, the samples fall into two groups: those with relatively low TOC values (below 0.5 %, and mostly below 0.4 %) in the lower part of the section (upper *spiralis* to upper *murchisoni* biozones) and those with relatively high TOC values (above 0.6 %) in the upper part. Although there is not an entirely consistent relationship between $\delta^{13}C_{org}$ and TOC (Fig. 3), it is clear that, with the exception of the single high *lapworthi* Biozone TOC value, the highest TOC values occur through the same stratigraphical interval as the highest $\delta^{13}C_{org}$ values (Fig. 2).

4. Correlation

The most remarkable correlation is that between the Banwy River carbon isotope record and those from the East Baltic region, recently summarized by Kaljo & Martma (2006). As with the Banwy River section, precise graptolite biostratigraphical correlation is possible in the East Baltic cores studied, enabling the timing of positive $\delta^{13}C$ excursions to be accurately constrained.

Uppermost Telychian strata are not present in Latvia and Estonia; there is an unconformity at this level resulting from the low eustatic sea-levels at this time (Loydell, 1998). In the lower Sheinwoodian, however, a thick sequence of graptolitic strata enables accurate relative dating of the onset of the early Sheinwoodian positive $\delta^{13}C$ excursion to the upper *murchisoni* Biozone (Fig. 4). High $\delta^{13}C$ values are maintained through the *riccartonensis* Biozone until the end of the excursion which is dated by *Monograptus flexilis* Elles (Fig. 4). Thus the timings of the beginning and end of the early Sheinwoodian positive $\delta^{13}C$ excursion are identical in the Banwy section and the East Baltic.

A Sheinwoodian positive $\delta^{13}C$ excursion has been recognized from many other regions, e.g. Australia (Andrew *et al.* 1994), Gotland (Munnecke, Samtleben & Bickert, 2003), the American mid-continent (Cramer & Saltzman, 2005) and Arctic Canada (Noble *et al.* 2005), but these studies lack the graptolite biostratigraphical control of the Banwy and East Baltic sections.

5. Discussion

5.a. Carbon burial and positive $\delta^{13}C$ excursions

There has been considerable debate (summarized by Melchin & Holmden, 2006a) as to the cause of positive $\delta^{13}C$ excursions in the Hirnantian and Silurian. Data from the Hirnantian in particular (Melchin & Holmden, 2006b) do not support enhanced global carbon burial as being a cause of positive $\delta^{13}C$

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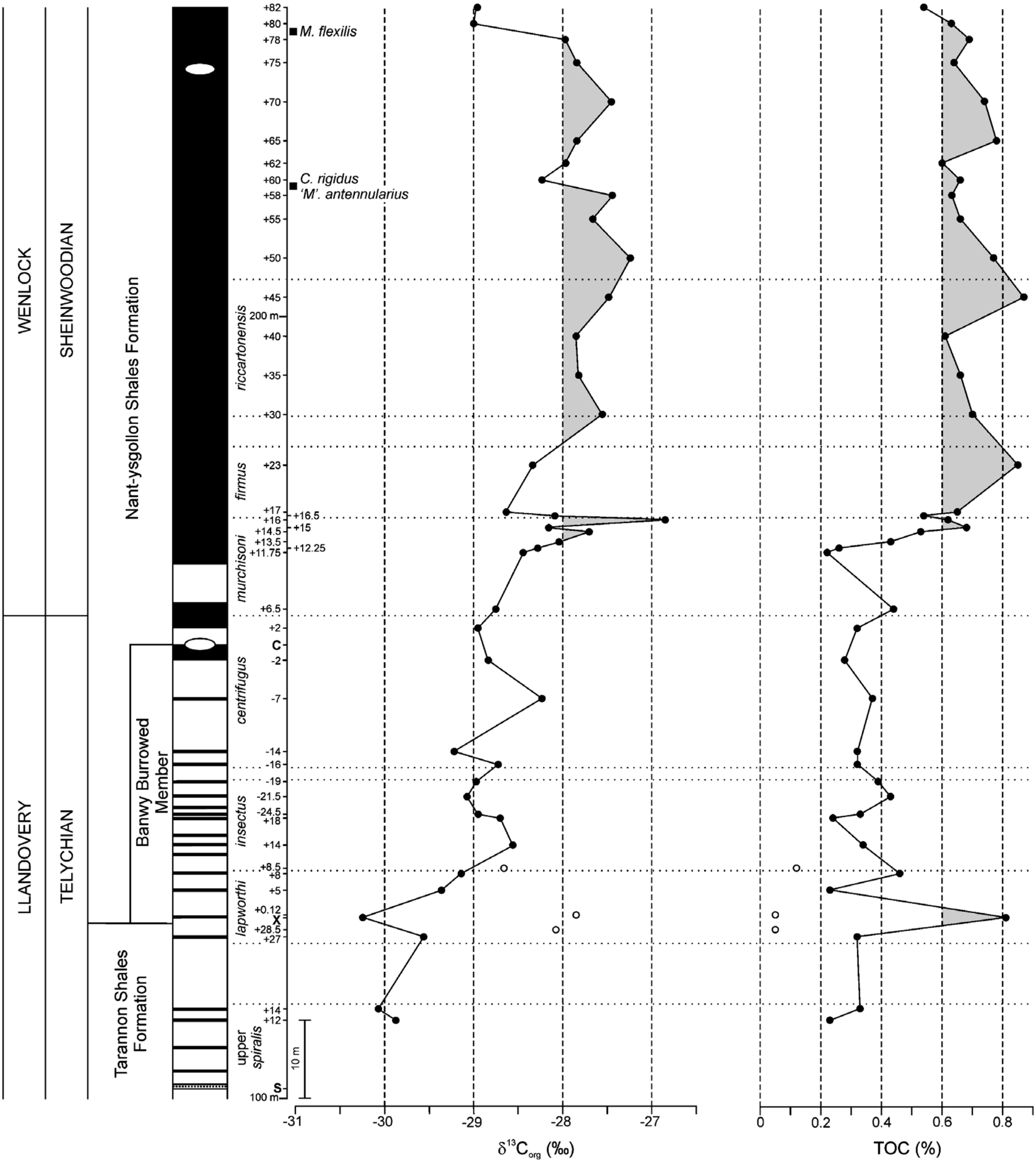

Figure 2. The $\delta^{13}C_{org}$ and TOC records through the upper Telychian and Sheinwoodian of the Banwy River section. S, X and C represent marker horizons (see Loydell & Cave, 1996). Shaded areas are above − 28 ‰ $\delta^{13}C_{org}$ and above 0.6 % TOC. In the lithologies column, black represents laminated hemipelagite; white represents bioturbated mudstones (see Loydell & Cave, 1996, for details). Open circles are bioturbated samples. Black circles are laminated hemipelagites.

excursions, leading to the proposal that increased carbonate weathering at times of low sea-level was responsible (Noble *et al.* 2005; Melchin & Holmden, 2006a, b).

The Banwy data, however, provide support for the carbon burial hypothesis. The highest $\delta^{13}C$ and TOC values all occur within the same interval, from the upper *murchisoni* Biozone through to nearly the top of the section (Fig. 1). It is interesting to note that Kump *et al.* (1999, cited by Noble *et al.* 2005, p. 1427) determined that a 50 % to 75 % increase in organic carbon burial would have been needed to generate the Hirnantian positive $\delta^{13}C$ excursion. In the Banwy River section average TOC approximately doubles between the lower and upper parts of the section. Kaljo, Kiipli & Martma (1997, p. 221) also recorded an 'increased

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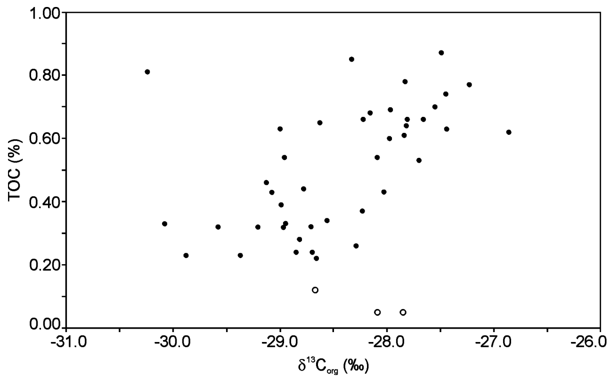

Figure 3. Plot of TOC (%) against $\delta^{13}C_{org}$ (‰). Open circles are bioturbated samples. Black circles are laminated hemipelagites.

content' of organic carbon in the *riccartonensis* Zone of the Ohesaare core, Estonia (4–6 % TOC) and Priekule core, Latvia (3–7 % TOC), demonstrating that increased carbon burial was a widespread phenomenon at this time. It will be interesting to see whether future studies demonstrate similar increases in TOC in strata recording the early Sheinwoodian positive $\delta^{13}C$ excursion.

The global sea-level curve for the early Silurian (Loydell, 1998) shows falling sea-level through the late *murchisoni–riccartonensis* zones. It is thus possible that enhanced carbon burial resulted from a higher sedimentation rate associated with regression. Carbonate weathering would also have increased at this time and thus a combination of increased carbon burial and carbonate weathering may be responsible for the positive $\delta^{13}C$ excursion.

5.b. Bioturbation, TOC and $\delta^{13}C$

The samples collected by Loydell & Cave (1996) were almost exclusively laminated hemipelagites (Fig. 1a), selected because these would yield the graptolites required for their biostratigraphical work. Between the sampled horizons, in both the Tarannon Shales Formation and Banwy Burrowed Member of the Nant-ysgollon Shales Formation, the strata were bioturbated and paler in colour (Fig. 1b, c). Three of these bioturbated samples were analysed for their $\delta^{13}C$ and TOC (indicated by open circles on Figs 2 and 3). In all three, TOC was much lower (0.05–0.12 %) than in the laminated hemipelagites. These analyses have been plotted separately to reflect the possibility that the isotopic composition does not represent a primary signal, but one modified by biostratinomic or diagenetic processes. As there are no other published $\delta^{13}C$ data from the uppermost Telychian it is difficult to known whether the dramatic fluctuations in $\delta^{13}C_{org}$ (e.g. from − 30.24 ‰ to − 27.85 ‰ over a stratigraphical thickness of 120 mm) are typical of this interval. It would be very interesting indeed to conduct a carbon isotope study through the upper Telychian and lower Sheinwoodian in Bohemia, where lithological changes are less pronounced and sections are consistently graptolitic, thus enabling more closely spaced sampling through the upper *spiralis* to *insectus* Biozone interval. In the Banwy River section there is a significant thickness of non-graptolitic strata between the upper *spiralis* and *lapworthi* biozones, reducing the stratigraphical precision possible in this part of the upper Telychian.

The Banwy hemipelagite data suggest a positive excursion commencing in the late *lapworthi* Biozone with peak $\delta^{13}C_{org}$ values in the lower *insectus* Biozone. This would coincide with the low eustatic sea-levels recognized by Loydell (1998). Including all of the $\delta^{13}C_{org}$ data (i.e. hemipelagites plus bioturbated strata) would generate a complex record, with high $\delta^{13}C_{org}$ values (− 28.09 ‰ and − 27.85 ‰) just below and just above the base of the Banwy Burrowed Member, but separated by the lowest $\delta^{13}C_{org}$ value (− 30.24 ‰) in the section. The coincidence of these major changes in $\delta^{13}C_{org}$ values with a lithological change would suggest a common cause. Based on the graptolites present in bed S+27 m and bed X, both clearly belong in the lower half of the *lapworthi* Biozone. From what level they are from within this interval is impossible to judge in the absence of graptolites from between S+14 and S+27 m.

6. Conclusions

The $\delta^{13}C_{org}$ record from the Banwy River section, Wales shows the widely recorded early Sheinwoodian positive $\delta^{13}C$ excursion. This can be correlated precisely, using graptolites, with the East Baltic $\delta^{13}C$ record. Increased TOC coincident with the positive $\delta^{13}C$ excursion suggests that increased carbon burial may have been responsible for generating the isotope excursion. More studies on the $\delta^{13}C$ record through the uppermost Telychian are required, particularly

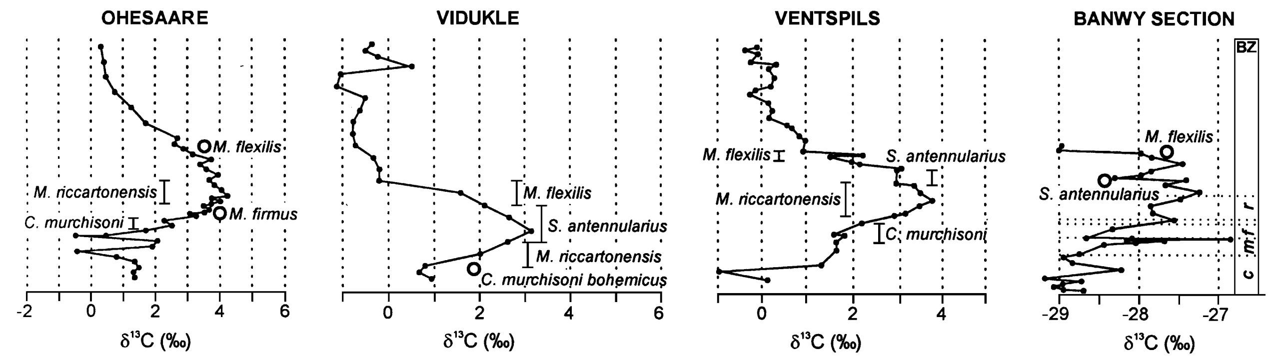

Figure 4. $\delta^{13}C_{carb}$ curves from three cores in the East Baltic region (from Kaljo & Martma 2006) compared with the Banwy River $\delta^{13}C_{org}$ curve. *c* = *centrifugus*; *m* = *murchisoni*; *f* = *firmus*; *r* = *riccartonensis*; BZ = biozone. For the East Baltic cores, stratigraphical ranges (bars) and occurrences (circles) of key biostratigraphical taxa are given; for the Banwy River section, biozonal boundaries are indicated for the *centrifugus–riccartonensis* biozones and the occurrences of two key taxa from higher in the Sheinwoodian are shown by open circles.

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in Bohemia. In the Banwy River data it is unclear whether bioturbated strata with low TOC are recording a primary geochemical signal or one modified by biostratinomic or diagenetic processes.

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