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Working towards a new stratigraphic calibration scheme for the Neoproterozoic-Cambrian

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Keywords: Precambrian-Cambrian, strontium, carbon, isotope stratigraphy, terminal Proterozoic

ABSTRACT

Recent improvements in the global correlation of the Neoproterozoic – Cambrian transition have revolutionised our understanding of the early fossil record. Foremost in this revolution has been isotope geochemistry, which provides an independent calibration scale for this time. In this article, global calibration schemes for the terminal Proterozoic are reconsidered. Crossreferencing $\delta^{13}\text{C}$ excursions with the $^{87}\text{Sr}/^{86}\text{Sr}$ record allows us 1) to correlate Neoproterozoic glaciations and, 2) to establish the rates and nature of early metazoan evolutionary expansion. The creation and continual perfection of such calibration schemes will be of crucial importance to the eventual subdivision and correlation of the Neoproterozoic.

RESUME

Ces dernières années, des progrès importants dans la corrélation des couches du passage Néoprotérozoïque-Cambrien à travers le monde ont été faits, et cela a révolutionné nos conceptions sur la répartition stratigraphique des premiers fossiles. La géochimie isotopique y a joué un rôle de premier ordre en nous fournissant une échelle de calibration indépendante pour l'époque en question. Dans cet article, les bases de calibration classiques pour le Protérozoïque terminal sont reconsidérées. La confrontation des courbes de $\delta^{13}\text{C}$ avec les enregistrements du $^{87}\text{Sr}/^{86}\text{Sr}$ nous permet 1) de corréler entre elles les glaciations néoprotérozoïques de différentes régions et, 2) de mieux suivre le rythme de l'expansion évolutive des premiers métazoaires. Au vu de l'absence de fossiles marqueurs, l'amélioration de tels schémas de calibration sera essentielle pour pouvoir définir et corréler les grandes subdivisions du Protérozoïque terminal.

1. Introduction

Over the past decade, our understanding of the events surrounding the appearance and subsequent diversity explosion of the earliest metazoans in the rock record has had to be constantly reassessed due to new fossil discoveries, significant improvements in dating and correlation, and the increasingly global nature of research efforts. In way of summary, some of these advances are described below:

1.1 New fossil finds

The Precambrian-Cambrian boundary global stratotype section was defined at the Kyoto IGC in 1992 at Fortune Head, Burin Peninsula in Canada, with the precise point being placed at the transition between a trace fossil assemblage characterised by *Harlaniella podolica* and the first occurrence of the branching trace fossil *Phycodes pedum* (Brasier et al. 1994b). This new emphasis on trace fossils, and not skeletal fossils, as stratigraphic markers is proving to be robust as 1) the sequence of appearance of trace fossil assemblages across the

Precambrian-Cambrian boundary appears to be consistent on a global scale (e.g. Crimes 1987, Narbonne et al. 1987, MacNaughton & Narbonne 1999, Jensen et al. 1999), and 2) the preservation of early sclerites is frequently dependent on diagenetic phosphatisation (Brasier 1990). One initial aim of the Precambrian-Cambrian boundary, which was to be placed as close as possible to the lowest known appearance of diverse shelly fossils (Cowie 1978, Cowie 1985), was to separate Precambrian, Ediacaran-type soft-bodied fauna from Cambrian small shelly fossils or SSF (Debrenne & Debrenne 1995). However, this aim has become ever more redundant as evidence for skeletal biomineralisation is found deeper in the Precambrian. For example, true sponges, which are perhaps the simplest of metazoans, are now known from Ediacarian age rocks in Australia (Gehling & Rigby 1996), Mongolia (Brasier et al. 1997), and China (Tang et al. 1978, Steiner et al. 1993, Xiao et al. 1998, but see Zhou et al. 1998) as well as from the lowermost Cambrian (e.g. Zhang & Pratt 1994). In addition, calcareous shells, other than *Cloudina*, have also been found in

upper Proterozoic rocks from Namibia (e.g. Grotzinger et al. 1995) and Mongolia (Brasier et al. 1997). Nevertheless, many skeletal fossil finds (e.g. Xue et al. 1992) as well as traces from the Precambrian remain controversial (Zhang et al. 1998, Jensen et al. 1999). On the other hand, unworked, soft-bodied fossil fronds, which are typical of the supposedly Proterozoic Ediacaran fauna, have now been found in Cambrian rocks of Australia (Jensen et al. 1998), well above the lowest appearance of diverse trace fossils, including the Cambrian marker fossil *Phycodes pedum*. These new discoveries allow the possibility that the expansion of Ediacaran soft-bodied fauna in the latest Proterozoic may simply represent one aspect of the so-called Cambrian explosion rather than being its direct precursor and that taphonomic and facies considerations, perhaps, may play a major role in determining the timing of faunal appearances around the Precambrian-Cambrian boundary (Lindsay et al. 1996b). As a result, the biological events which brought about the Cambrian radiation of shelled life-forms seem likely to have occurred in the Proterozoic (Fedonkin & Waggoner 1997), while the absence of palaeontological evidence for these primitive metazoans may be due to their small size (Fortey et al. 1996). In this regard, the recent discovery of fossil metazoan embryos from Cambrian as well as Proterozoic phosphorites (Bengston & Zhao 1997, Xiao et al. 1998; but see Xue et al. 1999) may open the door to an entirely new avenue of research on the origin of the Cambrian biotic explosion.

1.2 Improvements in dating

During the 1990's, a new geochronological scale has begun to be constructed based on the more reliable dating of individual minerals from volcanic tuffs (Bowring & Erwin 1998). Although such U/Pb zircon data can give consistent and accurate age information, the problems of international stratigraphic correlation of sections in which these tuffs are found can still give headaches. The Precambrian-Cambrian boundary GSSP at Newfoundland is lacking in stratigraphically useful body fossils (except for *Sabellidites* spp.), volcanic tuffs, or carbonates suitable for chemostratigraphy, which may aid in correlation, forcing many researchers to resort to the Siberian sections for correlation farther afield. It is generally argued that the boundary GSSP can be correlated into the Nemakit-Daldynian (= Manykaian) stage of the Olenek region, N Siberia, where volcanic breccias not far below the first appearance datum (FAD) of *Phycodes pedum* have yielded a U/Pb age of 543.6 (± 0.24) Ma (Bowring et al. 1993; Fig. 2). A similar age of 543.3 (± 1) Ma has been obtained from an ash layer at the top of the Schwarzsand Subgroup of Namibia, which contains a rich Ediacara fauna (Grotzinger et al. 1995; Fig. 2) but no Cambrian-type traces. Both ages, therefore, provide maximum ages for the Neoproterozoic-Cambrian boundary in their respective sections. Two stratigraphically lower tuffs from Namibia have yielded ages of 548.8 (± 1) and 545.1 (± 1) Ma, whereas the FAD of *Phycodes pedum* occurs above an unconformity in

sediments dated at 539.4 (± 1) Ma (Grotzinger et al. 1995). Thus, by using these proxy boundary sections, the base of the lowest stage of the Cambrian, and the upper boundary of the Terminal Proterozoic, can be regarded as well constrained in time to ca. 543 Ma, whereas the period of maximum diversity of Ediacaran-type fauna appears to have existed between 550 and 543 Ma. In consequence, the temporal distance between diverse Cambrian and diverse Ediacaran faunal assemblages has effectively been removed by these studies. Furthermore, it would appear that the assumed temporal relationship between the Ediacaran expansion and the last of the late Neoproterozoic glaciations, the Marinoan, ca. 600 Ma, has become less compelling. However, the Neoproterozoic glaciations are still clouded with uncertainties and misconceptions and will be discussed in more detail below.

1.3 Isotope studies

In recent years, stratigraphical studies of Neoproterozoic-Cambrian successions have turned their full attention to isotopes (Knoll et al. 1986, Kaufman et al. 1993, Kaufman & Knoll 1995), perhaps because of early difficulties in applying conventional biostratigraphy on a global scale to this time interval (Brasier et al. 1994a). As a result, faunal developments and stage boundaries in the Early Cambrian can now be calibrated against a wholly independent scale based on variations of $\delta^{13}\text{C}$ (Brasier et al. 1994a, Pelechaty 1998). The cross-referencing of this C isotope record with least altered Sr isotope ratios for Mongolia and Siberia has helped to reveal 1) the existence of significant hiatuses in E Siberia (Brasier et al. 1996); and 2) that small shelly fossils (SSFs), characteristic of the basal Tommotian, actually make their first appearances in pre-Tommotian rocks of Siberia and Mongolia (Knoll et al. 1995a, Shields & Brasier 1998). The resultant gradualisation of the Cambrian "explosion" can be seen by comparing generic diversities of classic Neoproterozoic-Cambrian sections (Fig. 1), illustrating further how the origin of the Cambrian radiations may be traced into the Precambrian. A great deal of isotope work has also been carried out for the Neoproterozoic, and preliminary coarse correlations based on both Sr and C isotopes have proved possible (Kaufman & Knoll 1995, Shields et al. 1997, Misi & Veizer 1998). In addition, work is underway to constrain more accurately variations in the sulphur isotope ratio of seawater through this time interval (Strauss 1993) for which trace sulphate in marine authigenic minerals such as francolite has already revealed potential as a stratigraphic tool (Shields et al. 1999). It is considered that future global stratotype sections and stages in the Neoproterozoic will require comprehensive isotopic definition in addition to any palaeontological significance they may have. This article explores in more detail the potential of isotope stratigraphy for this time interval using the most recent data available, while incorporating some new data from Mongolia, in an attempt at creating a more robust calibration scheme for Terminal Proterozoic-Early Cambrian time.

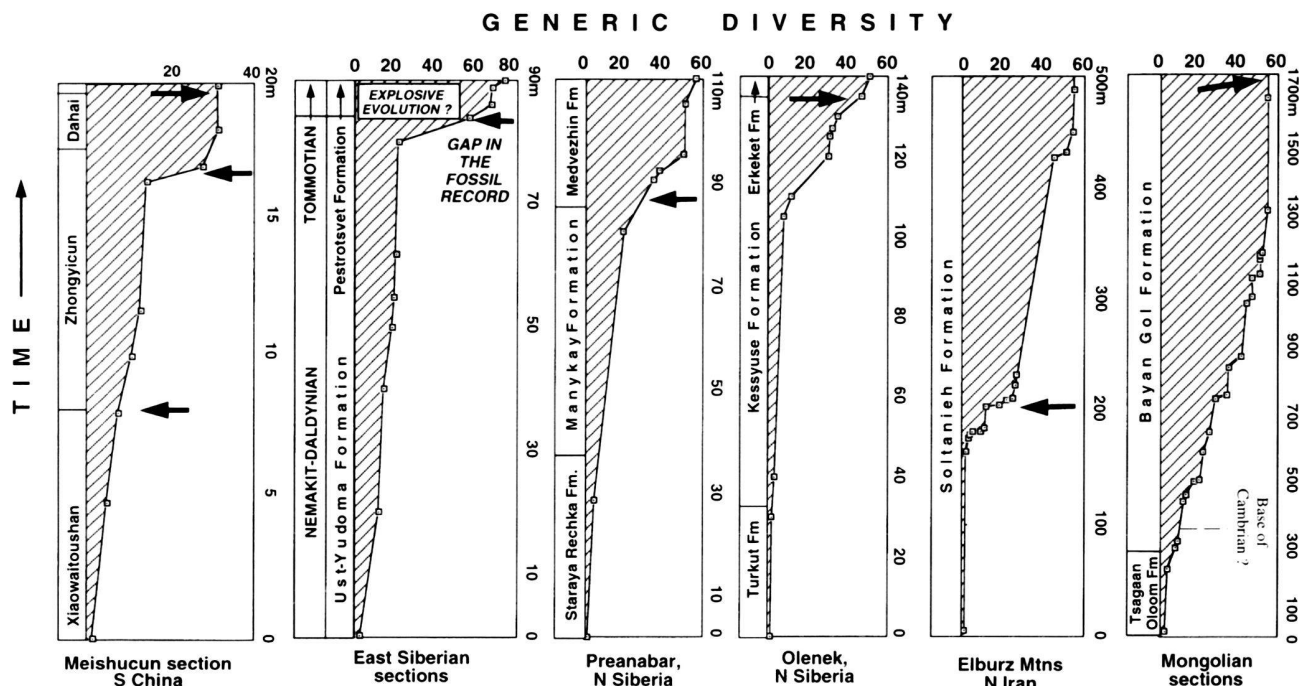


Fig. 1. Cumulative generic data (modified after Brasier et al. 1996) from the best known Neoproterozoic-Cambrian sections show that the Cambrian "explosion" of Tommotian SSF is likely to be an artefact of non-deposition in Siberia, and China (previous candidates for the Precambrian-Cambrian GSSP) and Iran. Due to the fortunate tectonic situation, the much thicker Mongolian palaeontological and isotopic records (Fig. 2) are more representative and show a more gradual pre-Tommotian faunal radiation, originating in the Proterozoic. Bold arrows indicate suspected gaps in those sedimentary sections.

2. Isotope stratigraphy

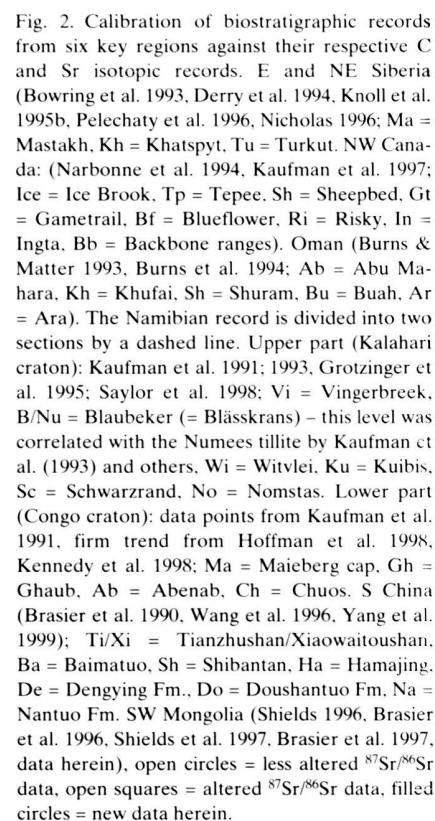
2.1 C Isotope stratigraphy

C isotope stratigraphy relies on the fact that the C isotopic ratios of seawater carbonate species fluctuate through time, something which occurs largely in response to changes in the net rate of organic matter burial. However, $\delta^{13}\text{C}$ shifts may also result from changes in biological productivity (Broecker 1982), vertical circulation (Brass et al. 1982), isotopic composition of carbon sources (Derry & France-Lanord 1996, Dickens et al. 1997), and carbonate alkalinity (Spero et al. 1997). These fluctuations may be recorded in authigenic carbonate rocks, which have undergone negligible post-depositional alteration. In order to constrain the possible effects of the incorporation of isotopically lighter carbon from organic matter during diagenesis, $\delta^{13}\text{C}$ values are frequently shown plotted against more easily altered geochemical parameters, such as $\delta^{18}\text{O}$ and Mn/Sr ratios (e.g. Marshall 1992). Several such studies suggest that trends in seawater $\delta^{13}\text{C}$ can be preserved intact in marine carbonate rocks (e.g. Kaufman et al. 1993), despite there being no necessity for any connection between the diagenetic alteration of Mn/Sr ratios, $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ values. Although the robustness of the C isotope system to diagenetic change can

make $\delta^{13}\text{C}$ trends of particular usefulness (Holser 1997), it is appropriate to retain a degree of healthy skepticism, especially in cases where absolute $\delta^{13}\text{C}$ values are the sole means of correlation (see discussion in Jensen et al. 1996). For a more reliable check on diagenetic alteration of carbonate C-isotope values, or for $\delta^{13}\text{C}$ studies in carbonate-poor sections, $\delta^{13}\text{C}_{\text{org}}$, isotopic analysis of bulk kerogen (Strauss et al. 1997) or individual organic marker molecules (Logan et al. 1997) may be undertaken. Parallel trends in both $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ are likely to indicate faithful preservation of seawater trends in $\delta^{13}\text{C}$ (Knoll et al. 1986) and are fast becoming a prerequisite for robust chemostratigraphic interpretation. Only few of the $\delta^{13}\text{C}$ records shown in Figure 2 are supported by equivalent $\delta^{13}\text{C}_{\text{org}}$ work, however, all major features of the final calibration scheme are so supported (Knoll et al. 1986, Shields et al. 1997, Kimura et al. 1997, Calver & Lindsay 1998).

2.2 Sr isotope stratigraphy

Despite the possibility of diagenetic alteration of seawater $\delta^{13}\text{C}$, the major problem with C isotope stratigraphy remains the lack of uniqueness of isotope events (e.g. Fig. 2), that is, the danger of correlating together superficially similar, but



wholly unrelated $\delta^{13}\text{C}$ excursions. Therefore, it is necessary to calibrate the C isotope record of any single section against an independent stratigraphic record, which in the persistent absence of distinct fossil markers in the pre-550 Ma Neoproterozoic, has come to mean the Sr isotope record. Sr isotope stratigraphy relies on the principle that the Sr isotopic ratio of seawater is invariant at any one time within analytical error. This is certainly the case today and the assumption that it was generally so in the past appears to be justified by thousands of measurements of well preserved, authigenic carbonate minerals that formed in past oceans, (e.g. McArthur 1994, Veizer et al. 1997). Temporal fluctuations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ can thus be recorded as for $\delta^{13}\text{C}$ and used for stratigraphy, provided that 1), seawater $^{87}\text{Sr}/^{86}\text{Sr}$ changed rapidly enough for trends to be resolvable, and 2), samples have retained their initial Sr isotopic compositions. The Terminal Proterozoic-Cambrian is one of the few parts of the geological record where the rate of change of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is high enough to be capable of providing stratigraphic resolution exceeding that from biostratigraphy or other methods (Kaufman et al. 1993). The second condition is more difficult to fulfill and requires the conscientious application of a barrage of geochemical tests in order to establish which samples retain more faithfully seawater $^{87}\text{Sr}/^{86}\text{Sr}$ (Veizer 1983, Stille & Shields 1997). The lack of shelly fauna in the Precambrian rock record means that only bulk samples can be measured, although effort must be made to select pure primary authigenic carbonate phases, such as early calcite cements, which requires a comprehensive petrographic study (e.g. Kaufman et al. 1993). Attempts at producing diagenetic trends using alteration proxies such as stable isotope values ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$), Mn/Sr ratios (Veizer 1983, Kaufman et al. 1993, Banner 1995), and Sr concentrations (Veizer 1978, Brasier et al. 1996) have proved invaluable. From such studies, it can be broadly concluded that the lowest ratios from any one particular stratigraphic level are most likely to represent coeval seawater. This is due to the fact that Rb and radiogenic Sr rich detritus (e.g. clay minerals) are most likely to effect the carbonate Sr isotope ratio during diagenesis. However, this 'rule of thumb' ought to be demonstrated for each study as exceptions to this rule are known, (e.g. Gao & Land 1991, Nicholas 1996) where Sr isotopic exchange has taken place during diagenesis with juvenile, volcanic material or other carbonate rocks and fluids possessing a lower isotopic ratio.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios from those samples considered most likely to have retained the Sr isotopic signature of the seawater in which they precipitated are called "least altered" $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Figure 2. In the case of the Mongolian, Chinese, Namibian and Siberian studies (Brasier et al. 1996, Yang et al. 1999, Kaufman et al. 1993, Kennedy et al. 1998, Nicholas 1996, Kaufman et al. 1996), this designation is based on numerous measurements and agreement between various diagenetic parameters. In the Omani case (Burns et al. 1994), only dolostones could be measured rendering many diagenetic proxies of limited use and implying substantial Sr loss. As with the Canadian study (Narbonne et al. 1994), where only few data are avail-

Tab. 1. Geochemistry of limestone leachates from samples of the Tsagaan Oloom Formation, western Mongolia. Techniques are as in Brasier et al. (1996) and in present text. NBS standard SRM 987 yielded 0.710256 (10), 0.710251 (10) and 0.710250 (7) during the period of measurement allowing values herein to be compared directly with those in the literature. b.d.l. = below detection limit with ICP-MS. Sr concentrations relate to the calcite fraction only.

Sample	height	$^{87}\text{Sr}/^{86}\text{Sr}$	2 s.e.	Rb/Sr	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}_{\text{carb}}$	Sr ppm
96TS06	7.5 m	0.706836	10	0.000002	-0.90	-10.07	-
96TS06 (HNO ₃)	7.5 m	0.706895	10	0.000340	-0.90	-10.07	1750
96TS06 (vein)	7.5 m	0.709138	11	b. d. l.	-	-	1405
96TS31	67 m	0.707094	10	0.000017	7.05	-10.83	4300
96TS31 (HNO ₃)	67 m	0.707084	11	0.000025	7.05	-10.83	4300
96TS42	137 m	0.707130	13	b. d. l.	8.35	-4.98	3020
96TS55	310 m	0.707343	10	b. d. l.	9.47	-4.79	1413
96TS66	420 m	0.707289	10	0.000036	7.38	-6.08	1118

able (although from apparently well preserved samples), it is assumed that the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values are "least altered" in the Omani data set. These "least altered" values represent, therefore, maximum estimates for coeval seawater and are shown above the respective $\delta^{13}\text{C}$ trends for any particular stratigraphic level. The Mongolian Sr isotopic record is the most continuous and is the only one shown in full (Fig. 2). In the case of Mongolia, the data set has been divided into "less altered" and "altered" ratios, whereby less altered values are from pure limestones having Sr contents >550 ppm and favourable trace element ratios (e.g. low Mn/Sr ratios), all of which suggest that these samples have retained the Sr isotopic ratio of seawater. Altered ratios in Figure 2 represent those samples which either fail to fulfill these conditions (see discussion in Brasier et al. 1996) or have not undergone such rigorous geochemical study.

2.3 Methods and Results

In order to complete the Mongolian data set, it has proved necessary to analyse several limestone samples in addition to those detailed in Brasier et al. (1996). Samples and analytical methods were selected specifically to show to which extent sampling biases and leaching techniques can have led to deviation from seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the western Mongolian samples. Data from these extra samples are shown in Figure 2 and Table 1: samples 96Ts06, 96Ts31, 96Ts42, 96Ts55, 96Ts66. All of these samples contain >95% CaCO_3 . Nevertheless, in order to minimise any possible contamination from non-carbonate species, all samples were dissolved, after washing in distilled water (slightly acidified by HCl) in a mild acid leach consisting of α -hydroxyisobutyric acid and ammonia at a pH of 4.5. This approach was preferred over using a strong acid (HCl or HNO_3) or a dilute, weak acid such as 5% acetic acid to avoid excessive leaching of radiogenic strontium from exchangeable sites in detrital material. Samples 96Ts06 and 96Ts31 were also prepared for analysis using HNO_3 which yielded a significant difference of 0.00006 in the resultant $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for 96Ts06, emphasising the need for such a mild

attack. Mild acid leaching (see McArthur 1994 for other suitable leaching possibilities) also reduces the need for Rb corrections caused by the decay of radioactive ^{87}Rb to ^{87}Sr by limiting the amount of Rb leaching from non-carbonate phases. Another possible source of more radiogenic strontium is post-lithification calcite veining, which is ubiquitous in the Tsagaan Gol Section as is commonly the case. Sample 96Ts06 (vein) yielded a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.709138) higher than any other sample from the entire Tsagaan Gol section, and 0.0023 higher than micrite of the same hand specimen (96Ts06), emphasising the need for careful and precise sample selection in a Sr isotope study (Stille & Shields 1997). Based on these results, it can be concluded that the Sr isotope variations recorded by Brasier et al. (1996), Shields (1996) and Shields et al. (1997) from western Mongolia represent seawater to an accuracy of approximately 0.0001.

3. Four important Terminal Proterozoic isotope records

3.1 The Mongolian isotopic record (Tsagaan Gol section)

At the base of the Tsagaan Gol Section (Gobi-Altai Province, western Mongolia) are found glaciogenic diamictites of possibly Sturtian age (Lindsay et al. 1996a), which lie unconformably on top of magmatic flows dated variously between 770 and 725 Ma (from studies cited in Brasier et al. 1996). The C isotope record (Fig. 2) shows a marked climb from -2‰ to 11‰ (anomaly S) below the second of two karstic surfaces (lower – middle Tsagaan Oloom) marking breaks in deposition (Shields 1996). Least altered $^{87}\text{Sr}/^{86}\text{Sr}$ ratios rise from 0.7067 to 0.7073 through the lowermost, post-glacial sequence and remain around 0.7072 (± 0.0001) through the plateau of high $\delta^{13}\text{C}$. This stasis in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ has been confirmed further by the additional measurement of three carefully selected samples, 96Ts42, 96Ts55, 96Ts66, which yielded 0.70713, 0.70734 and 0.70729, respectively (Fig. 2, Tab. 1). Above this karstic zone, $\delta^{13}\text{C}$ shows several peaks of 9‰ , 7‰ and 7‰ (anomaly U) and a continuation of the rise in least altered $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from 0.7072 to 0.7078. Above a third level of karstic collapse (middle – upper Tsagaan Oloom in Fig. 2), $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are abruptly higher, around 0.7084 (± 0.0001), and remain high throughout the remainder of the section, implying either that this karstic horizon represents a significant hiatus in deposition or that the sedimentological record becomes condensed at this point. Anomaly W corresponds to a low-point in the $\delta^{13}\text{C}$ curve just above the FAD of shelly fossils (sponge spicules and *Cambrotubulus* SSF) in this region (Brasier et al. 1997), above which $\delta^{13}\text{C}$ rises unsteadily towards another peak at about 5‰ (anomaly F). The gradual faunal expansion seen in Mongolia (Fig. 1) and the much larger thickness of sedimentary rock there indicate that the Precambrian-Cambrian transition is better represented in Mongolia than elsewhere (Fig. 1). However, it appears likely for similar reasons (absence of Ediacaran fauna, condensed sedimentation, and abruptness of isotopic changes) that the Terminal Proterozoic

is quite poorly represented in western Mongolia. Therefore, a continuation of the isotopic record deeper into the Proterozoic must be sought in other carbonate-rich sections, of which there are only few for this time interval: e.g. S. China, Oman or Namibia.

3.2 The Canadian isotopic record (MacKenzie Mountains)

One of the thickest and most fossiliferous of the Terminal Proterozoic sections is the upper Windermere Group of the MacKenzie Mountains, northwestern Canada. The general sequence architecture and the two distinct phases of glaciation recorded in the MacKenzie Mountains (Rapitan and Ice Brook) are commonly compared and correlated with the Australian stratigraphic record and glacial units there, i.e. Sturtian and Marinoan (Young 1995). Above the Rapitan glacials and just below the Ice Brook level are found simple discs of controversial origin overlain by a carbonate unit yielding anomalously high $\delta^{13}\text{C}$ values (up to $+11\text{‰}$) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios < 0.7072 (Narbonne et al. 1994). The Tepee unit, which directly overlies the Ice Brook glacial diamictites yields, by contrast, negative $\delta^{13}\text{C}$ values typical of cap-carbonates (Kennedy et al. 1998) accompanied by an unchanged $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7072. The overlying Sheepbed Formation, which contains nine genera of discoidal megafossils (e.g. *Ediacara*, *Medusinites* and *Hiemalora*) is not carbonate-rich but has nonetheless shown at least two significant $\delta^{13}\text{C}$ peaks within it (Kaufman et al. 1997). The uppermost $\delta^{13}\text{C}$ peak is immediately overlain by a $\delta^{13}\text{C}$ plateau of around $+2\text{‰}$ in units which have yielded a diverse assemblage of Ediacaran-type fauna accompanied by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.7084 and 0.7086 (Narbonne et al. 1994). The Canadian section has the advantage of being a continuous stratigraphic and tectonic unit as well as being richly fossiliferous. Isotopic correlation would tend to link the Mongolian glacial units with the Rapitan glacials, whereas anomalously high $\delta^{13}\text{C}$ values and unchanging $^{87}\text{Sr}/^{86}\text{Sr}$ ratios across the Ice Brook glacial would suggest an affinity between this phase of glaciation and the lower – middle Tsagaan Oloom Members in Mongolia. The continuous increase in Ediacaran fossil diversity found in NW Canada allows biozonations to be made (Kaufman et al. 1997) which can be correlated using isotopic stratigraphy (Ediac I, II, III in Fig. 3).

3.3 The South Chinese isotopic record (the Yangtse Gorges area, Hubei Province)

Recent isotopic studies (Wang et al. 1996; Yang et al. 1999) have greatly improved the data base for the classic Sinian sections of the Yangtse Gorges area, near Yichang, Hubei Province, S China. At their base, the Nantuo tillite is overlain by carbonate rocks of the Doushantuo and Dengying Formations. The presence of sponge spicules and even metazoan embryos (Xiao et al. 1998) near the top of the Doushantuo Formation implies that this formation is of Terminal Proterozoic (= Ediacarian) age. Post-glacial $\delta^{13}\text{C}$ data from the Doushantuo

Formation show two distinct peaks of up to 7‰ (Lambert et al. 1987; Wang et al. 1996) accompanied by least altered $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Yang et al. 1999) which are similar to those of anomaly “U” in Mongolia (TP1). The overlying Dengying Formation contains Ediacaran-type fronds and *Simotubulites* (*Cloudina*-type tubes) fossils, suggesting an affinity with palaeontologically similar strata in Namibia, Australia and Canada. One $\delta^{13}\text{C}$ peak of 7‰ is followed by a plateau of lower positive values averaging 2–3‰, while least altered $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are no lower than 0.7084. The southern Chinese, Terminal Proterozoic sections are the only ones which are carbonate-rich and show no signs of significant condensation from a late Neoproterozoic glacial unit to the Precambrian-Cambrian boundary. It is considered, therefore, that the C-isotopic record in this region represents the most complete set of features of any section for the Terminal Proterozoic (Fig. 2).

3.4 The Namibian isotopic record

Namibia contains some of the most comprehensively studied Neoproterozoic successions, which have caused a great deal of interest over recent years due to new fossil discoveries (Grotzinger et al. 1995, Narbonne et al. 1997), improvements in dating (Grotzinger et al. 1995) and isotope stratigraphy (Kaufman et al. 1991, Kaufman et al. 1993, Hoffmann et al. 1998). The Congo craton, especially, contains an intriguing pair of glaciogenic units: the lower Chuos and the upper Ghaub formations (Fig. 2). High $\delta^{13}\text{C}$ values of up to 10‰ characterise the interglacial Abenab Subgroup (Kaufman et al. 1991, Hoffman et al. 1998, Kennedy et al. 1998), whereas anomalously negative $\delta^{13}\text{C}$ values have been recorded from carbonate strata of the Maieberg Formation, which immediately overlie the Ghaub formation (Hoffman et al. 1998) as well as from above the Chuos Formation (Kaufman et al. 1991). Kennedy et al. (1998) report that $\delta^{13}\text{C}$ values increase through the Maieberg Formation reaching 6‰ accompanied by least altered $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7077 or higher, which is consistent with the previously discussed post-glacial carbonate section of South China. Unfortunately, the Namibian Neoproterozoic sedimentary record is complicated and fragmentary, which necessitates the use of composite sections (Saylor et al. 1998) and leads to controversial correlations between tectonic units. However, recent $\delta^{13}\text{C}$ data (up to 8.5‰) from the Gariep Belt of both South Africa and Namibia tend to suggest that the double diamictites there, the lower Kaigas and the upper Numees, are equivalents of the Chuos and the Ghaub, respectively, of the Congo Craton (Fölling et al. 1998). Chronological constraints (Frimmel et al. 1996) suggest that the lower of these glacial units is of Sturtian age. However, it is not clear whether the upper units of the Congo Craton and Gariep Belt (Ghaub and Numees) are age equivalent to the Blaubeker (= Blässkrans) mixtites of the Witvlei Group, Kalahari craton (Fig. 2), above which are also found negative $\delta^{13}\text{C}$ values, averaging –3‰ (Saylor et al. 1998).

Stratigraphically above the Neoproterozoic diamictites, the

Kalahari craton has yielded an excellent record of Ediacaran-type soft-bodied fauna (e.g. Grotzinger et al. 1995, Narbonne et al. 1997). Unlike in the MacKenzie Mountains, there is only one $\delta^{13}\text{C}$ peak (<7‰) in the Ediacara fauna-rich Nama and Witvlei Groups of Namibia (Kaufman et al. 1993). The rise in $\delta^{13}\text{C}$ towards this single peak is accompanied by least altered $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of between 0.7081 and 0.7084; a part of the terminal Neoproterozoic rise in $^{87}\text{Sr}/^{86}\text{Sr}$ which is wholly absent in Mongolia. It would appear, therefore, that the absence of Ediacaran fauna in W Mongolia might be partly explained by a hiatus in the Tsagaan Gol Section corresponding to the third zone of karstic collapse (middle – upper Tsagaan Oloom). The carbon isotope peak, which is missing in Mongolia, is shown as $\delta^{13}\text{C}$ event “V” in Figure 2. The associated period of greatest diversity of Ediacaran faunal types in Namibia, which has been dated at between 549 and 543 Ma (Grotzinger et al. 1995), is given the preliminary stage name: TP2 or Terminal Proterozoic II. These four regions provide the backbone of our Terminal Proterozoic isotopic record.

4. Globality of isotopic features

There is considerable discussion in the literature (*and far more in private circles*) of the validity of correlations based on isotopic “wiggles”, which are far from unique, may only be of local significance, and can also derive from post-depositional alteration. Although these deficiencies are borne out in some cases, it can also be argued that isotopic events which turn out to be of limited potential for correlation will tend to fall away from use just as marker fossils may turn out to be endemic, reworked or long-ranging. Furthermore, the possibility for double-checking $\delta^{13}\text{C}_{\text{carb}}$ isotope features with the $\delta^{13}\text{C}_{\text{org}}$ record or with the independent Sr isotope record can lead to extremely precise age correlation (e.g. Brasier et al. 1996, 1997). In order to assess the correlation potential and globality of the isotopic features from the above four regions, an attempt must be made to collate and compare all the data which are available for this time interval, i.e. incorporating the isotopic records of Oman, Siberia, Canada (Fig. 2) and elsewhere.

One $\delta^{13}\text{C}$ feature which is particularly widespread, if not ubiquitous, close to the Neoproterozoic-Cambrian boundary, is an extremely negative $\delta^{13}\text{C}$ excursion (Aharon et al. 1987, Kaufman & Knoll 1995, Kimura et al. 1997). The first occurrence of shelly fauna is found just below a negative $\delta^{13}\text{C}$ anomaly in Mongolia and E Siberia (Fig. 2) and is located within such an anomaly in S China (Hsü et al. 1985, Brasier et al. 1990), NW Siberia (Pokrovsky & Missarzhevsky 1993, Knoll et al. 1995a, Kaufman et al. 1996), NW Canada (Narbonne & Aitken 1995), India (Aharon et al. 1987), and Iran (Brasier et al. 1990, Kimura et al. 1997), with values commonly as low as –5‰. This isotopic excursion also coincides with the first appearances of diverse, penetrative trace fossils of Cambrian-type including *Phycodes* in Siberia and Mongolia. However, and probably for facies reasons, these traces appear further up

the section than the first occurrences of shelly fossils in such carbonate-rich sections (Lindsay et al. 1996b), contrary to the experience of workers from more siliciclastic sections (e.g. Landing 1994). Sr isotope ratios from Mongolia, Siberia and Canada reveal limited variation across the Neoproterozoic – Cambrian (Nemakit/Daldynian) transition strata, with least altered ratios around 0.7084 (± 0.0001), while Tommotian and Attdanian strata reveal markedly lower values in Mongolia (Brasier et al. 1996) and E Siberia (Nicholas 1996) of 0.7081 (± 0.0001). It is not the purpose of this paper to discuss isotopic features from the overlying parts of the early Cambrian; Brasier et al. (1994a; 1996) and Bartley et al. (1998) provide overviews.

Below the first appearance datum of small shelly fossils and diverse trace fossils, Ediacaran fauna-rich, latest Proterozoic successions from Namibia, China, Canada and Siberia reveal consistent isotopic features as discussed earlier for Namibia and China. Dating studies in Grotzinger et al. (1995) help us to calibrate backwards from the first appearance datum of *Phycodes* in Namibia at 539 Ma, to a $\delta^{13}\text{C}$ plateau $\sim 2\text{‰}$ at ca. 543 Ma, to a $\delta^{13}\text{C}$ peak of up to 7‰ , no earlier than 550 Ma (Fig. 2). Again, least-altered Sr isotope ratios reveal little variation, with evidence in Namibia of a slight increase in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ from about 0.7081 to 0.7084 during the rise to $\delta^{13}\text{C}$ event 'V'. Such isotopic signatures are unknown from Mongolia, but could easily be present in Oman (Fig. 2) where the presence of *Cloudina* tubes, a rise to $\delta^{13}\text{C}$ around 5‰ (Well MQ, Burns & Matter 1993) and least altered $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7085 (Burns et al. 1994) imply temporal affinity with the *Cloudina*-type fossil-bearing sediments of the Dengying Formation of S China and the Nama Group of Namibia.

Beneath the terminal Proterozoic $\delta^{13}\text{C}$ peaks of China, Oman and Canada are found additional positive $\delta^{13}\text{C}$ excursions accompanied by Ediacaran-type medusoids in Canada, only (Narbonne & Aitken 1995). The incomplete carbonate-rich stratigraphic records in Oman and Canada do not allow us to appreciate the full extent of $\delta^{13}\text{C}$ variation. However, the Chinese data are more complete and reveal two distinct peaks of up to 8‰ : feature "U" (Wang et al. 1996). Least altered $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for these peaks are similar (0.7077) to those for anomaly 'U' in Oman (<0.7079), Australia (0.7079; Calver & Lindsay 1998), and Namibia (0.7077) which are also similar to values from western Mongolia, where least altered $^{87}\text{Sr}/^{86}\text{Sr}$ ratios range from 0.7072 to 0.7078 (Fig. 2). Due to the similarity of their C and Sr isotopic records, the Doushantuo Formation of S China is considered to be correlative with the Middle Tsagaan Oloom Formation of W Mongolia (Pelechaty 1998), and thus to the $\delta^{13}\text{C}$ peaks of comparable magnitude in Canada, Namibia and Oman (Fig. 2). It is interesting to note that a single glaciogenic unit is found below anomaly "U" in Canada (Ice Brook), Oman (Abu Mahara) and S China (Nantuo), whereas in Mongolia there is a karstic disconformity at this level between the lower and middle Tsagaan Oloom. The existence of several $\delta^{13}\text{C}$ peaks and troughs in the Terminal Proterozoic is further confirmed by post-Marinoan Sr and C data

from Australia which are not shown in Figure 2 (Calver & Lindsay 1998).

Where measured, i.e. only in Mongolia and Canada, basal Terminal Neoproterozoic carbonate rocks and synglacial carbonates from the Ghaub Formation, Namibia (Kennedy et al. 1998) yield least altered $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of around 0.7072 (± 0.0001). Below this level in both these areas, $\delta^{13}\text{C}$ is consistently high (up to 11‰), whereas $^{87}\text{Sr}/^{86}\text{Sr}$ ranges between 0.7067 and 0.7073 in western Mongolia. Correlation of the isotopic records of Canada and Mongolia suggests not only that the Ice-Brook glacial phase may be correlative with a karstic hiatus in Mongolia but also that the two pulses of glaciation represented by the Mount Berg and Shezal tillites of NW Canada are likely to correspond to those of the Tsagaan Gol Formation of western Mongolia (Maikhan Uul member in Brasier et al. 1996 and Lindsay et al. 1996a). Unusually high $\delta^{13}\text{C}_{\text{carb}}$ ($>9\text{‰}$) have also been found above glaciogenic diamictites of possibly Rapitan / Sturtian age in Namibia (Kaufman et al. 1991, Halverson et al. 1998), Svalbard (Knoll et al. 1986), Greenland (Fairchild & Spiro 1987), E. Nevada & W. Utah (Wickham & Peters, 1993) and Brazil (e.g. Misi & Veizer 1998), leading to the possibility that all these glacial units are coeval.

5. A preliminary calibration scheme

Figure 3 represents a preliminary attempt at an isotopically based calibration scheme for Terminal Proterozoic – Cambrian time and early metazoan expansion. As such, it serves as a basis for discussion and is likely to be modified in the future. Nevertheless, it represents a significant advance over previous schemes which have only taken into account the carbon isotopic record (e.g. Kaufman & Knoll 1995, Pelechaty 1998) or lithostratigraphy (Brookfield 1995). The result of cross-referencing the $\delta^{13}\text{C}$ curve with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios results in a more complicated history of seawater $\delta^{13}\text{C}$ between 600 and 530 Ma (Fig. 3) than previously thought (Smith et al. 1994, Kaufman & Knoll 1995, Narbonne & Aitken 1995, Knoll 1996, Kaufman et al. 1997, Pelechaty 1998). One major difficulty derives from the often arbitrary correlation with the Varanger rock units of Norway, which ought to be resisted until the Varanger section can be brought more firmly into the global stratigraphic fold. Age constraints on supposedly Varanger-age rocks from eastern N America and Scotland are considered to constrain the age of the Varanger glaciation to between 605 Ma (references in Grotzinger et al. 1995, Brasier & McIlroy 1997) and 590 Ma (Halliday et al. 1989). However, it is not clear whether all these glacial units are age-equivalent to each other let alone to the Varanger glacials of Norway and so they cannot be used for constraining the age of the "Varanger" glaciation. Although, the ca. 600 Ma glaciation (pre-Ediacarian) is seen as a good palaeontological reference point by virtually all authors, it is perhaps wiser to call this phase the Marinoan (Australia) or the Ice Brook (NW Canada) glacial phase for the moment (Fig. 3).

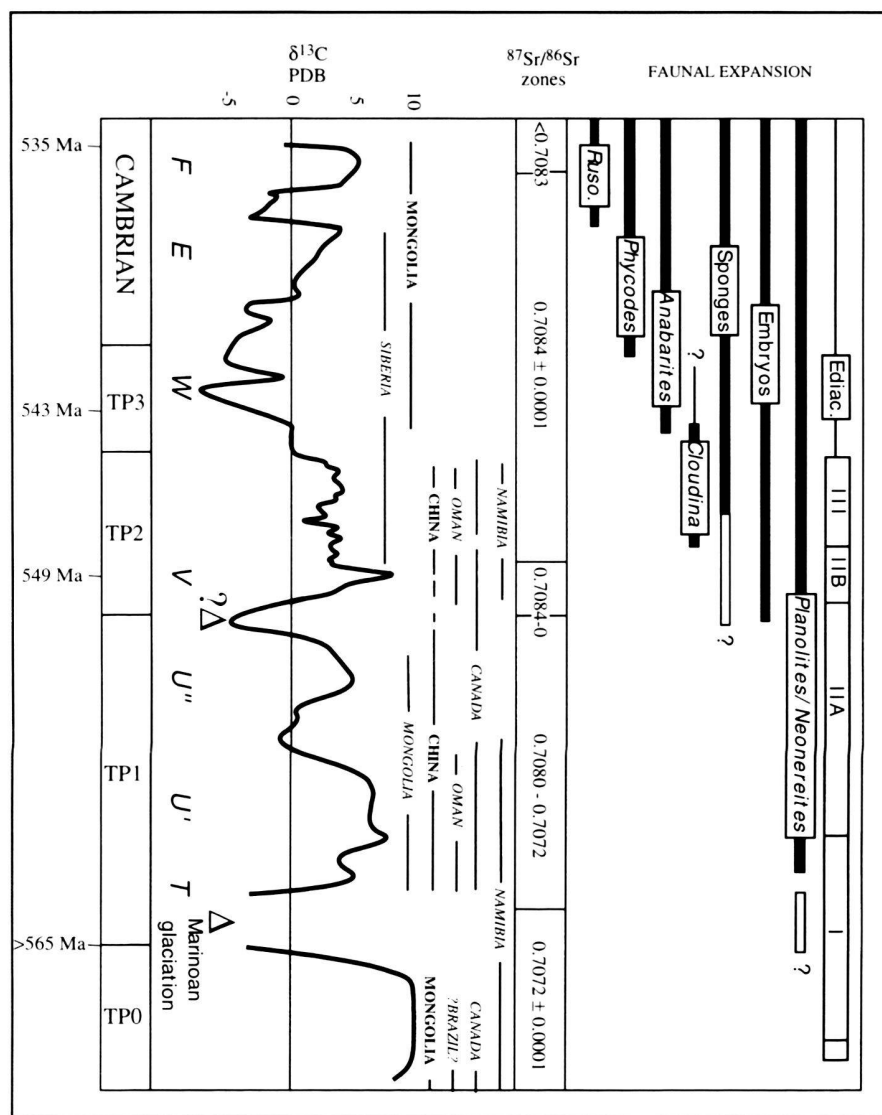


Fig. 3. Revised calibration of biostratigraphy and isotope stratigraphy through the terminal Neoproterozoic – Cambrian. Filled bars represent the stratigraphic ranges of fossils: Ruso. = *Rusophycus* or *Cruziana* arthropod traces, *Planolites* / *Neonereites* data are from Brasier & McIlroy (1997), Ediac. = Ediacara-type soft body fossils. Unfilled bars reveal possible extensions to these ranges. Ediacara-type faunal assemblages can be divided into zones: I, small simple discs; IIA, larger, radially symmetrical discs; IIB, complex discs and fronds; III, complex discs, fronds, dickinsoniids, abundant trace fossils, *Cloudina*, (Kaufman et al. 1997). The range of certain Ediacara-type fauna can be extended into the Cambrian (Crimes et al. 1995; Jensen et al. 1998). The C isotope curve has been constructed from the individual records of regions shown above the curve in capital letters (the actual curve is drawn from regions written in bold). Seawater Sr isotope evolution is shown in the form of zones as advised by McArthur 1994. Age constraints 535, 543 and 549 Ma are as in Bowring et al. 1993, Grotzinger et al. 1995.

This new calibration scheme identifies three (two of which are clearly distinct) glacial phases in the Neoproterozoic, from the two phases of the Sturtian, Australia (Lindsay 1989), Rapitan, NW Canada (Eisbacher 1985), Tsagaan Gol, W Mongolia (Lindsay et al. 1996a), Bebedouro (Brazil), Kaigas = Chuos (Namibia), Scott Mountain (Idaho, USA), and possibly also the Polarishreen Group, Greenland (Fairchild & Hambrey 1984), to the later, single phase of glaciation represented by the Nantuo (China), Marinoan (Australia), Ice Brook (NW Canada), Abu Mahara (Oman), Ghaub (? = Numees, ?=Blaubeker) (Namibia). Possibly younger Neoproterozoic or even Cambrian glaciogenic units, such as the tillites of W Africa (Bertrand-Sarfati et al. 1995), are still without firm age support and could possibly be correlative with Marinoan age tillites, for which age estimates are becoming progressively

younger (e.g. 565 Ma of Saylor et al. 1998). This interpretation of the Neoproterozoic stratigraphic record separates glaciations of this time period into two distinct episodes, something which has been lent support from the apparently globally characteristic petrographic and facies signatures of these two phases and their cap carbonate units (e.g. Young 1976, Kennedy et al. 1998). In particular, the earlier of the Neoproterozoic glaciations appears to be associated with haematitic iron-formations in Canada and Australia (Yeo 1984), Namibia (Chuos formation) and elsewhere, while cap rocks are laminated limestones. The younger Neoproterozoic glacial units are generally overlain by a thin brecciated dolomitic cap, which shows pseudo-tepee deformation (Kennedy et al. 1998). One major consequence of correlating the two Sturtian glaciogenic units of Mongolia, Canada and Australia with those of Greenland is

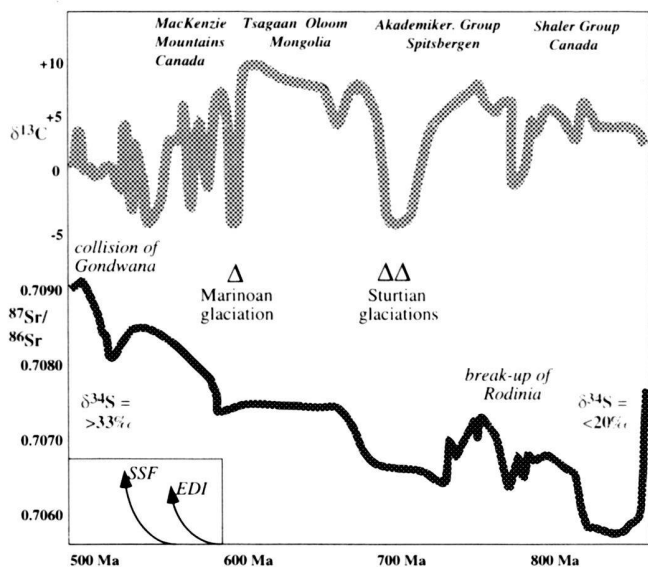


Fig. 4. Reconstruction of seawater isotopic variations between 800 and 500 Ma (Cryogenic – Ordovician) with Sr- and C-isotopes from Asmerom 1991, Brasier et al. 1996, Montanez et al. 1996, Fairchild et al. 1999 and S-isotopes from Strauss 1993, Shields et al. 1999.

that the term Varanger could become synonymous with Sturtian, as the Greenland glaciogenic units have been correlated with the classic Varanger glacials of Norway (Fairchild & Hambrey 1984). This would break a paradigm of Neoproterozoic geology, although we have to remember, for reasons which I have previously given, that the term Varanger is at present not a useful one. Furthermore, it implies that the long isotopic record of Spitsbergen, Greenland and Svalbard (Knoll et al. 1986, Derry et al. 1989, Asmerom et al. 1991, Derry et al. 1992, Fairchild et al. 1999) from below the lowermost unit of the double diamictite becomes pre-Sturtian in affinity (Kennedy et al. 1998), and by correlation older than about 750 Ma. Figure 4 sums up the subsequent Sr and C isotopic record for the whole period 800–500 Ma, which must inevitably result from such a conclusion. Recently, new Sr isotopic data from Greenland, which reveal pre-glacial Sr isotopic ratios as low as 0.7063 (Fairchild et al. 1999), similar to that from carbonates at a similar level in Arctic Canada (Kaufman et al. 1992) tend to support this older age for the Polarisbreen Group.

The resultant pattern of Neoproterozoic faunal radiation (Fig. 3) shows that silicic sponges (together with possible embryos, Xiao et al. 1998) are the first convincing metazoan body fossils to appear in the rock record (TP1), whereas simple metazoan trace fossils, such as *Neonereites* may first occur lower within the same stage TP1 (Brasier & McIlroy 1997).

More complicated trace fossils first occur very late in the Neoproterozoic, although several of these forms are still of only controversial metazoan origin (Jensen et al. 1999). The first penetrative traces and bioturbation typical of the Phanerozoic are found only very close to the presently defined Precambrian–Cambrian boundary (MacNaughton & Narbonne 1999). The first recognisably arthropod traces are found well below the first appearance datum of trilobites in many sections with *Monomorphichnus* and *Rusophycus* occurring in the pre-Tommotian Cambrian of Mongolia. Biostratigraphy and biozonation in the Terminal Proterozoic will undoubtedly prove possible in the future and a sound start has been made to establish faunal stages based on Ediacaran-type and associated fauna in Namibia and Canada (Kaufman et al. 1997).

6. Conclusion

High $\delta^{13}\text{C}$ values, up to 11‰, and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7072 ± 0.0001) in carbonate rocks appear to be characteristic of the period which followed the earliest two phases of the Neoproterozoic glaciations (ca. 700–600 Ma). Following a second period of glaciation (= Marinoan = Nantuo = Ice Brook) >565 Ma, one or more $\delta^{13}\text{C}$ peaks up to 9‰ accompany a rapid rise in $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.7072 to 0.7080, but a further $\delta^{13}\text{C}$ peak occurs later within or just prior to a $^{87}\text{Sr}/^{86}\text{Sr}$ plateau (0.7084 ± 0.0001). This latter $\delta^{13}\text{C}$ excursion is associated with the acme of Ediacaran fossil diversity in Namibia, S China and Canada between 549 and 543 Ma, which appears to be wholly missing from the otherwise representative Mongolian record. The Neoproterozoic–Cambrian transition strata and the first occurrence of diverse trace and shelly fossils are associated with ubiquitous, and multiple in Mongolia, negative $\delta^{13}\text{C}$ anomalies, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios which decrease from 0.7085 to 0.7081 by Tommotian times. By cross-referencing $\delta^{13}\text{C}$ excursions with the $^{87}\text{Sr}/^{86}\text{Sr}$ record, a more complicated pattern of isotopic evolution emerges, against which glacial phases and evolutionary events can be correlated. Such isotopically based calibration schemes will prove to be of crucial importance for the future subdivision and correlation of the Neoproterozoic.

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