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## Neoproterozoic variations in the C-isotopic composition of seawater: stratigraphic and biogeochemical implications

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### Abstract

The recent proliferation of stratigraphic studies of  $\delta^{13}\text{C}$  variation in carbonates and organic C in later Neoproterozoic and basal Cambrian successions ( $\sim 850\text{--}530\text{ Ma}$ ) indicates a strong oscillating trend in the C-isotopic composition of surface seawater. Alone, this trend does not adequately characterize discrete intervals in Neoproterozoic time. However, integrated with the vectorial signals provided by fossils and Sr-isotopic variations, C isotope chemostratigraphy facilitates the interbasinal correlation of later Neoproterozoic successions. Results of these studies are evaluated in terms of four stratigraphic intervals: (1) the Precambrian/Cambrian boundary, (2) the post-Varanger terminal Proterozoic, (3) the late Cryogenian, and (4) the early Cryogenian. Where biostratigraphic or radiometric data constrain the age of Neoproterozoic sedimentary sequences, secular variations in C and Sr isotopes can provide a level of stratigraphic resolution exceeding that provided by fossils alone. Isotopic data place strong constraints on the chemical evolution of seawater, linking it to major tectonic and paleoclimatic events. They also provide a biogeochemical framework for the understanding of the initial radiation of macroscopic metazoans, which is associated stratigraphically, and perhaps causally, with a global increase in the burial of organic C and a concomitant rise of atmospheric  $\text{O}_2$ .

### 1. Introduction

The elemental composition of seawater appears to have changed little during the past 545 million years (Holland, 1984). In contrast, the isotopic composition of C, O, S, and Sr in the oceans has varied markedly through this interval, imparting a significant record of tectonic and biogeochemical change to Phanerozoic sedimentary rocks (Holser, 1984). Because of the stratigraphic resolution provided by fossils, interest in the isotopic chemostratigraphy of Phanerozoic successions has, in general, been limited. However, at times of pronounced and rapid change, the isotopic record provides stratigraphic reso-

lution that matches or exceeds the best that paleontology can offer. Examples include O-isotopic variation during the Pleistocene (Shackleton, 1977), Sr-isotopic variation through the Tertiary (Richter et al., 1992), and C-isotope excursions at the Cenomanian–Turonian and Cretaceous–Tertiary boundaries (Scholle and Arthur, 1980; Zachos and Arthur, 1986).

It is reasonable to expect that isotopic variation should characterize Neoproterozoic as well as Phanerozoic rocks, so the *fact* of secular variation in the C-, S-, and Sr-isotopic composition of Neoproterozoic carbonates, organic matter, and sulfates is not unexpected. What does sur-

prise is the *magnitudes* of observed excursions— isotopic variations seen in Neoproterozoic successions match or exceed the strongest shifts recorded in Phanerozoic rocks. By analogy with the Phanerozoic record, this strongly suggests that the end of the Proterozoic Eon was a time of marked tectonic and biogeochemical change, and that isotopes have the potential to improve the relatively coarse stratigraphic resolution provided by Neoproterozoic fossils.

In this paper, we review the emerging record of C-isotopic abundances in Neoproterozoic carbonates and address three questions:

(1) Given the magnitude of reported shifts, can we have confidence that observed variations are primary and reflective of the world ocean?

(2) If we can establish that isotopic events are both primary and global, can we provide plausible tectonic and biogeochemical hypotheses to explain the shifts?

(3) What levels of stratigraphic resolution can we expect from the Neoproterozoic fossil and isotopic records?

## 2. Evaluating C-isotopic data

### 2.1. Primary isotopic compositions

The isotopic biogeochemistry of C is reviewed thoroughly in a number of publications (e.g., Broecker and Peng, 1982; Schidlowski et al., 1983; Goerike et al., 1994). In brief, the informational richness of the C-isotopic record arises because of photosynthesis. During the autotrophic fixation of CO<sub>2</sub>, <sup>12</sup>C is incorporated preferentially over <sup>13</sup>C by an amount determined by the kinetic properties of the CO<sub>2</sub>-fixing enzyme—commonly, but not always RUBISCO—and the availability of CO<sub>2</sub> at the molecular site of fixation. Photosynthetic uptake of isotopically light C leaves the dissolved inorganic carbon (DIC) of the surface ocean relatively enriched in <sup>13</sup>C.

Whereas the *difference* in isotopic composition between carbonate and organic C reflects photosynthetic fractionation, the *absolute* isotopic composition of each phase additionally re-

flects the fluxes of C into and out of the oceans. If we assume that the isotopic composition of C entering the oceans is constant or nearly so, secular variations in  $\delta^{13}\text{C}$  are determined in large part by variations in the relative rates at which carbonate and organic C are buried (Broecker, 1970; Hayes, 1983). Such variations are commonly ascribed to changes in the burial rate of organic matter, but this is not a necessary conclusion (Derry et al., 1992); if the total flux of C into the oceans is low,  $\delta^{13}\text{C}$  can be high even though *absolute* rates of organic C burial are modest. Furthermore, the assumption of isotopically constant input to surficial water masses is not always warranted. In particular, the weathering and erosion of organic-rich rocks or the vigorous ventilation of the deep sea following an interval of ocean stratification can contribute to negative excursions seen in the C-isotopic record. Both processes were probably important in determining the pattern of variation seen in Neoproterozoic successions.

Photosynthesis is restricted to surface waters, but the oxidation of photosynthetically produced organic matter proceeds throughout the water column, resulting in a gradient of  $\delta^{13}\text{C}$  values in dissolved inorganic carbon (DIC) that decreases with depth and is reflected in the isotopic composition of carbonates precipitated along the gradient (e.g., Broecker and Peng, 1982). Geographic variations in the intensity of deep water returning to the surface via upwelling and diffusion further increase the C-isotopic heterogeneity of the oceans.

Neoproterozoic stratigraphic successions usually include carbonates deposited in a range of sedimentary environments. If isotopic composition correlates strongly with facies rather than time, isotopic chemostratigraphy cannot work in these sections. For Sr, this is not at issue, because the long residence time of Sr (~4 Ma) insures that <sup>87</sup>Sr/<sup>86</sup>Sr is homogeneous throughout the world ocean. But the residence time of C is far shorter (~8 × 10<sup>4</sup> years), enforcing the geographic and depth-related variations in  $\delta^{13}\text{C}$  noted above.

These variations pose potential problems in the interpretation of the Proterozoic record. Indeed,

in several Paleoproterozoic basins containing iron-formation, carbonates inferred to have precipitated in a stratified ocean below the level of surface mixing are depleted in  $^{13}\text{C}$  by 4–6‰ relative to shallow marine carbonates (Beukes et al., 1990; Kaufman et al., 1990a; Winter and Knauth, 1992). However, in Neoproterozoic successions studied to date, no large or systematic variation among facies has been found within single sections (Knoll et al., 1986, 1995; Corsetti and Kaufman, 1994), along strike for distances as great as 650 km (Knoll et al., 1986; Narbonne et al., 1994; Corsetti and Kaufman, 1994), or perpendicular to strike across a basin from peritidal to slope environments (Narbonne et al., 1994; Knoll et al., 1995). These observations support sedimentological inferences that known Neoproterozoic carbonates formed within the mixed layer. Therefore, empirical data available to date suggest that facies variation in and of itself is not a principal determinant of stratigraphic trends within sections.

As shown below, contemporaneous carbonates from different Neoproterozoic basins may show geographic variation of 1–2‰, much as seen today. But stratigraphic trends and magnitudes in  $\delta^{13}\text{C}$  variation are conserved. Therefore, despite geographic heterogeneity in the C-isotopic composition of seawater, secular variations, particularly those of the *magnitude* seen in Neoproterozoic carbonates, appear to record global events and, therefore, provide reliable tools for correlation. Carbon isotope chemostratigraphy is possible in the Neoproterozoic because observed isotopic excursions are large. If the stratigraphic variations seen in individual sections were no more than 1 or 2‰, prospects for correlation in the absence of much better biostratigraphic control would be dim, as indeed they are for much of the preceding Mesoproterozoic Era.

## 2.2. Sources of C-isotopic alteration

The elemental and isotopic compositions of minor and trace elements in Proterozoic carbonates commonly reflect diagenetic alteration of primary abundances. However, for C, a major

constituent of carbonates, results of several studies indicate that essentially depositional C-isotopic compositions are commonly preserved in whole-rock samples of Neoproterozoic limestones and dolostones (Tucker, 1985; Knoll et al., 1986; Fairchild and Spiro, 1987; Burdett et al., 1990; Kaufman et al., 1991). Having stated this, it is important to emphasize that enough examples of post-depositional shifts in  $\delta^{13}\text{C}$  values have been documented (e.g., Zempolich et al., 1988; Fairchild et al., 1990; Kaufman et al., 1992) to warrant a detailed evaluation of potential alteration in *all* samples.

The C-isotopic composition of a carbonate rock sample can be altered by re-equilibration with fluids of different isotopic composition during neomorphism or recrystallization, by the addition of isotopically distinct carbonate to the rock, or by decarbonation reactions in the presence of siliciclastic rocks. In decarbonation, carbonates and quartz (or feldspar) react to produce Ca- or Mg-silicates plus  $\text{CO}_2$ . The  $\text{CO}_2$  is enriched in  $^{13}\text{C}$ , lowering the  $\delta^{13}\text{C}$  value of remaining carbonates (Shieh and Taylor, 1969). Decarbonation reactions occur under metamorphic conditions and occur only in the presence of silicate minerals. In their absence, even marble may retain essentially depositional  $\delta^{13}\text{C}$  values (Taylor and O'Neil, 1977; Valley and O'Neil, 1984; Ghent and O'Neil, 1985; Baker and Fallick, 1989a, b; Wickham and Peters, 1993). Metamorphic release of isotopically light volatiles can also result in the enrichment of  $^{13}\text{C}$  in residual organic C (Schidlowski, 1987; DesMarais et al., 1992). In consequence,  $\Delta\delta$  will decrease, but the stratigraphic co-variation between carbonate and organic carbon isotopic compositions may remain (e.g., Kaufman et al., 1991).

Dolomite in isotopic equilibrium with calcite will be enriched in  $^{13}\text{C}$  by about 2‰ (Sheppard and Schwarcz, 1970). Thus, the potential for isotopic alteration during dolomitization exists; however, studies of Proterozoic limestones and dolostones in single hand samples or closely interbedded layers demonstrate empirically that Proterozoic dolomites (especially, but not exclusively, mimetic dolomites) normally retain the C-isotopic composition of their precursor  $\text{CaCO}_3$ .

(Tucker, 1983; Knoll et al., 1986; Narbonne et al., 1994, and references cited therein). This presumably occurs because the overwhelmingly dominant source of C in the resulting dolomite was the precursor  $\text{CaCO}_3$ . Furthermore, Proterozoic dolomite formation was commonly a syngenetic reaction that took place in the presence of fluids isotopically similar to seawater. Also, penecontemporaneous cementation commonly occluded pore space, isolating dolostones from later diagenetic fluids (Tucker, 1983; Fairchild and Spiro, 1987).

Fairchild et al. (1990) demonstrated that  $\delta^{13}\text{C}$  of originally aragonitic limestones of the ~900 Ma Atar Group, Mauritania, were altered during late diagenetic neomorphism, apparently as a result of large-scale reaction with meteoric water following uplift. Beeunas and Knauth (1985) have also demonstrated isotopic alteration of limestones immediately beneath erosion surfaces in the ~1100 Ma Mescal Limestone, Arizona. Thus, given sufficient permeability and access to meteoric waters, isotopic alteration can accompany  $\text{CaCO}_3$  neomorphism (see also Rush and Chafetz, 1990).

Despite this, experience suggests that the processes most likely to have altered the C-isotopic compositions of Proterozoic carbonates are biological. The microbial metabolism of sedimentary organic matter commonly produces products of distinct isotopic composition. Photosynthetically derived organic C is strongly depleted in  $^{13}\text{C}$  relative to carbonate precipitated from the same water body. Respiration or fermentation of this organic matter yields isotopically light  $\text{CO}_2$  which can be quantitatively important in diagenetic carbonate precipitation. Dissimilatory sulfate reduction and methanogenesis also produce isotopically distinct products that can be incorporated into early diagenetic carbonate minerals (reviewed in Schidlowski et al., 1983). Abiological decomposition of volatile organic molecules at depth can mimic the isotopic effects of microorganisms, but the commonly low ratio of organic C to carbonate C and the occlusion of pore space by early diagenetic cements appear to have minimized this effect in Proterozoic rocks.

Additional biological influences are possible. Many algae and animals precipitate skeletons that are not in isotopic equilibrium with seawater (Lowenstam and Weiner, 1989; Grant, 1992). Because they irrigate sediments, animals can also facilitate diagenetic re-equilibration of carbonate sediments through bioturbation (Walter and Burton, 1990). Stream run-off charged with isotopically light  $\text{CO}_2$  from the decay of land plants can locally influence the isotopic composition of diagenetically stabilized carbonate sediments (Walter and Burton, 1990). In the absence or near absence of skeletons, bioturbation, and a land flora rich in biomass, Proterozoic carbonates are not plagued by these problems; however, they may significantly complicate the interpretation of Cambrian and younger carbonates (e.g., Grant, 1992).

### 2.3. *Evaluating sample quality*

A number of petrologic and geochemical tests have been developed to ascertain the degree of alteration of individual samples; relevant analytical techniques are discussed in publications by Fairchild and Spiro (1987), Kaufman et al. (1991, 1992, 1993), Derry et al. (1992), and Narbonne et al. (1994); a schematic flow chart of analyses is shown in Fig. 1.

(1) Initially, thin sections of micritic, oolitic, and/or stromatolitic carbonates are evaluated petrographically for grain size and degree of recrystallization, as well as abundance of authigenic and detrital components, stylolites, veins, and alteration associated with surficial weathering. The abundance and color of organic matter in thin section are also evaluated qualitatively. Screening of samples begins at this point. Those samples which are significantly recrystallized, which contain high concentrations of siliciclastic grains (especially clays), or which appear to be strongly oxidized are removed from the sample population.

(2) Highly polished thick sections cut from rock surfaces that are mirror images of those used to make thin sections, are used for cathodoluminescence (CL) examination. In carbonates, luminescence is activated by high concentra-

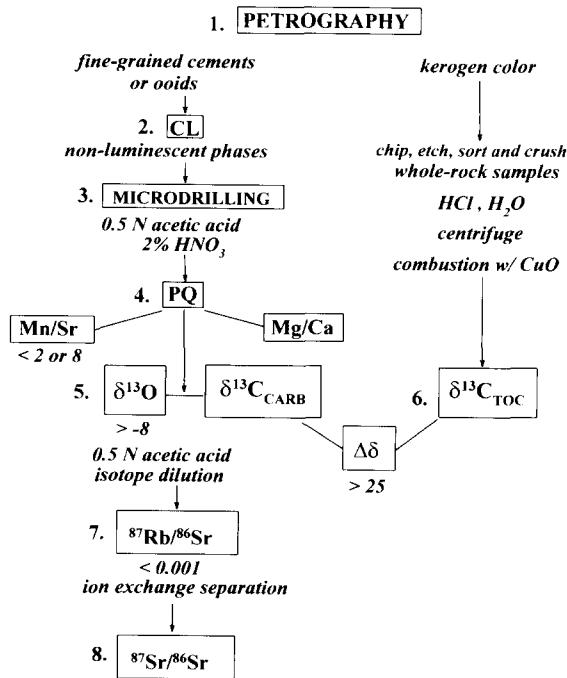


Fig. 1. A flow chart of petrologic and geochemical analyses used in studies of Neoproterozoic carbonates. Numbers are keyed to specific discussions (1)–(8) in the text.

tions of Mn and quenched by high concentrations of Fe (Hemming et al., 1989). Because seawater contains relatively little Mn compared to freshwater, this technique can be used to differentiate between samples which have been altered by meteoric diagenesis and samples which have not. CL examination shows that significant mm-scale intrasample variations in luminescence exist even in specimens which appear texturally homogeneous in optical microscopy (cf. fig. 5 in Kaufman et al., 1991); higher luminescence within a sample is often correlated with lower concentrations of organic C, an observation consistent with the suggestion that Mn-rich meteoric fluids were sufficiently rich in O<sub>2</sub> to oxidize organic matter. As a cautionary note, Rush and Chafetz (1990) have demonstrated that beneath exposure surfaces, even non-luminescent carbonate phases can have diagenetically altered C-isotopic compositions. Thus, while luminescence provides a guide to sample quality, it offers no guarantee.

(3) Because of apparent heterogeneities in both elemental and isotopic composition between various carbonate phases in whole-rock samples and to avoid obvious secondary veins and cements as well as weathered areas, it is necessary to micro-sample in detail (Hudson, 1977). Micro-samples are taken from fine-grained (i.e. micrite, ooids, and early diagenetic cements) and non- to moderately-luminescent portions of carbonate samples. Micro-samples of 5–10 mg are isolated, when possible, using a 3/4 or 1 mm diamond drill mounted to a small drill press. The sample is manipulated using an *x-y* positioning device while viewed under a binocular microscope. The fine powder produced by drilling is collected on weighing paper and stored.

(4) Powdered micro-samples are analyzed for their elemental and isotopic compositions. In particular, the elemental concentrations of Mn, Sr, Mg, and Ca are important for understanding the degree of alteration associated with meteoric diagenesis and dolomitization. Following the work of Veizer (1983, and later revisions), our studies have shown that the ratio of Mn/Sr is useful for screening samples. This is true because under the influence of meteoric fluids, Sr is expelled from marine carbonates while Mn is incorporated. Derry et al. (1992) and Kaufman et al. (1992, 1993) suggested that reliable Sr-isotopic values are likely to come only from carbonates having Mn/Sr < 2–3. Using this parameter to evaluate the degree of alteration of C-isotopic values is not as rigorous because the volumes of meteoric fluid that could easily alter Mn/Sr may have no effect on major element chemistry. Our experience suggests that carbonates (both limestones and dolostones) with Mn/Sr < 10 commonly retain near primary  $\delta^{13}\text{C}$  abundances.

(5) Further tests are provided by the isotopic data themselves. In the best case, C-, O-, and Sr-isotopic abundances are determined for the same carbonate microsample, and  $\delta^{13}\text{C}$  is also obtained from organic matter in the whole-rock sample. Oxygen-isotopic compositions are sensitive indicators of diagenesis, with a decrease in  $\delta^{18}\text{O}$  values often resulting from isotopic exchange with meteoric or hydrothermal fluids. Within individual Neoproterozoic carbonate

units, crossplots of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  commonly show little or no variation of  $\delta^{13}\text{C}$  with decreasing  $\delta^{18}\text{O}$ , again indicating that fluid volumes sufficient to re-equilibrate the O-isotopic composition of carbonates are commonly too small to have a significant effect on  $\delta^{13}\text{C}$ . On the other hand, in cases where individual sedimentary units show wide variations in C-isotopic abundances,  $\delta^{13}\text{C}$  commonly plots against  $\delta^{18}\text{O}$  as a straight line of positive slope. In such cases, only samples with the most enriched  $^{13}\text{C}$  and  $^{18}\text{O}$  compositions can be considered as potentially unaltered (Fairchild et al., 1990; Kaufman et al., 1992). Although the primary O-isotopic composition of Neoproterozoic seawater is still in question, values ranging between 0 and  $-5$  are indicated by recent studies (Zempolich et al., 1988; Hudson and Anderson, 1989), and these values are consistent with those recorded in our least-altered samples of limestone. Therefore, we consider that  $\delta^{18}\text{O}$  values of limestones less than  $-5$  represent some degree of O-isotopic alteration; samples with values below  $-10$  are considered unacceptably altered.

(6) Diagenetic effects can also be distinguished by analysis of co-existing carbonate and total organic carbon (TOC). In 1986, Knoll et al. noted that for thick, unmetamorphosed Neoproterozoic successions in Svalbard and East Greenland, stratigraphic plots of  $\delta^{13}\text{C}$  for carbonate and TOC co-varied smoothly with a  $\Delta\delta$  of  $28 \pm 2$ . Diagenetic processes can alter the isotopic composition of either carbonate C or organic C, but no process is currently known that can alter both signals by the same magnitude in the same direction. Thus, Knoll et al. (1986) concluded that in the sections under study, neither phase was strongly affected by post-depositional processes (see also Narbonne et al., 1994). There is no reason to assume that  $\Delta\delta$  has been constant through time; to the contrary, there is evidence that isotopic fractionation has varied as a function of  $p_{\text{CO}_2}$  and, perhaps, physiological evolution (Freeman and Hayes, 1992; DesMarais et al., 1992). Therefore, the number 28 is not magic and is not necessarily applicable to all carbonate–organic C pairs. In fact, Neoproterozoic samples with high TOC commonly ex-

hibit  $\Delta\delta$  values of  $> 30$ . For example, in the terminal Proterozoic Khorbusuonka Group of the Olenek Uplift, Siberia, samples with TOC concentrations  $< 1$  mg C/g generally exhibit  $\Delta\delta$  values of  $28 \pm 1$ ; samples whose TOC significantly exceeds 1 mg C/g have  $\Delta\delta$  values of  $33 \pm 2$  (Knoll et al., 1995; see also Walter et al., 1995). The reason for the relationship between  $\Delta\delta$  and TOC abundance is not clearly understood, but the empirical observation of correlation means that TOC must be factored into any attempt to use  $\Delta\delta$  values in the recognition of sample alteration (or  $\delta^{13}\text{C}_{\text{TOC}}$  as a proxy for  $\delta^{13}\text{C}_{\text{carb}}$  in isotopic chemostratigraphy). When samples contain very low concentrations of organic C ( $< 1$  mgC/g sample), there is a great potential for post-depositional contamination, and particular care must be taken in interpretation.

Total organic carbon is isolated in 9 mm wide Vycor tubing by repeated acidification of 100–300 mg of whole-rock powder with hot and cold HCl to remove carbonate C, followed by washing with deionized water to neutralize the sample. It is important that the sample be finely crushed so that carbonate is removed quantitatively. Organic isolates are dried with the residual siliciclastic fraction and CuO is added as an oxidant. The tubes are then evacuated and combusted at  $850^\circ\text{C}$  for 12 hours. Samples should be distilled as soon after combustion as possible.

(7) Prior to Sr-isotopic analyses, isotope dilution techniques are used to determine  $^{87}\text{Rb}/^{86}\text{Sr}$ , which indicates the abundance of radiogenic  $^{87}\text{Sr}$  derived from the decay of  $^{87}\text{Rb}$ ; values  $> 0.001$  are not considered for further analysis. Excess Rb in marine carbonates is generally found in detrital clays. Although some dolostone samples appear to give near primary Sr-isotopic compositions (cf. Derry et al., 1989, 1992), most appear altered and recently only data from limestones have been used to construct secular variations in Neoproterozoic successions (e.g., Asmerom et al., 1991; Kaufman et al., 1993).

(8) Strontium is separated from carbonates by dissolution of sample powders in ultra-clean 0.5 M acetic acid followed by standard ion-exchange techniques. After the Sr fraction is isolated and dried, it is transferred to a filament made of Re

or Ta ribbon and loaded into the sample chamber of a thermal ionization mass spectrometer for  $^{87}\text{Sr}/^{86}\text{Sr}$  analysis.

While screens based on petrography, cathodoluminescence, Mn/Sr, Mg/Ca,  $\delta^{18}\text{O}$  and  $^{87}\text{Rb}/^{86}\text{Sr}$  can identify most isotopically altered carbonates, no known combination of tests is guaranteed to reveal all samples with altered  $\delta^{13}\text{C}$  or  $^{87}\text{Sr}/^{86}\text{Sr}$ . The stratigraphic context and sedimentological features of individual samples and strata must additionally inform judgement. In particular it is important to show that isotopic variations are not associated with sequence boundaries, restricted conditions, high organic C and P contents, or nodular horizons (see Lambert et al., 1987, Aharon et al., 1987, and Brasier et al., 1990, for extreme variations of  $\delta^{13}\text{C}$  in carbonates occurring in C- and P-rich sediments), and that the variations are regionally consistent (e.g., Knoll et al., 1986, 1995; Corsetti and Kaufman, 1994; Narbonne et al., 1994). At the end of the day, the best way to be confident that isotopic variations recorded in individual sections correspond to secular variations in the world ocean is to demonstrate that the same variations occur in different sections shown by independent means to be of comparable age. As documented below, the principal features of the Neoproterozoic C-isotopic record fulfil this geographic criterion.

### 3. Construction of Neoproterozoic secular variation curves

#### 3.1. Age constraints on Neoproterozoic successions

For the first century of its existence, the geological time scale for the Phanerozoic Eon was unconstrained by radiometric age data. This did little to hinder the development of a chronostratigraphic scale in which the relative order of events could be determined with confidence. With time, a relatively small number of radiometric dates in key sections have permitted stratigraphers to calibrate the chronostrati-

graphic time scale in numerical terms (Harland et al., 1989).

A similar evolution is now taking place in Neoproterozoic stratigraphy. Time's arrow is clearly seen in the fossil record of Neoproterozoic eukaryotes, permitting the development of biostratigraphic zonation. Interdigitation of paleontological data with C- and Sr-isotopic curves indicates that chemostratigraphic signals also provide tools for correlation, tools that for many intervals of Neoproterozoic time permit finer resolution than do fossils. Radiometric dates that reliably calibrate this chronostratigraphy are at present limited, but by analogy to the Phanerozoic record there is every reason to expect that the Neoproterozoic record will be eventually calibrated, not by the dating of all or even many successions, but by the reliable dating of chronostratigraphic events that find widespread expression in Neoproterozoic rocks.

A comprehensive review of Neoproterozoic biostratigraphy is beyond the scope of this paper. Useful guides to Neoproterozoic stromatolites can be found in the literature (Walter, 1976; Semikhatov, 1991, and references therein), as can reviews of the Ediacaran, small shelly fossil, and ichnofossil animal records (Fedonkin, 1987; Lipps and Signor, 1992; Jenkins, 1995). Detailed discussions of the acritarch record are provided by Vidal and Knoll (1982), Jankauskas (1989), Moczyłowska (1991) and Knoll (1994).

Radiometric dates useful in calibrating chronostratigraphic events remain limited. Again, a critical review of Neoproterozoic geochronometric data is beyond the scope of this paper, but limiting ourselves to U–Pb data from zircons in volcanic horizons within chronostratigraphically significant sections, we can cite a number of dates that constrain age interpretations:

(1)  $534.6 \pm 1$  Ma for porphyry cobbles that immediately underlie basal Tommotian beds in the Kharaulakh Mountains, northern Siberia (Bowring et al., 1993).

(2)  $544 \pm 1$  Ma for a volcanic breccia within the basal part of the Nemakit–Daldyn succession in the Olenek Uplift, northern Siberia (Bowring et al., 1993).

(3)  $565 \pm 3$  Ma for volcanic ash interbedded with Ediacaran metazoans in Newfoundland (Benus, 1988; note, however, that the isotopic systematics have not been published for this date).

(4)  $602 \pm 3$  Ma and  $606 \pm_{2.4}^{3.4}$  Ma for volcanic rocks that immediately underlie Varanger tillites in Massachusetts and Newfoundland, respectively (Kaye and Zartman, 1980; Krough et al., 1988).

(5)  $723 \pm 3$  Ma for basalts that lie atop the Shaler Group on Victoria Island, northern Canada (Heaman et al., 1992), and dates of  $766 \pm 24$  Ma for diabase sheets that intrude the Little Dal Group but not overlying sediments in the Mackenzie Mountains, northwestern Canada (Armstrong et al., 1982).

(6)  $802 \pm 10$  Ma for the Rook Tuff that underlies the Burra Group of the Adelaide Geosyncline, South Australia (Fanning et al., 1986).

The significance of points (1)–(4) is self-evident; they calibrate chronostratigraphic events that can be correlated widely and reliably with chemostratigraphic data. Concerning (5), the radiometric constraints on correlative strata of the Shaler and Little Dal groups not only provide minimum dates for fossils and isotopic signatures in these rocks, but also constrain the ages of successions from Svalbard and East Greenland which are partly correlative with, but predominantly younger than these Canadian sections (Asmerom et al., 1991). If stratigraphic relationships between the Adelaide Geosyncline

and the Mackenzie Mountains can be sustained, then (6) may provide a maximum age for Shaler and Little Dal carbonates.

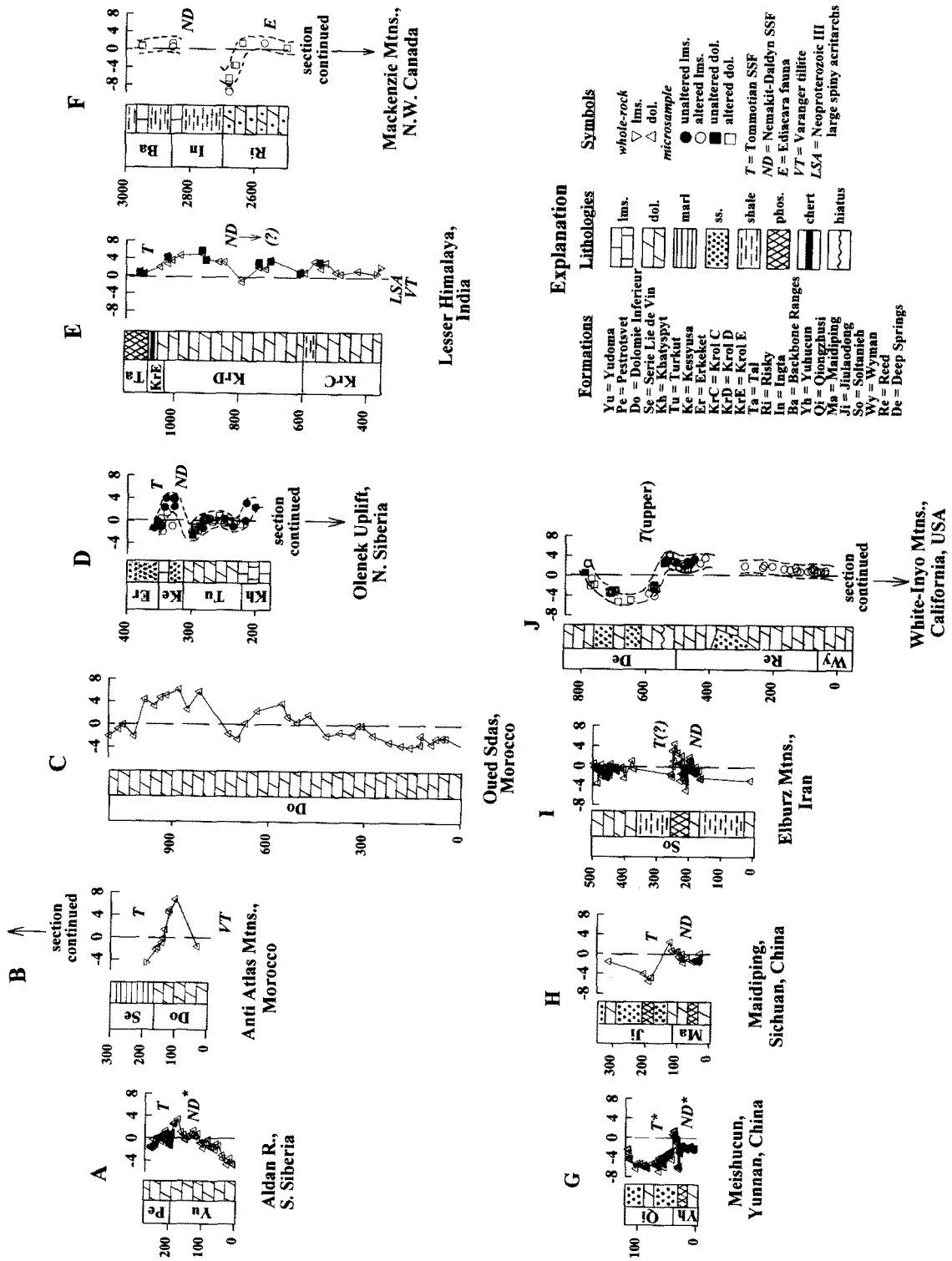
Certainly the dates cited here do not exhaust the age constraints on Neoproterozoic sedimentary successions. Rather, they illustrate the way in which a well-calibrated Neoproterozoic time scale is beginning to emerge.

### 3.2. Neoproterozoic chemostratigraphy

Prior to the 1980's secular changes in the C- and Sr-isotopic composition of Neoproterozoic seawater were not recognized due to the general lack of stratigraphic studies, and to the averaging of isotopic compositions over long time intervals (Schidlowski et al., 1975). This averaging method led to the conclusion that Precambrian seawater  $\delta^{13}\text{C}$  values were relatively constant around 0. However, since the early 1980's, stratigraphic studies have proliferated resulting in the recognition of strong and rapid secular changes in both the C- and Sr-isotopic composition of little-altered Neoproterozoic carbonates. In the discussion that follows, we have divided available data into four stratigraphic intervals. Detailed integration of isotopic and other stratigraphic data has been accomplished only for post-Varanger time (Knoll and Walter, 1992). Earlier Neoproterozoic periods are defined geochronometrically (Plumb, 1991); however, few Neoproterozoic sedimentary successions are well constrained by sound radiometric data. There-

Fig. 2. Secular variations in  $\delta^{13}\text{C}$  vs. stratigraphic depth (m) for carbonates deposited in the Precambrian–Cambrian boundary interval. (A) In southern Siberia (Magaritz et al., 1986); asterisk denotes that the Dvortsy section illustrated here contains fossils of the upper Nemakit–Daldyn *Purella antiqua* zone; lower Nemakit–Daldyn SSF occur elsewhere in the region. (B) In the Anti-Atlas Mountains of Morocco (Tucker, 1986); only the lower of two peaks in  $\delta^{13}\text{C}$  is shown. (C) In Oued Sdas in Morocco (Magaritz et al., 1991). (D) In the Olenek Uplift of northern Siberia (Knoll et al., 1995). (E) In the Lesser Himalaya of India (Aharon et al., 1987). (F) In the Mackenzie Mountains, Northwest Territories, Canada (Narbonne et al., 1994). (G) In Meishucun, China (Brasier et al., 1990); asterisk denotes that Kirschvink et al. (1991) have interpreted the same section as late Tommotian to Adtabanian in age. (H) In Maidiping, China (Brasier et al., 1990). (I) In the Elburz Mountains in Iran (Brasier et al., 1990). (J) In the White–Inyo Mountains, California, USA (Corsetti and Kaufman, 1994). General trends in secular variations of  $\delta^{13}\text{C}$  are shown for our more detailed elemental and isotopic studies of fine-grained carbonate micro-samples and organic C (D, F, and J); in these figures filled symbols (circles=limestones; squares=dolostones) represent our least-altered samples, while open symbols represent samples which, by the parameters outlined in the text, are considered altered. Ranges of key biostratigraphic assemblages and approximate positions of documented or inferred Varanger-age tillites in each succession are also indicated: *T*=Tommotian small shelly fossils; *ND*=Nemakit–Daldyn small shelly fossils; *Cl*= Cloudina; *E*=diverse Ediacaran faunas; *VT*=Varanger tillite.





fore, while there is a general correspondence between defined periods and both chemo- and biostratigraphic patterns, the correspondence is inexact.

### 3.3. *The Proterozoic–Cambrian boundary interval (~ 530–550 Ma)*

Several groups have reported C-isotopic variations across the erathem boundary (Fig. 2). The earliest work by Magaritz et al. (1986) was on whole-rock samples of dolostone from the upper Yudoma Formation collected at the Dvortsy section along the Aldan River in southern Siberia. The trends in these data indicate a significant and consistent positive rise in  $\delta^{13}\text{C}$  values within a 170 m stratigraphic interval, from  $-4$  in uppermost Proterozoic carbonates to  $+4$  in carbonates near the top of the basal Cambrian Nemakit–Daldyn interval; the Nemakit–Daldyn/Tommotian boundary is marked by a rapid decline in  $\delta^{13}\text{C}$  values (Fig. 2A; see also Magaritz, 1989, for C-isotopic variations in a nearby section from Ulakhan–Sulugur along the Lena River; Kirschvink et al., 1991 for additional data on sequences above the Nemakit–Daldyn interval; Brasier et al., 1993 for a discussion of the skeletal fossil assemblages in this succession). At about the same time, Tucker (1986) published an isotopic curve for a section in the Anti-Atlas Mountains of Morocco. Tucker's curve shows two positive  $\delta^{13}\text{C}$  excursions, but with poor biostratigraphic control. Later paleontological work by Latham and Riding (1990) showed that only the lower of the two isotopic peaks, with a maximum  $\delta^{13}\text{C}$  value of  $+7$  occurring in the Dolomie Inferieur, corresponds to the Nemakit–Daldyn excursion (Fig. 2B). A second Moroccan section at Oued Sdas yielded an isotopic curve similar in detail to that of the upper Yudoma section in southern Siberia (Fig. 2C; Magaritz et al., 1991).

The stratigraphic pattern of negative to markedly positive  $\delta^{13}\text{C}$  values from terminal Proterozoic into Nemakit–Daldyn carbonates, followed by a rapid drop near the base of the Tommotian, is also evident in carbonate-rich successions from the Kessyusa Formation in the

Olenek Uplift (Fig. 2D; Knoll et al., 1995) and the Staraya Rechka–Manykai succession of the Anabar region (Adams, 1993) in northern Siberia. Biostratigraphically constrained curves for part of this interval occur in the Krol D and Krol E horizons of the Lesser Himalaya in India (Fig. 2E; Aharon et al., 1987; Aharon and Liew, 1992) and the Ingta Formation in the Mackenzie Mountains, Northwest Territories, Canada (Fig. 2F; Narbonne et al., 1994). The end Nemakit–Daldyn peak also appears to occur in a number of “Tethyan” sections extending from China to Iran (Figs. 2G–2I; Brasier et al., 1990), although strong negative isotopic excursions associated with phosphorite deposition complicate interpretation. Finally, a peak in  $\delta^{13}\text{C}$  values in the lower Deep Spring Formation of the White–Inyo region, western USA (Fig. 2J; Corsetti and Kaufman, 1994) may also be correlative with the end Nemakit–Daldyn peak. However, in the absence of firm biostratigraphic control, it is impossible to rule out correlation of the White–Inyo peak with an earlier rise in  $\delta^{13}\text{C}$  values.

### 3.4. *The post-Varanger terminal Proterozoic interval (~ 550–590 Ma)*

The initial analyses from this interval of the Neoproterozoic were on carbonates that overlie Varanger tillites in Svalbard and East Greenland (Knoll et al., 1986; Fairchild and Spiro, 1987). In these successions, both carbonates and co-occurring organic C display negative  $\delta^{13}\text{C}$  values (ca.  $-3$  to  $-5$  for carbonates; Fig. 3A). In contrast, a stratigraphically higher interval that includes Ediacaran faunas in its upper part and (initially) represented by analyses of whole-rock samples from the Doushantuo and Dengying formations in the Yangtze Gorges of South China (Lambert et al., 1987) shows significant enrichment in  $^{13}\text{C}$  (Fig. 3B). Carbonates of the Doushantuo and lower Dengying formations record values as high as  $+7$ , but within the Doushantuo values are widely variable, most likely due to early organic diagenesis associated with high concentrations of both organic C and P. Dolostones from the upper Dengying Formation are characterized by relatively constant  $\delta^{13}\text{C}$  values

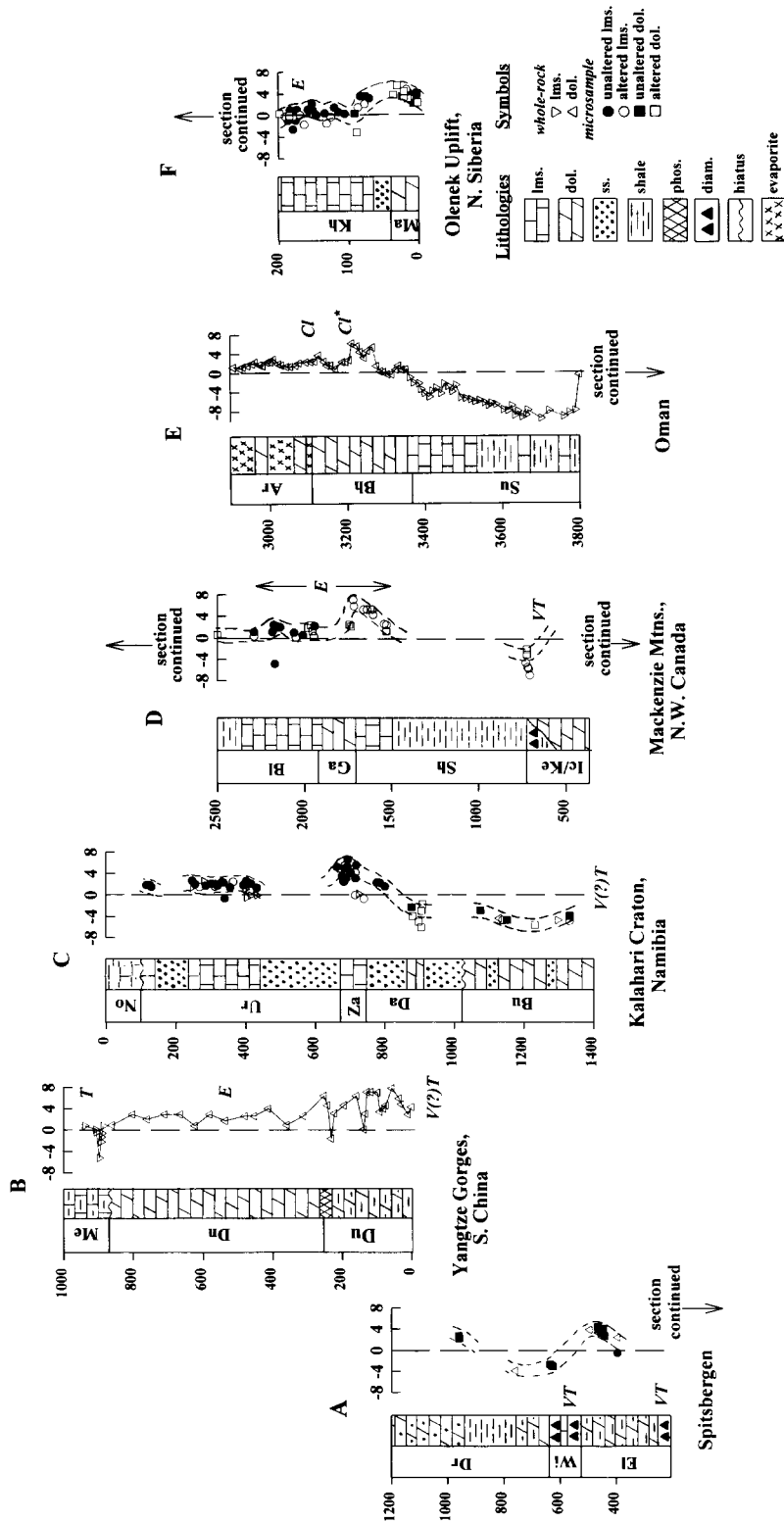


Fig. 3. Secular variations in  $\delta^{13}\text{C}$  vs. stratigraphic depth (m) for carbonates deposited in the post-Varanger terminal Proterozoic interval. (A) In Spitsbergen (Knoll et al., 1986; Fairchild and Spiro, 1987; Kaufman et al., 1993). (B) In South China (Lambert et al., 1987). (C) In Namibia (Kaufman et al., 1991, 1993; see also Saylor, 1993). (D) In the Mackenzie Mountains, Northwest Territories, Canada (Narbonne et al., 1994). (E) In Oman (Burns and Matter, 1993); asterisk denotes that although *Cloudina* is known to occur in the Buah Formation, its position within the formation has not been established. (F) In the Olenek Uplift, northern Siberia (Knoll et al., 1995). General trends from our more detailed studies are shown in (A), (C), (D), and (F). Ranges of key biostratigraphic assemblages and approximate positions of documented or inferred Varanger-age tillites in each succession are also indicated: *T* = Tommotian small shelly fossils; *Cl* = *Cloudina*; *LSA* = large spiny acritarchs of Terminal Neoproterozoic III aspect (the *Papillomembrana/Erechasphaera* zone); *E* = diverse Ediacaran faunas; *VT* = Varanger tillite. Formations: *El* = Elboreen; *Wi* = Wilsonbreen; *Dr* = Dracoisen; *Du* = Doushantuo; *Dn* = Dengying; *Me* = Meishucun; *Ma* = Buschmannsklippe; *Da* = Dabai; *Za* = Zaris; *Ur* = Urusis; *No* = Nomtsas; *Ib/Ke* = Ice Brook/Keele; *Sh* = Sheepbed; *Ga* = Gametrail; *Bt* = Blueflower; *Su* = Shuram; *Ar* = Ara; *Ma* = Mastakh; *Kh* = Khatyspyt.

near +2.  $\delta^{13}\text{C}$  data for a limited number of whole-rock samples from the Rodda Beds in the Officer Basin, central Australia, are broadly comparable with isotopic data from the equivalent interval in China (Jenkins et al., 1993), with  $\delta^{13}\text{C}$  values as high as +5.5 in carbonates of the lower Rodda Beds and values averaging around +1 in carbonates of the upper Rodda Beds (also see Pell et al., 1993 for similar isotopic excursions in the Ediacaran interval in the Flinders Ranges of South Australia).

In 1991, Kaufman et al. reported secular variations in C isotope abundances in the Vendian Witvlei and Nama groups of Namibia which cover both time intervals discussed above (Fig. 3C). Kaufman et al.'s (1991) results are consistent with the earlier reports, indicating a significant excursion from negative  $\delta^{13}\text{C}$  values in micro-samples of Witvlei and lower Nama limestones and dolostones to values as high as +6.5 in the overlying Zaris Formation. Stratigraphically above the Zaris Formation, carbonates of the Huns and Spitskop members of the Nama Group record  $\delta^{13}\text{C}$  values strikingly similar to those of the Dengying Formation.

In the upper Windermere Supergroup of the Northwest Territories, Canada, both the stratigraphic pattern of  $\delta^{13}\text{C}$  and its relationship to biostratigraphic data are similar to those in Namibia (Fig. 3D; Narbonne et al., 1994).  $\delta^{13}\text{C}$  values around -3 characterize cap carbonates above Varanger-age glacial sediments; a strong positive excursion to values as high as +7 is recorded in the upper part of the overlying Sheepbed Formation in carbonates associated with the lowermost diverse Ediacaran faunas in the section. (Simple organic discs of probable metazoan origin occur below the Varanger tillites in the Mackenzie Mountains; Hofmann et al., 1990.)  $\delta^{13}\text{C}$  values of carbonates in the overlying Gametrail, Blueflower, and lower Risky formations average around +2, but trend upsection to values near 0. In upper Risky and lower Ingta carbonates,  $\delta^{13}\text{C}$  values decline steeply to negative values and then rise again during the Nemakit–Daldyn interval, as described above.

A third succession which may span both the immediately post-glacial and Ediacaran time in-

tervals is the Huqf Group in Oman. In this sequence,  $\delta^{13}\text{C}$  values of limestones and shaley limestones from the siliciclastic-dominated lower half of the overlying Shuram Formation (shown most clearly in data from well MQ) start around -10 at the base of the unit (the extremely negative  $\delta^{13}\text{C}$  values are likely the result of early organic diagenesis) and then rise monotonically to values as high as +5.5 within the overlying Buah Formation (Burns and Matter, 1993; Fig. 3E). The high  $\delta^{13}\text{C}$  values are followed upsection by a plateau of values around +2 determined from dolostones of the upper Buah and Ara formations, both of which contain the shelly fossil *Cloudina* (Conway Morris et al., 1990; Knoll, unpublished observations). *Cloudina* was first described from Nama Group carbonates which, significantly, have C-isotopic compositions similar to those in the upper Buah and Ara formations. Burns and Matter (1993) accept a Rb–Sr date of  $554 \pm 10$  Ma for an ignimbrite within the Khufai Formation immediately below the Shuram Formation. If correct, this implies that the Shuram–Ara succession should correlate with the latest Neoproterozoic Nemakit–Daldyn excursion documented elsewhere. Furthermore, there must be a significant hiatus between the Khufai and glaciogenic strata of the underlying Abu Mahara Formation, and the local Nemakit–Daldyn fauna must contain *Cloudina*, but not small shelly fossils of the *Anabarites trisulcatus* zone.

We prefer an alternative interpretation in which the ignimbrite date is reset. In this interpretation, the Omani succession can be correlated as shown in Fig. 3D without necessitating unconventional assumptions about bio-, chemo-, or lithostratigraphy.

Comparable secular trends are also evident in the Khorbusuonka Group of the Olenek Uplift, northern Siberia (Fig. 3F; Knoll et al., 1995). At the base of this succession, Mastakh Formation dolostones display positive  $\delta^{13}\text{C}$  values as high as +5.5, similar to those in the Doushantuo, Zaris, Buah and Sheepbed formations. Above this, limestones of the Khatyspyt Formation, which contain Ediacaran metazoans, and overlying dolostones of the Turkut Formation yield

lying dolostones of the Turkut Formation yield values of +1 to +2 in their lower part, exhibit a minor positive excursion to ca. +3, and then gradually tail off to about 0 in the upper portion of the interval. With the exception of the mid-section excursion, this pattern approximates that seen in the Mackenzie Mountains, Namibian, Omani, and Chinese sections. As noted above, the uppermost Turkut and overlying Kessyusa formations display the sequential negative and positive isotopic excursions that mark the Proterozoic–Cambrian transition worldwide.

### 3.5. The late Cryogenian interval (~ 590–730 Ma)

At present, detailed information on secular variations in the interval between the Varanger and Sturtian ice ages is confined to studies of the Akademikerbreen and lowermost Polarisbreen groups in Spitsbergen (and their correlatives elsewhere in East Greenland and Nordaustlandet), the upper Otavi Group in Namibia, and the lower Huqf Group in Oman, with more scattered but consistent data from the Mackenzie Mountains Supergroup and other units in the North American Cordillera. As first shown by Knoll et al. (1986), this interval is characterized by a prolonged period of strongly positive  $\delta^{13}\text{C}$  values ( $> +5$  with values ranging up to +10), bounded by moderately negative  $\delta^{13}\text{C}$  values at the time of the Varanger and Sturtian ice ages (Figs. 4A–4C). The correlation of the negative C-isotopic excursion with Sturtian biogeochemical events in Svalbard and East Greenland is inferential (Sturtian tillites are not preserved there), albeit supported by available biostratigraphic and Sr-isotopic data (e.g., Asmerom et al., 1991).

There may also be a stratigraphically useful secondary structure in the Svalbard data. For example, the most positive  $\delta^{13}\text{C}$  values occur high in the section. Also, slightly negative values occur immediately beneath the lower glacial unit, and values of about +2 characterize intertillitic carbonates, rising to values of ca. +4 just below the upper tillite (Knoll et al., 1986; Fairchild and Spiro, 1987; see discussion in Fairchild and

Hambrey, 1995). Values of around +2 have also been reported from limestones of the Biri Formation that sit just beneath the single glacial diamictite (Moelv Tillite) in southern Norway (Tucker, 1985). Large acanthomorphic acritarch species in the associated Biskopås Conglomerate (Vidal, 1990) suggest that the Biri carbonates are closely related in time to the Varanger ice age.

It is possible that hiatuses in the Svalbard/East Greenland succession mask further secular variation of stratigraphic significance. For this interval, biostratigraphy does not provide the resolution needed to judge stratigraphic completeness. Necessarily, such evaluation must come from comparisons among sections. Detailed stratigraphic data from the Otavi Group, Namibia (Fig. 4D; Kaufman et al., 1991) corroborate the pattern of secular variation observed in the Arctic, and this succession contains a pre-Varanger diamictite attributed to the Sturtian ice age. A smaller data set from the Mackenzie Mountains, Canada (Fig. 4E; Narbonne et al., 1994), suggests comparable stratigraphic variation, with highly positive  $\delta^{13}\text{C}$  (+10 to +12) values in the main unit of the Keele Formation sandwiched between negative values in carbonates of the underlying (Sturtian) tillite-bearing Rapitan Group and overlying cap carbonates of the (Varanger) Ice Brook tillite (Klein and Beukes, 1993; Narbonne et al., 1994). This C-isotopic variation is also recorded in organic C, supporting interpretation of the variation as primary. Keele correlatives in the Upper Tindir Group, Yukon Territory (Young, 1982) not only contain positive  $\delta^{13}\text{C}$  values, but also large acanthomorphic acritarchs of Cryogenian aspect (Kaufman et al., 1992). Similarly, in Oman moderately positive  $\delta^{13}\text{C}$  values (up to +8) in the Kufai Formation are followed by significantly negative values in the overlying Shuram Formation (Fig. 4F; Burns and Matter, 1993); although no tillites have been documented near the Kufai/Shuram transition, this strong C-isotopic excursion likely records the climatic and paleoceanographic transition into the Varanger ice age.

In a recent study on the isotopic effects of metamorphism in Neoproterozoic carbonates of

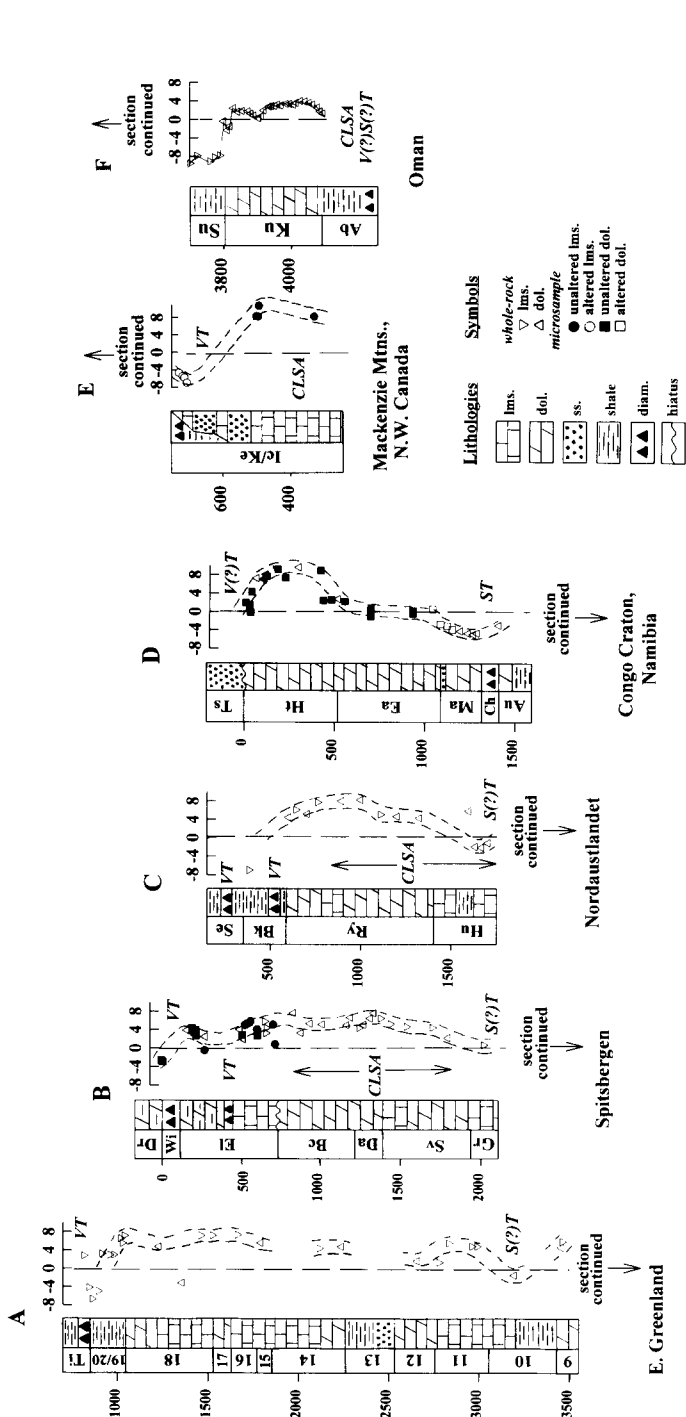


Fig. 4. Secular variations in  $\delta^{13}\text{C}$  vs. stratigraphic depth (m) for carbonates deposited in the late Cryogenian interval. (A) In East Greenland (Knoll et al., 1986). (B) In Spitsbergen (Knoll et al., 1986; Fairchild and Spiro, 1987; Kaufman et al., 1993). (C) In Nordaustlandet (Knoll et al., 1986). (D) In Namibia (Kaufman et al., 1991). (E) In the Mackenzie Mountains, Northwest Territories, Canada (Narbonne et al., 1994). (F) In Oman (Burns and Matter, 1993). General trends from our more detailed studies are shown in (A)-(E). Ranges of key biostratigraphic assemblages and approximate positions of documented or inferred Varanger- and Sturtian-age tillites in each succession are also indicated: CLSA = large acanthamorphic acritarchs of Cryogenian aspect (*Trachyhystriochosphaera/Cymatiosphaera zone*); VT = Varanger tillite; ST = Sturtian tillite. Formations: 9 = Bed 9, 10 = Bed 10, 11 = Bed 11, 12 = Bed 12, 13 = Bed 13, 14 = Bed 14, 15 = Bed 15, 16 = Bed 16, 17 = Bed 17, 18 = Bed 18, 19/20 = Bed 19/20; Tl = Tillite; Gr = Grusdievbreen; Sv = Sveanor; Au = Auros; Dr = Dracosen; Wi = Wilsonbreen; El = Elbobreen; Hl = Humberg; Ry = Rysso; Bk = Backaberget; Se = Seanoor; Ch = Chuos; Ma = Mateberg; Ea = Elandshoek; Ht = Huttenberg; Ic/Kc = Ice Brook/Keele; Ab = Abu Mahara; Ku = Khufai; Sr = Shuram.

western USA, Wickham and Peters (1993) show extremely positive  $\delta^{13}\text{C}$  values (between +10 and +14) in marbles, and argue convincingly that these values record sedimentary conditions. Even more phenomenal are values as high as +16 in carbonates from the relatively unmetamorphosed Sete Lagoas Formation in Brazil, which overlies a tillite of probable Sturtian age (Iyer et al., 1995). Although  $\delta^{13}\text{C}$  values of  $> +5$  characterize other intervals in the Neoproterozoic, Smith et al. (1994) argue that values as high as +10 and greater are confined to the interval between the Sturtian and Varanger glaciations, including carbonates in the Brigham Group that overlie the glaciogenic rocks of the Pocatello Formation in Idaho, USA.

### 3.6. *The early Cryogenian interval (~ 730–850 Ma)*

Early Cryogenian sedimentary successions for which chemostratigraphic data are available include the lower Akademikerbreen and Veteranen groups and equivalents in Spitsbergen, Nordaustlandet, and East Greenland (Knoll et al., 1986), the lower Otavi Group in Namibia (Kaufman et al., 1991), and the Shaler Group in Arctic Canada (Kaufman et al., 1990b; Asmerom et al., 1991; J.M. Hayes et al., unpublished data). Carbonates are a minor component of the Veteranen Group of Svalbard; therefore, much of our early understanding of C-isotopic variation in this interval came from analyses of organic C (see Figs. 5B and 5C where the indicated trends, shown as dashed and dotted lines, are provided by the  $\delta^{13}\text{C}$  values of organic C corrected by 28.5). We justified the use of organic C data alone because carbonate/organic C pairs analyzed throughout the entire succession show smooth covariation, and, where carbonates occur in the predominantly siliciclastic succession,  $\delta^{13}\text{C}$  matches the values predicted by the general organic C curve and a constant  $\Delta\delta$ . In Svalbard, the  $^{13}\text{C}$  depletion already noted at the time of the Sturtian glaciation is preceded by an interval of strong and then moderate C-isotopic enrichment ( $\delta^{13}\text{C}$  values as high as +7 have been noted), which, in turn, is preceded by yet another excursion

to negative  $\delta^{13}\text{C}$  values (Figs. 5A–5C). It is postulated that this negative excursion may represent a third period of Neoproterozoic glaciation; however, no direct stratigraphic association of pre-Sturtian tillite and the isotopic event has been documented.

The data from Namibia and northwestern Canada provide independent corroboration of strong C-isotopic variations during the early Cryogenian interval. In the lower Otavi Group, most carbonates below the inferred Sturtian diamictite are enriched in  $^{13}\text{C}$  by 2 to 6‰ relative to PDB, although one sample from immediately below the diamictite has a  $\delta^{13}\text{C}$  value of  $-3$  (Fig. 5D), similar to values recorded in carbonates immediately above the glacial horizon (Kaufman et al., 1991). Carbon-isotopic variations in Shaler Group carbonates also reflect those established for the early Cryogenian interval in Svalbard (Fig. 5E). In fact, four separate features of the isotope curves can be correlated including: (1) basal  $\delta^{13}\text{C}$  values near zero, (2) an interval of  $\delta^{13}\text{C}$  values between +3 and +4, (3) a  $\delta^{13}\text{C}$  peak of ca. +6, and, at the top of the succession (4) a significant negative excursion (Kaufman et al., 1990b; J.M. Hayes et al., unpublished data).

Acritarchs and Sr-isotopic data support C-isotopic correlations between the Shaler Group and succession in Svalbard (Asmerom et al., 1991).  $^{87}\text{Sr}/^{86}\text{Sr}$  values for the upper part of the Shaler Group (Wynniatt Formation) match those of the lower Akademikerbreen Group (ca. 0.7068), and below these,  $^{87}\text{Sr}/^{86}\text{Sr}$  values show a smooth and systematic decline to a remarkably low value of 0.7056 at the top of the Reynolds Point Formation.

### 3.7. *Summary of chemostratigraphic correlations*

Fig. 6 presents a generalized  $\delta^{13}\text{C}$  curve from ~ 850 Ma to the beginning of the Cambrian, synthesized from all analyzed successions. The known record of Sr-isotopic variations through this interval (Asmerom et al., 1991; Kaufman et al., 1993) and the biostratigraphic ranges of key fossil assemblages are also shown. For the two post-Varanger intervals described above, data

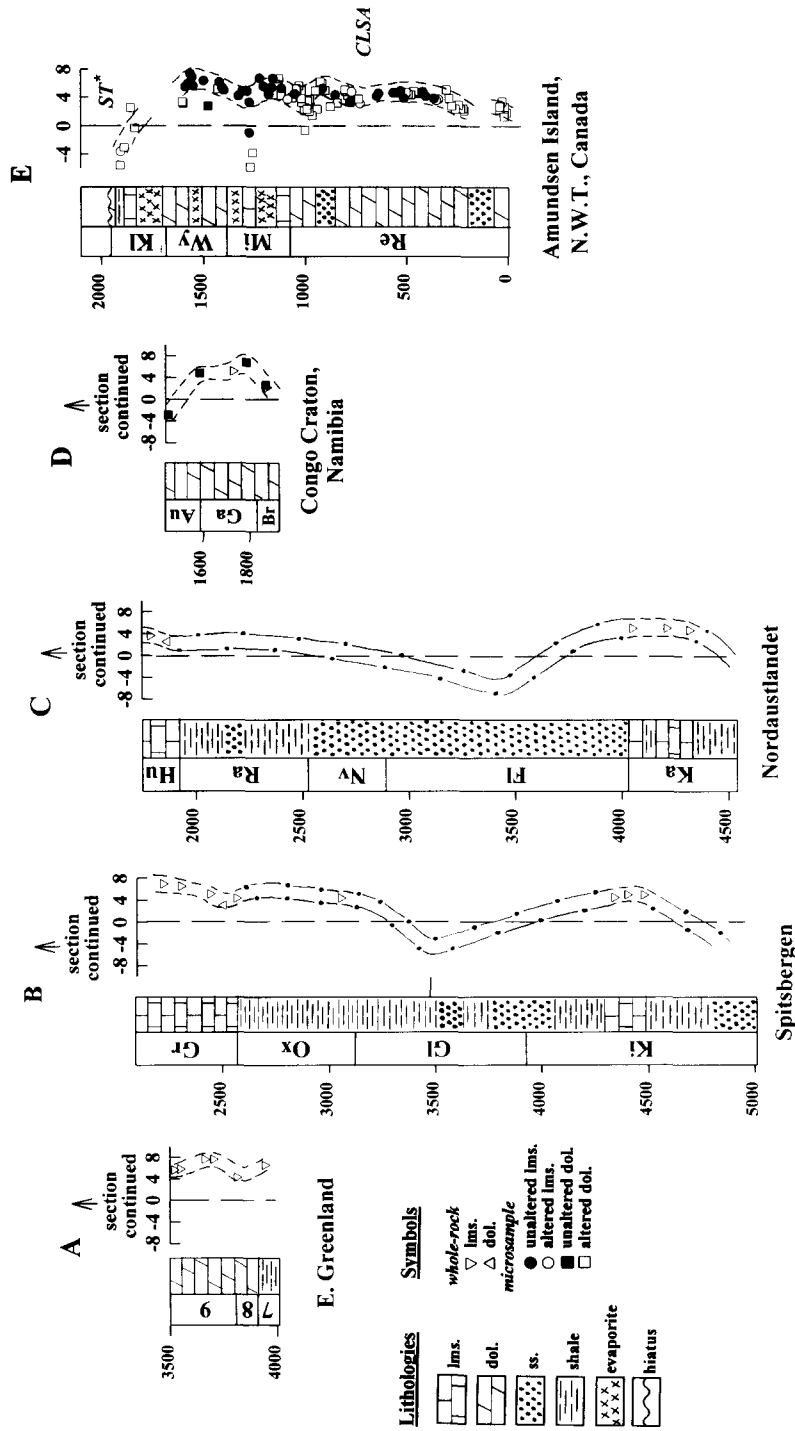


Fig. 5. Secular variations in  $\delta^{13}\text{C}$  vs. stratigraphic depth (m) for carbonates deposited in the early Cryogenian interval. (A) In East Greenland (Knoll et al., 1986). (B) In Spitsbergen (Knoll et al., 1986; Fairchild and Spiro, 1987; Kaufman et al., 1993). (C) In Nordaustlandet (Knoll et al., 1986). (D) In Namibia (Kaufman et al., 1991). (E) In Victoria Island, North West Territories, Canada (J.M. Hayes et al., unpubl. data); asterisk denotes that Sturtian tillites do not occur on Victoria Island but have been correlated with units immediately above the Kilian Formation. General trends from our more detailed studies are shown in all successions, but in (B) and (C) the trends are augmented by secular variations in the isotopic composition of organic C. Ranges of key biostratigraphic assemblages and approximate positions of Cryogenian aspect (*Trachytrichosphaera/Cymatospaera* zone); *ST* = Sturtian tillite. Formations: 7 = Bed 7; 8 = Bed 8; 9 = Bed 9; *Ki* = Kingreen; *Gl* = Glasgowbreen; *Ox* = Oxfordbreen; *Gr* = Grusdievbreen; *Ka* = Kapp Lord; *Fl* = Flora; *Nv* = Norvik; *Ra* = Raudstup/Salodd; *Hu* = Hunnberg; *Br* = Berg Aukas; *Ga* = Gauss; *Au* = Auros; *Re* = Reynolds Point; *Mi* = Minto Inlet; *Wy* = Wynniatt; *Kl* = Kilian.



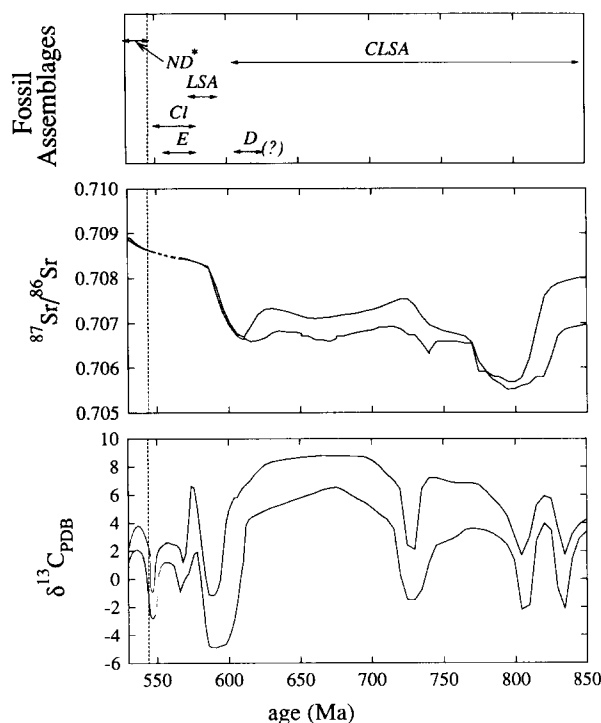


Fig. 6. Estimated ranges of fossil assemblages, secular variations in  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{13}\text{C}$  in Neoproterozoic to basal Cambrian carbonates ( $\sim 850$ – $530$  Ma). See previous figure captions for information on abbreviations of fossil assemblages. *D* = disc-shaped fossils of possible metazoan origin found in pre-Varanger sediments of the Mackenzie Mountains, Canada; asterisks denotes that a few SSFs of Nemakit–Daldyn aspect appear below the initial boundary of the stage (see Knoll et al., 1995).

strongly suggest that interbasinal correlations at the level of formation are feasible. For example, the peak values of  $\delta^{13}\text{C}$  in Ediacaran-aged carbonates support the direct correlation of the Doushantuo, Zaris, Sheepbed, Buah and Mastakh formations (Fig. 3). In some cases even finer resolution may be possible: second-order secular variations noted in the Nemakit–Daldyn interval in Morocco (Magaritz et al., 1991). India (Aharon et al., 1987; Aharon and Liew, 1992), and both southern and northern Siberia (Magaritz et al., 1986; Adams, 1993) may be correlative (Fig. 2). Formation-level correlations may also be possible for parts of the Cryogenian, particularly at extremes in the  $\delta^{13}\text{C}$  curve. However, given the small number of com-

parative studies and currently low biostratigraphic resolution, confidence in detailed correlations is lower for this interval. It is quite possible that the full range of secular variations has not yet been determined for the Cryogenian Period.

At present, the following generalization appears to hold. Where biostratigraphic and/or radiometric data are absent, interpretation of chemostratigraphic data can be problematic. However, where biostratigraphic data constrain interpretation, secular variations in C and Sr isotopes can provide a level of stratigraphic resolution exceeding that provided by fossils alone.

#### 4. Biogeochemical implications

The strongly positive  $\delta^{13}\text{C}$  values of many Neoproterozoic carbonates suggest that for much of this interval an unusually high proportion of the sedimentary C flux from the oceans was organic matter (Knoll et al., 1986). Controls on organic C burial are controversial, even for the modern ocean, although most students accept that in the modern oceans burial fluxes of organic matter are positively correlated with total sedimentation rate (Berner, 1989). There is, however, little reason to invoke extraordinarily high rates of total sedimentation during much of the Neoproterozoic Era, and Derry et al. (1992) have interpreted Sr-isotopic data to indicate just the reverse: that during the Cryogenian, at least, total erosional flux to the oceans was low. In this interpretation, high proportional rates of organic C burial during the Cryogenian were not associated with high absolute rates of burial. The high proportional rates of organic C burial must then be related to unusual fluxes of reductants into the oceans, presumably via volcanoes and/or hydrothermal ridges; the Cryogenian Sr-isotopic record is consistent with such a hypothesis. As an alternative end-member hypothesis, one could posit that Cryogenian erosional fluxes into the oceans were similar to modern values, but this would necessitate truly extraordinary hydrothermal activity to produce the low  $^{87}\text{Sr}/^{86}\text{Sr}$  values recorded in Cryogenian carbonates. In either

case, and for all intermediate hypotheses, hydrothermal and/or volcanic input of reduced gases and metals accounts for the pattern of organic C burial inferred from C-isotopes, while simultaneously preventing a consequent increase in  $p_{O_2}$ . Cryogenian oceans may have been stratified, with anoxic deep water depleted in  $^{13}C$  relative to surface water masses.

Negative excursions punctuate the Cryogenian C isotope record. In sections containing glaciogenic rocks, these excursions are invariably associated stratigraphically with evidence of continental glaciation, and it is possible that all observed excursions correlate with Neoproterozoic ice ages. Possible causal mechanisms include the breakdown of stratification and mixing of  $^{13}C$ -depleted deep water into the surface ocean, the erosion of organic-rich rocks exposed during low sea-level stands, and a mixing-related reduction in the proportional burial of organic C (Kaufman et al., 1991). These mechanisms are consistent with the additional stratigraphic association of Neoproterozoic tillites with iron-formation (Young, 1976), and, quite possibly, all contributed to the observed pattern of C isotopes.

High proportional rates of organic C burial returned following the post-Varanger negative excursion, but during this interval, seawater  $^{87}Sr/^{86}Sr$  was high. Derry et al. (1992) interpreted the Sr-isotopic record, combined with limited data on secular variations in the Nd-isotopic composition of Neoproterozoic to Cambrian seawater, to indicate a strong increase in rates of continental erosion, ascribed to Pan-African uplift (see also Asmerom et al., 1991; Kaufman et al., 1993). The post-Varanger C isotope peak would, therefore, have been a time of high absolute global rates of organic C burial associated with high levels of primary productivity and high rates of total sedimentation. In consequence,  $p_{O_2}$  would likely have increased substantially. If one accepts the alternate end member hypothesis of invariant erosion rates during the Neoproterozoic, then the sharp post-Varanger increase in  $^{87}Sr/^{86}Sr$  must be interpreted in terms of a dramatic decline in oceanic hydrothermal activity, once again with increased  $p_{O_2}$  the likely result.

The point is that given the empirical records of C- and Sr-isotopic variation, post-Varanger  $p_{O_2}$  is the predicted outcome of biogeochemical models under a wide range of model assumptions. Limited data on seawater  $\delta^{34}S$  for this interval suggest that an approximately contemporaneous shift in the oceanic S cycle would have exacerbated rather than counterbalanced this change (Knoll, 1991; Ross et al., 1991).

In this respect, it is significant that the first appearance of diverse Ediacaran metazoans occurs in sediments that document the post-Varanger C-isotopic rise. In the absence of well-developed circulatory systems, early macroscopic animals would have required high  $O_2$  concentrations in ambient waters (Runnegar, 1982), providing a plausible physiological link between atmospheric change and evolution (Knoll, 1991). After rising sharply, perhaps to present-day or greater concentrations (Derry et al., 1992; Kaufman et al., 1993),  $p_{O_2}$  may subsequently have decreased as global erosion rates subsided into the Cambrian; this provides a speculative but plausible mechanism by which those elements of the Ediacaran biota that were dependent on diffusion for the oxygenation of tissues, could have become extinct while small animals that had evolved circulatory and respiratory sophistication survived to populate the Cambrian seas.<sup>1</sup>

## 5. Conclusions

The recent proliferation of stratigraphically detailed C isotope studies in Neoproterozoic successions documents secular variations in the Neoproterozoic C cycle that are remarkable on

<sup>1</sup>In the modern ocean the coupling of high productivity with low rates of deep ocean ventilation will result in phosphorus starvation as P-rich organic matter rains out of the mixed layer, predominantly as fecal pellets. In the absence of widespread metazoans, it is reasonable to suggest that P was cycled differently in Neoproterozoic oceans. Particulate organic matter falling slowly through the water column may have been stripped of its nutrients by bacteria before it left the photic zone, resulting in the rapid remineralization of P in oxygenated surface waters (necessary to sustain primary productivity) while refractory organic C descended into the deep ocean and sediments.

the scale of the last 2000 Ma. Because of their magnitude, repeated variation, and fidelity of preservation, C isotopes provide chronostratigraphic tools that are being integrated with paleontological and other isotopic (Sr, S) data to yield a new framework for the interbasinal correlation of later Neoproterozoic successions. For the post-Varanger and Proterozoic/Cambrian boundary intervals, the principal patterns of variation appear to have been documented, but much work is needed to bring the Cryogenian record to a comparable level.

The prolonged intervals of marked  $^{13}\text{C}$  enrichment in later Neoproterozoic carbonates and organic C, and the magnitude of the isotopic excursions that bracket these intervals require an unusual combination of paleoceanographic and paleoclimatic events. Independent and stratigraphically correlative evidence for the required conditions comes from the Sr-isotopic record and the sedimentary records of glaciogenic rocks and iron-formation. In a practical vein, C isotopes highlight the hydrocarbon potential of Neoproterozoic, especially post-Varanger, successions. As yet, there is no consensus on the mechanisms that produced this extraordinary biogeochemical record, but it can hardly be doubted that the combined geochemical and sedimentary data document first-order events in the history of Earth's surface environment.

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### Appendix

A Jandel Scientific SigmaPlot computer file including the stratigraphic depth and  $\delta^{13}\text{C}$  composition of all samples used in this compilation, as well as disk copies of the figures, is available from the authors. Please send a formatted 1.44 Mbyte 3.5" floppy disk with all requests. A number of the stratigraphic curves were digitized from original figures using a digitizing pad and Jandel Scientific SigmaScan. This effort resulted in minor uncertainties in the true position and isotopic composition of individual samples. However, the relative position and isotopic composition of samples were preserved in all cases.

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