

Review article

Chemostratigraphy of Neoproterozoic carbonates: implications for 'blind dating'

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ABSTRACT

The $\delta^{13}\text{C}_{\text{carb}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ secular variations in Neoproterozoic seawater have been used for the purpose of 'isotope stratigraphy' but there are a number of problems that can preclude its routine use. In particular, it cannot be used with confidence for 'blind dating'. The compilation of isotopic data on carbonate rocks reveals a high level of inconsistency between various carbon isotope age curves constructed for Neoproterozoic seawater, caused by a relatively high frequency of both global and local $\delta^{13}\text{C}_{\text{carb}}$ fluctuations combined with few reliable age determinations. Further complication is caused by the unresolved problem as to whether two or four glaciations, and

associated negative $\delta^{13}\text{C}_{\text{carb}}$ excursions, can be reliably documented. Carbon isotope stratigraphy cannot be used alone for geological correlation and 'blind dating'. Strontium isotope stratigraphy is a more reliable and precise tool for stratigraphic correlations and indirect age determinations. Combining strontium and carbon isotope stratigraphy, several discrete ages within the 590–544 Myr interval, and two age-groups at 660–610 and 740–690 Myr can be resolved.

Terra Nova, 13, 1–11, 2001

Introduction

Over the last few decades, Neoproterozoic sedimentary formations have been investigated intensively for carbon, oxygen, sulphur and strontium isotope ratios. These studies were motivated by several reasons, among which deciphering the composition of ancient seawater and the search for regional stratigraphic correlations were of great importance. A substantial database has been created, leading to the reconstruction of temporal trends in the carbon and strontium isotopic composition of Neoproterozoic seawater. One result suggests that whereas the elemental composition of seawater appears to have changed little during the past 545 Myr (Holland, 1984), the isotopic composition of carbon, oxygen, sulphur and strontium in seawater has varied significantly through this interval (Kaufman and Knoll, 1995). The present authors find these two statements somewhat internally inconsistent, as both elemental and isotopic compositions should be closely linked via, and

controlled by, the same tectonic and biogeochemical changes. However, the elemental composition of seawater does not concern us here.

A second result was the demonstration that carbon and strontium isotope signatures in Neoproterozoic carbonate sequences can serve as important tools for both regional and global correlations (Table 1). Recently, the temporal isotopic trends of Neoproterozoic seawater have been applied for age determination and correlations of Neoproterozoic carbonate sequences of the Una Group, Irece Basin, Brasil (Misi and Veizer, 1998) and for indirect age determinations of nonfossiliferous, medium- to high-grade marbles in the Norwegian Caledonides (Trønnes and Sundvoll, 1995; Melezhik *et al.*, 1997). These age assessments of the Caledonian marbles constituted a 'blind dating' since no additional stratigraphic controls were available. During these Norwegian studies several problems were experienced that are addressed further here. The main objective of this article is not to resolve these problems, nor to contribute a significant amount of new data, but rather to highlight some obstacles in the practical application of carbon and strontium isotope chemostratigraphy in the Neoproterozoic.

Temporal trends of carbon isotopes

Since Knoll and Walter (1992) and Derry *et al.* (1992) constructed the first $\delta^{13}\text{C}_{\text{carb}}$ age curve for the Neoproterozoic–early Cambrian time interval, at least seven other reference curves covering various time intervals of the Neoproterozoic have been presented (Fig. 1a). It is readily apparent that when the different age curves are plotted together they produce a rather confusing pattern. Below, this complication is considered in terms of (i) the age of rocks, (ii) the age of articles, and (iii) possible spatial and temporal isotopic fluctuations in dissolved inorganic carbon at any given time.

Inconsistencies related to the age of rocks

The time interval reviewed in this article, 544–850 Ma, may be separated into three sections characterized by: (i) no agreement (except two points of convergence) between $\delta^{13}\text{C}_{\text{carb}}$ age curves published by different authors (interval 675–850 Ma); (ii) a relatively high degree of agreement [interval *c.* 610–675 Ma, Walter *et al.* (2000) data are excluded]; and (iii) a very low level of agreement (interval 544–610 Ma).

It is obvious (Fig. 1) that the degree of coincidence between different

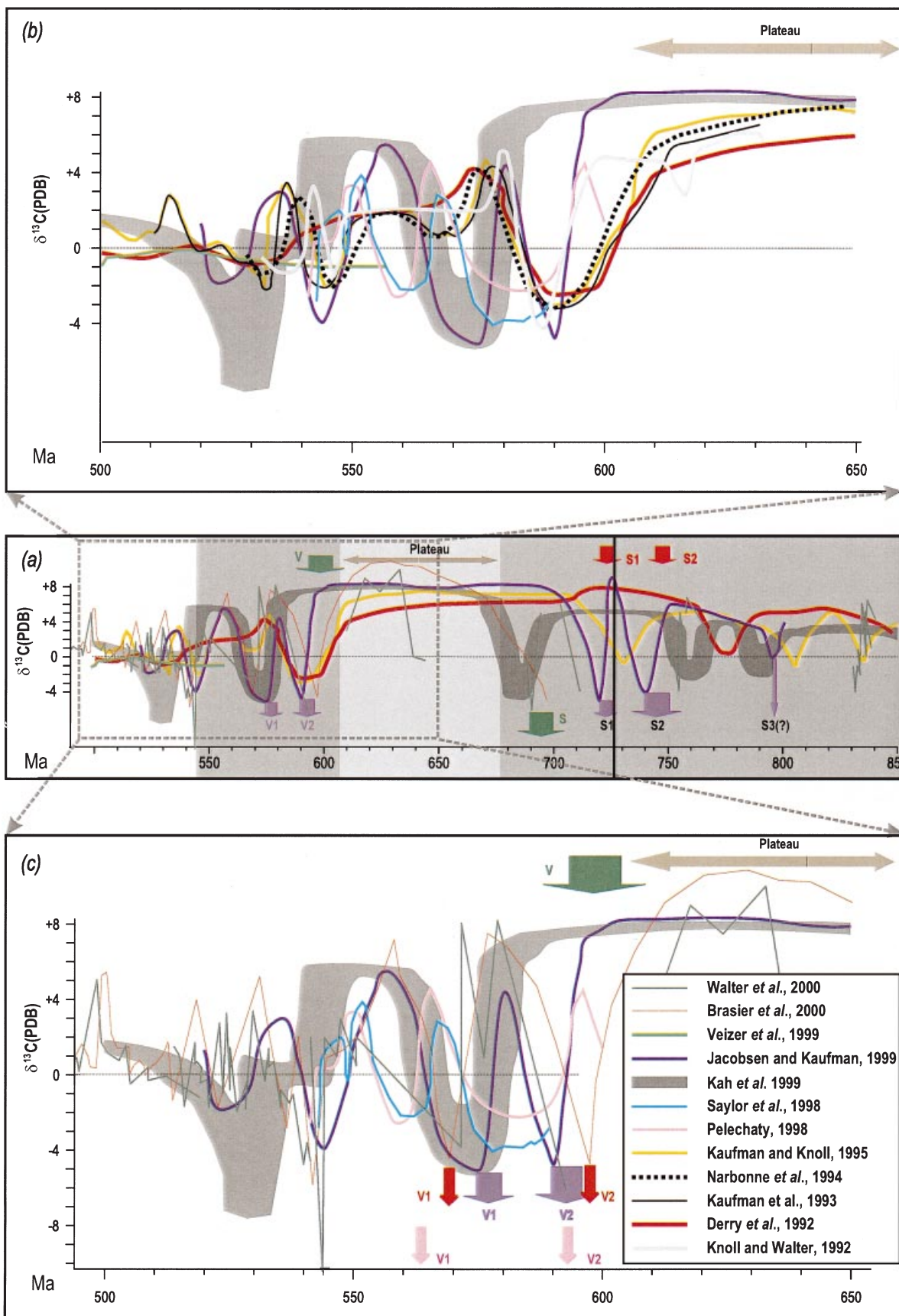
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Table 1 List of references to the work with contributions to carbon and strontium isotope signatures in Neoproterozoic carbonate sequences

Author(s)	Area of study	Time interval
Pre-1996 studies with limited reliable age constraints		
Veizer <i>et al.</i> (1983)	Africa and Australia	1000–600 Ma
Knoll <i>et al.</i> (1986)	Svalbard and E. Greenland	900–550 Ma
Magaritz <i>et al.</i> (1986)	Siberian Platform	PC/C*
Tucker (1986a)	S. Morocco	PC/C
Aharon <i>et al.</i> (1987)	Lesser Himalaya	PC/C
Lambert <i>et al.</i> (1987)	Yangtze Platform	PC/C
Magaritz (1989)	S. Siberia	PC/C
Derry <i>et al.</i> (1989)	Svalbard and E. Greenland	Upper Proterozoic
Fairchild <i>et al.</i> (1990)	Mauritania	Neoproterozoic
Kaufman <i>et al.</i> (1991)	NW. Canada	780–620 Ma
Kirschvink <i>et al.</i> (1991)	Siberia, Morocco and S. China	PC/C
Asmeron <i>et al.</i> (1991)		
Pokrovsky and Vinogradov (1991)	Central Siberia	Upper Proterozoic
Aharon and Liew (1992)	Compilation	PC/C
Brasier (1992)	SE. Newfoundland and England	Early Cambrian
Derry <i>et al.</i> (1992)	Namibia, Svalbard, E. Greenland and Central Australia	900–540 Ma
Kaufman <i>et al.</i> (1992)	NW. Canada	1000–540 Ma
Knoll and Walter (1992)	Compilation	630–500 Ma
Brasier <i>et al.</i> (1993)	Siberia	PC/C
Kaufman <i>et al.</i> (1993)	Namibia, Svalbard, East Greenland and Arctic Canada	610–540 Ma
Pokrovsky and Gertsev (1993)	S. Central Siberia	PC/C
Pokrovsky and Missarzhevsky (1993)	Central Siberia	PC/C
Wickham and Peters (1993)	W. North America	770–540 Ma
Corsetti and Kaufman (1994)	E. California and W. Nevada	PC/C
Brasier <i>et al.</i> (1994a,b)	Siberia	Lower Cambrian
Narbonne <i>et al.</i> (1994)	NW. Canada	Neoproterozoic
Smith <i>et al.</i> (1994)	Idaho, USA	Neoproterozoic
Wang <i>et al.</i> (1994)	NW. China	PC/C
Kaufman and Knoll (1995)	Compilation	Neoproterozoic
Knoll <i>et al.</i> (1995a,b,c)	NW. Siberia	(a) 1600–1200 Ma, (b), (c) PC/C
Post-1996 studies		
Kaufman <i>et al.</i> (1996)	N. Siberia	PC/C
Kennedy (1996)	Australia	Ca. 600 Ma
Banerjee <i>et al.</i> (1997)	India	PC/C
Kaufman <i>et al.</i> (1997)	Compilation	PC/C
Kimura <i>et al.</i> (1997)	N. Iran	PC/C
Shields <i>et al.</i> (1997)	W. Mongolia	750–545 Ma
Bartley <i>et al.</i> (1998)	NW. Siberian Platform	PC/C
Calver (1998)	Tasmania	650–545 Ma
Hofmann <i>et al.</i> (1998)	Compilation	Neoproterozoic
Kah <i>et al.</i> (1998)	Canada	1270–723 Ma
Kennedy <i>et al.</i> (1998)	Congo craton	750–570 Ma
Pelechaty (1998)	Siberia	565–545 Ma
Saylor <i>et al.</i> (1998)	Southern Namibia	548–543 Ma
Jacobsen and Kaufman (1999)	Compilation	Neoproterozoic
Calver (2000)	Australia	Neoproterozoic III
Hill and Walter (2000)	Australia	~ 830–750 Ma
Walter <i>et al.</i> (2000)	Canada and Australia	840–544 Ma

*PC/C – Precambrian/Cambrian boundary.

Fig. 1 $\delta^{13}\text{C}_{\text{carb}}$ reference curves for Neoproterozoic seawater. The reference curves representing time interval (a) 850–500 Ma, (b) 650–500 Ma, all data, and (c) 650–500 Ma, only data published after 1996. Blue arrows indicate age positions of the early (S3), middle (S2), and late (S1) Sturtian glaciations as well as of the early (V2), and late (V1) Varangerian glaciations by Jacobsen and Kaufman (1999). Pink arrows indicate age positions of the early (V2), and late (V1) Varangerian glaciations by Pelechaty (1998). Red arrows indicate age positions of the early (S2) and late (S1) Sturtian glaciations as well as of the early (V2) and late (V1) Varangerian glaciations by Brasier *et al.* (2000). Green arrows indicate age positions of the Sturtian–Rapitan (V) and Marinoan–Varangerian (V) glaciations by Walter *et al.* (2000).



age- $\delta^{13}\text{C}_{\text{carb}}$ curves depends on two major factors: (i) the availability of reliable age determinations, and (ii) the frequency of $\delta^{13}\text{C}_{\text{carb}}$ fluctuations. A high level of disagreement for the time interval of 675–850 Ma has apparently been caused by a relatively high frequency of $\delta^{13}\text{C}_{\text{carb}}$ fluctuations (Fig. 1a) combined with but few reliable U–Pb age determinations. One age is 746 ± 2 Myr obtained on zircons for the Lower Naauwpoort Formation in the northern Damara Belt, Namibia (Hoffman *et al.*, 1996), which has been assumed to be a maximum age for the Sturtian–Rapitan (as defined by Young, 1995) glacial deposits. Another U–Pb age of 723 ± 3 Myr for baddeleyite from the rocks overlying the Shaler Group, Canada (Heaman *et al.*, 1992) establishes a minimum age constraint for one of the negative $\delta^{13}\text{C}_{\text{carb}}$ excursions (Jacobsen and Kaufman, 1999). In addition, a U–Pb age of 777 ± 7 Myr obtained from volcanites at or near the base of the Burra Group from the Adelaide Geosyncline in South Australia (Preiss, 2000) has been used to constrain the age of the Skilogalee Dolomite (Hill and Walter, 2000). The limited number of age determinations results in a high degree of inconsis-

tency among different curves. Consequently, three(?) negative $\delta^{13}\text{C}_{\text{carb}}$ excursions reported from the time interval 675–850 Ma (e.g. Kaufman and Knoll, 1995) have been assigned to different ages (Fig. 1a). As all these negative carbon isotope excursions have been tightly connected to post-glacial events, it follows that their age is completely dependent on the age constraints of the Sturtian glaci-ation(s). However, ongoing debates [Kaufman *et al.* (1997) and Hoffman *et al.* (1998) vs. Kennedy *et al.* (1998) and Prave (1999)] have demonstrated that it is unclear whether there was one or three glaciations around Sturtian time. Consequently, one should demonstrate not only exact ages for the Sturtian glaci-ation(s), but also prove that there were three negative $\delta^{13}\text{C}_{\text{carb}}$ excursions, and not one. Such an attempt has been made by Brasier *et al.* (2000), who reported two new ages, $723 + 16/-10$ and 544 ± 3.3 Myr, from Oman. The first was assigned to a Sturtian age. Brasier *et al.* (2000; p. 178) reported that ‘the revised chronology confirms four negative $\delta^{13}\text{C}$ excursions between c. 723 and 543 Ma, of which the lower two are associated with glaciations’. Thus, the date of the Sturtian glaci-ation

($723 + 16/-10$ Ma; Brasier *et al.* 2000) has been refined. The latest research on and correlation between Canadian and Australian Neoproterozoic sequences (Walter *et al.*, 2000) has revealed only two major glaci-ations, namely Sturtian (Rapitan glaci-als) at about 700 Ma, and Marinoan (Ice Brook glaci-als) at around 600 Ma; a possible minor glaci-ation at 570 Ma has been recognized.

The section of convergence, or a ‘plateau’, placed between c. 610 and 675 Ma, initially appears to be firmly established, though conflicting with the curve reported by Walter *et al.* (2000). However, this ‘isotopic plateau’ has not yet been supported by any reliable age determinations. Consequently, the younger and particularly the older age limit for this section of convergence still require definition (Fig. 1a).

The younger Neoproterozoic section (between 544 and 610 Ma; Fig. 1b) has been supported by two reliable U–Pb date determinations on zircons: 543.9 ± 1 Ma for the Precambrian/Cambrian boundary and 548.8 ± 1 Ma for a late Vendian, postglacial, positive $\delta^{13}\text{C}_{\text{carb}}$ excursion and first global appearance of Ediacaran fossils (Bowring *et al.*, 1993;

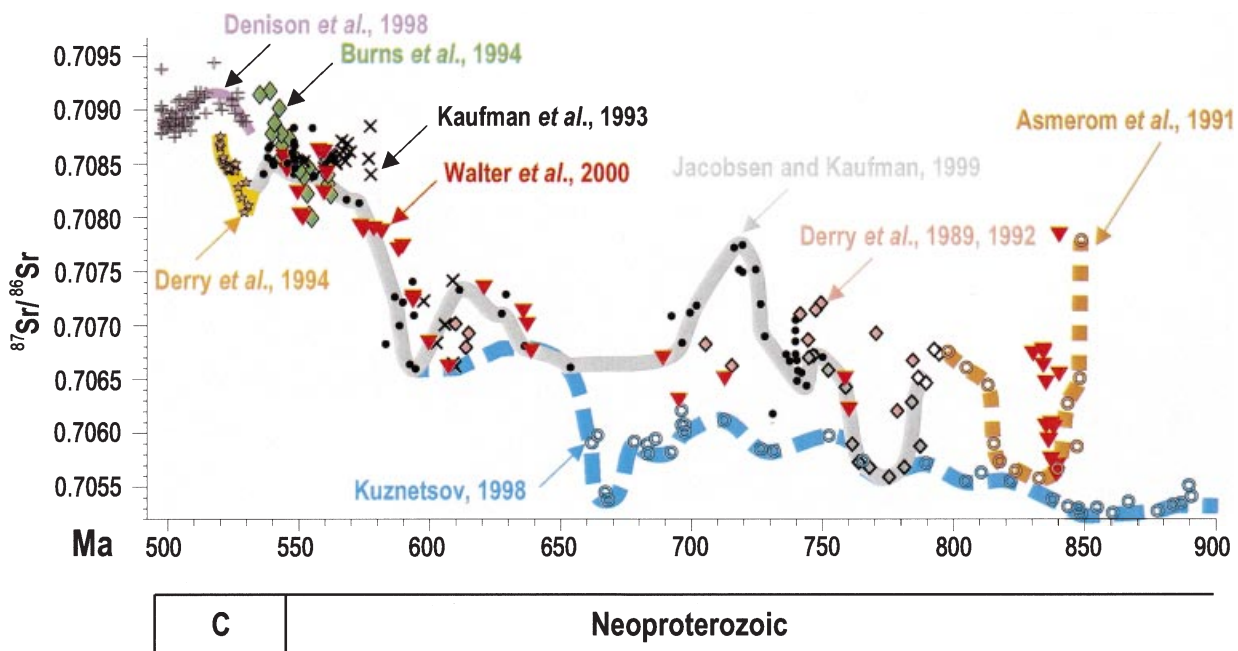


Fig. 2 Temporal variations of $^{87}\text{Sr}/^{86}\text{Sr}$ in Neoproterozoic carbonates. Sources of data: Asmerom *et al.* (1991), Burns *et al.* (1994), Denison *et al.* (1998), Derry *et al.* (1989, 1992, 1994), Jacobsen and Kaufman (1999), Kaufman *et al.* (1993), Kuznetsov (1998), Walter *et al.* (2000).

Grotzinger *et al.*, 1995). A series of studies has demonstrated the presence of three negative $\delta^{13}\text{C}_{\text{carb}}$ excursions occurring sometime between 544 and 610 Ma (Fig. 1b). However, there is a very low level of agreement on age constraints amongst various papers. The problem of whether there was one or three negative $\delta^{13}\text{C}_{\text{carb}}$ excursions, separated by a series of returns to highly positive $\delta^{13}\text{C}_{\text{carb}}$ values, return us to the number of glacial episodes: three (e.g. Hoffman *et al.*, 1998) or only one (e.g. Kennedy *et al.*, 1998; Prave, 1999). The result of this debate is a very confusing age- $\delta^{13}\text{C}_{\text{carb}}$ curve pattern as illustrated by Fig. 1(b).

Finally, considering the number of glaciations, it is worth pointing out that the only evidence for multiple glaciations is from chemostratigraphy. There is no rock sequence bearing robust evidence for more than two total Neoproterozoic glaciations (e.g. Kennedy *et al.*, 1998; Prave, 1999; Condon and Prave, 2000).

Inconsistencies related to the time of investigations

Articles devoted to $\delta^{13}\text{C}_{\text{carb}}$ reference curves may be separated into two groups. The first group, including all studies performed prior to 1996 (Table 1), should be considered as less reliable, as the reference $\delta^{13}\text{C}_{\text{carb}}$ curves were characterized by poor age constraints. The first reliable age constraints for the time interval of 544–850 Ma were obtained in 1993–96 (Heaman *et al.*, 1992; Bowring *et al.*, 1993; Grotzinger *et al.*, 1995; Hoffman *et al.*, 1996). Consequently, the second group of papers, published after 1996 (Table 1), might be expected to show more agreement. However, this latter group actually shows very few points of convergence between various $\delta^{13}\text{C}_{\text{carb}}$ curves (Fig. 1a,c). The reference $\delta^{13}\text{C}_{\text{carb}}$ curve for 550–580 and 600–670 Ma (Fig. 1), reported by Kah *et al.* (1998), perfectly matches the curve appearing in Jacobsen and Kaufman (1999). However, these two curves are totally in conflict between 670 and 800 Ma (Fig. 1). As they were based essentially on the same database, it is not possible, at this stage, to account for the discrepancy. Two other reference $\delta^{13}\text{C}_{\text{carb}}$ curves generated for 540–

590 Ma – one by Pelechaty (1998), and the other by Saylor *et al.* (1998) – exhibit good agreement (Fig. 1c). However, both of them conflict with the interpretation of Jacobsen and Kaufman (1999) and Kah *et al.* (1998). This kind of discrepancy leads us again to the problem of Neoproterozoic glaciations. It can be exemplified by the disagreement between Jacobsen and Kaufman's (1999) interpretation, on the one hand, and the data reported by Pelechaty (1998), on the other hand. Different age assignments to the younger Varangerian glaciation in these two contributions (Fig. 1c) are automatically reflected in a 20-Myr-shift for one of the negative $\delta^{13}\text{C}_{\text{carb}}$ excursions.

Inconsistencies related to spatial and temporal isotopic fluctuations in dissolved inorganic carbon

Particularly problematical, and addressed by Veizer (e.g. Misi and Veizer, 1998; Veizer *et al.*, 1999), are the complex and unclear reasons for the quite large variations in $\delta^{13}\text{C}_{\text{carb}}$ at any given time. In the Phanerozoic, and even today, $\delta^{13}\text{C}_{\text{carb}}$ fluctuates by the order of 5‰ (Veizer *et al.*, 1999). This important fact has apparently rarely been considered as a potential cause for the discrepancies observed in the Neoproterozoic database. For instance, the section of convergence, or the 610–670 Ma isotopic plateau, exhibits no internal, age-related fluctuations of $\delta^{13}\text{C}_{\text{carb}}$. However, the upper $\delta^{13}\text{C}_{\text{carb}}$ limit of the section has changed (Fig. 1a) from +6‰ (Derry *et al.*, 1992) to +7.5‰ (Kaufman and Knoll, 1995) through +8.5‰ (Jacobsen and Kaufman, 1999) to c. +12‰ (Brasier *et al.*, 2000). This could well be caused by a spatial isotopic variation in dissolved inorganic carbon influenced by local factors. Consequently, the global seawater $\delta^{13}\text{C}_{\text{carb}}$ value, equilibrated with atmospheric CO_2 , might not yet have been unambiguously established.

Another example is the remarkably variable magnitude of both negative and positive $\delta^{13}\text{C}_{\text{carb}}$ excursions, as evident from the comparison of different databases. For instance, the negative $\delta^{13}\text{C}_{\text{carb}}$ excursion occurring at the post-earlier Varangerian ice age has been estimated at –2.5‰ (Derry *et al.*, 1992; Pelechaty, 1998), –3‰

(Kaufman and Knoll, 1995), –4‰ (Saylor *et al.*, 1998), and –5‰ (Jacobsen and Kaufman, 1999). Pokrovsky and Gertsev (1993) have even reported $\delta^{13}\text{C}_{\text{carb}}$ as low as –8 to –10‰. The latter values were obtained from a 250–1000 m-thick, well-preserved carbonate formation developed over a distance of 1000 km. All these inconsistencies might well be caused by local isotopic variations in dissolved inorganic carbon, and therefore the representative global $\delta^{13}\text{C}$ values remain unclear. Moreover, the problem of stratigraphic applications of strong, basin-wide ^{13}C depletion recorded in marine carbonates has been discussed in detail by Calver (2000). Based on a study of the Adelaide Rift Complex in Australia, he concluded that ‘the strong overprint of stratification on both organic and carbonate $\delta^{13}\text{C}$ stratigraphy needs to be recognized before global correlation... can be attempted’ (Calver, 2000, p. 140). He also argued that $\delta^{13}\text{C}_{\text{carb}}$ values (ranging from –3 to –10‰) obtained from the Wonoka Formation do not mirror a global seawater signal. Yet, $\delta^{13}\text{C}_{\text{carb}}$ of –10.5‰ appeared in a compilation by Walter *et al.* (2000; Fig. 29, p. 414) as a marine $\delta^{13}\text{C}_{\text{carb}}$ at 545 Ma.

A series of $\delta^{13}\text{C}_{\text{carb}}$ negative shifts could be advantageous in carbon isotope stratigraphy, providing a potential tool for detailed stratigraphic correlations. However, all puzzling aspects of the Neoproterozoic negative $\delta^{13}\text{C}$ excursions are compounded by the enigmatic nature of postglacial ‘cap carbonates’ (Walter and Bauld, 1983; Tucker, 1986b; Singh, 1987; Fairchild, 1993). With the existing lack of consensus on the nature of the Neoproterozoic cap carbonates, the stratigraphic implication of $\delta^{13}\text{C}_{\text{carb}}$ negative shifts is largely a matter of debate.

Grotzinger and Knoll (1995) suggested an interesting interpretation: the postglacial cap dolostones and limestones in the Neoproterozoic might well be related to an early stage of overturn of the stratified ocean. They suggested further that the carbonates were associated with the upwelling of deep, anoxic, ^{13}C -depleted, HCO_3 -saturated water supplemented by that from perpetually Ca- and Mg-supersaturated shallow water. Several consequences follow. First, although upwelling of deep water was a

large-scale phenomenon it was not a global one. There must have been vast shelf zones, inter- and intracontinental seas which were not affected by the deep, anoxic, ^{13}C -depleted, upwelled water. Secondly, it is unlikely that carbonates precipitated from upwelled water were in isotopic equilibrium with the coeval atmosphere and surface water. Thirdly, the isotopic composition of such carbonates should exhibit a wide range depending on deep water/surface water ratios (e.g. Kennedy, 1996). Consequently, the correlation of postglacial carbonates by means of carbon isotope chemostratigraphy, which is solely based on negative $\delta^{13}\text{C}$ values, could be totally misleading.

Neoproterozoic trends of strontium isotopes

Veizer and Compston (1976) reported a first seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve for the whole of the Precambrian and demonstrated a sharp increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater between 2.5 and 2.0 Ga. Later, more detailed data obtained for the Neoproterozoic (Veizer *et al.*, 1983) exhibited low $^{87}\text{Sr}/^{86}\text{Sr}$ values at around 900 Ma. This was assigned to the ocean's response to a major hydrothermal event. A substantial amount of new isotopic data has been generated through the years by Derry *et al.* (1989, 1992, 1994), Asmerom *et al.* (1991) and Kaufman *et al.* (1993, 1996). This database has recently been screened for postsedimentary alteration, and age constraints which 'significantly improves the resolution of the $^{87}\text{Sr}/^{86}\text{Sr}$ record for the late Neoproterozoic to Early Cambrian' (Jacobsen and Kaufman, 1999; p. 44). However, the Neoproterozoic–early Cambrian time interval can usefully be divided into two sections. The younger section demonstrates a marked rise in the $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.7066 at 590 Ma up to 0.7085 at the Precambrian–Cambrian boundary (Fig. 2), which seems to be well established. In contrast, the $^{87}\text{Sr}/^{86}\text{Sr}$ temporal trend for the older section, spanning from 850 to 590 Ma, has no consensus (Fig. 2). Jacobsen and Kaufman (1999) have already discussed the inconsistency between their database and that reported from the Karatau Group which terminates the Riphean stratotype section on the

western slope of the southern Urals (e.g. Kuznetsov *et al.*, 1997; Kuznetsov, 1998). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained from 890 to 670 Myr-old carbonate formations of the Karatau Group are uniquely low, ranging between 0.7053 and 0.7062, whereas the data compiled by Jacobsen and Kaufman (1999) exhibit far more radiogenic values (Fig. 2).

Below, these discrepancies are considered in terms of (i) the age constraints, (ii) the depositional environments, (iii) the screening for postdepositional alteration, and (iv) the laboratory techniques.

Inconsistencies related to the age constraints

It is apparent that the discrepancies associated with the older time interval of 850–590 Ma, which is represented by the Shaler, Akademikerbreen, Polarisbreen, and Karatau groups, might well be caused by the lack of reliable age determinations.

The Shaler Group, from Victoria Island in Canada (Asmerom *et al.*, 1991) lies unconformably on a sequence containing 1.2-Gyr-old lavas. It is overlain unconformably by basaltic lavas dated by the U–Pb method on baddeleyite to be 723 ± 3 Myr old. The palaeomagnetic data for the Mackenzie Supergroup, correlated with the Shaler Group, indicate that the latter is younger than 880 Myr (Asmerom *et al.*, 1991 and references therein). More recent isotopic work has demonstrated that the maximum age of Shaler Group carbonate rocks is not more than 802 ± 10 Myr (Jacobsen and Kaufman, 1999 and references therein). Although Jacobsen and Kaufman (1999) have refined the age of Shaler carbonate rocks and assigned it to 740 Myr, they largely used circular arguments involving the carbon and strontium isotopic trends for the correlation. Moreover, in the recent publication by Walter *et al.* (2000) the age of the Shaler Group carbonate rocks (840–834 Myr, table 7, p. 407) was adopted from Asmerom *et al.* (1991). As far as the Akademikerbreen and Polarisbreen groups are concerned, there has been no isotopic age published yet. It is only known that the Akademikerbreen Group rocks contain acritarchs of latest Late Riphean age, and the

shales at the base of the Polarisbreen Group might be a correlative of the Varanger tillites in northern Norway (e.g. Knoll *et al.*, 1986). However, the age estimate of the two-stage Varangerian glaciation determined by the Rb–Sr method on fine clay minerals from the Norwegian tillites exhibits a wide range of ages from 630 to 560 Myr (Gorokhov *et al.*, 1996).

The geochronological baseline for the 850–670 Ma interval of Kuznetsov's $^{87}\text{Sr}/^{86}\text{Sr}$ curve (Fig. 2) is based on the Pb–Pb and Rb–Sr dates for the carbonate and siliciclastic rocks of the Karatau Group consisting of (bottom to top) the Inzer, Minyar and Uk formations. Two Pb–Pb dates of 836 ± 25 and 780 ± 80 Ma on lower Inzer Formation limestone (Ovchinnikova *et al.*, 1998) and middle Minyar Formation dolostone (Ovchinnikova *et al.*, 2001) provide depositional age constraints for the lower part of the Karatau Group. Both the ages and the $^{87}\text{Sr}/^{86}\text{Sr}$ values are roughly consistent with the Shaler Group data (Jacobsen and Kaufman, 1999).

However, the upper portion of the Karatau Group, with an inferred age of 760–670 Myr, specifically demonstrates low $^{87}\text{Sr}/^{86}\text{Sr}$ values (Fig. 2), thus conflicting with the previously reported data (see Jacobsen and Kaufman, 1999). The age of the Uk Formation based on Rb–Sr and K–Ar techniques on glauconites has been constrained to 688 ± 10 and 670 ± 10 Myr, respectively (Gorozhanin and Kutuyavin, 1986). Podkovyrov *et al.* (1998), however, inferred several stratigraphic hiatuses of unknown duration in the Karatau carbonate succession and thus opened the possibility that the geological record of the Karatau succession is not complete. At the same time, there is a paucity of strontium isotopic data from the time interval 690–600 Ma (Fig. 2). Jacobsen and Kaufman (1999) have not reported any $^{87}\text{Sr}/^{86}\text{Sr}$ data from between 690 and 650 Ma, and thus Kuznetsov's data (0.07054–0.07060) are the only isotopic record available for this period of time.

Inconsistencies related to depositional environments

Sr isotopic ratios measured from sedimentary carbonates reflect mixing

of strontium delivered by continental runoff and that derived from seawater–basalt interaction (e.g. Veizer, 1989). Therefore, transitions from open marine to restricted marine to lacustrine environments exhibit regular changes in $^{87}\text{Sr}/^{86}\text{Sr}$: restricted and lacustrine carbonates become enriched in ^{87}Sr . There are some exceptions: in a certain type of rift basin floored by basalts (e.g. Red Sea, Friedman, 1996) shore-associated carbonates may be depleted in ^{87}Sr as compared to coeval carbonates precipitated from well-mixed seawater. However, examples of unambiguous resolution between marine vs. nonmarine environments in transgressive/regressive carbonate sequences have been reported from both the Cenozoic (McCulloch *et al.*, 1989) and the Palaeoproterozoic (Gorokhov *et al.*, 1998; Kuznetsov *et al.*, 1999). It is not entirely clear whether all Neoproterozoic carbonate formations studied for strontium isotopes were deposited in open marine basins. As far as the Karatau Group is concerned, the carbonate rocks of the Inzer, Minyar and Uk formations were accumulated in relatively deep-water marine and shallow-marine settings. No evidence of evaporitic sediments has been found in the Karatavian carbonate sequences (Maslov, 1997). In contrast, the lower part of the Shaler Group includes several horizons of deltaic sediments, and the upper part contains evaporitic intercalations, restricted coastal carbonates and red beds (Asmerom *et al.*, 1991 and references therein). Akademikerbreen Group carbonate sediments also might have been precipitated in a partly restricted basin, as they are enriched in Mn relative to the high background Sr content, and include calcian dolomites (Derry *et al.*, 1989, 1992). Based on these facts, the Karatau carbonate sequences are by far the best match with deposition in an open marine setting.

Inconsistencies related to the screening of carbonate material

Conventional geochemical assessment for postdepositional alteration of carbonate is based largely on the relative abundances of Mn, Fe, Rb and Sr (e.g. Brand and Veizer, 1980; Gorokhov, 1996). Elemental ratios, such as Mn/Sr, Fe/Sr, Ca/Sr and Rb/Sr, as well

as carbon and oxygen isotopes, are widely used as geochemical criteria for revealing the least disturbed Rb–Sr systems. Different authors, however, use not only dissimilar values of the same ratios, but also dissimilar combinations of these ratios. Asmerom *et al.* (1991) used Mn/Sr < 1.5 and Rb/Sr < 0.004 to identify altered samples, whereas Derry *et al.* (1992) suggested for Mn/Sr < 1, Rb/Sr < 0.002, and Ca/Sr < 1000. Kaufman *et al.* (1993) suggested Mn/Sr < 1.5 and Rb/Sr < 0.0005, whereas Kuznetsov *et al.* (1997) and Semikhatov *et al.* (1998) advocated Mn/Sr ≤ 0.2, Fe/Sr ≤ 5.0 and Rb/Sr ≤ 0.0010. In all cases the choices of the elemental ratios and their values are empirical and arbitrary. However, the elemental ratios depend not only on the extent of postsedimentary alteration, but also on the initial carbonate composition. The consequences of different criteria applied for the recognition of altered samples can be exemplified by the following. If Mn/Sr ≤ 0.2 (as suggested by Kuznetsov *et al.*, 1997) is applied for five 609–610 Myr-old limestone samples from Svalbard and East Greenland (Table 1, p. 416, Kaufman *et al.*, 1993), only two, each having $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7066, would pass this test. Yet the ‘best preserved’ 610 Myr-old samples (as based on other criteria) shown by Jacobsen and Kaufman (1999) have $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7074. Thus, it is believed that at least some of the inconsistencies presented in Fig. 2 might well be related to different approaches applied to geochemical screening.

The work by Montañez *et al.* (1996) documenting an elaborate screening approach is considered to represent state-of-the-art in isotopic studies of ancient carbonates. Another related and serious problem is that only a very limited number of samples per time unit (very often a single sample) has been used in most studies of reconstruction of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Neoproterozoic seawater. Evidently, a limited number of samples is seldom sufficient even to recognize alteration trends and therefore should not be used for the reconstruction of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

Inconsistencies related to the laboratory processing of carbonate material

Many authors who measured strontium isotopes on marine carbonate

rocks have used a preliminary laboratory leaching of carbonate material for removal of late, recrystallized carbonate phases and/or contaminating constituents (Gao, 1990; Kupecz and Land, 1991; Ohde and Elderfield, 1992; Gorokhov *et al.*, 1995; Kuznetsov *et al.*, 1997; Semikhatov *et al.*, 1998; McArthur *et al.*, 1993a, 1993b). Acetic acid, ammonium acetate and chloride are the reagents commonly used. Details of the technique have been discussed by McArthur (1994). Although some scientists (Gao, 1990; Kupecz and Land, 1991) use leaching strictly for removal of the Sr bound to clay components, others (Gorokhov *et al.*, 1995) suggest this procedure for removal of both clay-bound Sr and late, ^{87}Sr -rich, calcite cement. The 1 N ammonium acetate procedure appears to involve the most appropriate leaching reagent: it removes not only the clay-bound Sr (Morton, 1985; Gorokhov *et al.*, 1994), but also late calcite phases (Wada and Furumura, 1994). An experimental study has shown that $^{87}\text{Sr}/^{86}\text{Sr}$ values, obtained from Rhiphean nonmetamorphosed limestones by selective leaching, are lower by 0.0002–0.0019 than values measured from bulk carbonate components without leaching (e.g. Gorokhov *et al.*, 1995). Thus, Sr isotopic values obtained with the leaching procedure are less enriched in ^{87}Sr and likely the best proxy for initial seawater composition. Therefore, the inconsistencies exposed in Fig. 2 should also be considered in terms of various laboratory techniques.

Concluding remarks: efficacy of isotope stratigraphy

The compilation presented in Fig. 1 demonstrates that, in general, it is very unlikely that carbonate formations deposited between 850 and 544 Ma can currently be correlated unambiguously or dated indirectly by means of carbon isotope stratigraphy if no other independent stratigraphic or isotopic (i.e. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios) controls are provided (‘blind experiments’). If a carbonate sequence is characterized by negative $\delta^{13}\text{C}_{\text{carb}}$ (to less than -4‰), this may provide an approximate age restriction: it could not have been deposited between 670 and 610 Ma, or even as long ago as 700 Ma providing that the 680 Ma

assignment for the negative $\delta^{13}\text{C}_{\text{carb}}$ excursion, which appeared in Kah *et al.* (1998), is an artefact or error (Fig. 1a). Rather, it might have formed either at around 740–700 Ma (Sturtian glaciation) or between 590 and 540 Ma (late to post-Varangerian glaciation) (Fig. 1a). These alternatives may be further resolved by means of 'strontium isotope stratigraphy' (see discussion below). $\delta^{13}\text{C}_{\text{carb}}$ values fluctuating around zero might be found throughout the 850–544 Ma interval, whereas $\delta^{13}\text{C}_{\text{carb}} > +5\text{‰}$ indicates that the carbonates might have been deposited between 670 and 610 Ma.

Although the causes of the $^{87}\text{Sr}/^{86}\text{Sr}$ inconsistencies in Fig. 2 for 760–670 Ma are not fully understood, one should prefer the lower $^{87}\text{Sr}/^{86}\text{Sr}$ curve (e.g. Veizer and Compston, 1974) unless the inconsistencies involve improper age constraints (Fig. 2). Under these conditions strontium isotope data, even when used alone, can clearly discriminate carbonate formations deposited prior to 670 Ma ($^{87}\text{Sr}/^{86}\text{Sr} \leq 0.7063$) from those formed between 670 and 544 Ma ($^{87}\text{Sr}/^{86}\text{Sr} \geq 0.7063$, Fig. 2). Moreover, as the result of a progressive and rather uniform increase of $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.7061 to 0.7085, several discrete age-groups of carbonate formations may be resolved within the time interval 590–544 Ma (Fig. 2).

The combined application of strontium and carbon isotope data may further resolve the age uncertainties for the low- $\delta^{13}\text{C}_{\text{carb}}$ carbonates (see above). Low strontium isotope ratios (< 0.7063) combined with low- $\delta^{13}\text{C}_{\text{carb}}$ values are indicative of an age > 670 Myr, whereas $^{87}\text{Sr}/^{86}\text{Sr} > 0.7061$ would place the age of the rocks between 590 and 544 Myr.

Thus, following an earlier statement by Veizer (e.g. Misi and Veizer, 1998), it is concluded herein that, at the present time, strontium isotope stratigraphy provides a more definitive and precise tool for stratigraphic correlations and indirect age determinations compared to the $\delta^{13}\text{C}_{\text{carb}}$ approach.

Some specific steps recommended in future isotope stratigraphy studies

The current practice in isotope studies of Precambrian carbonates rarely

includes thorough investigation and documentation of depositional environments. As contemporaneous open marine, restricted marine, lagoonal, and lacustrine carbonates may be characterized by very different isotopic compositions, the study of depositional environments and palaeofacies analysis are strongly suggested to be an essential part of all isotopic studies attempting to reconstruct the composition of seawater.

It is already apparent that the isotopic composition of carbonates is subject to considerable internal variability, and therefore the isotopic data obtained from any single section should not be used for the reconstruction of the seawater composition until it is established, by comparison with a series of coeval distant sections, to be representative for the time interval studied.

Without exceptions, all ancient carbonates experienced some degree of postdepositional alteration and modification of carbon, oxygen and strontium isotope systems. Given the condition that all necessary geochemical, mineralogical, and petrological precautions have been undertaken to identify the alteration trends, a limited number of samples and analyses are considered to be insufficient for the recognition of alteration trends and thus such databases should not be used for the reconstruction of the seawater composition.

Acknowledgements

This work was supported by the Geological Survey of Norway (Project 270500), the Russian Foundation of Basic Research (Grants 99–05–65181 and 00–05–64915 for IG and AK), and the Scottish Universities Environmental Research Centre, Glasgow. Ø. Nordgulen is acknowledged for comments on an earlier draft. M. Schidlowski and L. Derry, the official referees, are thanked for providing comments that improved the manuscript.

References

Aharon, P. and Liew, T.C., 1992. An assessment of the Precambrian/Cambrian transition events on the basis of carbon isotope records. In: *Early Organic Evolution: Implications for Mineral and Energy Resources* (M. Schidlowski *et al.*, eds), pp. 212–223. Springer-Verlag, Heidelberg.

- Aharon, P., Schidlowski, M. and Singh, I.B., 1987. Chronostratigraphic markers in the end-Precambrian carbon isotope record of the Lesser Himalaya. *Nature*, **327**, 699–702.
- Asmerom, Y., Jacobsen, S., Knoll, A.H., Butterfield, N.J. and Swett, K., 1991. Strontium isotope variations of neoproterozoic seawater: implications for crustal evolution. *Geochim. Cosmochim. Acta*, **55**, 2883–2894.
- Banerjee, D.M., Schidlowski, M., Siebert, F. and Brasier, M.D., 1997. Geochemical changes across the Proterozoic – Cambrian transition in the Durmala phosphorite mine section, Mussoorie Hills, Garhwal Himalaya, India. *Palaeogeogr. Palaeoclim. Palaeoecol.*, **132**, 183–194.
- Bartley, J.K., Pope, M., Knoll, A.H., Semikhatov, M.A. and Petrov, P.Yu., 1998. A Vendian – Cambrian boundary succession from the northwestern margin of the Siberian Platform: stratigraphy, chemostratigraphy and correlation. *Geol. Mag.*, **135**, 473–494.
- Bowring, S.A., Grotzinger, J.P., Isachsen, C.E. *et al.*, 1993. Calibrating rates of EARLY Cambrian evolution. *Science*, **261**, 1293–1298.
- Brand, U. and Veizer, J., 1980. Chemical diagenesis of a multicomponent carbonate system – 1: Trace elements. *J. Sediment. Petrol.*, **50**, 1219–1236.
- Brasier, M.D., 1992. Global ocean – atmosphere change across the Precambrian – Cambrian transition. *Geol. Mag.*, **129**, 161–168.
- Brasier, M.D., Corfield, R.M., Derry, L.A., Rozanov, A.Yu. and Zhuravlev, A.Yu., 1994a. Multiple $\delta^{13}\text{C}$ excursions spanning the Cambrian explosion to Botomian crisis in Siberia. *Geology*, **22**, 455–458.
- Brasier, M.D., Khomentovsky, V.V. and Corfield, R.M., 1993. Stable isotopic calibration of the earliest skeletal fossil assemblages in eastern Siberia (Precambrian – Cambrian boundary). *Terra Nova*, **5**, 225–232.
- Brasier, M., McCarron, G., Tucker, R., Leather, J., Allen, P. and Shields, G., 2000. New U–Pb zircon dates for the Neoproterozoic Ghubrah glaciation and for the top of the Huqf supergroup, Oman. *Geology*, **28**, 175–178.
- Brasier, M.D., Rozanov, A.Yu., Zhuravlev, A.Yu., Corfield, R.M. and Derry, L.A., 1994b. A carbon isotope reference scale for the Lower Cambrian succession in Siberia: report of IGCP Project 303. *Geol. Mag.*, **131**, 767–783.
- Burns, S.J., Haudenschild, U. and Matter, A., 1994. The strontium isotopic composition of carbonates from the late Precambrian (~560–540 Ma) Huqf Group of Oman. *Chem. Geol. (Isot. Geosci. Sect.)*, **111**, 269–282.

- Calver, C.R., 1998. Isotope stratigraphy of the Neoproterozoic Togari Group, Tasmania. *Aus. J. Earth Sci.*, **45**, 865–874.
- Calver, C.R., 2000. Isotope stratigraphy of the Ediacarian (Neoproterozoic III) of the Adelaide Rift Complex, Australia, and the overprint of water column stratification. *Precamb. Res.*, **100**, 121–150.
- Condon, D.J. and Prave, A.R., 2000. Two from Donegal: Neoproterozoic glacial episodes on the northern margin of Laurentia. *Geology*, **28**, 951–954.
- Corsetti, F.A. and Kaufman, A.J., 1994. Chemostratigraphy of Neoproterozoic – Cambrian units, White-Inyo Region, eastern California and western Nevada: implications for global correlation and faunal distribution. *Palaios*, **9**, 211–219.
- Denison, R.E., Koepnick, R.B., Burke, W.H. and Hetherington, E.A., 1998. Construction of the Cambrian and Ordovician seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve. *Chem. Geol. (Isot. Geosci. Sect.)*, **152**, 325–340.
- Derry, L.A., Brasier, M.D., Corfield, R.M., Rozanov, A.Yu. and Zhuravlev, A.Yu., 1994. Sr and C isotopes in Lower Cambrian carbonates from the Siberian craton: a paleoenvironmental record during the 'Cambrian explosion'. *Earth Planet. Sci. Lett.*, **128**, 671–681.
- Derry, L.A., Kaufman, A.J. and Jacobsen, S.B., 1992. Sedimentary cycling and environmental changes in the Late Proterozoic: Evidence from stable and radiogenic isotopes. *Geochim. Cosmochim. Acta*, **56**, 1317–1329.
- Derry, L.A., Keto, L.S., Jacobsen, S.B., Knoll, A.H. and Swett, K., 1989. Sr isotope variations in Upper Proterozoic carbonates from Svalbard and East Greenland. *Geochim. Cosmochim. Acta*, **53**, 2331–2339.
- Fairchild, I.J., 1993. Balmy shores and icy waters: The paradox of carbonates associated with glacial deposits in Neoproterozoic times. *Sed. Rev.*, **1**, 1–15.
- Fairchild, I.J., Marshall, J.D. and Bertrand-Sarafati, J., 1990. Stratigraphic shifts in carbon isotopes from Proterozoic stromatolitic carbonates (Mauritania): Influences of primary mineralogy and diagenesis. *Am. J. Sci.*, **290-a**, 46–79.
- Friedman, G.M., 1996. Improved chronostratigraphic reference curve of late Neogene seawater $^{87}\text{Sr}/^{86}\text{Sr}$: Comment. *Geology*, **24**, 284–285.
- Gao, G., 1990. Geochemical and isotopic constraints on the diagenetic history of a massive stratal, late Cambrian (Royer) dolomite, Lower Arbuckle Group, Slick Hills, SW Oklahoma, USA. *Geochim. Cosmochim. Acta*, **54**, 1979–1989.
- Gorokhov, I.M., 1996. Diagenesis of carbonate sediments: the behaviour of trace elements and the strontium isotopes. In: *Lithology and Paleogeography* (Yu. L. Verba, ed.), 4, pp.141–164 (in Russian). St. Petersburg State University.
- Gorokhov, I.M., Clauer, N., Turchenko, T.L. et al., 1994. Rb-Sr systematics of Vendian-Cambrian claystones from the east European Platform: Implications for a multi-stage illite evolution. *Chem. Geol.*, **112**, 71–89.
- Gorokhov, I.M., Melezhik, V.A., Kuznetsov, A.B., Konstantinova, G.V. and Melnikov, N.N., 1998. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in Early Paleoproterozoic seawater: Implications for the $\delta^{13}\text{C}_{\text{carb}}$ positive anomaly (Abstr.). In: *The 9th International Conference on Geochronology, Cosmochronology and Isotope Geology*, 20–26. August, 1998, Beijing, China. *Chinese Sci. Bull.*, **43**, 47.
- Gorokhov, I.M., Semikhatov, M.A., Baskakov, A.V. et al., 1995. Sr isotopic composition in Riphean, Vendian, and Lower Cambrian carbonates from Siberia. *Stratigr. Geol. Corr.*, **3**, 1–28.
- Gorokhov, I.M., Siedlecka, A., Roberts, D. et al., 1996. A Rb-Sr investigation of illite-forming events in diagenetic grade Neoproterozoic shales, Varanger Peninsula, North Norway. *Norsk Geo. Unders. Rep.*, **96.154**, 1–28.
- Gorozhanin, V.M. and Kutyavin, E.P., 1986. Rubidium-Strontium Dating on Glauconites from the Uk Formation. In: *Dokembrii I Paleozoi Yuzhnogo Urala* (V.I. Kozlov, V.A. Maslov and N.D. Sergeeva, eds) Ufa: Bashkir. Nauch. Tsentr Ural. Otd. Akad. Nauk SSSR, 60–63 (in Russian).
- Grotzinger, J.P. and Knoll, A.H., 1995. Anomalous carbonate precipitates: Is the Precambrian the key to the Permian? *Palaios*, **20**, 578–596.
- Grotzinger, J.P., Bowring, S.A., Saylor, B.Z. and Kaufman, A.J., 1995. Biostratigraphic and geochronologic constraints on early animal evolution. *Science*, **270**, 298–604.
- Heaman, L.M., Lecheminant, A.N. and Rainbird, R.H., 1992. Nature and timing of Franklin igneous events, Canada: implications for a Late Proterozoic mantle plume and the break-up of Laurentia. *Earth Planet. Sci. Lett.*, **109**, 117–131.
- Hill, A.C. and Walter, M.R., 2000. Mid-Neoproterozoic (~830–750 Ma) isotope stratigraphy of Australia and global correlation. *Precamb. Res.*, **100**, 181–211.
- Hoffman, P.F., Hawkins, D.P., Isachsen, C.E. and Bowring, S.A., 1996. Precise U-Pb zircon ages for early Damaran magmatism in the Summas and Welwitschia inlier, northern Damara Belt, Namibia. *Geol. Surv. Namibia Comm.*, **11**, 47–52.
- Hoffman, P.F., Kaufman, A.J. and Halverson, G.P., 1998. A Neoproterozoic snowball Earth. *Science*, **281**, 1342–1346.
- Holland, H.D., 1984. *The Chemical Evolution of the Atmospheric and the Oceans*. Princeton University Press, Princeton.
- Jacobsen, S.B. and Kaufman, A.J., 1999. The Sr, C and O isotopic evolution of Neoproterozoic seawater. *Chem. Geol.*, **161**, 37–57.
- Kah, L., Sherman, A.G., Narbonne, G.M., Knoll, A.H. and Kaufman, A.J., 1998. $\delta^{13}\text{C}$ stratigraphy of the Proterozoic Bylot Supergroup, Baffin Island, Canada: implications for regional lithostratigraphic correlations. *Can. J. Earth Sci.*, **36**, 313–332.
- Kaufman, A.J. and Knoll, A.H., 1995. Neoproterozoic variations in the C-isotopic composition of seawater: stratigraphic and biogeochemical implications. *Precamb. Res.*, **73**, 27–49.
- Kaufman, A.J., Hayes, J.M., Knoll, A.H. and Germs, G.J.B., 1991. Isotopic compositions of carbonates and organic carbon from upper Proterozoic successions in Namibia: stratigraphic variation and the effects of diagenesis and metamorphism. *Precamb. Res.*, **49**, 301–327.
- Kaufman, A.J., Jacobsen, S.B. and Knoll, A.H., 1993. The Vendian record of Sr and C isotopic variations in seawater: Implications for tectonics and paleoclimate. *Earth Planet. Sci. Lett.*, **120**, 409–430.
- Kaufman, A.J., Knoll, A.H. and Awramik, S.M., 1992. Biostratigraphic and chemostratigraphic correlation of Neoproterozoic sedimentary succession: Upper Tindir Group, north-western Canada, as a test case. *Geology*, **20**, 181–185.
- Kaufman, A.J., Knoll, A.H. and Narbonne, G.M., 1997. Isotopes, ice ages, and terminal Proterozoic earth history. *Proc. Natl. Acad. Sci.*, **95**, 6600–6605.
- Kaufman, A.J., Knoll, A.H., Semikhatov, M.A. et al., 1996. Integrated chronostratigraphy of Proterozoic–Cambrian boundary beds in the western Anabar region, northern Siberia. *Geol. Mag.*, **133**, 505–553.
- Kennedy, M.J., 1996. Stratigraphy, sedimentology, and isotopic geochemistry of Australian Neoproterozoic postglacial cap dolostones: deglaciation, $\delta^{13}\text{C}$ excursions, and carbonate precipitation. *J. Sedim. Res.*, **66**, 1050–1064.
- Kennedy, M.J., Runnegar, B., Prave, A.R., Hoffman, K.-H. and Arthur, M.A., 1998. Two or four Neoproterozoic glaciations? *Geology*, **26**, 1059–1063.
- Kimura, H., Matsumoto, R., Kakuwa, Y., Hamdi, B. and Zibaseresht, H., 1997. The Vendian – Cambrian $\delta^{13}\text{C}$ record, North Iran: evidence for overturning of the ocean before the Cambrian Explosion. *Earth Planet. Sci. Lett.*, **147**, E1–E7.
- Kirschvink, J.L., Magaritz, M., Ripperdan, Zhuravlev, A.Y. and Roznov, A.Y., 1991. The Precambrian/Cambrian

- boundary: magnetostratigraphy and carbon isotopes resolve correlation problems between Siberia, Morocco, and south China. *GSA Today*, **1**, 69.
- Knoll, A.H., Grotzinger, J.P., Kaufman, A.J. and Kolosov, P., 1995c. Integrated approaches to terminal Proterozoic stratigraphy: an example from the Olenek Uplift, northeastern Siberia. *Precamb. Res.*, **73**, 2521–2270.
- Knoll, A.H., Hayes, J.M., Kaufman, A.J., Swett, K. and Lambert, I.B., 1986. Secular variation in carbon isotope ratios from Upper Proterozoic successions of Svalbard and East Greenland. *Nature*, **321**, 832–838.
- Knoll, A.H., Kaufman, A.J. and Semikhatov, M.A., 1995a. The carbon-isotopic composition of Proterozoic carbonates: Riphean succession from northwestern Siberia (Anabar Massif, Turukhansk Uplift). *Am. J. Sci.*, **295**, 823–850.
- Knoll, A.H., Kaufman, A.J., Semikhatov, M.A., Grotzinger, J.P. and Adams, W., 1995b. Sizing up the sub-Tommotian unconformity in Siberia. *Geology*, **23**, 1139–1143.
- Knoll, A.H. and Walter, M.R., 1992. Latest Proterozoic stratigraphy and Earth history. *Nature*, **356**, 673–678.
- Kupez, J.A. and Land, L.S., 1991. Late-stage dolomitization of the Lower Ordovician Ellenburger Group, West Texas. *J. Sediment. Petrol.*, **61**, 551–574.
- Kuznetsov, A.B., 1998. *Evolution of Sr isotopic composition in late Riphean seawater: the Karatau Group carbonates, Southern Urals*. Unpubl. doctoral dissertation, St.-Petersburg, Inst. Precamb. Geol. Geochronol., Russian Acad. Sci., Russia. (in Russian).
- Kuznetsov, A.B., Gorokhov, I.M., Melezhik, V.A. et al., 1999. Evolution of the Palaeoproterozoic Tulomozero palaeobasin, south-eastern Karelia, Russia: chemical and isotopic evidence. EUG-10, 28 March–1 April, 1999, Strasbourg, France. *J. Conf. Abstr.*, **4**, 810.
- Kuznetsov, A.B., Gorokhov, I.M., Semikhatov, M.A., Melnikov, N.N. and Kozlov, V.I., 1997. Strontium isotopic composition from the Inzer Formation limestones, the Upper Riphean type section in southern Urals. *Trans. Russian Acad. Sci., Earth Sci. Sections*, **353**, 319–324.
- Lambert, I.B., Walter, M.R., Wenlong, Z., Songnian, L. and Guogans, M., 1987. Palaeoenvironment and carbon isotope stratigraphy of the Upper Proterozoic carbonates of the Yangtze Platform. *Nature*, **325**, 140–142.
- Magaritz, M., 1989. ^{13}C minima follow extinction events: a clue to faunal radiation. *Geology*, **17**, 337–340.
- Magaritz, M., Holser, W.P. and Kirschvink, J.L., 1986. Carbon-isotope events across the Precambrian/Cambrian boundary on the Siberian Platform. *Nature*, **320**, 258–259.
- Maslov, A.V., 1997. *Sedimentary associations of the Riphean in its stratotype area (the evolution of the views on depositional environment, and lithofacies zoning)*. Russian Academy of Sciences, the Ural Division: Yekaterinburg (in Russian).
- McArthur, J.M., 1994. Recent trends in strontium isotope stratigraphy. *Terra Nova*, **6**, 331–358.
- McArthur, J.M., Chen, M., Gale, A.S., Thirwall, M.F. and Kennedy, W.J., 1993a. Strontium isotope stratigraphy for the Late Cretaceous: age models and intercontinental correlations for the Campanian. *Paleoceanography*, **8**, 859–873.
- McArthur, J.M., Thirwall, M.F., Gale, A.S. et al., 1993b. Strontium isotope stratigraphy for the Late Cretaceous: a new curve, based on the English Chalk. In: *High Resolution Stratigraphy* (E. Hailwood and R. Kid, eds). *Spec. Publ. Geol. Soc. London*, **70**, 195–209.
- McCulloch, M.T., de Deckker, P. and Chivas, A.R., 1989. Strontium isotope variations in single ostracod valves from the Gulf of Carpentaria, Australia: a palaeoenvironmental indicator. *Geochim. Cosmochim. Acta*, **53**, 1703–1710.
- Melezhik, V.A., Roberts, D., Pokrovsky, B.G., Gorokhov, I.M. and Ovchinnikova, G.V., 1997. Primary isotopic features in metamorphosed Caledonian carbonates: implications for depositional age. (Extended abstract). *Norges Geol. Unders. Bull.*, **433**, 22–23.
- Misi, A. and Veizer, J., 1998. Neoproterozoic carbonate sequences of the Una Group, Irece Basin, Brasil: chemostratigraphy, age and correlations. *Precamb. Res.*, **89**, 87–100.
- Montañez, I.P., Banner, J.L., Osleger, D.A., Borg, L.E. and Bosserman, P.J., 1996. Integrated Sr isotope variations and sea-level history of Middle to Upper Cambrian platform carbonates: Implications for the evolution of Cambrian seawater $^{87}\text{Sr}/^{86}\text{Sr}$. *Geology*, **24**, 917–920.
- Morton, J.P., 1985. Rb-Sr dating of diagenesis and source age of clays in Upper Devonian black shales of Texas. *Bull. Geol. Soc. Am.*, **96**, 1043–1049.
- Narbonne, G.M., Kaufman, A.J. and Knoll, A.H., 1994. Integrated chemostratigraphy and biostratigraphy of the Windermere Supergroup, north-western Canada: Implications for Neoproterozoic correlations and the early evolution of animals. *Bull. Geol. Soc. Am.*, **106**, 1281–1292.
- Ohde, S. and Elderfield, H., 1992. Strontium isotope stratigraphy of Kita-daitojima Atoll, North Philippines Sea: Implications for Neogene sea level change and tectonic history. *Earth Planet. Sci. Lett.*, **113**, 473–486.
- Ovchinnikova, G.V., Vasil'eva, I.M., Semikhatov, M.A. et al., 1998. U-Pb systematics of Proterozoic carbonate rocks: the Inzer Formation of the Upper Riphean stratotype (southern Urals). *Stratigr. Geol. Corr.*, **6**, 336–347.
- Ovchinnikova, G.V., Vasil'eva, I.M., Semikhatov, M.A. et al., 2001. Potentialities of the Pb-Pb dating of carbonate rocks with disturbed U-Pb systems: the Min'yar Formation of the Upper Riphean stratotype, southern Urals. *Stratigr. Geol. Corr.*, in press.
- Pelechaty, S.M., 1998. Integrated chronostratigraphy of the Vendian System of Siberia: implications for a global stratigraphy. *J. Geol. Soc. London*, **155**, 957–973.
- Podkovyrov, V.N., Semikhatov, M.A., Kuznetsov, A.B. et al., 1998. Carbonate carbon isotopic composition in the Upper Riphean stratotype, the Karatau Group, southern Urals. *Stratigr. Geol. Corr.*, **6**, 319–335.
- Pokrovsky, B.G. and Gertsev, D.D., 1993. Upper Precambrian carbonates with anomalously light isotopic composition of carbon (south central Siberia). *Lith. Miner. Dep.*, **1**, 64–80 (in Russian).
- Pokrovsky, B.G. and Missarzhevsky, V.V., 1993. Isotopic correlation of the Precambrian – Cambrian boundary strata of the Siberian Platform. *Trans. Russian Acad. Sci.*, **329**, 768–771.
- Pokrovsky, B.G. and Vinogradov, V.I., 1991. Isotopic composition of strontium, oxygen and carbon in the Upper Precambrian carbonates of the western slope of the Anabar Uplift (Kotuikan River). *Trans. USSR Acad. Sci.*, **320**, 1245–1250 (in Russian).
- Prave, A.R., 1999. Two diamicites, two cap carbonates, two $\delta^{13}\text{C}$ excursions, two rifts: The Neoproterozoic Kingston Peak Formation, Death Valley, California. *Geology*, **27**, 339–342.
- Preiss, W.V., 2000. The adelaidite Geosyncline of South Australia and its significance in Neoproterozoic continental reconstruction. *Precamb. Res.*, **100**, 21–63.
- Saylor, B.Z., Kaufman, A.J., Grotzinger, J.P. and Urban, F., 1998. A composite reference section for terminal Proterozoic strata of southern Namibia. *J. Sediment. Res.*, **68**, 1223–1235.
- Semikhatov, M.A., Gorokhov, I.M., Kuznetsov, A.B. et al., 1998. The strontium isotopic composition in early Late Riphean seawater: Limestones of the Lakhandanda Group, the Uchur-Maya region, Siberia. *Trans. (Dokl.) Russian Acad. Sci./Earth Sci. Sections*, **360**, 488–492.
- Shields, G., Stille, P., Brasier, M.D. and Atudorei, N.-V., 1997. Stratified oceans

- and oxygenation of the late Precambrian environment: a post-glacial geochemical record from the Neoproterozoic of W. Mongolia. *Terra Nova*, **9**, 218–222.
- Singh, U., 1987. Ooids and cements from the late Precambrian of the Flinders Ranges, South Australia. *J. Sedim. Petrol.*, **57**, 117–127.
- Smith, L.H., Kaufman, A.J., Knoll, A.H. and Linl, P.K., 1994. Chemostratigraphy of predominantly siliciclastic Neoproterozoic successions: a case study of the Pocatelto Formation and Lower Brigham Group, Idaho, USA. *Geol. Mag.*, **131**, 301–314.
- Trønnes, R.G. and Sundvoll, B., 1995. Isotopic composition, depositional ages and environments of Central Norwegian Caledonian marbles. (Extended abstract). *Norges Geol. Unders. Bull.*, **427**, 44–47.
- Tucker, M.E., 1986a. Carbon isotope excursions in Precambrian/Cambrian boundary beds, Morocco. *Nature*, **319**, 48–50.
- Tucker, M.E., 1986b. Formerly aragonitic limestones associated with tillites in the Late Proterozoic of Death Valley, California. *J. Sedim. Petrol.*, **56**, 818–830.
- Veizer, J., 1989. Strontium isotopes in seawater through time. *Ann. Rev. Earth Planet. Sci.*, **17**, 141–167.
- Veizer, J. and Compston, W., 1974. $^{87}\text{Sr}/^{86}\text{Sr}$ composition of seawater during the Phanerozoic. *Geochim. Cosmochim. Acta*, **38**, 1461–1484.
- Veizer, J. and Compston, W., 1976. $^{87}\text{Sr}/^{86}\text{Sr}$ in Precambrian carbonates as an index of crustal evolution. *Geochim. Cosmochim. Acta*, **40**, 905–914.
- Veizer, J., Compston, W., Clauer, N. and Schidlowski, M., 1983. $^{87}\text{Sr}/^{86}\text{Sr}$ in Late Proterozoic carbonates: Evidence for a 'mantle event' at 900 Ma ago. *Geochim. Cosmochim. Acta*, **47**, 295–302.
- Veizer, J., Ala, D., Azmy, K. et al., 1999. $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ evolution of Phanerozoic seawater. *Chem. Geol.*, **161**, 59–88.
- Wada, S.-I. and Furumura, S., 1994. Solubility of CaCO_3 in 1 mol L^{-1} ammonium acetate for extracting exchangeable bases. *Soil. Sci. Plant. Nutr.*, **40**, 361–364.
- Walter, M.R. and Bauld, J., 1983. The association of sulphate evaporites, stromatolitic carbonates and glacial sediments: Examples from the Proterozoic of Australia and Cainozoic of Antarctica. *Precamb. Res.*, **21**, 129–146.
- Walter, M.R., Veevers, J.J., Calver, C.R., Gorjan, P. and Hill, A.C., 2000. Dating the 840–544 Ma Neoproterozoic interval by isotopes of strontium, carbon, and sulfur in seawater, and some interpretative models. *Precamb. Res.*, **100**, 371–433.
- Wang Da-Rui, Bai Yu-Lei and Jia Cheng-Zao, 1994. Carbon isotope anomaly and significance at the boundary between Precambrian and Cambrian on Keping Section, Xinjiang, Northwest China. *Chinese Sci. Bul.*, **39**, 1285–1289.
- Wickham, S.M. and Peters, M.T., 1993. High $\delta^{13}\text{C}$ Neoproterozoic carbonate rocks in western North America. *Geology*, **21**, 165–168.
- Young, G.M., 1995. Are the Neoproterozoic glacial deposits preserved on the margins of Laurentia related to the fragmentation of two supercontinents? *Geology*, **23**, 153–156.

Received 18 May 2000; revised version accepted 5 April 2001