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Correlation of the Askyn River section, Southern Urals, Russia, with the Mid-Carboniferous Boundary GSSP, Bird Spring Formation, Arrow Canyon, Nevada, USA: implications for global paleoceanography

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Abstract

Isotopic data of unaltered low-Mg calcite brachiopods from type Bashkirian strata of the Askyn River section (southern Urals, Russia) are correlated with those from the Mid-Carboniferous Boundary Global Stratotype Section and Point (GSSP) at Arrow Canyon (southern Nevada, USA). Strontium isotope and conodont data of precisely located samples from the sub- to tropical locations spanning the Mid-Carboniferous boundary facilitate the correlation of the two sequences and support the discontinuous nature of the sequence at Askyn. Carbon isotopic trends of the two sites are generally divergent and demonstrate the influence (overprinting) of local oceanographic conditions on global parameters. Oxygen isotopes show a similar divergence for the latest Mississippian time period, with concurrence of values for the earliest Pennsylvanian at the two sites. In both instances, differences-variations in water temperature, currents, salinity and burial rate/amount of organic matter or combinations of these factors may have played roles of influencing water chemistry at the local level. It is possible to achieve global correlations at a finer scale than biozones with precisely located material from stratotype and ancillary sections, especially if a Global stratotype POINT has been identified and selected according to universally accepted biostratigraphic criteria. Consequently it is possible to resolve oceanographic influences at the local level and reconcile them with truly global oceanographic conditions and ultimately define global causes/effects such as cryospheric and tectonic events. Seawater chemistry at Arrow Canyon probably represents Panthalassan global Mid-Carboniferous oceanic conditions, supported by its similarity with data from other locations and modern global oceanographic parameters. Askyn represents Paleotethys and global oceanographic conditions, but in part, overprinted by local influences. The Mid-Carboniferous seems to be a time of expansion of the cryosphere as documented by a positive shift in seawater oxygen isotope composition of about 0.5‰ (SMOW) from the latest Mississippian (−1.2‰) to earliest Pennsylvanian (−0.7‰).

Keywords: Mid-Carboniferous; global correlation Askyn–GSSP; strontium; carbon; oxygen isotopes

1. Introduction

Chemostratigraphic correlation of sequences

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older than Cenozoic, until recently, has been largely hampered by imprecise and inaccurate analytical and stratigraphic (including biostratigraphic) data/results. Problems with preservation and resolution of the geologic record coupled with obtaining geochemically unaltered material further complicate the task of precisely correlating Mesozoic and older sequences. The concern with analytical accuracy and precision has been largely overcome in the past 20 yr with major improvements in methodology and instrumentation. Problems with accuracy of chemical data have been largely resolved by using 'unaltered' source material, identified after a rigorous selection process (cf. Brand and Veizer, 1980). The secondary layer of brachiopods in many instances is both morphologically as well as chemically preserved in its pristine state (e.g., Grossman, 1994), and guards of belemnites may hold similar application potential (e.g., Brand, 1995; Veizer et al., 1997b).

Resolution of the geologic record and precise placement of samples/units/formations is probably the greatest stumbling block to high-resolution chemostratigraphic correlation. According to Veizer et al. (1999, p. 62) "...highest resolution can be achieved with biostratigraphy, with a resolution limit rarely better than 0.5 Ma and more often on the order of 1 Ma or more". Global correlations can be refined to no less than to individual biozones for Paleozoic sequences, except in a situation where the biozones are defined both within a stratotype section and more importantly are characterized by a stratotype point. In this case, geochemical correlation resolution in sequences should far exceed the limits espoused by Veizer et al. (1999), and may approach the limit of bioturbation, if present, on scales of about 15 cm or better. Using a combination of stratotype sections and points, it should be possible to correlate Mesozoic and Paleozoic sequences at resolutions currently achieved for, or approaching Cenozoic ones. The Global Stratotype Section and Point (GSSP) for the Mid-Carboniferous boundary, among others, should be a prime candidate for demonstrating the potential of high-resolution chemostratigraphic correlation.

The GSSP for the Mid-Carboniferous boundary has been established at Arrow Canyon, Nevada in a carbonate sequence of the Bird Spring Formation (Brenckle et al., 1997; Lane et al., 1999). Brand and Brenckle (2001) presented detailed stratigraphic and geochemical information on the unaltered brachiopods from the Mid-Carboniferous GSSP. Sinitsyna et al. (1995) and Bruckschen et al. (1999) described in detail an ancillary section in Russia covering the Mid-Carboniferous interval.

The Mid-Carboniferous shift in carbon isotopes recorded in brachiopods has been ascribed in part to increased burial of organic matter (carbon) and changes in ocean circulation patterns (e.g., Bruckschen et al., 1999; Mii et al., 1999). In contrast, the shift observed in the seawater oxygen isotope composition has been linked to changes in climate; specifically expansion of the cryosphere (Mii et al., 1999). With precise positioning of samples from the two studied sections (GSSP and Askyn), a clearer picture should evolve as to changes in paleoceanography and paleoclimates, and their causes and effects during this time period.

The primary objective of this paper is to demonstrate the concept and viability of correlating Paleozoic sections within biozone intervals using chemostratigraphy. Another objective is to decipher global oceanographic and climatologic parameters from local ones using carbon and oxygen isotopes. Specifically, the purpose of this paper is to correlate an equivalent ancillary section in southeastern Russia with the Mid-Carboniferous GSSP in Nevada, USA.

2. Geological setting

Arrow Canyon is situated in the western United States (Nevada) and during Mid-Carboniferous time was located close to the equator. Based on paleogeographic re-construction, the GSSP site, part of the Great Western Basin, probably was connected to the Panthalassan Ocean to the west (Fig. 1; Lane et al., 1999) by a seaway that extended from southern California to Alaska. The boundary beds at Arrow Canyon were deposited about 75 km from the cratonic highlands to the east and about 200 km from the Antler Orogenic

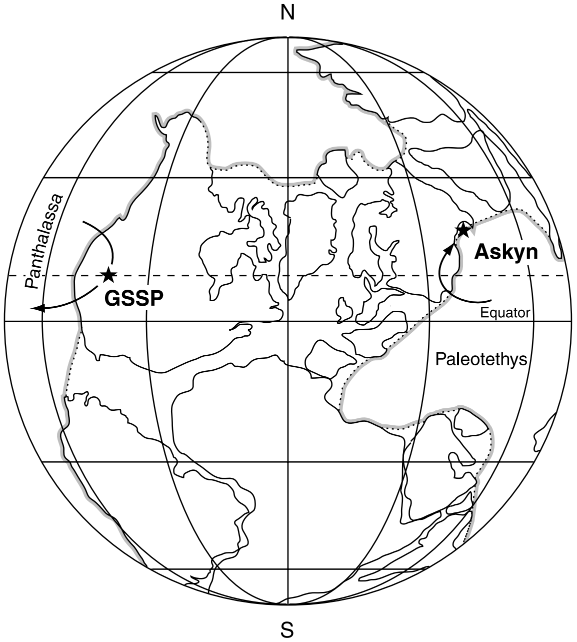

Fig. 1. Paleogeography of Mid-Carboniferous time showing plate configuration and major oceans/seas (Panthalassa and Paleotethys; plate reconstruction after Scotese and McKerrow, 1990). The Mid-Carboniferous GSSP represents the GSSP at Arrow Canyon, Nevada, USA, and Askyn is a boundary section located along the Askyn River, southern Urals, southeast of the town of Ufa, Russia. Ocean currents at the GSSP and Askyn are inferred from the Carboniferous paleoceanographic reconstruction of Ziegler et al. (1981). Dotted line represents possible continental outline/edge during the Mid-Carboniferous. For detailed paleogeographic elements and descriptions of the two locations see Lane et al. (1999) and Sinitsyna et al. (1995).

Highland to the west (Lane et al., 1999). At the same time, the Askyn River section of Russia (southern Urals) was deposited on the other side of the emerging global continent along the edge of the Paleotethys Ocean (Fig. 1). Both localities occupied low-latitude, tropical to sub-tropical, positions during Mid-Carboniferous time, but within different provinces of oceanic circulation (Ziegler et al., 1981).

2.1. Arrow Canyon, Nevada – GSSP

The GSSP section at Arrow Canyon consists of laterally extensive (tens of kilometers), generally undisturbed and almost completely exposed shelf-edge deposits. The predominantly carbonate succession at Arrow Canyon represents numerous shallowing–deepening events with a rich invertebrate fauna. These glacioeustatic fluctuations were probably the direct result of glacial events in southern Gondwana (Lane et al., 1999). Specifically the GSSP boundary falls within a 1.5-m-thick neritic packstone to grainstone with a faunule suggesting deposition in a relatively shallow, open marine shelf environment. The precise lithostratigraphy and biostratigraphy are described in detail by among many papers by Brenckle et al. (1997) and Lane et al. (1999), and superimposed with geochemical (trace element, carbon, oxygen and strontium isotope) data by Brand and Brenckle (2001).

2.2. Askyn River section, Russia

The Askyn River section is situated in the western part of the Asatau Anticline. Successively older stratigraphic units ranging from the Vendian (Zigan Unit) to the Upper Carboniferous are exposed near the core of the anticline. The sediments at the Askyn section range from the upper Serpukhovian to the upper Moscovian. Limestones and dolostones of the Yuldybaevsky, Protvinsky and Staroutkinsky horizons represent the uppermost Serpukhovian with a total thickness of 32 m. The Serpukhovian/Bashkirian boundary coincides with the base of the Bogdanovsky horizon, which is a 14-m-thick unit of shallow marine limestone. The Bashkirian deposits at the Askyn section represent the most complete succession for this stage in the type region. Shallow marine carbonates (limestones and dolostones) are rich in foraminifers, conodonts, brachiopods, and algae. The total thickness of the Bashkirian is 226.1 m with 146.6 and 79.5 m for the lower and upper substages, respectively. These deposits represent open marine shelf to semi-restricted shallow bank environments (Sinitsyna et al., 1995, fig. 16.2).

3. Methodology

The brachiopods used in this study underwent rigorous trace element, micro-structural and cathode luminescence tests to identify those specimens that are morphochemically unaltered (cf. Brand and Veizer, 1980; Brand, 1989). The preservation tests (mineralogy, micro-structures and geochemistry) for the GSSP brachiopods are extensively discussed in Brand and Brenckle (2001). Studies on micro-textural preservation of the Askyn shells were performed on a GEO 1530 Gemini SEM (kV) utilizing freshly broken fragments and splinters of the shells. The diluted phosphoric acid that remained after dissolution of carbonates for stable isotope preparation (cf. Bruckschen et al., 1999) was used to determine the Mg, Sr, and Mn concentrations on a Philips PU 7000 ICP-AES spectrometer. The trace element and stable isotope data are therefore from the same portion of the brachiopod shell. Since the phosphoric acid cannot be transferred quantitatively from the y-tube reaction vessel to the ICP, the trace element concentrations were normalized by a factor needed to adjust the ICP calcium values to 40

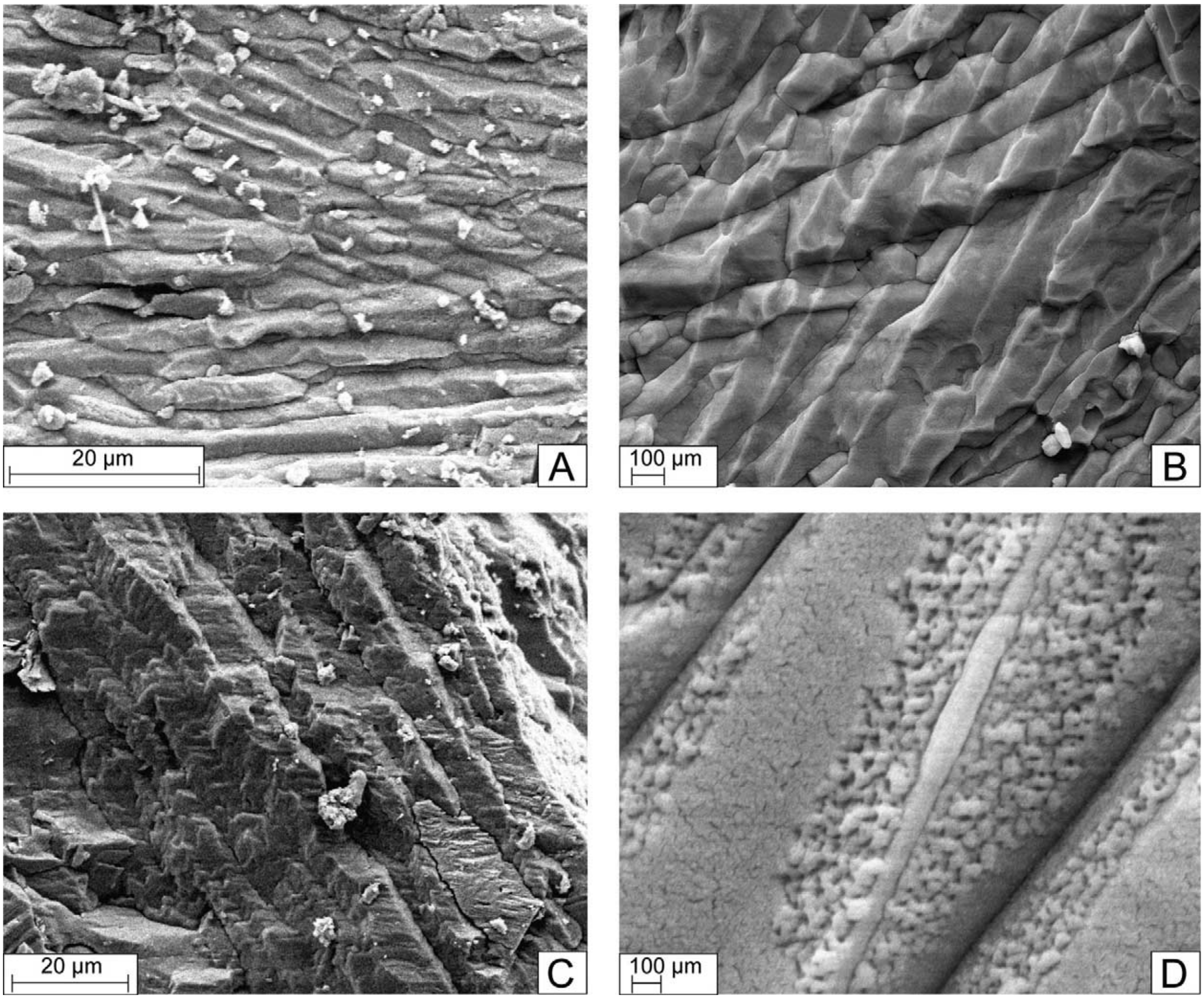

Fig. 2. SEM micrographs of micro-structures in brachiopod shells from the boundary interval at the Askyn River section. (A) Well preserved trabecular fibers of the secondary layer within specimen PB 906b (latest Serpukhovian). (B) Trabecular fibers exhibiting excellent preservation in specimen PB 908a (earliest Bashkirian). (C) Well preserved fibers in specimen PB 909c (earliest Bashkirian). (D) Excellent preserved trabecular fibers of the secondary layer with some minor signs of dissolution (pits) in specimen PB 910b (earliest Bashkirian; Appendix).

wt%. The detection limits for Mn and Sr, depending on sample size, were between 10 and 5 ppm, and the precision was within 10 relative percent (Appendix).

Carbon and oxygen isotopes were measured off- or on-line to test the voracity of the two evaluation methods. For off-line analyses, an aliquot of 1–6 mg of shell powder was reacted with 100% phosphoric acid for 24 h at 50°C. The released gas was measured on a Finnigan MAT 251 mass-spectrometer, calibrated against PDB and corrected to a temperature of 25°C. On-line measurement involved drilling of samples from 200-μm-thick thin-sections, after cathode luminescence work, and analysis of powder by mass-spectrometer utilizing the Finnigan Kiel II device. Data for carbon and oxygen isotopes, from either method, were not normalized to but compared to NBS standard reference materials (e.g., NBS SRM #19 and 20; Appendix).

About 0.5–1.0 mg of shell powder was analyzed for $^{87}Sr/^{86}Sr$. For complete description of preparation procedures and technical details see Diener et al. (1996). All strontium isotope values were normalized to a nominal value of 0.710240 for NBS SRM #987 (McArthur, 1994; Appendix). GSSP data used in this study are from previous work, the reader is referred to the article for additional information (Brand and Brenckle, 2001) on details of sampling strategy, sample preparation, analysis and evaluation.

4. Potential diagenetic alteration of $\delta^{13}C$ and $\delta^{18}O$ in Askyn brachiopods

In contrast to $^{87}Sr/^{86}Sr$, the upper Serpukhovian $\delta^{18}O$ and $\delta^{13}C$ values of unaltered brachiopods from the Askyn section, are significantly lower than those measured at Arrow Canyon (Appendix; Brand and Brenckle, 2001). At first glance, one might attribute this discrepancy to potential diagentic alteration of the Askyn samples. Since we want to focus on the importance of detecting and differentiating between local and global isotope trends/signals we need to rule out this possibility.

All analyzed shells from the Askyn section were screened for diagenetic alteration by the trace element and cathode luminescence techniques and for preservation of micro-texture by scanning electron microscopy (SEM) (cf. Brand and Veizer, 1980; Brand, 1989; Veizer et al., 1997a). None of the samples (e.g., PB 906, 908, 909 or 910) show any signs of re-crystallization of low-Mg calcite fibers (secondary layer) by these criteria (Fig. 2). Only some minor dissolution (pitting) was noted in the fibers of specimen 910 (Fig. 2D). Further-

Table 1

One-way ANOVA of isotopic compositions of unaltered brachiopods from the Askyn section, southern Urals, Russia, analyzed by the macro-(Bochum University) and micro-method (Erlangen University/TAMU)

Parameter	Macro-method (Bochum)			Micro-method (Erlangen)			*P*
(‰)	*N*	mean	SD	N	mean	SD	
$\delta^{13}C$	21	−0.183	3.313	18	0.211	3.431	0.718
$\delta^{18}O$	21	−4.181	1.133	18	−4.035	1.566	0.737
$\delta^{13}C$[a]	8	−0.249	3.485	8	−0.185	3.362	0.971
$\delta^{18}O$[a]	8	−3.905	1.765	8	−4.179	1.076	0.714
$\delta^{13}C$[b]	2	−3.090	0.269	2	−3.445	0.771	0.601
$\delta^{18}O$[b]	2	−5.345	0.092	2	−5.550	0.071	0.130
$\delta^{13}C$[c]	3	−0.623	0.940	6	−0.450	1.928	0.890
$\delta^{18}O$[c]	3	−3.947	0.973	6	−4.368	0.319	0.343
$\delta^{13}C$[d]	3	+6.627	0.215	3	+6.810	0.740	0.701
$\delta^{18}O$[d]	3	−2.227	0.454	3	−1.620	0.212	0.104

Note: N = Total of unaltered brachiopod data (replicate samples averaged), SD = standard deviation.

[a] Averages of sampling horizons.

[b] Sampling level 904 (4/3–3.75 m).

[c] Sampling level 908 (5/4–0.00 m).

[d] Sampling level 909 (6/7+3.00 m; replicate samples averaged).

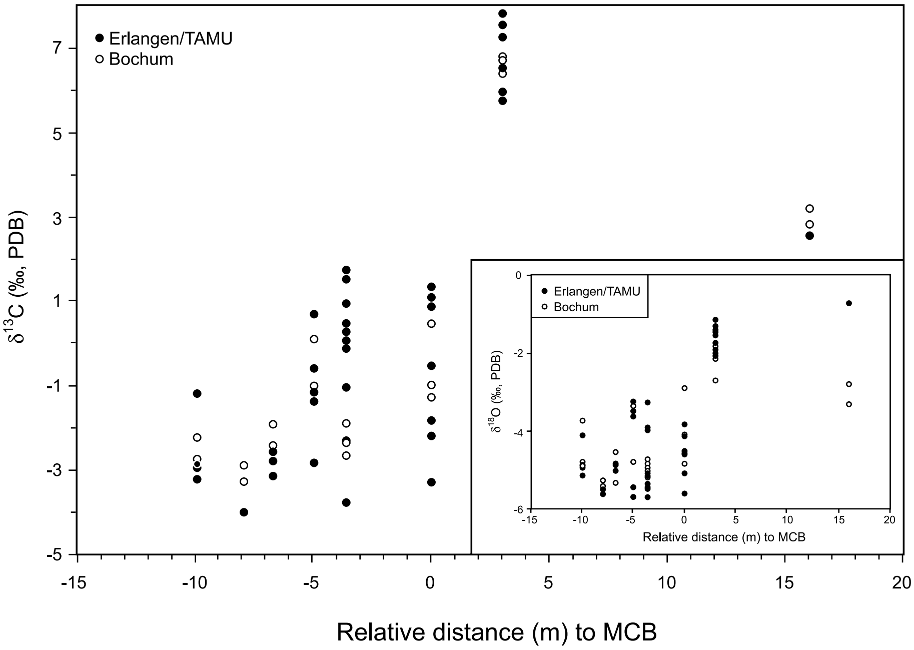

Fig. 3. Comparison of carbon isotope carbon results using two different sampling techniques for stable isotope analyses on brachiopod calcite from the Askyn River section across the Mid-Carboniferous boundary (MCB). The Bochum method represents the combined trace element, micro-structural sampling approach, whereas the Erlangen/TAMU method uses cathode luminescence and micro-sampling of shell to obtain preserved calcite material for stable isotope analysis (Table 1). Similar results and trends are observed for the oxygen isotope values (inset).

more the trace chemistry of the Askyn brachiopods are similar to those recorded in their modern counterparts (Appendix; Brand and Logan, 1991). However, the trace element–SEM screening technique in conjunction with the off-line preparation technique for stable isotopes, routinely utilized at Bochum and other institutions, has recently been suggested as a potential source of uncertainty in identifying and analyzing original shell carbonate and thus obtaining depositional isotope values (E. Grossman, pers. comm. 1999).

In order to test our screening and analysis approach, we re-analyzed our Askyn samples at Erlangen University, utilizing the selection and analytical procedures of Grossman et al. (1993) and Mii (1996) of obtaining online analyses of non-luminescent aliquots drilled from 200-μm-thick sections of shells. The $\delta^{18}O$ and $\delta^{13}C$ show no significant difference between the results of the two techniques. No significant differences were found in the isotope values whether we tested the whole data set (first evaluation set, Table 1), averaged horizon data set (second evaluation set), or individual samples (analyses) from stratigraphically equivalent strata (subsequent evaluations, Table 1). Overall, the Erlangen/TAMU (Texas A&M University) approach results in a significant scatter in $\delta^{13}C$ for contemporaneous samples (i.e. samples from one horizon or multi measurements within one shell) that clearly exceeds those obtained with the Bochum technique (Fig. 3). The $\delta^{18}O$ values show a similar pattern as exhibited by the $\delta^{13}C$ values between the 'Bochum' and 'Erlangen/TAMU' techniques (Fig. 3, inset). This clearly disproves the suggestion that one test method is better than the other in obtaining 'preserved' samples and consequently chemical signatures. The greater scatter of Erlangen values may simply be related to seasonal trends resolved by its more intricate sampling scheme. However, the general agreement of the mean values for a given sample, trace chemistry, micro-structural evaluation, and cathode luminescence support the suggestion of preservation of the original isotope composition in the shells from Askyn.

The degree of calcium carbonate alteration is mainly controlled by the water–rock ratio (Brand and Veizer, 1980; Banner and Hanson, 1990) and the 'openness' of the diagenetic system, and can vary for different constituents/layers of a shell. For a given diagenetic system, some trace elements or isotopes may be altered, while others may retain their near-original chemical composition (Veizer, 1983). In terms of preservation of original $\delta^{13}C$ values, marine limestones and low-Mg calcite shells embedded in such limestones, are believed to react as a closed system, where the system is buffered by marine $\delta^{13}C$ values and, therefore, are not strongly affected by diagenesis. For this reason, $\delta^{13}C$ of micritic limestones, which represent diagenetically re-crystallized carbonates have been frequently used as proxies for $\delta^{13}C$ of marine DIC (e.g., Veizer, 1983). Ascribing the low $\delta^{13}C$ values at Askyn to diagenesis would require a significant degree of post-depositional alteration on the section, which should be also reflected by the $^{87}Sr/^{86}Sr$ values but is not. Instead, the Sr isotope values at Askyn are indistinguishable from those measured at Arrow Canyon, providing supporting evidence for original $\delta^{13}C$ in the Askyn brachiopod calcite. Because none of the test criteria and results point to diagenetically influenced isotope signatures in brachiopods from the Askyn River section, we prefer to attribute the observed isotopic differences to local effects such as seasonal variations; and further discussed in the subsequent text.

5. Correlation trends

Global correlation between intercontinental Paleozoic sections/strata at a more refined level than biozones is deemed problematic and unrealistic by Veizer et al. (1997a,b), although it was not precluded for sections/sequences at the local and possibly regional level. Some researchers use 'limited' biostratigraphic assignments for formations/horizons/beds coupled with ages derived from geologic time charts to achieve local/regional/global correlations, which by its very nature makes correlations at better than biozone extremely difficult (e.g., Mii et al., 1999). The problem of contiguous and complete sequences is a major stumbling block to achieving a level of correlation precision in Paleozoic strata that is attainable in younger ones. Stratotype sections are the preferred means of attempting and establishing chemocorrelation between units, because this allows for the combination of biological and chemical tools in achieving high-precision correlation. Possibly even better are stratotype points (GSSPs), where a specific point/horizon separates sub- and superjacent depositional/biological events, based on globally accepted paleontological evidence such as the first appearance of the conodont *noduliferous* at the

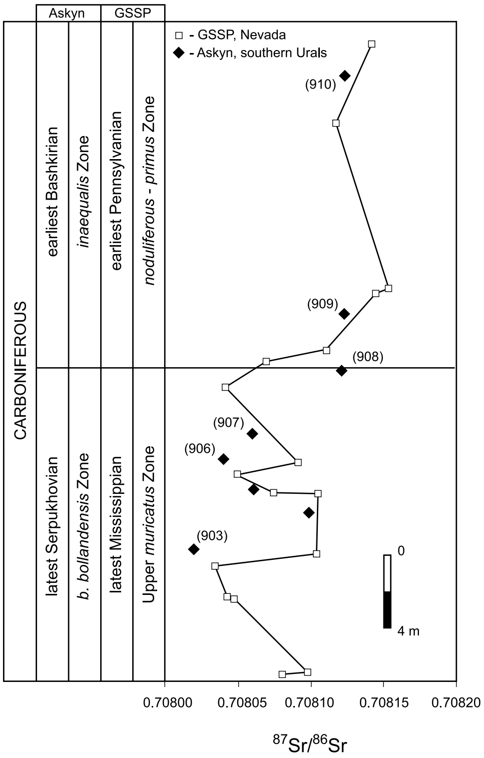

Fig. 4. Chemostratigraphic trend of strontium isotopes in unaltered brachiopods from the Mid-Carboniferous GSSP, Nevada, and Askyn, southern Urals. Stratigraphic position of isotopic data from Askyn was not adjusted to facilitate correlation with strontium isotope data and trends established about the Mid-Carboniferous at the GSSP (Brand and Brenckle, 2001). Note: Size of symbols represents analytical (GSSP and Askyn) and stratigraphic (GSSP) uncertainty of individual samples.

Mid-Carboniferous boundary (Brenckle et al., 1997; Lane et al., 1999). This allows for precise placement of samples and their geochemical information relative to a globally recognized and fixed point in space and time. From this perspective it should be possible to correlate global oceanographic events using such tracers as strontium isotopes. The role of carbon and oxygen isotopes is less clear because they may be controlled to some degree by local, regional or other oceanographic influences (cf. Bates and Brand, 1991; Mii et al., 1999; Veizer et al., 1999).

5.1. Strontium isotope chemostratigraphy

The recently designated Mid-Carboniferous GSSP at Arrow Canyon is an ideal candidate for testing the hypothesis of chemostratigraphic correlation; of course in conjunction with biostratigraphic information. Brand and Brenckle (2001) presented a detailed isotopic chemostratigraphic sequence and Lane et al. (1999) presented an equivalent detailed conodont biostratigraphy for the GSSP. The sequence exhibits some distinct and resolvable perturbations (oceanographic oscillations–isotopic trends) leading up to the Mid-Carboniferous boundary (Fig. 4), which should be identifiable in isochronous data sets from other locations. To test this hypothesis, the strontium isotope trend of the unaltered brachiopods from the GSSP was to be overlaid with the information gathered from the Mid-Carboniferous sequence at Askyn.

Using lithostratigraphic measurements and boundary placement, the strontium isotope data from the horizons at Askyn were directly superimposed onto the data from the GSSP (Fig. 4). Several problems arise from this ‘direct’ placement and correlation of data. Namely, the strontium values of samples PB 903, 906 and 908 do not correspond to those for equivalent horizons from the GSSP, and furthermore their ranges are outside acceptable variation (± 0.000023 based on modern shallow water brachiopods; Brand and Logan, pers. comm., 2001) for isochronous horizons. Especially disconcerting is the apparent mismatch between the ‘boundary’ value from Askyn (0.708122) with that from the GSSP (0.708056; Fig. 4). Statistical analysis of corresponding data from equivalent horizons of the two sections confirms that there is no significant difference ($P = 0.417$) but neither is there great similarity between the two data sets (Table 2). This raises the question of a possible hiatus (break) about the Mid-Carboniferous boundary at Askyn, a concern that has been extensively debated over the last several decades by conodont biostratigraphers (H.R. Lane, pers. comm., 2001).

Chemostratigraphic agreement between the two sequences required the separation of the Askyn data set between samples 907 and 908 (Fig. 4), resulting in a slight downward shift by about 7 m for the latest Serpukhovian samples and a somewhat larger one of about 12 m for the earliest Bashkirian ones. Considering the hiatus at Askyn, the data are re-plotted and superimposed

Table 2
One-way ANOVA of isotopic compositions between unaltered brachiopods of the Mid-Carboniferous GSSP Bird Spring Formation, Arrow Canyon, Nevada, and the Askyn section, southern Urals, Russia

Parameter	Arrow Canyon			Askyn			*P*
	*N*s	mean	SD	*N*s	mean	SD	
$^{87}Sr/^{86}Sr$[a]	11	0.708096	0.000034	8	0.708081	0.000041	0.417
$^{87}Sr/^{86}Sr$[b]	7	0.708083	0.000042	6	0.708084	0.000036	1.000
$\delta^{13}C$ (‰)[b]	7	+2.474	0.754	6	−0.233	3.415	0.064
$\delta^{13}C$ (‰)[c]	7	$\underline{+2.474}$	0.754	5	$\underline{-1.556}$	1.208	0.001
$\delta^{18}O$ (‰)[b]	7	$\underline{-2.451}$	1.018	6	$\underline{-4.277}$	1.244	0.014

Evaluations were performed on corresponding data (sampling) intervals. Underlined values are significantly different at the 95% confidence level ($P < 0.050$). *N*s = number of samples/horizons (total of unaltered brachiopod data), SD = standard deviation.

[a] No stratigraphic adjustment of Askyn samples.

[b] With stratigraphic adjustment of Askyn samples.

[c] Without the ‘heavy’ $\delta^{13}C$ sample/horizon (Appendix).

on those from the GSSP. The revised placement of the Askyn data on the GSSP realizes agreement in both chemostratigraphy and biostratigraphy (Fig. 5), while it assumes some constancy in sedimentation rates above and below the break as well as around the globe; concepts which deserve future detailed attention. Nevertheless, this agreement is tested once more statistically on data from corresponding horizons and concludes that there is now significant similarity between the two strontium data sets ($P = 1.000$; Table 2). Additional tests confirm excellent correlation between the two data sets of corresponding samples (GSSP $^{87}\mathrm{Sr} = 0.0000098$ position $+0.708011$, $r^2 = 0.957$; Askyn $^{87}\mathrm{Sr} = 0.0000087$ position $+0.708025$, $r^2 = 0.921$). It is recommended that due to the paucity of data the position of the earliest Bashkirian in the Askyn section needs further study and may be subject to further revision (Fig. 5).

The fit of the two data sets suggests that correlation at the better than biozone appears to be readily attainable for well constrained sequences with sufficient amount of unaltered material, definitive bio- and stratigraphic reference points, and precise sampling location measurements. The observations of the GSSP and Askyn trends demonstrate that global correlation at a level, not achieved before, is possible for Paleozoic strata. This should expand the potential of chemostratigraphy of providing enhanced correlation of fossil-rich Paleozoic units.

If all applicable criteria (tight lithostratigraphic control, exact stratigraphic measurements coupled with unequivocal biostratigraphic identification and strontium isotope data from preserved and precisely located brachiopods) are fulfilled not only should it be possible to correlate global sequences at better than biozone levels, but it should also be possible to exclude samples/data that do not match but still represent a sequence of chronologically ‘equivalent’ oceanographic events.

Data from formations/members/units without precise stratigraphic information may be useful in constructing only general trends of oceanographic seawater-strontium evolution. Superimposed on the GSSP oceanographic trend are strontium isotope ranges for unaltered brachio-

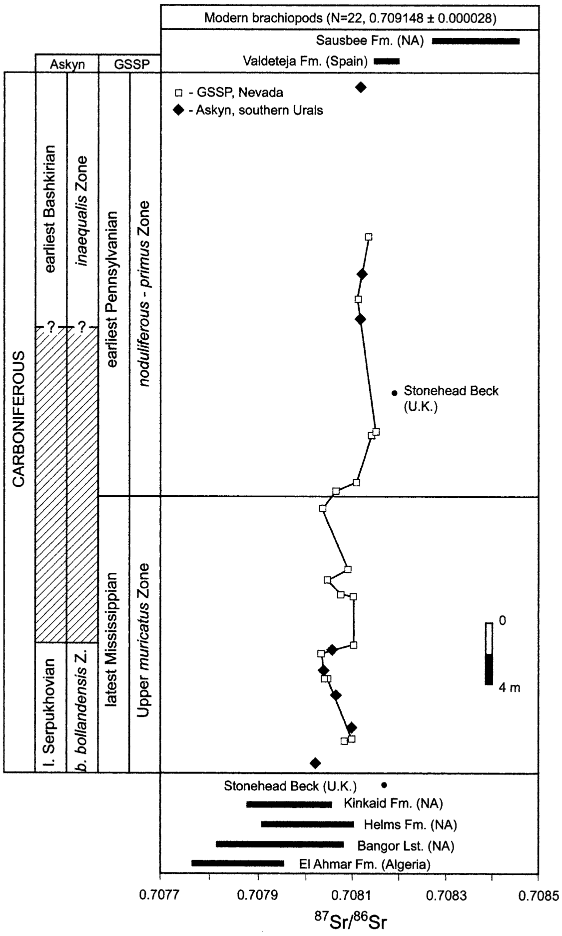

Fig. 5. Chemostratigraphic trend of strontium isotopes in unaltered brachiopods from the Mid-Carboniferous GSSP (Brand and Brenckle, 2001), Nevada, and Askyn, southern Urals. Position of strontium data from the Serpukhovian at Askyn was adjusted to account for differences in sampling interval, sedimentation rates and most importantly biostratigraphic concurrence. The position of strontium data from the Bashkirian at Askyn required a more significant adjustment to agree with conodont biostratigraphic information (Lane, pers. comm., 2001). The strontium isotope data for the Kinkaid (late Chesterian-brachiopods) and Sausbee (Morrowan-brachiopods) formations are from Bruckschen et al. (1999). The data of the El Ahmar (basal Serpukhovian-brachiopods) and Valdeteja (Bashkirian-brachiopods) formations are from Popp et al. (1986). The data of modern shallow-water brachiopods are from Brand and Logan (1991). The solid datum point is of conodont material from the Mid-Carboniferous section at Stonehead Beck, UK (Riley et al., 1993). Note: Size of symbols represents analytical (GSSP and Askyn) and stratigraphic (GSSP) uncertainty of individual samples.

pods from the Late Mississippian El Ahmar, Bangor, Helms, and Kinkaid formations and Early Pennsylvanian Valdeteja and Sausbee formations (Fig. 5). Conodont ^{87}Sr/^{86}Sr data from the European ancillary Mid-Carboniferous boundary section at Stonehead Beck are also included to attempt stratigraphic placement and possibly even correlation (Fig. 5). Except for the data from Stonehead Beck, these units/samples are not stratigraphically well constrained, and thus are plotted as ranges outside the GSSP trend. The isotopic ranges for the latest Mississippian data sets are much greater than that for GSSP trend espoused in this report. This reflects either greater isotopic seawater variation during their respective time periods, samples covering a great amount of geologic time, or the inclusion of some altered material (cf. Brand, 1991). Furthermore, their numerical divergence from that of the GSSP Mid-Carboniferous Sr isotope trend confirms that data from these units do not represent latest Mississippian time, instead there was possibly a hiatus or non-marine deposition across the boundary at these other locations, or they simply reflect a collection/sampling/availability bias. The data of these units were placed in order of general biostratigraphic information, and there seems to be a trend of increasing strontium isotopic similarity with decreasing stratigraphic separation of the aforementioned units (Fig. 5). This incontrovertibly proves that none of those samples from these specific units represent the latest Mississippian or a boundary interval, but eventually expansion of the GSSP Sr curve should perhaps facilitate the chemostratigraphic placement of these and other units/formations.

The datum of the Pennsylvanian conodont sample from Stonehead Beck is only slightly similar to time-equivalent data from the GSSP (Fig. 5). Correlation of the GSSP trend for this particular stratigraphic interval is difficult with a singular point. In addition, the possible lack of diagenetic integrity of the strontium isotope value of the conodont material makes correlation of the Stonehead Beck sequence with other boundary sequences a difficult proposition. Other latest Pennsylvanian data sets show decreasing isotopic similarity with increasing stratigraphic separation. Although the isotopic data of the Valdeteja brachiopods are somewhat similar to those from the GSSP, they infer deposition some time after earliest Pennsylvanian time, and a even later time of deposition is inferred for the brachiopod material from the Sausbee Formation (Fig. 5).

5.2. Carbon isotope chemostratigraphy

With the strontium isotope trend established for the Mid-Carboniferous boundary interval, the other geochemical parameters should follow that trend if they too reflect global oceanographic conditions. Fig. 6 shows the carbon isotope data trends from the Mid-Carboniferous GSSP and Askyn sections, as well as carbon values of modern low-latitude brachiopods, and of counterparts from seven formations/horizons representing Serpukhovian and Bashkirian times.

The carbon isotope values from the GSSP for the latest Mississippian have a mean of +1.92‰, and range from +0.46 to +3.43‰, which corresponds to a large degree with the values obtained for preserved brachiopods from the sub-boundary Kinkaid, Bangor and El Ahmar formations as well as the Tarusskian Horizon. In contrast, the carbon isotope values from preserved brachiopods of the Askyn section do not concur with those of corresponding levels from the latest Mississippian at the GSSP at the 95% confidence level (Table 2; computation of data without the heavy carbon values does not improve the situation). Although there seems to be no similarity in values between the latest Mississippian GSSP and Askyn, their trends do seem to bear some resemblance (Fig. 6).

The earliest Pennsylvanian (Bashkirian) brachiopods from the GSSP have a mean carbon isotope value of +1.85‰, with a range of +0.006 to +3.24‰ (Brand and Brenckle, 2001). This range concurs to some degree with values obtained on unaltered brachiopods from the Morrowan Sausbee Formation (Fig. 6). In contrast, the δ^{13}C from the Valdeteja Formation and Krasnopolyanskian Horizon differ significantly from those recorded at the GSSP for the earliest Pennsylvanian. The data from the Askyn brachiopods show a wide scatter about the trend depicted at the GSSP, and their paucity of data precludes any

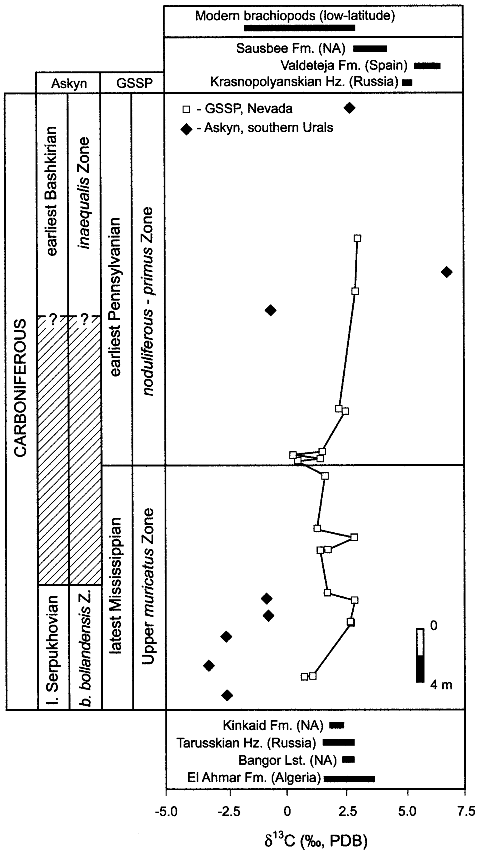

Fig. 6. Chemostratigraphic trend of carbon isotopes in unaltered brachiopods from the Mid-Carboniferous GSSP, Nevada (Brand and Brenckle, 2001), and Askyn section, southern Urals. The data of the El Ahmar (basal Serpukhovian-brachiopods) and Valdeteja (Bashkirian-brachiopods) formations are from Popp et al. (1986). The data of the Kinkaid (late Chesterian-brachiopods), and Sausbee (Morrowan-brachiopods) formations are from Mii et al. (1999). Russian Platform data of brachiopods are from the Tarruskian (Serpukhovian) and Krasnopolyanskian (Bashkirian) horizons are from Mii et al. (2001). Data of Bangor (Chesterian-brachiopods) and additional Sausbee (Morrowan-brachiopods) units are from Brand (1989). The data of modern low-latitude (sub- to tropical) brachiopods are from Brand and Logan (1991) and Carpenter and Lohmann (1995). Note: Size of symbols represents stratigraphic (GSSP) uncertainty of samples.

correlation between the two sequences based on carbon isotope values (Fig. 6).

It is proposed that the Askyn values, in part, reflect local environmental conditions and the influences of a continental hinterland. A number of causes may be responsible for the observed divergence in the carbon trends from the GSSP and Askyn, as well as Valdeteja and Krasnopolyanskian, such as differences in organic matter production, removal, burial, and oxidation–reduction, and water circulation due to plate movement (cf. Mii et al., 1999), or simply temporal differences between the GSSP and these formations/horizons. Bruckschen et al. (1999) espoused a shift towards heavier $\delta^{13}C$ values at the Mid-Carboniferous boundary based on Askyn data from Russia and other data sets from the Ukraine. Mii et al. (1999) observed a similar shift in $\delta^{13}C$ values but with a divergence between North American and Eurasian data during the middle Carboniferous. More definitive data-information covering in greater detail and with more precise sample placement this particular time span is required to resolve this important issue in the middle of the Carboniferous.

5.3. Oxygen isotope chemostratigraphy

The carbon isotope data from the GSSP and Askyn suggests a dichotomy in them reflecting global oceanographic conditions. The following is an examination of their respective and correlative oxygen isotope values of comparable samples and horizons (Fig. 7). The oxygen isotope values from the GSSP are similar to those recorded in modern low-latitude brachiopods. The latest Mississippian brachiopod data from Askyn follow the general pattern exhibited by that from the GSSP, but their values are in general more negative (Fig. 7). In contrast, although few, two data for the earliest Pennsylvanian from Askyn are similar to those from the GSSP at comparable stratigraphic levels. The difference in oxygen isotope values between the two sections is significant at the 95% confidence level (Table 2).

Four of the five late Mississippian data sets are similar to that from the GSSP, whereas the data from the Bangor limestone are similar to the data from the Askyn. This appears to confirm that local environmental variation in seawater chemistry may be a greater influence than previously recognized. In contrast the earliest Pennsylvanian data from the GSSP, Askyn and the other early

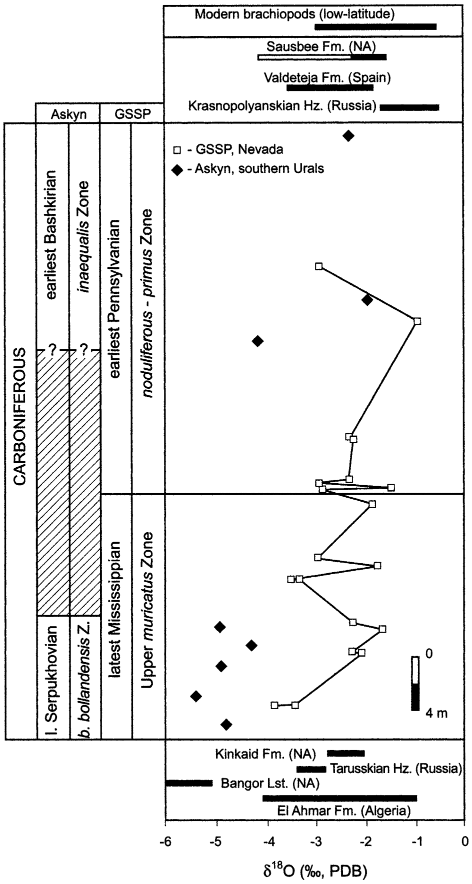

Fig. 7. Chemostratigraphic trend of oxygen isotopes in unaltered brachiopods from the Mid-Carboniferous GSSP, Nevada (Brand and Brenckle, 2001), and Askyn section, southern Urals. The data of the El Ahmar and Valdeteja formations are from Popp et al. (1986). The data of the Kinkaid, and Sausbee formations are from Mii et al. (1999). Russian Platform data of the Tarruskian and Krasnopolyanskian horizons are from Mii et al. (2001). Data of Bangor and additional Sausbee units are from Brand (1989). Data of the Goddard shale (Chesterian-brachiopods) are from Lowenstam (1961). The data of modern low-latitude (sub-tropical to tropical) brachiopods are from Brand and Logan (1991) and Carpenter and Lohmann (1995). Note: Size of symbols represents stratigraphic (GSSP) uncertainty of samples.

Pennsylvanian are similar and show significant overlap but wide variation (Fig. 7).

The strontium, carbon and oxygen isotope values of preserved brachiopods from correlative units seem to be an invaluable tool in recognizing both global oceanographic and local environmental variations. Therefore caution is mandatory when interpreting isotopic values and trends of Paleozoic brachiopods.

6. Discussion

A number of researchers are on record that "...isotopic data clearly have enormous power to help us to determine the nature of climatic and oceanographic change throughout geologic time" (Marshall, 1992, p. 143; Lowenstam, 1961; Popp et al., 1986; Bates and Brand, 1991; Grossman, 1994; Veizer et al., 1997a,b; Bruckschen et al., 1999; Kump and Arthur, 1999; Mii et al., 1999). In particular, they may document changes associated with supercontinent formation and breakup, glacial events, mid-ocean ridge events, and the overall tectonic evolution of the Earth system and biosphere (e.g., Muehlenbachs, 1998; Bruckschen et al., 1999; Lécuyer and Allemand, 1999; Veizer et al., 1999).

The Carboniferous has drawn most of the attention of isotope researchers in part due to its abundance of suitable test material and relatively contiguous sequences throughout the world. Since all of the marine record during the Carboniferous comes from epeiric seas, the isotopic compositions of marine invertebrates may be subject to greater than normal water chemistry fluctuations especially in restricted settings (cf. Grossman, 1994). Although controversial, it is accepted by some that oceanic water was buffered by low- and high-temperature submarine processes at an oxygen isotope value near 0‰ (e.g., Muehlenbachs, 1998). Others believe that changes in seawater chemistry indeed were the controlling parameters for carbonate isotope compositions (e.g., Veizer et al., 1997a,b). In contrast, the carbon isotope composition of the ocean is largely dependent on the size of the organic carbon reservoir which includes the terrestrial/marine biomass and organic carbon stored in sedimentary rocks. The strontium isotopic composition of the ocean represents a delicate balance between continental and oceanic processes such as weathering, exchange and diagenesis in these realms (e.g., Taylor and Lasaga, 1999). Since the strontium isotopic compositions of preserved brachiopods from the GSSP and Askyn (after minor adjustments as demonstrated in Fig. 5) are in concordance with each other, they must reflect original signatures and with it the isotopic composition of the Mid-Carboniferous ocean. Furthermore, this agreement should facilitate the interpretation of the observed carbon and oxygen isotope trends for the two data sets (Figs. 6 and 7).

The Mid-Carboniferous was marked by apparent drastic changes in oxygen isotopic compositions as recorded by preserved brachiopods (Bruckschen et al., 1999; Mii et al., 1999). Lacking adequate resolution, Bruckschen et al. (1999) deferred final interpretation of Mid-Carboniferous oxygen isotope trends to a re-evaluation of data. Nevertheless, they suggested that three parameters may be responsible for their observed $\delta^{18}O$ oscillations: (1) tectonically driven changes in seawater-^{18}O, (2) superimposed ice mass effects, and (3) climatic SST (shallow, surface temperature) changes. Mii et al. (1999, 2000) found compelling evidence to support global changes in seawater-^{18}O related to changes in the global cryosphere. This change was apparently documented by a shift of about 2‰ for the Late Chesterian–early Morrowan (Serpukhovian–Bashkirian) transition (Mii et al., 1999).

The carbon isotopic record in Carboniferous brachiopods suggests a divergence in values between the Mississippian and Pennsylvanian. This apparent shift in carbon of about 3‰ for the Mid-Carboniferous was interpreted by Popp et al. (1986) to reflect a global increase in burial of organic carbon, which subsequently was demonstrated not to be of a global nature (Grossman, 1994). The latest thought on this apparent shift is that in North America it is limited to a change of 1.5‰, whereas in Europe there is an additional change of the same magnitude for a total of 3‰ (Mii et al., 1999; Bruckschen et al., 1999). The North American shift in the carbon record was ascribed to an increase in organic carbon burial, with changes in ocean circulation patterns accounting for those observed in the European material. No such clear-cut separation is noted in the data from the GSSP and other sequences (Fig. 6). Instead, it is believed that the carbon isotope distribution is to a large degree affected by local events such as at Askyn. Therefore, it is of paramount importance in evaluating concurrent sequences to decipher and separate global from local and regional oceanographic events/conditions. Ultimately, with material from stratigraphically well-constrained sections such as the Mid-Carboniferous GSSP and Askyn, we should be able to resolve problems of global versus local events and overprinting of these, and consequently derive interpretations that more closely reflect actual oceanographic changes and secular variations.

Using an upper limit of about 35°C, realistic water temperatures may be calculated with the oxygen isotope values of the latest Pennsylvanian/Serpukhovian GSSP and Askyn brachiopods

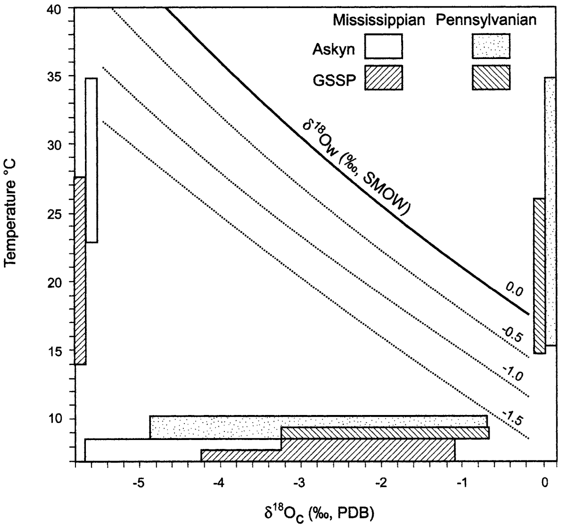

Fig. 8. Temperature–oxygen isotope (carbonate and water) trends for the latest Mississippian/earliest Pennsylvanian at the GSSP (Brand and Brenckle, 2001) and latest Serpukhovian/earliest Bashkirian Askyn River section (Sinitsyna et al., 1995). The upper temperature limit of ∼38°C is based on the de-naturation of proteins (cf. Brock, 1985; Brand, 1989) with a corresponding one of 35°C for brachiopods (Brand and Logan, 1991; Carpenter and Lohmann, 1995). The limiting factor for oxygen isotope composition of seawater is the lowest value of −5.68‰ (latest Serpukhovian) and −4.84‰ (earliest Bashkirian) from the Askyn section (Appendix). Postulated seawater temperatures ranged from 14 to 28°C at the GSSP, and from 23 to 35°C at Askyn during latest Mississippian with a proposed water isotope value of −1.2‰ (SMOW), and from 15 to 27°C at the GSSP and from 16 to 35°C at the Askyn during earliest Pennsylvanian with a proposed water isotope value of −0.7‰ (SMOW).

(Fig. 8; cf. Thompson and Newton, 1988). These conditions suggest a water temperature range of about 23–35°C for the Askyn locality and a range of 14–28°C for the GSSP; with a water oxygen isotope composition of about −1.2‰ (SMOW). This is reasonable in light of their tropical locations and postulated water current directions and conditions (Fig. 1). The slightly higher and more limited temperature range at Askyn may reflect more restricted oceanic conditions relative to more open ones noted at the GSSP (Lane et al., 1999). Similar temperature ranges can be calculated with the oxygen values of the earliest Bashkirian counterparts, but with a seawater oxygen isotope value of −0.7‰ (Fig. 8). In this instance, calculations suggest a water temperature range of about 16–35°C for the Askyn area and a range of 15–27°C for the GSSP. Overall there is a general cooling trend of several degrees from the latest Serpukhovian to earliest Bashkirian, which is coupled with an increase in seawater-^{18}O by about 0.5‰. Mii et al. (1999, 2001) and Bruckschen et al. (1999) suggested that the cryosphere started to expand before the end of the Mississippian that continued into the Pennsylvanian. The trend observed in this study supports that concept of Carboniferous glaciation being underway by Mid-Carboniferous time (Dickins, 1996; Lopez-Gamundi and Martinez, 2000) or at least cooling of the hydrosphere (Fig. 7).

7. Conclusions

Preserved low-Mg calcite brachiopods those from the type Bashkirian Askyn River section (southern Urals, Russia) are used to correlate this section with the Mid-Carboniferous GSSP at Arrow Canyon (southern Nevada, USA). Strontium isotope data of precisely located and preserved brachiopods facilitates the correlation of isochronous sections and horizons. Conodont biostratigraphy and strontium isotope data suggest that a hiatus exists in the Askyn sequence about the Mid-Carboniferous boundary. Once this hiatus is considered, chemostratigraphic correlation of the Askyn sequence is achievable with the GSSP. The two sites exhibit generally divergent carbon isotopic trends that demonstrate the influence (overprinting) of local oceanographic conditions on global parameters. Oxygen isotopes show a similar divergence for the latest Mississippian, with similar values for the earliest Pennsylvanian at the two sites. In both instances, differences–variations in local water temperature, salinity and burial rate/amount of organic matter or combinations of these factors may have played roles in influencing water chemistry.

It is possible to achieve global correlations more refined than biozones with precisely located material from stratotypes and ancillary sections, especially if a Global stratotype POINT has been identified and selected according to universally accepted criteria. Consequently it is possible to resolve oceanographic influences at the local level and reconcile them with truly global oceanographic events. It is proposed that seawater chemistry at Arrow Canyon reflect Panthalassan Mid-Carboniferous oceanic conditions, supported by its similarity to data from other 'mid'-Carboniferous sections and modern global oceanographic material. In contrast, Askyn seawater represents global oceanographic conditions that were strongly overprinted by local Paleotethyan environmental conditions during the latest Serpukhovian.

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Appendix

Geochemical data of brachiopods from the Mid-Carboniferous Askyn River section, southern Urals, Russia

Sample #	Allochem	Strat. Level	Horizon	Strat Pos. (m)	Mn	Sr	Mg	Oxygen	Carbon	Sr isotope
PB 903-E	brach	3 bound 4/3–5.75 m	Yuldybaevsky	−9.95	7	531	2368	−4.93	−2.95	0.708020
903-E								−4.86	−3.21	
903-B								−4.91	−2.81	
903b-E					4	510	3734	−5.14	−2.87	
903b-E								−4.11	−1.20	
903b-B								−4.80	−2.24	
PB 904-E	brach	3 bound 4/3–3.75 m	Yuldybaevsky	−7.95	89	245	6052	−5.50	−2.90	0.708099
904-E								−5.60	−3.99	
904-B								−5.28	−2.90	
904b					85	536	2897	−5.41	−3.28	
PB 905-E	brach	3 bound 4/3–2.50 m	Yuldybaevsky	−6.70	3	296	2590	−4.85	−2.66	0.708061
905-E								−4.87	−2.80	
905-B								−5.33	−1.92	
905b-E					15	352	2276	−4.88	−3.18	
905b-E								−5.01	−2.46	
905b-B								−4.54	−2.44	
PB 906-E	brach	3 bound 4/3–0.80 m	Yuldybaevsky	−5.00	106	464	2804	−3.62	−2.84	0.708040
906-E								−3.24	−1.37	
906-E								−3.49	0.68	
906-E								−5.45	−0.59	
906-E								−5.68	−1.17	
906-B								−4.78	−1.04	
906b-B					3	711	3174	−3.37	0.10	
PB 907-B	brach	4 bound 4/3+0.60 m	Yuldybaevsky	−3.60	116	201	2147	−5.20	−1.90	0.708060
907b-B					46	175	1841	−4.72	−2.34	
907c-B					18	284	1713	−4.94	−2.37	
907d-B					5	371	2171	−4.85	−1.92	
907e-B					2	299	1706	−5.02	−2.66	
907-1-E								−5.16	−3.78	
907-2-E								−5.07	−1.04	
907-3-E								−3.27	1.71	
907-4-E								−3.98	0.45	
907-5-E								−3.91	1.52	
907-6-E								−4.72	0.95	
907-7-E								−5.49	0.45	
907-8-E								−5.70	0.09	
907-9-E								−5.47	−0.10	
907-10-E								−5.38	0.23	
907-11-E								−5.44	0.07	
PB 908-B	brach	4 bound 5/4	Yuldybaevsky	0.00	38	313	3212	−4.84	−1.30	0.708122
908b-B					17	335	2983	−4.09	−1.02	
908c-B					50	398	2882	−2.91	0.45	
908-1-E								−4.56	−0.53	
908-2-E								−4.12	−2.20	
908-E								−4.60	−3.30	

(*Continued*)

Sample #	Allochem	Strat. Level	Horizon	Strat Pos. (m)	Mn	Sr	Mg	Oxygen	Carbon	Sr isotope
908-E								−4.52	0.90	
908-E								−4.58	1.09	
908-E								−3.83	1.34	
PB 909-B	brach	6 bound 6/7	Bogdanovsky	3.00	2	512	1601	−1.81	6.73	0.708178
909b-B					19	593	1541	−2.71	6.38	
909c-B					16	532	1632	−2.16	6.77	
909-E								−1.15	7.52	
909-E								−1.54	7.77	
909-1-E								−1.46	7.55	
909-2-E								−1.33	6.38	
909-3-E								−2.02	7.25	
909-4-E								−1.75	6.39	
909-5-E								−2.06	5.78	
909-6-E								−1.73	6.49	
909-7-E								−1.41	6.35	
909-8-E								−1.90	5.96	
PB 910-B	brach	8 upper part	Sjuransky	16.00	255	319	2977	−2.82	3.02	0.708124
910b-B					104	312	2639	−3.32	2.84	
910-E								−0.73	2.55	

E = Erlangen/TAMU diagenetic evalution method; B = Bochum University diagenetic evaluation method.

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