Carboniferous paleoclimate and global change: Isotopic evidence from the Russian Platform

Ethan L. Grossman¹, Peter Bruckschen²*, Horng-sheng Mii³, Boris I. Chuvashov⁴, Thomas E. Yancey¹, and Ján Veizer⁵

¹Department of Geology & Geophysics, Texas A&M University, College Station, Texas 77843, U.S.A. (egrossman@tamu.edu)

²Geolofisches Institut, Universität zu Köln, Köln, Germany

³Department of Earth Sciences, National Taiwan Normal University, 88 Sec. 4, Ting-Chou Rd., Taipei, Taiwan 116, R.O.C.

⁴Institute of Geology & Geochemistry, Russian Academy of Science, Urals Branch, Pochtovyi per. 7, Ekaterinburg, Russia
⁵Institut fur Geologie, Ruhr-Universität, D-44780 Bochum, Germany, and Ottawa–Carleton Geoscience Centre, University of Ottawa, Ontario, Canada K1N 6N5

*Present address: Bergheimer Steig 41, 45357 Essen, Germany; email. Peter.Bruckschen@t-online.de

A preprint of the following published paper: Grossman, E.L., Bruckschen, P., Mii, H-S., Chuvashov, B.I., Yancey, T.E., and Veizer, J., 2002. Carboniferous paleoclimate and global change: Isotopic evidence from the Russian Platform. *In* Carboniferous stratigraphy and Paleogeography in Eurasia. Institute of Geology and Geochemistry, Russian Academy of Sciences, Urals Branch, Ekaterinburg, p. 61-71.

ABSTRACT

We present new and published isotopic data on brachiopod shells from the Urals and Moscow Basin to explore paleoclimate, global change, and chemostratigraphy in the Carboniferous. A total of 134 shells were analyzed from the Askyn, Sokol, Zilim, and Kamen Perevolochny sections in the Urals. The most important feature of this record is a sharp increase in δ^{18} O and δ^{13} C at the Serpukhovian-Bashkirian boundary. A Mid-Carboniferous increase had been reported for Moscow Basin and North American sections, but the timing had never been so well constrained. This shift bears witness to the transition from greenhouse to icehouse climate in the Carboniferous. The magnitude of the δ^{18} O and δ^{13} C shifts in the Urals (Askyn section) appears exaggerated because of anomalously low Serpukhovian values. Using the δ^{18} O increase recorded in North American and Moscow Basin sections as conservative estimates, this shift implies an ice sheet at least the size of modern glaciers, and perhaps a lowering of tropical temperature several degrees celsius. The simultaneous increase of δ^{18} O and δ^{13} C provides evidence that cooling was promoted by increased burial of organic carbon. These δ^{18} O and δ^{13} C shifts appear global and should be useful as chronostratigraphic markers for the Serpukhovian-Bashkirian boundary. Mid-Kasimovian δ^{18} O and δ^{13} C minima in the Moscow Basin may represent a warm interval in the otherwise icehouse Late Carboniferous. Future investigations will test the global nature of this and other isotopic events.

INTRODUCTION

The mid-Carboniferous was a time of great global environmental change. The Pangean supercontinent was beginning to assemble with the collision of Laurussia and Gondwana. Earth's climate was entering an icehouse mode, with cooling and glaciation indicated by glacial sediments (Dickins, 1996; Frakes et al., 1992; González, 1990), brachiopod migration patterns (Raymond et al., 1989), sea level decline (Ross and Ross, 1988), and δ^{18} O increases (Mii et al., 1999, 2001; Bruckschen et al., 2001). A major Paleozoic bio-event corresponds to the Mid-Carboniferous boundary (Sepkoski, 1995), with major extinctions and originations of conodont and ammonoid faunas, as well as turnover in crinoids, corals, and foraminifera (House, 1993; Nemirovskaya and Nigmadganov, 1994; Walliser, 1995).

Stable isotopes are a fundamental tool for the study of paleoclimate and paleoceanography. Carbon isotopic studies of Mid-Carboniferous brachiopod shells from the North American and European cratons reveal a dramatic global increase in the δ^{13} C of seawater, suggestive of enhanced burial of organic carbon in sediments (Popp et al., 1986; Mii et al., 1999, 2001; Bruckschen et al., 1999). A simultaneous increase in brachiopod δ^{18} O indicates cooling, evidence for a

linkage between carbon burial and climate change. These apparently global shifts in carbon and oxygen isotopes recorded in brachiopod shells testify to the utility of stable isotopes as chemostratigraphic markers. Furthermore, carbon isotopic analyses of fine-grained carbonates have revealed other carbon-cycle perturbations in the Carboniferous (Buggisch, 2001; Saltzman, 2002).

The Russian Platform provides one of the best records of Carboniferous sediments in the world. Not surprising, it has been the subject of three isotopic studies (Bruckschen et al., 1999; 2001; Mii et al., 2001). In this paper we will compile new and published isotopic stratigraphies for the Askyn, Sokal, Kamen Perevolochny, and Zilim sections in the Urals, compare these results with those for the Moscow Basin, and present and interpret a composite Carboniferous isotope record for the Russian Platform.

STUDY AREA

We present for the first time detailed isotopic stratigraphies for Mid-Carboniferous carbonate sections in the Urals. These sections include the Sokol and Kamen Perevolochny sections in the middle Urals (Mii et al., 2001), and the Askyn and Zilim sections in the southern Urals, 300 km to the south (Bruckschen et al., 2001).

The Askyn section provides upper Serpukhovian through Bashkirian carbonate sediments. The limestones and dolostones of the 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 are the most complete succession for this stage in the type region. The total thickness is 226 m, with 147 m and 79 m for the lower and upper substages, respectively. These shallow marine carbonates (limestones and dolostones) are rich in foraminifera, conodonts, brachiopods, and algae, and have been interpreted as open marine shelf to semi-isolated shallow bank deposits (Sinitsyna et al., 1995). Brachiopod shells were analyzed from the upper Serpukhovian and all horizons of the Uralian Bashkirian section.

The Sokol section is located on the northwest bank of the Chussavaya River 6 km downstream from the Staroutkinsk settlement. It consists of Upper Serpukhovian to lower Moscovian bedded limestones with nodular cherts. Brachiopod shells were collected throughout the roughly 270 m of Bashkirian deposits. However, only seven intervals yielded well-preserved fossils. These lie within the Siuransky, Tashastinsky, and Asatausky Uralian horizons.

Recently Proust et al. (1998) proposed a carbonate ramp interpretation for the depositional environments of the Askyn and Sokol sections. The environment fluctuated between inner- and mid-ramp in the late Sepukhovian and early Bashkirian, and between mid- and outer-ramp in the later Bashkirian.

The 50-m Kamen Perevolochny section near Martyanovo provides spiriferid brachiopods from four intervals in thickbedded detrital and fossiliferous limestone with nodular chert. These sediments are of late Moscovian (Myachkovian) age. The Zilim section comprises upper Bashkirian to upper Moscovian limestones, dolostones, and cherts, terminated by a thin suite of Kasimovian sandstones (15 m) and Gzhelian dolostones and limestones (6 m). Brachiopod shells were collected from the upper Bashkirian and lower Moscovian. The upper Bashkirian is represented by 16 m of alternating thin- to thick-bedded limestones with intercalations of banded chert. The lower Moscovian is composed of interbedded fossiliferous limestone and chert. Chert nodules occur within the limestones. The total thickness of the Moscovian section is 204 m, with 89 m representing the lower Moscovian.

MATERIALS AND METHODS

Isotopic studies of "deep time" require careful screening of sample material for diagenetic alteration, which generally lowers δ^{18} O and δ^{13} C values. Details of the screening and sampling methods are described in Bruckschen et al. (1999) and Mii et al. (2001). Briefly, sample preservation is evaluated based on textural and chemical preservation (Grossman, 1994). Brachiopod shells have characteristic microstructures that can be examined by petrographic microscope and by scanning electron microscope (SEM). Preservation of original microstructure is a primary criterion for overall shell preservation. Another primary criterion is brachiopod shell chemistry. Shell chemistry should reflect the chemistry of seawater and the appropriate chemical distribution coefficients (Veizer, 1983). Superimposed on this are biological controls (that is, "vital effects"). Original brachiopod shell calcite should be enriched in Mg, Sr, Na, and S, and contain little or no Mn and Fe (Brand and Veizer, 1980; Grossman et al., 1996).

For the data reported here, sample screening and preparation were performed by either of two methods. The first method, used by Ján Veizer and his colleagues at University of Ottawa and Ruhr University, involves crushing of shell and routine examination for diagenesis using optical and scanning electron microscopes. This is followed by sampling of 1 to 6 mg of crushed carbonate for isotopic and chemical analysis. Bruckschen et al. (1999) consider samples "well preserved" if Mn concentrations are less than 200 ppm. Carbonate samples are reacted offline at 50°C for 24 h, and the resulting CO_2 is analyzed on an isotope ratio mass spectrometer (IRMS). The second method, used at Texas A&M University and Erlangen University, involves microstructural evaluation of each shell in thin-section under the petrographic microscope (Grossman, 1994; Mii et al., 1999; Bruckschen et al., 1999). Chemical preservation is evaluated using cathodoluminescence microscopy, which provides a qualitative indication of Mn content. This is supplemented by chemical analysis of select shells. Photomicrographs taken under plain-light and cathodoluminescence are used to target texturally-preserved, nonluminescent shell areas for isotopic analysis. About 0.1 to 0.2 mg of carbonate is reacted online at 70°C for roughly 15 minutes, and the resulting CO₂ is subsequently analyzed on an IRMS. For samples from the Moscow Basin and Urals, the two methods do not appear to yield significantly different results (Bruckschen et al., 2001; P. Bruckschen, unpublished data). All brachiopod data presented here are calibrated to the PDB standard using NBS-19 ($\delta^{13}C = 1.95\%$ and $\delta^{18}O = -2.20\%$ versus PDB).

Isotopic studies of the Sokol and Kamen Perevolochny sections used the spiriferid brachiopods *Choristites, Martinia, Spirifer,* and *Neospirifer,* the athyrid *Composita,* and the productid *Gigantoproductus.* For the Askyn and Zilim sections, brachiopod taxa were not always identified, but taxa include *Chonetes, Productus. Linoproductus, Striatrifera, Orthotetes,* and *Choristites.* A total of 134 shells were analyzed from the Urals.

ISOTOPIC RECORDS FOR THE URALS AND MOSCOW BASIN

The Askyn section provides an isotopic record for the mid Serpukhovian (Protvinsky horizon) through late Bashkirian (Asatausky horizon), with the most continuous record across the Serpukhovian-Bashkirian boundary yet produced (Fig. 2). Both the oxygen and carbon isotopic compositions of this section are characterized by a sharp increase at the Serpukhovian-Bashkirian boundary (Bruckschen et al., 2001). Oxygen isotopic values are low in the Serpukhovian (ca. -5%), and increase to roughly -2%above the boundary. The δ^{18} O values remain relatively high but variable in the Bashkirian. Carbon isotopic values for Serpukhovian brachiopods from the Askyn Section are unusually low (-2 to -3%), and increase to a maximum of 6% at the Serpukhovian-Bashkirian boundary, before settling upon a mean value of about 4.5‰ throughout the Bashkirian.

Sokol section data do not include samples for the Serpukhovian, thus the sharp shift for the Askyn section cannot be duplicated with the existing data. Compared with the Askyn section data, oxygen isotopic compositions are relatively constant. Carbon isotopic data for the Sokol section also are relatively constant at 5 - 6%, except for the uppermost sample (4.7‰).

Where they overlap, the carbon and oxygen isotopic values for the Askyn and Sokol section generally agree. The significance of small shifts, such as the $\delta^{18}O$ minimum at the Tashastinsky-Asatausky boundary (Sokol section) and the $\delta^{13}C$ and $\delta^{18}O$ minima at the Bashkirian-Moscovian boundary (Zilim section), is uncertain without more detailed records.

The Zilim section shows δ^{18} O and δ^{13} C minima at the Bashkirian-Moscovian boundary, and Moscovian values similar to Bashkirian data above the boundary. The upper Moscovian samples from the Kamen Perevolochny section yield relatively low δ^{18} O and high δ^{13} C values.

Because the Urals and Moscow Basin are separated by more than 1200 km, comparison of isotopic records from the regions provides an opportunity to identify regional and even global change. The Serpukhovian and Bashkirian are well represented by Uralian samples, while the records for the Visean and Moscovian through Gzelian are anchored with Moscow Basin samples (Fig. 3). For the interval where the records overlap, Serpukhovian through Moscovian, the isotopic trends are generally similar. Both the Uralian and Moscow Basin records show increases in $\delta^{18}O$ and $\delta^{13}C$ from early Serpukhovian to early Bashkirian. Unfortunately, Moscow Basin data for this interval are sparse, so the timing of this dramatic isotopic event cannot be resolved. The $\delta^{18}O$ and $\delta^{13}C$ values for both regions reach a maximum in the earliest Bashkirian and decrease to lower values in the late Bashkirian or early Moscovian. In the Moscovian, oxygen and carbon isotopic trends diverge. Uralian and Moscow Basin δ^{13} C values increase. Uralian δ^{18} O values decline throughout the Moscovian, while Moscow Basin values remain low throughout the stage. Limited Moscow Basin data suggest correlative δ^{18} O and δ^{13} C minima in the early Kasimovian, with a return to higher values in the late Kasimovian and Gzelian.

ENVIRONMENTAL SIGNIFICANCE OF THE ISOTOPIC RECORDS

Oxygen Isotopes

Oxygen isotopic shifts in marine carbonates can be caused by temperature change (increase = cooler) or changes in the isotopic composition of the water (O'Neil et al., 1969). The latter can vary as a function of glacial ice volume or, like salinity, vary with evaporation and river input. Higher brachiopod δ^{18} O can thus indicate greater ice volume, higher salinity, or lower temperature. Restricting Paleozoic isotopic studies to brachiopods helps constrain the effects of salinity change. Sedimentological evidence for glaciation and paleobiological climate data provide constraints on the interpretation of δ^{18} O data, and vice versa. Continental glaciation has a global effect on seawater δ^{18} O. Thus, synchronous worldwide shifts in fossil δ^{18} O provide convincing evidence for glaciation.

Isotopic paleotemperature calculations require an estimate of the δ^{18} O of the water (δ_w) in which shells were precipitated. As a working model, many researchers use the δ_w of the modern ocean (0% versus SMOW) for icehouse oceans, and the δ_{w} of an "ice-free" ocean (modern ocean if glaciers melt; -1‰ versus SMOW; Savin, 1977) for greenhouse oceans (Fig. 3). This working model is in accord with model calculations and $\delta^{\rm 18}O$ measurements of ophiolites and meteoric cements that suggest little change in the hydrosphere δ^{18} O since at least the Carboniferous (Muehlenbachs, 1986; Gregory, 1991; Hays and Grossman, 1991). For an alternative view, see Veizer et al. (2000) and Wallmann (2001). For this time interval the two approaches lead to differences in interpretation of absolute paleotemperatures, but not to differences in interpretation of temperature change.

The oxygen isotopic records from the Russian Platform show Earth's transition from greenhouse to icehouse climate mode in the Mid Carboniferous, and perhaps a warm interlude in the Late Carboniferous. Our record begins in the late Visean with δ^{18} O values (-4 to -2‰; Moscow Basin) typical for the Late Paleozoic (Fig. 3). Assuming an ice-free world (δ^{18} O of water = -1‰), these translate to temperatures of 20° to 30°C, comparable to modern tropical and subtropical sea-surface temperatures. $\delta^{18}O$ appears to decrease 4‰ in the Serpukhovian, but this change may be an artifact of the anomalously low δ^{18} O values (ca. -5‰) for Serpukhovian brachiopods from the Askyn section. These low values yield Serpukhovian paleotemperatures of $34 \pm$ 2°C (assuming an ice-free world; Fig. 3). Such high temperatures are unusual for the open ocean, and are substantially greater than those obtained for the Visean. Bruckschen et al. (2001) suggest that the Serpukhovian brachiopods at the Askyn section may have lived in a local, restricted environment with lower salinity. Tentatively, we accept this explanation for the low δ^{18} O values pending further study.

The Askyn section in the Urals records a dramatic δ^{18} O increase at the Serpukhovian-Bashkirian boundary. A similar shift is observed for the Moscow Basin (Bruckschen et al., 1999; Mii et al., 2001) and the North American craton (Mii et al., 1999), but a hiatus at the Mid-Carboniferous boundary does not allow temporal resolution of the event (Fig. 4). The magnitude of the shift at the Askyn section (ca. 4‰) is larger than that observed for the Moscow Basin (1.8‰) and the North American craton (2-3‰), but again that may be an artifact of low salinities during Askyn deposition in the Serpukhovian. Quaternary studies help constrain the δ^{18} O shift expected with glaciation. The transition from ice-free conditions to a full Pleistocene glaciation would increase

seawater δ^{18} O by roughly 2‰, based on foraminifera and ice core measurements and mass balance calculations (e.g., Shackleton and Opdyke, 1973; Lea et al., 2000). Decreasing temperature in nearshore, tropical waters could account for an additional 1‰ increase in brachiopod δ^{18} O (Beck et al., 1992; Guilderson et al., 1994). If we accept 2‰ as a conservative estimate of the δ^{18} O shift at the Serpukhovian-Bashkirian boundary, at minimum ice volume increased to that comparable to the modern ice sheets (29 x 10⁶ km³ ≈ 1‰ δ_w increase). An additional 1‰ δ^{18} O increase is equivalent to a 5°C cooling or an increase in ice volume to Pleistocene levels (59 x 10⁶ km³). Coupled climate-ice sheet models indicate that either scenario is reasonable (Hyde et al., 1999).

The isotopic evidence for cooling in the Mid-Carboniferous is supported by sedimentological evidence for Mid-Carboniferous glaciation (e.g., Frakes et al., 1992; Dickins, 1996; González, 1996; Fig. 4). The δ^{18} O shift corresponds to a shift from indistinct to distinct zonal climate in the region (Eynor et al., 1970). Furthermore, paleobotanical evidence points to abrupt cooling at the Serpukhovian-Bashkirian boundary on the Russian Platform (Durante, 1995). Sea level drops precipitously at this boundary (Fig. 4; Ross and Ross, 1988; Alekseev et al., 1996).

By late Moscovian, δ^{18} O values decreased to those similar to the Visean, suggesting a warming trend and decline in ice volume. This δ^{18} O decrease is seen in the measurements of Kamen Perevolochny section brachiopods from the Urals (Fig. 2). Supporting a warming trend, there is some evidence of shrinkage of the Gondwanan ice sheets at this time (Dickins, 1996; González, 1990). δ^{18} O values do not rise to the early Bashkirian maximum until the latest Carboniferous-earliest Permian (Fig. 3), a time considered by many to be the peak of Pangean glaciation.

Carbon Isotopes

Carbon isotopic compositions of brachiopod shells reflect the δ^{13} C of dissolved inorganic carbon (DIC) in seawater. Seawater δ^{13} C is higher in the surface ocean than the deep ocean because phytoplankton preferentially utilize ¹²CO₂ in photosynthesis. At depth, respiration exceeds photosynthesis and there is a net release of ¹³C-depleted carbon during the oxidation of organic matter (Anderson and Arthur, 1983). DIC δ^{13} C values may increase with increased productivity, but the process that influences productivity most, upwelling, mitigates this effect by lowering the $\delta^{13}C$ of surface seawater. Thus, using δ^{13} C in brachiopod shells as productivity indicators is tenuous. On the other hand, ocean DIC δ^{13} C is sensitive to changes in the burial of organic matter. Increased organic matter burial increases δ^{13} C, whereas increased weathering of organic matter decreases δ^{13} C (Kump and Arthur, 1999). Generally it is believed that increased burial of organic carbon will lower the pCO₂ of the atmosphere. Thus, the $\delta^{13}C$ of carbonate sediments provides a rough proxy of atmospheric CO₂ levels.

Visean and early Serpukhovian brachiopod shells from the Moscow Basin yield δ^{13} C values typical for modern marine carbonates, averaging about 2.5‰. δ^{13} C values appear to dramatically decrease within the Serpukhovian. However, the low δ^{13} C (and δ^{18} O) values for these Askyn section brachiopods may be anomalous, as discussed earlier. The prominent feature of the δ^{13} C record is the >2‰ increase at the Serpukhovian-Bashkirian boundary. The increase appears even more precipitous because of the anomalously low Askyn values for the Serpukhovian. This mid-Carboniferous δ^{13} C was noted by Popp et al. (1986) for Europe, Mii et al. (1999) for North America, and Bruckschen et al. (1999) and Mii et al. (2001) for the western Russian Platform. All of these studies have attributed this increase to enhanced burial of organic carbon, especially burial on land as coal. Alternatively, the cooling climate may have lead to cold bottom waters and the formation of gas hydrates. Bruckschen et al. (1999) and Mii et al. (1999) noted a positive correlation between δ^{13} C and δ^{18} O in the mid-Carboniferous, and proposed that burial of organic carbon lead to drawdown of CO₂ and consequently cooling and glaciation. The new data for the Urals sections provide further evidence for this coupling of carbon cycle and paleoclimate. Applying this model, the δ^{13} C and δ^{18} O minima in the Kasimovian record from the Moscow Basin is interpreted as enhanced weathering (or decreased burial) of organic carbon, release of CO₂, and increased greenhouse warming and glacial retreat (Figs. 3, 4).

CONCLUSIONS, IMPLICATION, AND FUTURE DIRECTIONS

We have presented isotopic records for brachiopods from Carboniferous sediments in the Urals, and compared them with similar records from the Moscow Basin and North America. The most significant feature is a dramatic increase in δ^{18} O and δ^{13} C at the Serpukhovian-Bashkirian (S-B) boundary. All evidence indicates that this isotopic shift is recording Earth's transition from a greenhouse mode to an icehouse climate mode. The carbon isotope shift provides evidence that cooling was promoted by increased burial of organic carbon. This global isotopic event is a useful chemostratigraphic marker for the S-B boundary. The Askyn section in the Urals provides the most detailed record of this event produced to date, but the magnitude of the shifts is uncertain because of anomalous results for Serpukhovian samples. Replication of the isotopic record across the S-B boundary should be a priority. Where well-preserved brachiopods are lacking, fine-grained carbonate can be used to provide a detailed δ^{13} C stratigraphy correlatable on a global scale (Baud et al., 1989; Buggisch, 2001; Saltzman, 2002).

Other coupled δ^{13} C and δ^{18} O events worth investigating are minima at the Bashkirian-Moscovian boundary in the Urals, and a mid-Kasimovian minima in the Moscow Basin. The latter may represent a warm interval in the otherwise icehouse Late Carboniferous. Future investigations will further strengthen the application of stable isotopes as stratigraphic markers and markers of the linkage between the global carbon cycle and paleoclimate.

REFERENCES

Alekseev, A.S., Kononova, L.I., and Nikishin, A.M., 1996. The Devonian and Carboniferous of the Moscow Syneclise (Russian Platform): stratigraphy and sea-level changes. Tectonophysics 268, 149-168.

Anderson, T.F., and Arthur, M.A., 1983. Stable isotopes of oxygen and carbon and their application to sedimentologic and paleoenvironmental problems. *In* Arthur, M.A., et al., Stable Isotopes in Sedimentary Geology, SEPM Short Course #10, pp. 1-1 – 1-151.

Baud, A., Magaritz, M., and Holser, W. T., 1989. Permian-Triassic of the Tethys: Carbon isotope studies. Geologische Rundschau 78, 649-677.

Brand, U., and Veizer, J., 1980. Chemical diagenesis of a multicomponent carbonate system. 1. Trace elements. Jour. Sed. Petrology 50, 1219-1236.

Bruckschen, P., Oesmann, S., and Veizer, J., 1999. Isotope stratigraphy of the European Carboniferous. Proxy signals for ocean chemistry, climate, and tectonics. Chemical Geology 161, 127-163.

Bruckschen, P., Veizer, J., Schwark, L., and Leythaeuser, D., 2001. Isotope stratigraphy for the transition from the late Palaeozoic geenhouse in the Permo-Carboniferous icehouse–new results. Terra Nostra, 2001/4, 7-11.

Buggisch, W., 2001. Whole-rock carbon isotope analysis $(\delta^{13}C)$ of Devonian to Permian sediments. Terra Nostra 2001/4, 12-15.

Dickins, J.M., 1996. Problems of a Late Palaeozoic glaciation in Australia and subsequent climate in the Permian. Palaeogeography, Palaeoclimatology, Palaeoecology 125, 185-197.

Durante, M.V., 1995. Reconstruction of Late Paleozoic climatic changes in Angaraland according to phytogeographic data. Stratigraphy and Geological Correlation, 3, 123-133.

Eynor, O.L., Bel'govskiy, G.L., and Smirnov, G.A., 1970. Carboniferous geology and paleogeography of the USSR. International Geology Review 12, 105-113.

Eynor ["Einor"], O.L., Brazhnikov, N.E., Vassilyuk, N.P., Gorak, S.V., Dunaeva, N.N., Kireeva, G.D., Kotchetkova, N.M., Popov, A.B., Potievskaya, P.D., Reitlinger, E. A., Rotai, A.P., Sergeeva, M. T., Teteryuk, V.K., Fissunenko, O.P., and Furduy, R.S., 1979. The Lower-Middle Carboniferous boundary, *in* Wagner, R.H., Higgins, A.C., and Meyen, S.V., eds., The Carboniferous of the USSR. Leeds, England, Yorkshire Geological Society, Occasional Publication 4, 61-81.

Frakes, L.A., Francis, J.E., and Syktus, J.I., 1992. Climate modes of the Phanerozoic: The history of the Earth's climate over the past 600 million years. Cambridge University Press, Cambridge, Great Britain, 274 p.

Garzanti, E., and Sciunnach, D., 1997. Early Carboniferous onset of Gondwanian glaciation and Neo-tethyan rifting in South Tibet. Earth and Planetary Science Letters 148, 359-365.

González, C.R., 1990. Development of the Late Paleozoic glaciations of the South American Gondwana in western Argentina. Palaeogeography, Palaeoclimatology, Palaeoecology 79, 275-287.

Gregory, R. T., 1991, Oxygen isotope history of seawater revisited: Timescales for boundary event changes in the oxygen isotope composition of seawater, *in* Taylor, H.P., Jr., O'Neil, J. R., and Kaplan, I. R., eds., Stable isotope geochemistry: A tribute to Samuel Epstein, The Geochemical Society, Special Publication No. 3, San Antonio, pp. 65-76.

Grossman, E.L., 1994. The carbon and oxygen isotope record during the evolution of Pangea: Carboniferous to Triassic, *in* Klein, G.D., ed., Pangea: Paleoclimate, tectonics, and sedimentation during accretion, zenith, and breakup of a supercontinent. Geological Society of America Special Paper 288, 207-228.

Grossman, E.L., Mii, H-S., Zhang, C-L., and Yancey, T.E., 1996. Chemical variation in Pennsylvanian brachiopod shells—effects of diagenesis, taxonomy, microstructure, and paleoenvironment. Jour. Sed. Research 66, 1011-1022.

Guilderson, T.P., Fairbanks, R.G., and Rubenstone, J.L., 1994. Tropical temperature variations since 20,000 years ago: Modulating interhemispheric climate change. Science 263, 663-665.

Hays, P.D., and Grossman, E.L., 1991. Oxygen isotopes in meteoric calcite cements as indicators of continental climate. Geology 19, 441-444.

Hess, J.C., and Lippolt, H.J., 1986. ⁴⁰Ar/³⁹Ar ages of tonstein and tuff sanidines: new calibration points for the improvement of the Upper Carboniferous time scale. Chem. Geol. (Isotope Geosciences Section) 59, 143-154.

House, M.R., 1993. Fluctuations in ammonoid evolution and possible environmental controls. *In* House, M.R., ed., The Ammonoidea: Environment, Ecology, and Evolutionary Change. Systematics Assoc. Spec. Vol. 47, Clarendon Press, Oxford, pp. 13-34.

Hyde, W.T., Crowley, T.J., Tarasov, L., and Peltier, W.R., 1999. The Pangean ice age: studies with a coupled climate-ice sheet model. Climate Dynamics, 15, 619-629.

Kump, L.R., and Arthur, M.A., 1999. Interpreting carbonisotope excursions: carbonates and organic matter. Chem. Geol., 161, 181-198.

Lea, D.W., Pak, D.K., and Spero, H.J., 2000. Climate impact of Late Quaternary equatorial Pacific sea surface temperature variations. Science 289,1719-1723.

Manger, W.L., and Sutherland, P.K., 1990. Comparative ammonoid/conodont-based and foraminifer-based Middle Carboniferous correlations. Courier Forschungsinstitut Senckenberg, 130, 345-350.

Mii, H-S., Grossman, E.L., Yancey, T.E., Chuvashov, B., Egorov A., 2001. Isotope records of brachiopod shells from the Russian Platform—evidence for the onset of mid-Carboniferous glaciation. Chemical Geology, 175, 133-147.

Mii, H-S., Grossman, E.L., and Yancey, T.E., 1999. Carboniferous isotope stratigraphies of North America: Implications for Carboniferous paleoceanography and Mississippian glaciation. Geol. Soc. America Bull. 111, 960-973.

Miller, K.G., Fairbanks, R.G., and Mountain, G.S., 1987. Tertiary oxygen isotope synthesis, sea level history, and continental margin erosion. Paleoceanography 2, 1-19.

Muehlenbachs, K., and Clayton, R. N., 1976. Oxygen isotope composition of the oceanic crust and its bearing on seawater: Journal of Geophysical Research 81, 4365-4369.

Nemirovskaya, T., and Nigmadganov, I., 1994. The Mid-Carboniferous conodont event. Courier Forschungsinstitut Senckenberg 168, 319-333.

O'Neil, J. R., Clayton, R. N., and Mayeda, T. K., 1969. Oxygen isotope fractionation in divalent metal carbonates. Journal of Chemical Physics, 51, 5547-5558.

Popp, B.N., Anderson, T.F., and Sandberg, P.A., 1986. Brachiopods as indicators of original isotopic compositions in some Paleozoic limestones. Geological Society of America Bulletin 97, 1262-1269. Proust, J.N., Chuvashov, B.I., Vennin, E., and Boisseau, T., 1998. Carbonate platform drowning in a foreland setting. The Mid-Carboniferous platform in western Urals (Russia). Jour. Sed. Research 68, 1175-1188.

Raymond, A., Kelley, P.H., and Lutken, C.B., 1989, Polar glaciers and life at the equator: The history of Dinantian and Namurian (Carboniferous) climate. Geology, 17, 408-411.

Ross, C.A., and Ross, J.R.P., 1988. Late Paleozoic transgressive-regressive deposition. The Society of Economic Paleontologists and Mineralogists Special Publication, no. 42, 227-247.

Saltzman, M.R., 2002. Carbon and oxygen isotope stratigraphy of the Lower Mississippian (Kinderhookianlower Osagian), western United States: Implications for seawater chemistry and glaciation. Geol. Soc. America Bull. 114, 96-108.

Savin, S.M., 1977. The history of the Earth's surface temperature during the past 100 million years: Ann. Rev. Earth Planet. Sci. 5, 319-355.

Sepkoski, J.J., Jr., 1995. Patterns of Phanerozoic extinction: a perspective from global data bases. *In* Walliser, O.H., ed., Global Events and Event Stratigraphy, Springer, Berlin, pp. 35-51.

Shackleton, N.J., and Opdyke, N.D., 1973. Oxygen isotope and palaeomagnetic stratigraphy of equatorial Pacific core V28-238: Oxygen isotope temperatures and ice volumes on a 10⁵ year and 10⁶ year scale. Quat. Res., 3, 39-55.

Sinitsyna, Z.A., Kulagina, E.I. Pazukhin, V.N., Kochetkova, N.M., 1995. 5. Askyn section. In: Kozlov, V.I., Sinitsyna, Z.A., Kulagina, E.I., Pazukhin, V.N., Puchkov, V.N., Kochetkova, N.M., Abramova, A.N., Klimenko, T.V., Sergeeva, N.D., eds., Guidebook of excursion for the Palezoic and Upper Precambrian sections of the Western slope of the Southern Urals and Preuralian regions. Geol. Inst. Ufa Sci. Center RASci., pp. 106-121.

Vail, P., Mitchum, R.M., and Thompson, S., 1977. Seismic stratigraphy and global changes of sea level, part 4: Global cycles of relative sea level, in Payton, C.E., ed., Seismic Stratigraphy–Applications to Hydrocarbon Exploration. Amer. Assoc. Petrol. Geol. Memoir 26, pp. 83-97.

Veevers, J.J., and Powell, C. McA., 1987. Late Paleozoic glacial episodes in Gondwanaland reflected in transgressive-regressive depositional sequences in Euramerica. Geological Society of America Bulletin 98, 475-487.

Veizer, J., 1983. Chemical diagenesis of carbonates: Theory and application of trace element technique. In Arthur, M.A., et al., 1983. Stable Isotopes in Sedimentary Geology, SEPM Short Course #10, pp. 3-1 – 3-100.

Veizer, J., Godderis, Y. and François, L.M., 2000. Evidence for decoupling of atmospheric CO₂ and global climate during the Phanerozoic eon. Nature 408, 698-701.

Walliser, O.H., 1995. Global events in the Devonian and Carboniferous. *In* Walliser, O.H., ed., Global Events and Event Stratigraphy, Springer, Berlin, pp. 225-250.

Wallmann, K., 2001. The geological water cycle and the evolution of marine δ^{18} O values. Geochim. Cosmochim. Acta 15, 2469-2485.

- 1. Simplified geologic map of the Urals with sampling localities (modified from Proust et al., 1998).
- Carbon and oxygen isotopic records for the Sokol, Askyn, Zilim, and Kamen Perevolochny sections in the Urals. Data points represent analyses of individual shells. Stippled bar is the average value for each interval. Its width is arbitrary.
- Comparison of isotopic data for the Urals and the 3. Moscow Basin. Data are from this paper, Bruckshen et al. (1999, 2001), and Mii et al. (2001). Time scale from Mii et al. (1999, 2001) based on the work of Hess and Lippolt (1986), Roberts et al. (1996), and Manger and Sutherland (1990). Bands represent running means with a 3-million-year window and a 1-million-year time step, based on the data for 362 shells. Band width is $\pm 2 x$ standard error. Dashed lines represent breaks in the data or intervals with less than 3 analyses per time-step. Calibration of oxygen isotopic values to paleotemperature is based on the calcite-water fractionation relation of O'Neil et al. (1969) using the polynomial regression of Hays and Grossman (1991). Temperatures are shown for two estimates of the $\delta^{18}O$ of seawater (δ_w). One is for the modern (icehouse) ocean (0% SMOW) and the other is for an ice-free greenhouse ocean (-1‰ SMOW; modern ocean with glaciers melted).
- Comparison of Russian Platform isotopic record with geological indicators of glaciation (VP, Veevers and Powell, 1987; D, Dickins, 1996; F, Frakes et al., 1992; G, González, 1990; GS, Garzanti and Sciunnach, 1997) and sea level (Ross and Ross, 1988; Alekseev et al., 1996; Vail et al., 1977). Because of limited stratigraphic control, the exact upper and lower limits of many glacial deposits are unknown.





Figure 2.



Figure 3.

