

Global changes during Carboniferous–Permian glaciation of Gondwana: Linking polar and equatorial climate evolution by geochemical proxies

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ABSTRACT

The most prevalent Phanerozoic glaciation occurred during the Carboniferous–Permian on the Southern Hemisphere Gondwana supercontinent. Sediments from the Pennsylvanian Dwyka Group deposited in the Karoo Basin of South Africa provide a complete record of glaciation and deglaciation phases. The direct correlation of glaciation events in southern Gondwana basins with the well-studied climate evolution of equatorial regions was previously hampered by lack of precise radiometric dating. As dating has now become available for the Karoo Basin, the Gondwana glaciation can be viewed in a global paleoclimatic framework with high temporal resolution. Element geochemical proxies (CIA [chemical index of alteration], Zr/Ti, Rb/K, V/Cr) record three confined shifts in climate and paleoenvironment of the Karoo Basin. These shifts were induced by changes in sea level, weathering rate, provenance, and redox conditions. Because of the low availability and diagenetic overprint of carbonates, ocean and atmosphere $p\text{CO}_2$ variations had to be reconstructed from $\delta^{13}\text{C}_{\text{org}}$ values of marine organic matter. The $\delta^{13}\text{C}_{\text{org}}$ signatures are affected by variable proportions of marine versus terrestrially derived organic matter and its state of preservation. Organic geochemical investigations (TOC [total organic carbon], C/N, lipid biomarkers) indicate the organic matter in the central Karoo Basin was primarily of algal origin. In agreement with element proxies, the varying $\delta^{13}\text{C}_{\text{org}}$ values mirror shifts in $p\text{CO}_2$, rather than variations of organic-matter type. A covariation trend between carbon isotope signatures of equatorial carbonates and $\delta^{13}\text{C}_{\text{org}}$ values from the Karoo Basin argues against local forcing factors and instead implies a global climate-control mechanism. The 5–7 m.y. duration of a complete glacial cycle is not in tune with any known orbital frequency. Processes such as changes in equator-pole temperature gradients or newly developing atmosphere-ocean circulation pathways can be regarded as controlling factors.

Keywords: paleoclimate, Paleozoic, Carboniferous–Permian glaciation, Karoo Basin, Dwyka Group.

INTRODUCTION

The global climate comprises a complex interplay between atmosphere, land, and ocean. For a better understanding of global interaction of climate-forcing factors, it is important to investigate paleoclimate records (Crowley and Baum, 1992; Berner, 1994; Frakes et al., 1992; Martini, 1997). In the view of today's discussion on future climate change (IPCC, 2001), the study of a fossil icehouse-greenhouse transition may prove valuable. The most extensive Phanerozoic glaciation lasted 90 m.y. (Crowell, 1978) and its termination occurred during the Carboniferous–Permian on the southern hemispherical Gondwana supercontinent.

Glacial conditions in the Southern Hemisphere and their contemporaneous effect on marine and terrestrial life in equatorial regions influenced the atmospheric CO_2 content. The drop in $p\text{CO}_2$ (Berner, 1994) at the end of the Carboniferous coincides with times of contrasting climate evolution between polar and equatorial regions. Carbon isotopes record

these global changes because of isotopic exchange among atmospheric, organic, and inorganic carbon reservoirs (Hayes et al., 1999). The influence of the Gondwana glaciation on global climate is documented by variations in $\delta^{13}\text{C}$ measured on brachiopods from equatorial regions (Bruckschen et al., 1999; Veizer et al., 1999).

The Karoo Basin of South Africa was part of a major depocenter during the late Paleozoic (Fig. 1). Equivalent glacial sedimentary deposits exist in South America, South Africa, Namibia, Tanzania, Antarctica, India, and Australia (Crowell, 1978; Caputo and Crowell, 1985; Veevers and Powell, 1987). Sedimentological and mineralogical investigations (Bühmann and Bühmann, 1990) have been carried out for glacial sedimentary sequences of the Karoo Basin, but only preliminary geochemical analyses of the Dwyka Group sedimentary rocks exist (Visser and Young, 1990). This study provides the first detailed geochemical record covering the entire glacial-in-

terglacial sequence in the Karoo Basin of South Africa. By comparing climate proxy signatures from polar and equatorial regions, we gain insight into the synchronicity of climate processes. Because geochemical proxies are affected by diagenesis, provenance change, or weathering, we tried to extract reliable information on climatic and sedimentary evolution by combining several independent proxies.

RESULTS

Geologic Overview

The geology of the Karoo Basin was summarized by Visser (1997) and Visser and Young (1990). The Dwyka Group can be differentiated into four deglaciation sequences (DS I–IV, Fig. 2A), each with a glacial and an interstadial phase (Visser, 1997). Absolute age determinations based on sensitive high-resolution ion microprobe (SHRIMP) analysis of single zircons defined the duration of each cycle to ~5–7 m.y. (Bangert et al., 1999; Stollhofen et al., 2000). Each deglaciation sequence consists of a basal zone with massive diamictites overlain by a terminal mudrock (Fig. 2A). Visser (1997) documented changes in ice-flow direction over southern Africa during DS I–IV (Fig. 1). Interpretation of geochemical proxy signatures must differentiate climatically induced from provenance-controlled variations.

Geochemical Proxies

Multiple geochemical investigations reveal climate variations during deposition of the Pennsylvanian Dwyka and Lower Permian Ecca Group in the Karoo Basin. Zr/Ti ratios indicate provenance change (Fig. 2B) for the interstadial phases (DS II median Zr/Ti = 0.076; DS III median Zr/Ti = 0.044), whereas glacial phases exhibit constant Zr/Ti ratios (median 0.058). Higher Zr contents point to a granitic rock composition, thus identifying the northern highlands as sediment source region during the interglacial phases of DS I and II. Sequences DS III and IV received clastic debris from source regions located near the southern magmatic arc associated with subduction along the paleo-Pacific plate margin (Visser, 1997).

Glacial deposits are interrupted by intersta-

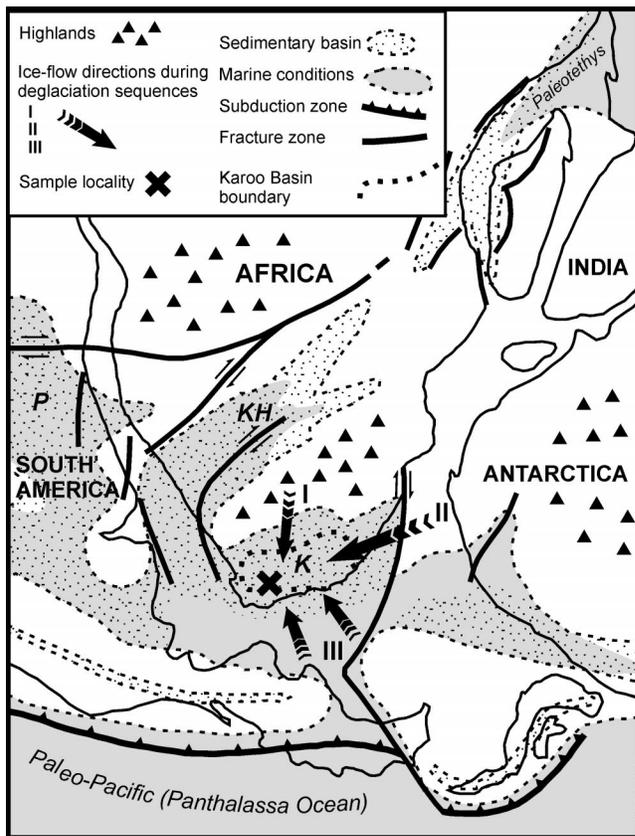


Figure 1. Paleogeographic reconstruction of Karoo Basin during late Paleozoic (after Visser and Prækelt, 1996). Major ice-flow directions recorded in deglaciation sequences I, II, and III (after Visser, 1997) indicate clockwise change in provenance. P—Paraná Basin; K—Karoo Basin; KH—Kalahari Basin.

dial sedimentary units representing temperate climate conditions. Cyclic climate variations during DS I–IV induced severe sea-level change because the ice volume accumulated almost exclusively on land. These changes are recorded by various proxy signatures, including the chemical index of alteration (CIA; after Nesbitt and Young, 1982), Rb/K ratio (Campbell and Williams, 1965), V/Cr ratio (Jones and Manning, 1994), and organic-matter content (Figs. 2C–2F).

Variations in CIA indicate rapid transitions from glacial to interglacial phases (Fig. 2C). Low temperatures and rare vegetation favor physical weathering during glacial periods. The diamictites were deposited as subaqueous aprons and fans forming close to the ice-grounding line (Visser, 1997). Vegetation expansion, soil formation, and warmer and more humid climate during interstadials increased chemical weathering rates, as indicated by elevated CIAs.

Differentiation between fully marine phases during the interstadials and limnic or brackish conditions induced by sea-level drawdown during glaciation is reflected by the Rb/K ratio (Fig. 2D). Stadial phases reveal median Rb/K ratios of 4.09, DS I and II interstadials yield Rb/K ratios of 4.78, and DS III and IV interstadials give Rb/K ratios of 5.56 (Fig. 2D). This agrees with the most pronounced sea-level rise, the *Eurydesma*-transgression of DS III (Visser, 1997) inducing oxygen deficient bottom water conditions associated with water column stratification upon sea-level highstand. Anoxia is indicated by higher V/Cr ratios correlating with elevated accumulation and preservation of organic carbon (Fig. 2E and F).

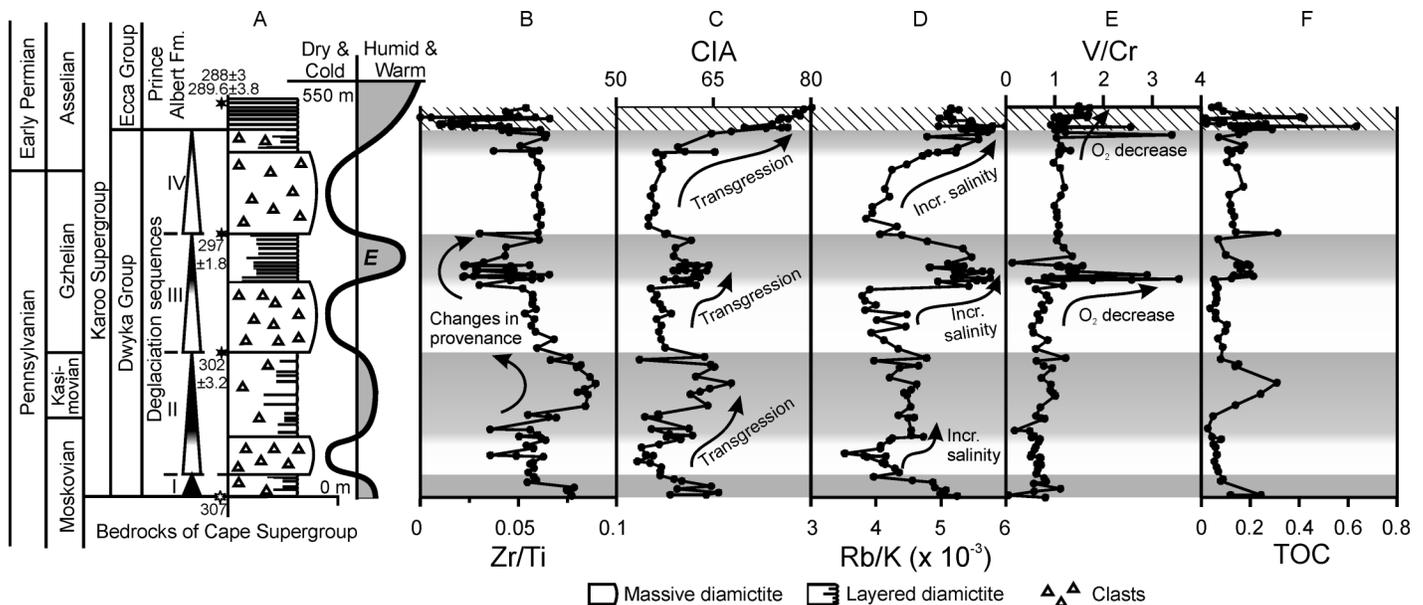


Figure 2. Stratigraphy and facies evolution of glacial Dwyka Group sedimentary succession; shading indicates interstadial phases. E—*Eurydesma* transgression; filled stars—sensitive high-resolution ion microprobe (SHRIMP) ages after Bangert et al. (1999); open star—age by Visser (1997). A: Simplified lithology and climate. B: Zr/Ti (a provenance proxy). C: CIA (chemical index of alteration; weathering proxy). D: Rb/K (salinity proxy). E and F: V/Cr and total organic carbon (TOC) (redox proxies).

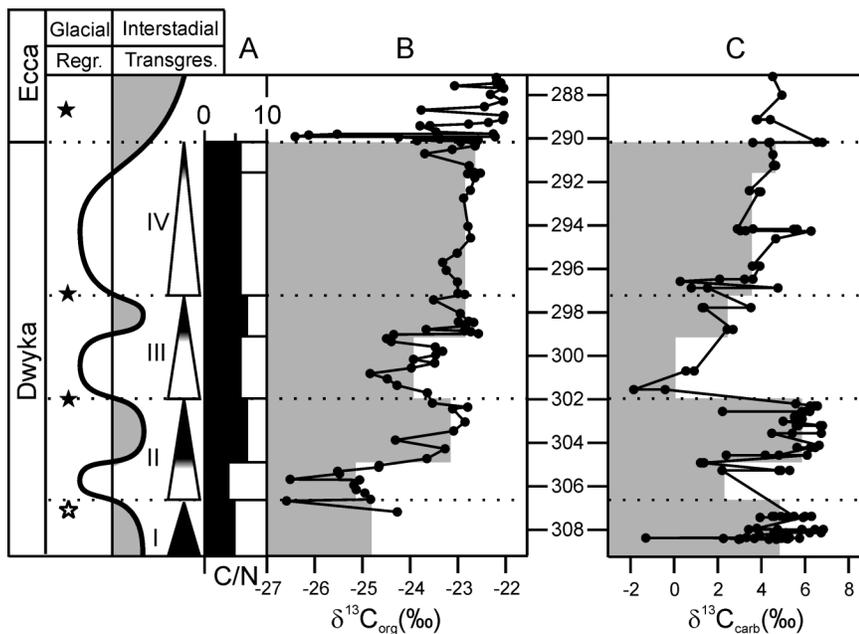


Figure 3. Carboniferous–Permian climate evolution within the Karoo Basin. Filled stars—sensitive high-resolution ion microprobe ages after Bangert et al. (1999); open star—age by Visser (1997). A: Invariable mean C/N ratios for glacial and interstadial phases indicate a constant marine organic-matter source. In B and C, median $\delta^{13}\text{C}$ values for glacial and interstadial phases are shown by gray shading. B: $\delta^{13}\text{C}_{\text{org}}$ for Dwyka sequence. C: $\delta^{13}\text{C}_{\text{carb}}$ for equatorial regions after Veizer et al. (1999); ages corrected by -1 m.y. Synchronous evolution of proxies from polar and equatorial regions indicates global control.

The cyclicity of the lower Dwyka Group, as shown by different element ratios, can also be seen in the carbon isotope composition of organic matter (Fig. 3B). More negative $\delta^{13}\text{C}_{\text{org}}$ values mark the full glacial environments (for stadials of DS II, median is -25.13‰ , and for stadials of DS III, median is -23.95‰), whereas interstadial phases in general are characterized by less negative $\delta^{13}\text{C}_{\text{org}}$ values (interstadials of DS I have a median of -24.83‰ , those of DS II have a median of -23.19‰ , and those of DS III have a median of -22.86‰). Organic matter derived from marine primary production incorporates the $\delta^{13}\text{C}$ signature of atmospheric CO_2 and thus reveals the changes between glacial and interglacial $p\text{CO}_2$ values (Jasper and Hayes, 1990). Variation in proportions of marine versus terrigenous organic matter sources, stage of degradation, and burial history can alter the carbon isotopes of bulk organic matter (Meyers, 1997). Origin and degree of diagenetic overprint of organic matter were assessed by determination of C/N ratios and biomarker composition. C/N ratios <10 indicate an origin of organic matter from marine algae (Meyers, 1997), whereas terrigenous organic matter yields C/N ratios of >20 . Samples from the Dwyka sequence give C/N ratios of <8 , indicative of marine-derived organic matter. Glacial and interglacial phases show no significant variation in C/N ratios (Fig. 3A). Gas chromatography–mass spectrometry (GC-MS)

analyses of aliphatic hydrocarbon fractions (Fig. 4A and 4B) show a predominance of alkanes with carbon numbers in the $n\text{-C}_{16}$ to $n\text{-C}_{18}$ range. These compounds derive from algal biomass and are in strong contrast to land plant–lipids, which maximize around $n\text{-C}_{29}$ in their n -alkane distribution (Meyers, 1997). As for the C/N ratios, no obvious differences can be measured between samples from glacial or interglacial phases. This similarity points toward a consistent marine origin for the organic matter deposited in the basin center. Deltaic sedimentation systems with strong terrigenous input were established along the northeastern basin margin (Visser, 1997). High C/N ratios (>30), pristane/phytane ratios greater than 8, and the presence of long-chained aliphatic hydrocarbons indicate a strong terrestrial input into the basin margins (Figs. 4C and 4D). By comparing the geochemical fingerprints of organic matter from central and marginal basin positions, we demonstrate that the distal basin received no significant amounts of terrestrial organic matter during deposition of the entire Dwyka Group. Because the organic carbon was derived exclusively from marine organic matter, variations in its carbon isotopes must originate from CO_2 variations between glacial and interglacial phases. Admixture of terrigenous organic matter from vegetation cover of the southern Gondwana continent during ice-free phases can be excluded.

In DS IV carbon isotopic signatures do not

reflect the cyclicity shown by the element ratios. The transition from the upper Dwyka Group (mean $\delta^{13}\text{C}$ of -22.75‰) into postglacial Ecce Group (mean $\delta^{13}\text{C}$ of -22.25‰) is characterized by a conspicuous excursion to lighter $\delta^{13}\text{C}$ values of -26.5‰ . This excursion correlates with enhanced tectonic and volcanic activity, which is documented by decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ca. 290 Ma (Veizer et al., 1999).

Climate information can be extracted from the $\delta^{13}\text{C}$ record of marine bicarbonate. Marine carbonates suitable for reliable carbon isotope determinations were not deposited during sedimentation of the Dwyka Group. Therefore, we used $\delta^{13}\text{C}$ values of the organic carbon in the sedimentary rocks to infer climate changes. The isotope variations are driven by the CO_2 content in the atmosphere, which affects the organic carbon reservoir. Paired carbonate and organic carbon isotopes have been used to decipher changes in atmospheric $p\text{CO}_2$ over Earth's history (Hayes et al., 1999). Veizer et al. (1999) compiled an extensive set of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ data from paleotropical carbonate fossils. The $\delta^{13}\text{C}_{\text{org}}$ values from south Gondwana and $\delta^{13}\text{C}_{\text{carb}}$ values from equatorial regions (Fig. 3B and C) show co-evolutionary trends during the Pennsylvanian. Variability lies within the error range of the age determinations. The marked drop ca. 303 Ma and the subsequent increase in the $\delta^{13}\text{C}_{\text{carb}}$ values (Fig. 3C) indicate a transition from a warm to a cold climate phase (Bruckschen et al., 1999). The co-variations of $\delta^{13}\text{C}_{\text{org}}$ from the Karoo Basin in southern Gondwana and the equatorial $\delta^{13}\text{C}_{\text{carb}}$ of Bruckschen et al. (1999) confirm a global change in the carbon isotope composition during the Pennsylvanian.

DISCUSSION AND CONCLUSION

Independent geochemical proxies reflect climate variations during deposition of stadal and interstadial sediments of the glacial Dwyka Group within the central Karoo Basin. During stadal phases, sea-level lowstand caused sediment deposition under nonmarine conditions, as indicated by sedimentological and paleoecological evidence (Visser, 1997). Organic matter deposited in distal regions, however, reveals no terrestrial influence. During interstadial phases, sea level rose significantly, establishing full-marine conditions that persisted throughout deposition of the postglacial Ecce Group.

The global nature and synchronous onset of regionally observed climate variations are documented by the simultaneous shifts in the $\delta^{13}\text{C}$ values of equatorial carbonates and the $\delta^{13}\text{C}$ values of organic carbon from the southern-latitude Karoo Basin. The ~ 5 m.y. periodicity in the duration of stadal-interstadial

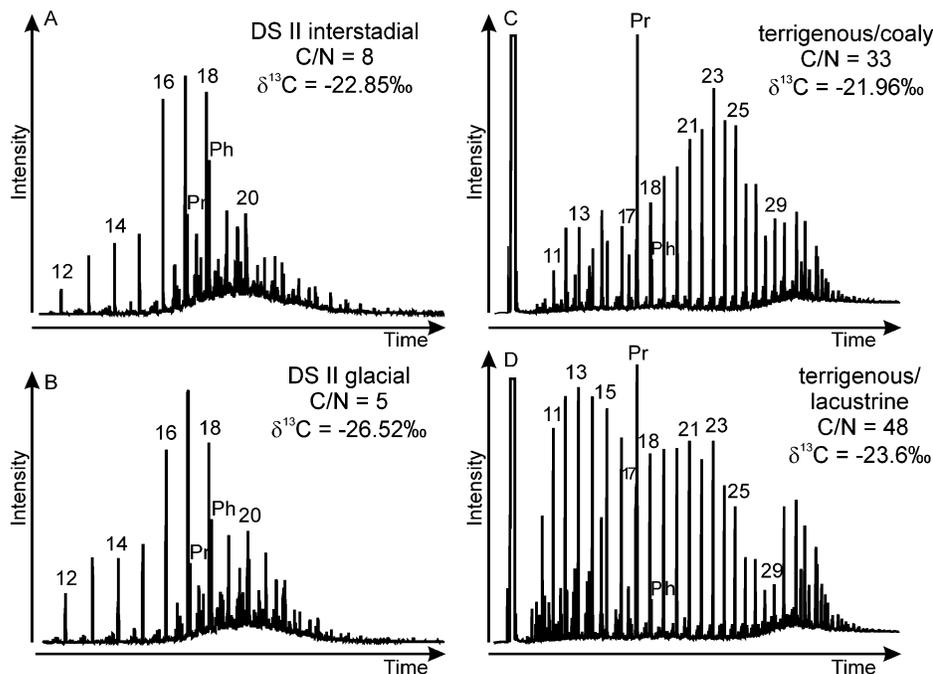


Figure 4. Dwyka sedimentary lipid distribution; *n*-alkanes indicated by carbon number, and pristane and phytane denoted as Pr and Ph, respectively. A and B: Aliphatic hydrocarbon compositions of samples from (A) interstadial and (B) glacial phases document a fully marine origin of organic matter. C and D: Distribution of *n*-alkanes from basin margins reveals a strong input of land-plant material. Variation of $\delta^{13}\text{C}_{\text{org}}$ values in central basin thus results from change in $p\text{CO}_2$.

cycles does not fit any known orbital frequency and requires further investigation.

The clockwise drift of the southern Gondwana continent shifted the Karoo Basin into polar cold regions and can be regarded as the primary trigger for glaciation processes. This mechanism is, however, insufficient to explain the cyclic climate variations as well as the terminal and abrupt breakdown of the ice shields. Warm currents along the eastern coast of Pangea (Kutzbach et al., 1990) transported moist air to polar regions. In combination with high albedo rates and low $p\text{CO}_2$, icehouse conditions were established and glaciers started to accumulate in high latitudes. High temperature gradients between equatorial and polar regions favored the development of a psychrosphere where deep ocean cold-water currents reached equatorial regions. Feedback mechanisms intensified the cooling rates and favored the fixation of water as glaciers on southern continents. This in turn caused a global fall in sea level. During regression phases, CO_2 fixing carbonate-complexes were exposed above sea level and carbonate weathering led to increasing $p\text{CO}_2$. In concert with phases of enhanced tectonic activity (Stollhofen et al., 2000), elevated atmospheric CO_2 release initiated greenhouse conditions. Elevated temperatures established new air-ocean circulation pathways and possibly a retreat of the CO_2 -fixing psychrosphere. Most importantly, the Pangean closure of the equatorial seaway

(Saltzman, 2003) decoupled the evolution of the Panthalassian and Paleotethys Oceans.

As a result of reduced equatorial to polar temperature gradients, glaciers retreated and sea level rose. The processes of CO_2 release and temperature increase, linked in a positive feedback, caused global warming. The final termination of the Carboniferous–Permian glaciation phase in southern Africa must be viewed to have resulted from the interaction of different climate-controlling factors, including variations in $p\text{CO}_2$ values, the continent-ocean configuration, and continental topography, as well as changing atmospheric and oceanic circulation pathways. As the solar system passes through one of the four galactic spiral arms, the cosmic ray flux increases, which may trigger global glaciation (Shaviv, 2002). The poor correlation between the cosmic ray flux maximum and the timing of the Pennsylvanian glaciation excludes this external forcing mechanism and underlines the need for further investigation.

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REFERENCES CITED

Bangert, B., Stollhofen, H., Lorenz, V., and Armstrong, R., 1999, The geochronology and significance of ash-fall tuffs in the glaciogenic Carboniferous–Permian Dwyka Group of Namibia and South Africa: *Journal of African Earth Science*, v. 29, p. 33–49.

- Berner, R.A., 1994, Geocarb II: A revised model of atmospheric CO_2 over Phanerozoic time: *American Journal of Science*, v. 294, p. 56–91.
- Bruckschen, P., Oesmann, S., and Veizer, J., 1999, Isotope stratigraphy of the European Carboniferous: Proxy signatures for ocean chemistry, climate, and tectonics: *Chemical Geology*, v. 161, p. 127–163.
- Bühmann, C., and Bühmann, D., 1990, Clay minerals as palaeoenvironment indicators exemplified on a Karoo Sequence from the Bothaville area, South Africa: *South African Journal of Geology*, v. 93, p. 505–513.
- Campbell, F.A., and Williams, G.D., 1965, Chemical composition of shales of Mannville Group (Lower Cretaceous) of central Alberta, Canada: *American Association of Petroleum Geologists Bulletin*, v. 49, p. 81–87.
- Caputo, M.V., and Crowell, J.C., 1985, Migration of glacial centers across Gondwana during Paleozoic Era: *Geological Society of America Bulletin*, v. 96, p. 1020–1036.
- Crowell, J.C., 1978, Gondwana glaciation, cyclothem, continental positioning, and climate change: *American Journal of Science*, v. 278, p. 1345–1372.
- Crowley, T.J., and Baum, S.K., 1992, Modeling late Paleozoic glaciation: *Geology*, v. 20, p. 507–510.
- Frakes, L.A., Francis, J.E., and Syktus, J.I., 1992, Climate modes for the Phanerozoic: Cambridge, Cambridge University Press, 274 p.
- Hayes, J.M., Strauss, H., and Kaufman, A.J., 1999, The abundance of ^{13}C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma: *Chemical Geology*, v. 161, p. 103–125.
- IPCC (Intergovernmental Panel on Climate Change), 2001, Third assessment report: Climate change 2001: <http://www.ipcc.ch> (February 2003).
- Jasper, J.P., and Hayes, J.M., 1990, A carbon isotope record of CO_2 levels during the late Quaternary: *Nature*, v. 347, p. 462–464.
- Jones, B., and Manning, D.A.C., 1994, Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones: *Chemical Geology*, v. 111, p. 111–129.
- Kutzbach, J.E., Guetter, P.J., and Washington, W.M., 1990, Simulated circulation of an idealized ocean for Pangean time: *Paleoceanography*, v. 5, p. 299–317.
- Martini, I.P., 1997, Late glacial and postglacial environmental changes, Quaternary, Carboniferous–Permian, and Paleozoic: Oxford, Oxford University Press, 343 p.
- Meyers, P.A., 1997, Organic geochemical proxies of palaeoceanographic, paleolimnologic and paleoclimatic processes: *Organic Geochemistry*, v. 27, p. 213–250.
- Nesbitt, H.W., and Young, G.M., 1982, Early Proterozoic climates and plate motions inferred from major element chemistry of lutites: *Nature*, v. 299, p. 715–717.
- Saltzman, M.R., 2003, Late Paleozoic ice age: Oceanic gateway or $p\text{CO}_2$? *Geology*, v. 31, p. 151–154.
- Shaviv, N.J., 2002, Cosmic ray diffusion from galactic spiral arms, iron meteorites, and a possible climatic connection: *Physical Review Letters*, v. 89, 051102.
- Stollhofen, H., Stanistreet, I.G., Bangert, B., and Grill, H., 2000, Tuffs, tectonism and glacially related sea level changes, Carboniferous–Permian, southern Namibia: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 161, p. 127–150.
- Veivers, J.J., and Powell, C.A., 1987, Late Paleozoic glacial episodes in Gondwanaland reflected in transgressive-regressive depositional sequences in Euramerica: *Geological Society of America Bulletin*, v. 98, p. 475–487.
- Veizer, J., Ala, D., Azmy, K., Bruckschen, P., Buhl, D., Bruhn, F., Carden, G.A.F., and Diener, A., 1999, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ evolution of Phanerozoic seawater: *Chemical Geology*, v. 161, p. 59–88.
- Visser, J.N.J., 1997, Deglaciation sequences in the Permo–Carboniferous Karoo and Kalahari basins of southern Africa: A tool in the analysis of cyclic glaciomarine basin fills: *Sedimentology*, v. 44, p. 507–521.
- Visser, J.N.J., and Praekelt, H.E., 1996, Subduction, megashear systems and late Paleozoic basin development in the African segment of Gondwana: *Geologische Rundschau*, v. 805, p. 632–646.
- Visser, J.N.J., and Young, G.M., 1990, Major element geochemistry and paleoclimatology of the Permo–Carboniferous glaciogenic Dwyka Formation and postglacial mudrocks in southern Africa: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 81, p. 49–57.

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