

Late Paleozoic ice age: Oceanic gateway or $p\text{CO}_2$?

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ABSTRACT

The cause of the late Paleozoic (ca. 355–255 Ma) ice age remains uncertain. A lowering of atmospheric carbon dioxide levels near the beginning of this time period occurred in response to the rise of land plants and likely cooled Earth, but the rapid growth of extensive Gondwanan ice sheets was delayed for tens of millions of years, until the Late Mississippian. The $\delta^{13}\text{C}$ values from a thick succession at Arrow Canyon, Nevada, indicate a divergence between North America and Europe ($\sim 2\text{‰}$) across the Mississippian-Pennsylvanian transition, and support a scenario in which the closure of a subequatorial oceanic gateway during the assembly of Pangea altered the oceanic distribution of nutrients (^{12}C) and led to enhanced poleward transport of heat and moisture. This change marks the transition from a cool, moisture-starved Gondwana to the icehouse world of the Pennsylvanian and Early Permian.

Keywords: Carboniferous, glaciation, carbon isotope, Arrow Canyon, oceanic gateway.

INTRODUCTION

The late Paleozoic ice age was one of the most severe in Earth history, lasting nearly 100 m.y. and extending to sea level around the margins of the Gondwanan continents (Crowell, 1999). Relatively small, discontinuous glacial centers characterize the early part of the Mississippian (Veevers and Powell, 1987), and the rapid growth of extensive continental ice sheets near the Mississippian-Pennsylvanian (mid-Carboniferous) boundary produced a maximum area of expanded ice comparable to the Pleistocene ($\sim 23.5 \times 10^6 \text{ km}^2$) (Crowley and Baum, 1991; Fig. 1). A lowering of atmospheric CO_2 levels, brought about in part by the rise of land plants and their effect on silicate weathering and organic carbon burial, is thought to have played a major role in global cooling during the Carboniferous (Berner, 1990), although long-term decreases in the cosmic ray flux reaching Earth may also be important (Shaviv, 2002). A significant increase in global organic carbon burial has been argued on the basis of a large $\delta^{13}\text{C}$ shift to values of $\geq +6\text{‰}$ documented across the Mississippian-Pennsylvanian transition in the paleo-Tethyan region (Popp et al., 1986; Bruckschen et al., 1999), and this is supported by widespread coals in the Pennsylvanian of North America and Europe (Calder and Gibling, 1994). However, recent studies have indicated significant interoceanic variability in the magnitude of the $\delta^{13}\text{C}$ shift at the Mississippian-Pennsylvanian transition (Mii et al., 1999, 2001), raising the possibility that the $+6\text{‰}$ values recognized in Tethyan sections signal a restructuring of oceanic circulation patterns in response to the suturing of Euramerica and Gondwana (Fig. 1), rather than elevated global organic carbon burial rates. Such a scenario is consistent with the proposal that closure of this subequatorial oceanic gateway in the Late

Mississippian enhanced poleward transport of heat and vapor and played a critical role in maintaining large polar ice sheets over southern Gondwana (Smith and Read, 2000).

The purpose of this paper is to evaluate the

hypothesis that oceanic $\delta^{13}\text{C}$ values differed significantly on opposite sides of Pangea during the Pennsylvanian and to examine the implications for the buildup of continental ice sheets. Present knowledge of Carboniferous $\delta^{13}\text{C}$ values for North America is limited in part by the spatial and temporal resolution available in the relatively thin, shallowly dipping strata of the Midcontinent region (Mii et al., 1999), and therefore this study focused on high-resolution $\delta^{13}\text{C}$ analyses from a thick ($\sim 1.3 \text{ km}$), richly fossiliferous, and continuously exposed sequence in the Arrow Canyon Range of Nevada (Fig. 2). The Arrow Canyon $\delta^{13}\text{C}$ curve provides a reference section for western North America that can be integrated biostratigraphically with the Midcontinent region as well as sections in the paleo-Tethys that record values $\geq +6\text{‰}$ in the Pennsylvanian (Fig. 1).

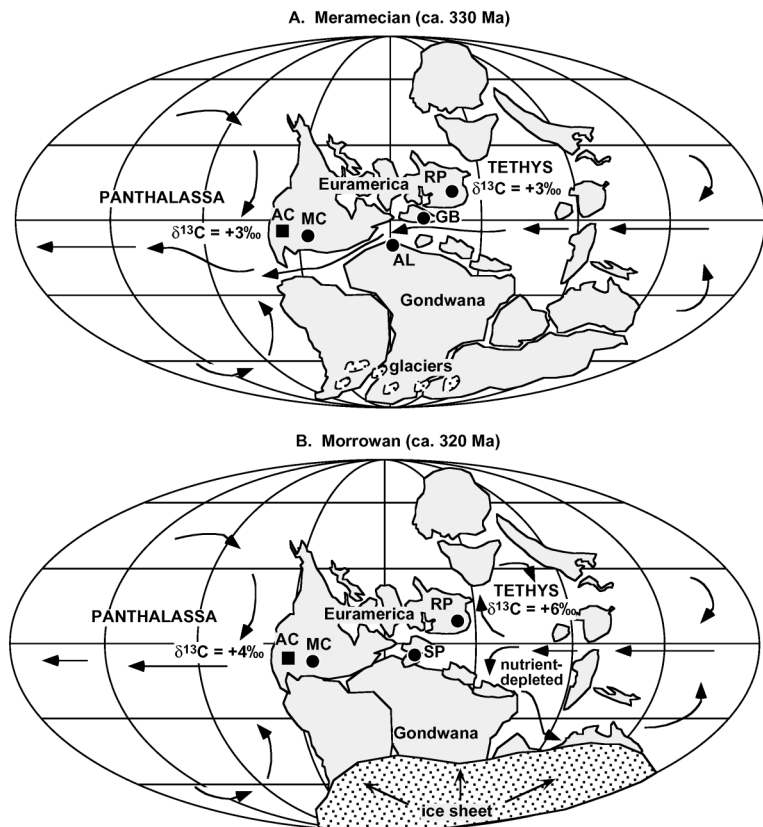


Figure 1. Paleogeographic maps showing simplified ocean circulation, extent of glaciation, and generalized carbon isotopic values for Panthalassan and paleo-Tethyan water masses (Popp et al., 1986; Veevers and Powell, 1987; Grossman, 1994; Smith and Read, 2000). A: Subequatorial current flowed freely between Gondwana and Euramerica (Laurussia) in Meramecian. B: Closure of oceanic gateway between Gondwana and Euramerica deflected heat and moisture poleward, resulting in major period of ice-sheet advance by Morrowan time and development of interoceanic $\delta^{13}\text{C}$ divergence reflecting nutrient depletion in paleo-Tethyan realm. AC—Arrow Canyon, Nevada; MC—Midcontinent, United States; RP—Russian Platform; GB—Great Britain; AL—Algeria; SP—Spain.

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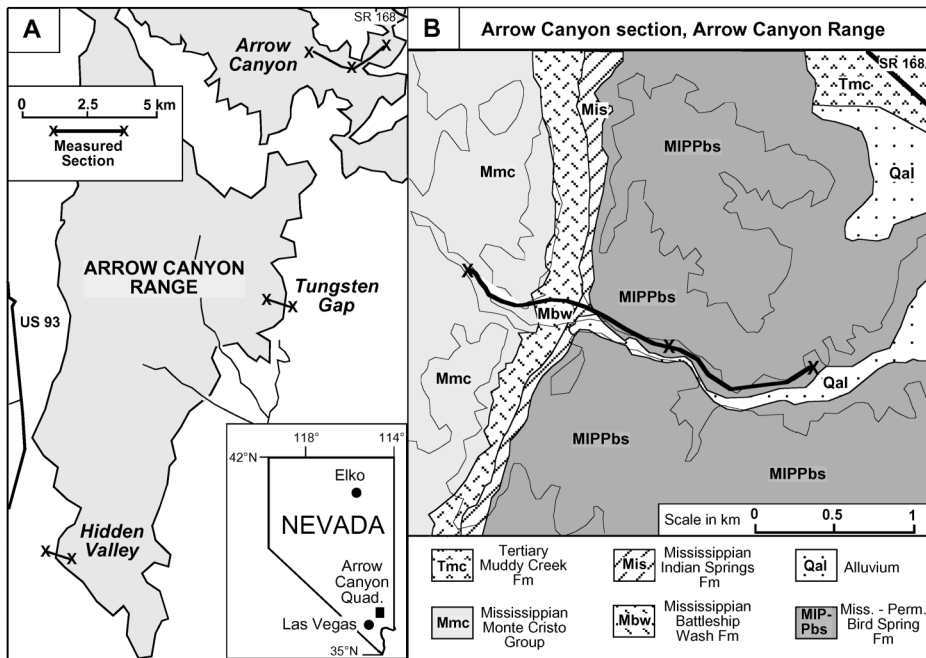


Figure 2. Locality map of Arrow Canyon Range, southeastern Nevada. A: Location of three measured sections sampled for $\delta^{13}\text{C}$. B: Simplified geologic map of Arrow Canyon showing location of thick Carboniferous section (Cassity and Langenheim, 1966) (SR—state road).

GEOLOGIC SETTING AND DATA

The Carboniferous succession in the Arrow Canyon Range (Fig. 2) was selected for $\delta^{13}\text{C}$ study because a half century of paleontologic and sedimentologic investigation by academic, government, and industry geologists has shown it to be among the most complete records of open-marine carbonate platform (ramp) deposition known in the world (e.g., Cassity and Langenheim, 1966; Heath et al., 1967; Pierce and Langenheim, 1974; Poole and Sandberg, 1991). Most recently, the International Subcommittee on Carboniferous Stratigraphy recognized this uniquely developed stratigraphic framework by designating the global stratotype section and point (GSSP) for the Mississippian-Pennsylvanian boundary at Arrow Canyon (Lane et al., 1999). The $\delta^{13}\text{C}$ curve for the Arrow Canyon Range (Fig. 3) was generated from samples of micritic limestone matrix drilled from fresh rock surfaces. The curve begins with a large increase to values of $\geq +7\%$ in the Lower Mississippian (Kinderhookian) Dawn Limestone (Fig. 3). It is the preservation of this transient positive excursion (Saltzman, 2002), which can be correlated with brachiopod-based curves in both North America (Mii et al., 1999) and Europe (Bruckschen et al., 1999), that perhaps

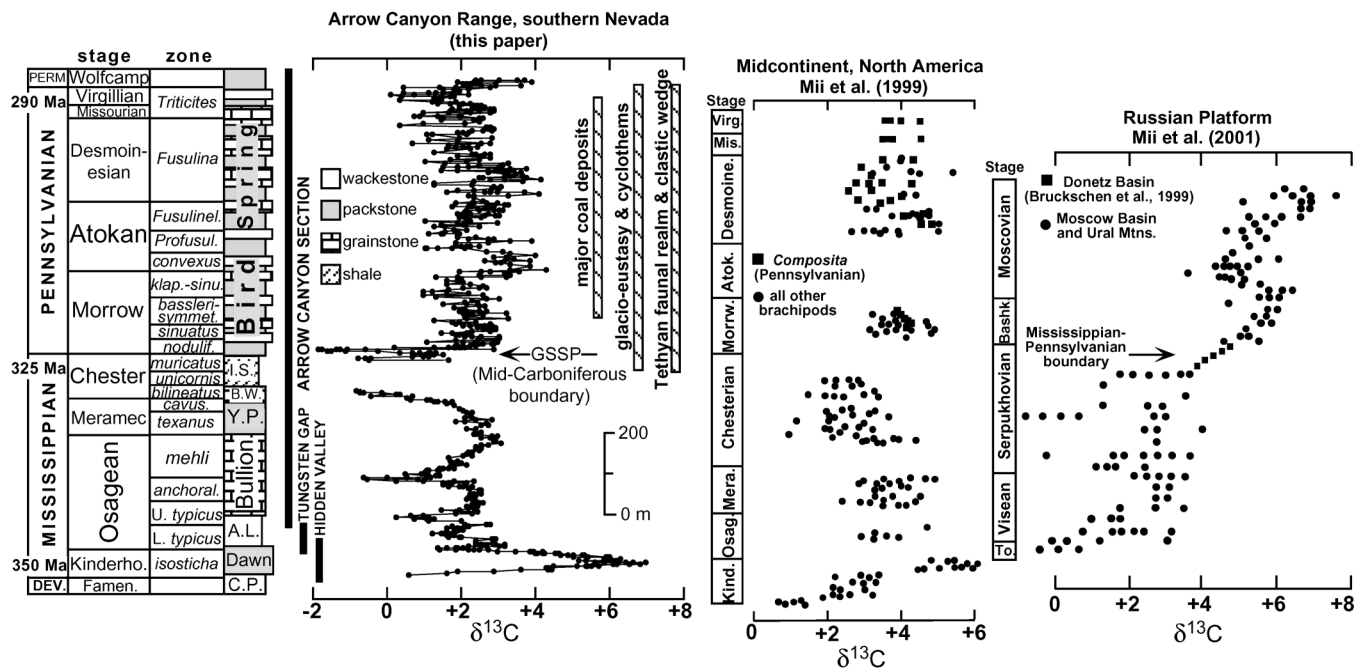


Figure 3. Integrated $\delta^{13}\text{C}$ and biostratigraphy and generalized measured section for Arrow Canyon Range succession (C.P.—Crystal Pass Limestone; A.L.—Anchor Limestone; Y.P.—Yellowpine Limestone; B.W.—Battleship Wash Formation; I.S.—Indian Springs Formation) and its correlation with brachiopod calcite curves from Midcontinent of North America and from Russian Platform. Arrow Canyon Range biostratigraphic zonation is after Cassity and Langenheim (1966), Pierce and Langenheim (1974), Poole and Sandberg (1991), and Lane et al. (1999). Black bars to right of Arrow Canyon stratigraphic column indicate range of each of three sample locations (see Fig. 2). Arrow points to global stratotype section and point (GSSP) for Mississippian-Pennsylvanian boundary at Arrow Canyon. See $\delta^{18}\text{O}$ curve in Data Repository (see footnote 1). Ruled bars to right of Arrow Canyon $\delta^{13}\text{C}$ curve approximate major intervals of coal deposition and glacio-eustatic sedimentation in southern Euramerica, and development of paleo-Tethyan faunal realm in Europe (see text for discussion and references). In Russian Platform section, upper Serpukhovian samples from Donetz Basin (Bruckschen et al., 1999) are inserted into section of Mii et al. (2001) because of incomplete record in Moscow Basin (Nemirovskaya et al., 1990). No scale is placed on Midcontinent and Russian Platform sections because corresponding measured sections are not available.

best illustrates the suitability of the Arrow Canyon succession for investigation of $\delta^{13}\text{C}$ trends and the potential for global correlation. Following this large positive shift in the Kinderhookian, $\delta^{13}\text{C}$ values remain near +2‰ to +3‰ through most of the Mississippian before falling to below 0‰ in the Chesterian. A positive shift to values above +3‰ occurs in the Lower Pennsylvanian (Morrowan); maximum values of $\sim +4\%$ are higher up in the Atokan and Missourian Stages. The $\delta^{18}\text{O}$ values show significantly more scatter and have a mean of -4.8% in the Mississippian and -3.4% in the Pennsylvanian (see Data Repository¹).

DISCUSSION

The $\delta^{13}\text{C}$ curve for the Arrow Canyon Range (Fig. 3) does not record the shift to values of $\geq +6\%$ observed in the Pennsylvanian of European (paleo-Tethyan) basins (Mii et al., 2001). The Arrow Canyon curve is, however, in agreement with brachiopod calcite data from the Midcontinent region of North America (Mii et al., 1999), which argues against local or basin-scale diagenetic alteration as a cause of the lower $\delta^{13}\text{C}$ values measured in the two North American sections. A primary seawater signal is also consistent with the absence of evidence for exposure surfaces in the majority of the Arrow Canyon Pennsylvanian strata (e.g., no karst pits or brecciated limestone) and the only rare occurrence of strongly negative $\delta^{18}\text{O}$ values ($\leq -6\%$) (see footnote 1) that are commonly interpreted as indicators of extensive resetting of primary $\delta^{13}\text{C}$ values (Algeo et al., 1992; Grossman, 1994; Immenhauser et al., 2002). If interpreted as a primary, surface-mixed-layer water-mass signature, the $\sim 1.5\%$ – 2.0% divergence in $\delta^{13}\text{C}$ values between North American and European basins must reflect regional differentiation in terms of temperature (thermodynamic imprint) or nutrient contents (biological influence). For example, a shift in circulation patterns that resulted in net downwelling and a relatively nutrient-depleted (^{12}C -enriched) paleo-Tethyan water mass compared to Panthalassa has been suggested (Mii et al., 1999, 2001; Fig. 1). In addition, a warming of the western paleo-Tethyan surface ocean may have resulted in net outflow of $^{12}\text{CO}_2$, enriching the local water mass in ^{13}C . This bulk-transfer (kinetic) effect, which can account for an estimated 0.6‰ difference in the modern oceans (Lynch-Stieglitz et al., 1995), may be opposed by equilibrium exchange of CO_2 between the surface ocean and atmosphere that involves a temperature-

dependent fractionation of $\sim -0.1\%$ K^{-1} . Thus, cold surface waters in equilibrium with the atmosphere will have higher $\delta^{13}\text{C}$ values compared with warmer waters (Gruber et al., 1999). However, because the sections from which Carboniferous $\delta^{13}\text{C}$ values are known are thought to represent tropical to subtropical water masses (Fig. 1) that likely had a relatively narrow temperature range (20–30 °C), the most likely explanation for the $\delta^{13}\text{C}$ gradient at the Mississippian-Pennsylvanian transition involves lower nutrient contents in the western paleo-Tethys as a result of biological pumping of ^{12}C -enriched organic matter in a region characterized by downwelling or a strong pycnocline that prevented return of ^{12}C .

Although it may not be possible to uniquely determine the role of various biological and thermodynamic factors, a reasonable hypothesis for the North American versus European divergence in $\delta^{13}\text{C}$ values at the Mississippian-Pennsylvanian transition is a reorganization of the ocean circulation that resulted in a semi-restricted paleo-Tethyan water mass and promoted nutrient depletion along its western margin (Fig. 1).

Independent biogeographic evidence for a temporal link between the disruption of free circulation of water masses on opposite sides of Pangea (closure of the subequatorial oceanic gateway) and the Mississippian-Pennsylvanian boundary $\delta^{13}\text{C}$ divergence can be seen in the development of strongly provincial Tethyan and non-Tethyan bryozoan, foraminifer, and coral faunas (Rodríguez, 1984; Ross and Ross, 1985). A significant episode of brachiopod migrations near the Mississippian-Pennsylvanian boundary (Raymond et al., 1989) may also signal high-latitude temperature changes associated with gateway closure. In addition, geochronologic and sedimentologic data place the early stages of collision between Euramerica and Gondwana ca. 315–325 Ma (Dallmeyer et al., 1986; Chesnut, 1991), close to the biostratigraphically defined Mississippian-Pennsylvanian boundary. However, a somewhat analogous gateway closure during the middle Pliocene uplift of the isthmus of Panama led to an $\sim 1.0\%$ difference in the deep oceans of the Atlantic and Pacific, but apparently produced only small ($<0.5\%$), transitory shifts in surface-ocean $\delta^{13}\text{C}$ values (Keigwin, 1982). This difference in the effects of the two gateway closures suggests that increased water-mass residence times in the late Paleozoic epicontinental sea environment (e.g., Holmden et al., 1998; Immenhauser et al., 2002) may have exaggerated a relatively small $\delta^{13}\text{C}$ gradient developed in the surface waters of the open ocean. The effects of oceanic gateway closure on circulation patterns during the Pliocene have been modeled (e.g., Maier-Reimer and Mikolajewicz, 1990), and

use of a fully coupled atmosphere-ocean model in the Carboniferous would provide a key test of the gateway hypothesis.

Interpretation of the $\delta^{13}\text{C}$ divergence between European and North American carbonates in the middle part of the Carboniferous as a response to a restructuring of ocean-circulation patterns has implications for the cause of the widespread ice-sheet advances in southern Gondwana. Following periods of relatively minor glacial buildup in the Mississippian, the onset of this main period of glaciation is dated to the Namurian (Chesterian) by widespread tillites on Gondwana (Veevers and Powell, 1987; Crowell, 1999) and may have begun slightly earlier on the basis of the onset of glacio-eustatic cyclothemic deposition and incised valleys in depositional sequences in Euramerica (*Gnathodus bilineatus* zone; Smith and Read, 2000) (Fig. 3). The $\delta^{13}\text{C}$ divergence between Europe and North America is perhaps best dated by comparing curves from Arrow Canyon and the U.S. Midcontinent with the Donetsk Basin in the Ukraine, which preserves the most complete record through this interval on the Russian platform (Nemirovskaya et al., 1990). The positive $\delta^{13}\text{C}$ shift in the Donetsk begins at a level (D7/5 limestone bed = $+4.1\%$; Bruckschen et al., 1999) that is just beneath the Mississippian-Pennsylvanian boundary (Nemirovskaya et al., 1990), a horizon well marked by the first occurrence of the species *Declinognathodus noduliferous* that defines the GSSP at Arrow Canyon (Lane et al., 1999). That $\delta^{13}\text{C}$ values are well below $+4\%$ in the lowermost Pennsylvanian *D. noduliferous* zone and uppermost Mississippian *muricatus* zone at Arrow Canyon (a result in good agreement with brachiopod calcite data in Brand and Brenckle, 2001) gives a minimum age for the $\delta^{13}\text{C}$ divergence in the uppermost Chesterian. Thus, it seems plausible that the poleward deflection of a warm, circumequatorial current associated with the joining of the Euramerican and Gondwanan land masses brought substantial heat and moisture to southern Gondwana at some stage during the Chesterian and facilitated the expansion of ice sheets (Smith and Read, 2000). Although $\delta^{18}\text{O}$ values from Arrow Canyon increase by $\sim 1\%$ across the Mississippian-Pennsylvanian boundary (see footnote 1) and are consistent with ice buildup (Grossman et al., 2002), the values as a whole are somewhat lower than values in coeval brachiopod calcite (Mii et al., 1999, 2001) and have likely been diagenetically altered to some degree.

Although the gateway hypothesis for ice buildup in the Pennsylvanian may be consistent with the timing of $\delta^{13}\text{C}$ changes and the pattern of physical evidence for glaciation, a critical question having implications for glob-

¹GSA Data Repository item 2003013, $\delta^{18}\text{O}$ curve for Arrow Canyon Range succession, is available from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, editing@geosociety.org, or at www.geosociety.org/pubs/ft2003.htm.

al climate and $p\text{CO}_2$ estimates lingers. Which $\delta^{13}\text{C}$ signature, North American or European, most closely represents global seawater values during the Pennsylvanian? Mii et al. (2001) hypothesized that (1) the $\sim +6\%$ $\delta^{13}\text{C}$ values in Europe were representative of the global oceans and thus due entirely to burial of organic carbon (primarily terrestrial coals) and (2) the lower $\delta^{13}\text{C}$ signature in North America recorded enhanced coastal upwelling. However, it appears that the onset of widespread coal deposition in southern Euramerica is younger than the $\delta^{13}\text{C}$ shift by several conodont zones (middle Morrowan–late Morrowan *klapperi-sinuosus* zone; Groves, 1983; Peppers, 1996; Fig. 3 herein), and the evidence for strong upwelling in western Euramerica is even later (Desmoinesian; Heckel, 1986). A lowering of the global $\delta^{13}\text{C}$ curve by 1‰–2‰ (from the $\sim +5\%$ – 6% peak used in Berner, 1990) raises the possibility that atmospheric CO_2 values in the Pennsylvanian were as much as several times higher than the current estimates of 250–300 ppm and highlights the importance of future studies aimed at more accurately determining the timing of organic carbon burial, upwelling, and changes in $\delta^{13}\text{C}$ on a global scale.

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