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Mississippian $\delta^{13}C_{carb}$ and conodont apatite $\delta^{18}O$ records — Their relation to the Late Palaeozoic Glaciation

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ABSTRACT

Carbon isotopes of whole rock carbonates and oxygen isotopes of conodont apatite from Late Devonian to Early Pennsylvanian sections in Europe and Laurentia were measured in order to reconstruct variations in the carbon cycle, marine palaeotemperature, and ice volume during the Mississippian. Conodont apatite $\delta^{18}O$ values show two major positive shifts of +2‰ and +1.5‰ V-SMOW in the late Tournaisian and Serpukhovian, respectively, that are interpreted to reflect climatic cooling and changes in ice volume. Carbon isotope ratios of inorganic and organic carbon show a major positive excursion with an amplitude of +6.5‰ V-PDB in the Tournaisian and a positive shift of up to +5‰ V-PDB in the Serpukhovian. The positive $\delta^{13}C$ excursions coincide with the deposition of organic carbon-rich black shales which indicate that organic carbon burial, lowering of atmospheric pCO_2, and climatic cooling may have occurred during these time intervals. However, while in the Tournaisian the positive shifts in $\delta^{18}O_{apatite}$ and $\delta^{13}C$ coincide, in the Serpukhovian the positive shift in $\delta^{18}O_{apatite}$ precedes the positive shift in $\delta^{13}C$ and raises the question as to whether changes in the global carbon cycle were the ultimate cause of the inferred climatic changes. The conodont apatite $\delta^{18}O$ values suggest that a first major cooling and potential glaciation event occurred in the Tournaisian with ice masses persisting into the Visean. The second glaciation event occurred in the Serpukhovian and culminated in the first glacial maximum of the Late Palaeozoic Glaciation.

1. Introduction

The Mississippian time interval represents the transition from Devonian greenhouse to Permo-Carboniferous icehouse modes. After a Frasnian temperature maximum and two short-term cooling episodes in the latest Frasnian and earliest Famennian (Joachimski and Buggisch, 2002; Joachimski et al., 2004), the first glacial deposits are recorded from the Amazon Basin of Brazil, Bolivia, and Peru at the Devonian–Carboniferous (D–C) boundary (Caputo, 1985; Streel et al., 2000). A pronounced positive $\delta^{13}C$ excursion during the Tournaisian (Mii et al., 1999; Buggisch and Haas, 2000; Saltzman et al., 2000; Saltzman, 2002, 2003a,b) was interpreted as the result of enhanced organic carbon burial inducing a lowering of atmospheric CO_2 levels and climatic cooling. However, no glacial deposits are known from this time interval. Ice rafted debris and tillites have been reported from the Visean and Serpukhovian with a maximum extent during the Bashkirian (Garzanti and Sciunnach, 1997). Miller and Eriksson (2000) recorded glacioeustatic sequences from late Mississippian (Arnsbergian; Table 1) strata in southwest Virginia. Smith and Read (2000) interpreted Chesterian incised valleys of the Illinois basin to have formed by an abrupt lowering of sea level of up to 95 m, probably as a consequence of the onset of ice build-up at high latitudes. Late Namurian glacial deposits are well known from numerous areas in South America (López-Gamundi, 1997; López-Gamundi and Martínez, 2000).

The evolution of Mississippian sea water temperatures has been reconstructed using oxygen isotope ratios of well-preserved brachiopod shells (Grossman et al., 1993; Banner and Kaufmann, 1994; Bruckschen et al., 1999, 2001; Mii et al., 1999, 2001; Veizer et al., 1999; Stanton et al., 2002). The $\delta^{18}O$ values reported by Grossmann et al. (1993) and Mii et al. (1999, 2001) gave realistic palaeotemperatures, assuming that the isotopic composition of Mississippian sea water was in the same range as that of the Pleistocene and Holocene. Other reported $\delta^{18}O$ values (e.g. Veizer et al., 1999) are in part too low and result in unrealistically warm palaeotemperatures if no secular change in the oxygen isotopic composition of sea water is assumed.

In this study, we use oxygen isotope ratios measured on conodont apatite in order to reconstruct the ice volume and palaeotemperature history during the Mississippian. Oxygen isotopes ratios of PO_4^{3-} of conodont apatite have been shown to represent an alternative and reliable palaeotemperature proxy (Wenzel et al., 2000; Joachimski and Buggisch, 2002; Joachimski et al., 2004, 2006), especially since the abundance of conodonts in shallow- as well as deep-water carbonates allows the construction of isotope records that have a much higher

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Table 1
Stratigraphic time table and correlation of conodont Zones for the Mississippian

Stage	Subdivision	Age (Ma)	Substage	Regional substage (UK)	Belgium
Serpukhovian		320		H2 Alportian / H1 Chokierian	
Serpukhovian		320–324	Euoposmrhcera	Arnsbergian (E2)	
Serpukhovian		324–326,5	Euoposmrhcera	Pendleian (E1)	
Viséan	(O.)	–332	(V3c)	Brigan-tian	Warnantian
Viséan	(O.)	332–337.5	(V3b)	Asbian	Warnantian
Viséan	(M.)	337.5	(V3a)	Hol-kerian	Livian
Viséan	(M.)		(V2b)	Hol-kerian	Livian
Viséan	(U.)	–341.5	(V2a)	Arundian	Moliniacian
Viséan	(U.)	341.5–343.5	(V1b)	Arundian	Moliniacian
Viséan	(U.)	343.5–	(V1a)	Chadian	Moliniacian
Tournaisian	(O.)	347.5	(Tn3)	Chadian	Ivorian
Tournaisian	(O.)	–351.5	(Tn3)	Cour-ceyan	Ivorian
Tournaisian	(M.)	351.5–355.5	(Tn2)	Cour-ceyan	Hastarian
Tournaisian	(U.)	355.5–	(Tn 1b)	Cour-ceyan	Hastarian

Age (Ma)	Age (Ma)	Europe	USA / Ireland	North American series
319	319–320	*Declinognathodus noduliferus*	*D. noduliferus*	Chesterian
	320–322	*Gnathodus postbilineatus*	*R. muricatus*; *A. unicornis*	Chesterian
	322–324	*G. bilineatus bollandensis*	*C. naviculus*	Chesterian
	324–326,5	*Lochriea ziegleri*	*C. naviculus*	Chesterian
326,5	326,5–328,5	*Lochriea nodosa*	*Gnathodus bilineatus*	Chesterian
	328,5–335	*Gnathodus bilineatus*	*Gnathodus bilineatus*	Chesterian / Meramecian
336.5	335–337	*Gnathodus praebilineatus*	**Ireland**	Meramecian
340	337–345.5	*Gnathodus texanus*	*M. beckmanni*	Meramecian / Osagean
345.5	345.5–347.5	*Scaliognathus anchoralis*	*Scaliognathus anchoralis*	Osagean
	347.5–349	*Gnathodus typicus*	*Scaliognathus anchoralis*	Osagean
	349–350	*Gnathodus semiglaber*	*Pol. communis carina*	Osagean
	350–350.8	*Neopolygnathus communis carina*	*Pol. communis carina*	Osagean
	350.8–351.5	*Gnathodus punctatus*	*Ps. multistriatus*	Osagean
351.5	351.5–353	*S. isosticha–Late S. crenulata*	*Pol. inornatus/ Siphonodella*	Osagean / Kinderhookian
	353–354	*Early S. crenulata*	*Pol. spicatus*	Kinderhookian
	354–356	*Siphonodella sandbergi*	*Pol. spicatus*	Kinderhookian
	356–356.5	Lt. *Siphonodella duplicata*		Kinderhookian
	356.5–357.3	E. *Siphonodella duplicata*		Kinderhookian
358	357.3–358	*Siphonodella sulcata*		Kinderhookian

Numerical ages after STG (2002). European conodont zonation after Weyer and Menning (2006).

time resolution in comparison to records reconstructed from oxygen isotope ratios of brachiopod shells. Carbon isotopes of inorganic and organic carbon derived from whole rock carbonate analysis are used as proxies to unravel changes in the global carbon cycle that may be responsible for major climatic changes or, alternatively, may result from climatic and oceanographic circulation changes. The conodont