Available online at www.sciencedirect.com
ScienceDirect
Palaeogeography, Palaeoclimatology, Palaeoecology 256 (2007) 254–272
PALAEO
www.elsevier.com/locate/palaeo

Carbon–oxygen isotope signal of Mississippian slope carbonates, Appalachians, USA: A complex response to climate-driven fourth-order glacio-eustasy

Thomas C. Wynn *, J. Fred Read

Department of Geosciences, Virginia Tech, Blacksburg, Virginia 24061, United States

Accepted 15 February 2007

Abstract

Mississippian (Chesterian) ramp-slope muds in Virginia, deposited on the margin of a rapidly subsiding foreland basin, were not significantly reset isotopically by regional meteoric aquifer systems that affected units on the adjacent platform. Carbon and oxygen isotopic ratios of these muds tend to covary at the scale of the twelve 4th-order sequences that dominate the platform succession. The $\delta^{13}C$ values of the slope muds range from +0.5 to +4‰ PDB and lie in the range of least-altered contemporaneous brachiopods from North America, indicating little resetting of carbon isotopes by diagenesis. There is an approximately 1 to 2‰ decrease in $\delta^{13}C$ in the maximum flooding zone relative to the lowstand, followed by a positive shift upward in the highstand before becoming more negative toward 4th-order correlative conformities. Meteoric diagenesis might have reset some sediments just beneath a sequence boundary to lighter values; it cannot account for the observed shifts evident throughout the sequences. The ^{13}C-enriched values in $\delta^{13}C$ profiles could be due to increased productivity during glacial stages. The increased productivity during glacial stages was probably due to increased ocean circulation, coupled with shallowing, which brought the ramp top into waters with more ^{13}C-enriched dissolved inorganic carbon, with the opposite effects occurring during deglaciation.

The $\delta^{18}O$ values of muds range from about −2.2 to about −4.6‰ PDB, falling within and beyond the lighter part of the range of contemporaneous North American brachiopods [Mii, H.S., Grossman, E.L., Yancey, T.E., 1999. Carboniferous isotope stratigraphies of North America; implications for Carboniferous paleoceanography and Mississippian glaciation. Geol. Soc. Am. Bull., 111, 960–973]. These values likely have been reset by burial diagenesis, and perhaps by some meteoric diagenesis just beneath correlative conformities. The sequences show negative excursions of 1 to 2‰ in $\delta^{18}O$ in the maximum flooding zone relative to the lowstand, and then become more positive upward in the highstand, then decrease toward the correlative conformities. Some of the preserved signal could reflect ice-volume changes, although this would account for only 0.5 to 1‰ change. The ice-volume effect during lowstands, plus cooling of ramp-top waters and small increases in salinity due to increased aridity in the Appalachian Basin, could account for the remaining 0.5 to 1.5‰ of oxygen isotope excursions, with the opposite effect occurring during high sea levels. The $\delta^{18}O$ and $\delta^{13}C$ of the Appalachian ramp-slope facies lack the strong 3rd-order trends of the mid-continental United States and Europe. The remnant 4th-order carbon and oxygen isotope signal is similar in structure to Cenozoic deep-sea isotope profiles that are due in large part to 4th-order glacio-eustasy. This would be compatible with onset of Late Paleozoic glaciation of Gondwana.

Keywords: Greenbrier Limestone; Appalachian Basin; Stable isotopes; Lower Carboniferous; Mississippian; Sequence stratigraphy

* Corresponding author. Present address: Department of Geology and Physics, Lock Haven University, Lock Haven, PA 17745, United States. Tel.: +1 570 484 2081.

E-mail address: twynn@lhup.edu (T.C. Wynn).

0031-0182/$ - see front matter
doi:10.1016/j.palaeo.2007.02.033

1. Introduction

Many studies have been done on the carbon and oxygen isotopic ratios of Early Carboniferous or Mississippian Period marine carbonates (see Bruckschen et al., 1999; Mii et al., 1999). In North America, carbon and oxygen isotope profiles have been constructed using brachiopods from, shallow-platform carbonates of the cratonic interior. The matrix of these platform carbonates underwent considerable diagenetic resetting to lighter isotopic values (Mii et al., 1999). However, brachiopods are not always distributed uniformly throughout the stratigraphic record, thus limiting sampling to brachiopod-bearing beds. Also, it is not clear how well these cratonic interior settings (or foreland basins for that matter) are representative of the global oceans.

Another approach is the use of "whole-rock" in which the matrix is sampled, but in order to avoid the intense early diagenesis that commonly affects platform carbonates, sampling is limited to slope carbonates. The advantage of "whole-rock" sampling is that it yields a continuous isotopic stratigraphic record and is not dependent on the distribution of brachiopods in the section. Such an approach was used by Saltzman (2002) to develop a carbon–oxygen isotope stratigraphy for Lower Mississippian strata in the western United States and by Immanhauser et al. (2002) for Pennsylvanian carbonates in Spain. In Paleozoic deeper-water carbonates, the bulk of the carbonate is generated on the ramp or platform top, and exported to the slope. Hence these slope deposits originally were representative of the stable isotope compositions of the platform waters, but they have commonly not been modified by subsequent meteoric diagenesis.

In this paper, we sampled the mud matrix of Mississippian (Chesterian) Greenbrier Group strata on the ramp-slope bordering the deeper foreland basin of the Appalachians in order to generate carbon and oxygen isotopic profiles and to evaluate if a primary isotope signal was present. Furthermore, we wished to determine whether an identified primary signal could be related to the climatic and eustatic fluctuations documented from the adjacent shallow-ramp succession (Al-Tawil and Read, 2003; Al-Tawil et al., 2003), and with associated changes in water, temperature and biological productivity. Previous studies have shown that the diagenetic resetting of these slope and basinal micritic carbonates by regional meteoric aquifer systems was relatively minor compared to platform carbonates updip (Niemann and Read, 1988; Nelson and Read, 1990). During burial, carbon isotopic ratios were buffered by the rock carbon, but oxygen isotopic values were altered to varying degrees depending on the permeability of the rocks to burial fluids (Meyers and Lohmann, 1985).

Most of the isotopic studies in the Paleozoic have shown long-term isotopic excursions related to 2nd-order (~ 5 to 20 m.y.) and 3rd-order (~ 0.5 to 5 m.y.) sea-level events. In this study, the carbon and oxygen isotopic excursions appear to be at the 4th-order scale (<0.5 m.y.). This is similar to the signal seen in the later Cenozoic, where glacio-eustasy has been especially pronounced (Hays et al., 1976; Zachos et al., 1997).

2. Geologic setting

The Appalachian Basin is an elongate foreland basin bordered on the east by overthrust Precambrian and Cambrian metasedimentary rocks, and on the west by the Cincinnati Arch (Fig. 1; Colton, 1970; de Witt and McGrew, 1979). In the western part of the basin, the Paleozoic rocks are undeformed to gently folded (Appalachian Plateau), whereas the eastern portion of the basin, including the sections sampled in this study, lies within the fold–thrust belt (Fig. 1). The Mississippian carbonates are relatively thin over much of the distal foreland in the northwest, but to the southeast they thicken rapidly across a major hinge into the foreland basin. They thicken more gradually to the southwest down the axial plunge of the foreland basin.

2.1. Formational and sequence stratigraphic framework

The Mississippian stratigraphy and biostratigraphy of Virginia and West Virginia (Figs. 2, 3) were studied by Butts (1922, 1940, 1941), Reger (1926), Wells (1950), Flowers (1956), de Witt and McGrew (1979), and Maples and Waters (1987). Greenbrier Group carbonates unconformably overlie deltaic and shelf siliciclastics of the Price/Borden Formation (Kinderhookian to Middle Osagean) throughout much of northeastern Kentucky, Virginia and West Virginia (Branson, 1912; Butts, 1940, 1941; Bartlett, 1974; Kammer et al., 1990; Pashin and Ettensohn, 1995). However in southern Kentucky, Greenbrier Group carbonates overlie Late Osagean–Early Meramecian Fort Payne–Salem Formation carbonates that are developed on and in front of deltaic siliciclastics of the Borden Formation (Bjerstedt and Kammer, 1988; Sable and Dever, 1990; Khetani and Read, 2002).

The Late Meramecian to Chesterian Greenbrier Group (Hillsdale to Alderson interval) and the Lillydale Shale and Glenray Limestone of the lower Bluefield Formation (Mauch Chunk Group) make up the studied interval (Figs. 1–3). Regionally, Greenbrier carbonates are relatively thin over much of the shallow-ramp area in