



Carboniferous–Permian carbon isotope stratigraphy of successions from China (Yangtze platform), USA (Kansas) and Russia (Moscow Basin and Urals)

Werner Buggisch*, Xiangdong Wang, Alexander S. Alekseev, Michael M. Joachimski

ARTICLE INFO

Article history:

Received 5 May 2010

Received in revised form 18 November 2010

Accepted 16 December 2010

Available online 25 December 2010

Keywords:

Carbon isotopes

Glaciation

Diagenesis

Pennsylvanian

Permian

ABSTRACT

The Pennsylvanian and Early Permian were times of extreme sea-level changes of >100 to perhaps up to 200 m. For example, glacio-eustatic sea-level changes are well documented from the US Midcontinent, Moscow Basin and Yangtze Platform, where more than 100 stacked subtidal to supratidal sequences have been described. In contrast, carbonates developed in the Ural Mountains and South Guizhou of the Yangtze Platform were deposited in ramp and slope settings. $\delta^{13}\text{C}$ values of whole rock samples from the US Midcontinent and Moscow Basin were intensively affected by diagenesis. Only well-preserved brachiopod shells maintained their original carbon isotope ratios. In contrast, limestones deposited in the deeper water slope environments were not affected by meteoric diagenesis and are interpreted to have mainly retained their carbon isotope ratios. Mean $\delta^{13}\text{C}$ values of slope carbonates of the Yangtze Platform increase from about 3‰ during the Viséan and Serpukhovian to 5‰ at the Carboniferous–Permian boundary and decrease to values around 2‰ in the early Kungurian. This positive $\delta^{13}\text{C}$ excursion coincides with low $\delta^{13}\text{C}$ values in the Yangtze Platform successions, which were reset by meteoric diagenesis. The highest $\delta^{13}\text{C}$ values recorded in the slope succession coincide with the inferred maximum glaciation that caused pronounced sea-level lowstands. Short-lived, but significant negative $\delta^{13}\text{C}$ excursions in the Chinese slope succession are interpreted to reflect changes in ocean circulation due to sea-level rises which caused enhanced production and/or preservation of organic matter which influenced the subsequent early diagenetic cementation.

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1. Introduction

The Pennsylvanian to Early Permian was a time of icehouse conditions that led to extensive glaciations in the southern hemisphere on Gondwana (Veevers and Powell, 1987). The Late Devonian greenhouse ceased near the Devonian–Carboniferous (D–C) boundary and gave way to a short-lived glaciation at the D–C transition (Caputo, 1985; Streel et al., 2000). The Carboniferous glaciation probably started during the Tournaisian (Buggisch et al., 2008) and reached a first acme in Serpukhovian–Bashkirian times (Crowell, 1999; Frakes et al., 1992; Garzanti and Sciunnach, 1997; Powell et al., 2009; Smith and Read, 2000; Wright and Vanstone, 2001). Frakes et al. (1992) reported minimum distribution of glacial deposits during the latest Moscovian and Kasimovian. Consequently, a contraction of ice masses was assumed (Montañez et al., 2007) with ice sheets increasing again during the Early Permian, reaching a second maximum during the Asselian to Sakmarian. In contrast, Veevers and Powell (1987), and Crowell (1999) argued that ice sheets reached their maximum extent during the latest Moscovian to Gzhelian. The waxing and waning of continental ice sheet causing high-frequency sea-level fluctuations is

well documented in the cyclic sedimentation pattern in the US Midcontinent, the so-called Kansas cyclothems (Crowley and Baum, 1992; Heckel, 1977, 1994; Veevers and Powell, 1987; Wanless and Sheppard, 1936). The magnitude of sea-level changes is estimated to have been potentially up to 200 m (Buggisch et al., 2008; Ross and Ross, 1987) although other authors give more conservative values (Fielding et al., 2008a; Isbell et al., 2003; Joachimski et al., 2006; Mazzullo et al., 2007; Rygel et al., 2008).

Carbon isotope ratios of Palaeozoic carbonates were traditionally measured on low-Mg calcitic brachiopod shells that are considered to be relatively resistant to diagenetic alteration. Whole-rock carbonates are also suitable for carbon isotope analyses (Brand, 2004; Holser, 1997) provided that they were not altered during diagenesis. Palaeozoic carbonates were predominantly precipitated in tropical shallow-water environments. Carbonates found in deeper water settings were usually exported from shallow-water platforms, although microbial micrites and diagenetic cements may have been formed in greater water depths.

It is well known that secular variations in $\delta^{13}\text{C}$ can provide information on the transfer of carbon between reservoirs. An increase in $\delta^{13}\text{C}$ of carbonates indicates excess burial and preservation of organic carbon whereas a decrease suggests a transfer from the organic to the inorganic reservoir. Additional factors like preferential precipitation of aragonite versus calcite (Sandberg, 1983; Swart, 2008) may affect the carbon isotope signal of carbonates. During the

* Corresponding author.

E-mail addresses: werner@buggisch.com (W. Buggisch), xdwang@nigpas.ac.cn (X. Wang), aaleks@geol.msu.ru (A.S. Alekseev), joachimski@geol.uni-erlangen.de (M.M. Joachimski).

last decade, it has become evident that local water masses may be decoupled from open marine oceans and that geochemical signals may reflect local environments rather than global changes (Holmden et al., 1998; Mii et al., 2001; Swart, 2008; Swart and Eberli, 2005). Covariance of $\delta^{13}\text{C}$ values measured on carbonate rocks and organic matter as well as synchronous changes of $\delta^{13}\text{C}$ values in spatially distant successions can be used to argue for changes in the global carbon reservoir (Holser, 1997; Magaritz et al., 1992) although Swart (2008) reported global synchronous changes in $\delta^{13}\text{C}$ unrelated to the global carbon cycle.

Studies have documented the significance of early diagenesis for alteration of carbonates (Allan and Matthews, 1982; Elrick and Scott, 2009; Grossman et al., 2008; Immenhauser et al., 2002; Joachimski, 1994). Shallow water carbonates may be affected by meteoric diagenesis. The influence of meteoric water can extend several meters below emersion surfaces. This process is most effective during rapid glacio-eustatic sea-level falls and lowstands. Carbonates rich in organic matter or intercalated between shales and marlstones rich in organic carbon can interact with CO_2 produced by the remineralisation of isotopically light organic carbon in the oxic or sulfate reduction zone (Irwin et al., 1977).

$\delta^{13}\text{C}$ values of carbonates deposited in deeper waters should be more resistant to early diagenesis because cementation took place in marine pore water. Nevertheless, some variations in $\delta^{13}\text{C}$ may be induced by sea-level changes (Swart, 2008). Carbonates are produced mostly on shallow-water platforms during sea-level high-stands and may be exported into deeper periplatform environments. The $\delta^{13}\text{C}$ values of recent platform carbonates such as from the Great Bahama Bank (Swart et al., 2009) are elevated by 4 to 5‰ due to high salinity, the preferential formation of aragonite, and high organic productivity. The carbonate factory may be shut down during sea-level lowstands, with meteoric diagenesis altering the initial $\delta^{13}\text{C}$ values of the platform carbonates. Sea-level changes may also influence ocean circulation and thus the $\delta^{13}\text{C}$ of deep water through preservation and/or oxidation of organic carbon (Katz et al., 2007).

In this study, we present data from the U.S. Midcontinent, Moscow Basin (Russia), Ural foredeep (Russia) and Yangtze platform and its platform margin (South China; Fig. 1) (i) to evaluate the extent to which shallow-water carbonates were altered during Pennsylvanian and Early Permian sea-level lowstands, and (ii) to test whether primary carbon isotope ratios are preserved in deep water environments.

2. Methods

Slabs were cut from carbonate rock samples taken in the US Midcontinent, Moscow Basin (Russia), and Ural foredeep sections (Russia). Carbonate powders were collected from the slabs using a dental drill. In the Chinese sections, carbonate powders were collected in the field from fresh surfaces using a hand drill. Stable isotope analyses were performed on whole rock samples and brachiopod shells using a Kiel III carbonate preparation device connected to a ThermoFisher 252 mass spectrometer. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are reported in per mil relative to V-PDB (Vienna Pee Dee belemnite). Accuracy and precision of the carbon isotope measurements were monitored by replicate analysis of standards NBS19 and laboratory standards. Reproducibility for carbon and oxygen isotopes was better than ± 0.05 and $\pm 0.10\%$ (1σ), respectively. Oxygen isotope values of dolomite were corrected using the acid fractionation factor published by Rosenbaum and Sheppard (1986).

Some brachiopod shells were examined under cathodoluminescence. However, most $\delta^{13}\text{C}$ analyses were performed on unchecked brachiopod shells.

3. Geological setting

3.1. Moscow basin

The Moscow Basin (or Moscow Syncline) is located in the central part of the vast Precambrian Russian Platform. Devonian to Lower Permian shallow-water carbonates constitute the main part of the Moscow Basin sedimentary succession (Alekseev et al., 1996). The biostratigraphic scheme of the Carboniferous of the Moscow Basin and the sea-level history were recently discussed by Alekseev et al. (2004). Palaeomagnetic and palaeoclimatic data indicate a tropical to subtropical position (about 20–25°N) of the Moscow Basin during Pennsylvanian time (Scotese, 1997; Witzke, 1990). A semi-arid climate prevailed with caliche horizons forming during glacio-eustatic lowstands (Kabanov, 2005; Kabanov and Baranova, 2007). Due to the lack of a prominent siliciclastic input, sedimentary cycles are not as obvious as in the US Midcontinent. Nevertheless, numerous subaerial unconformities and calcsols developed during sea-level falls, alternating with intertidal and subtidal highstand deposits. The latter part of the cycles are more argillaceous and sometimes contain tempestite deposits. The regressive parts of the cycles are greater in thickness with most cycles being asymmetrical (Kabanov and Baranova, 2007).

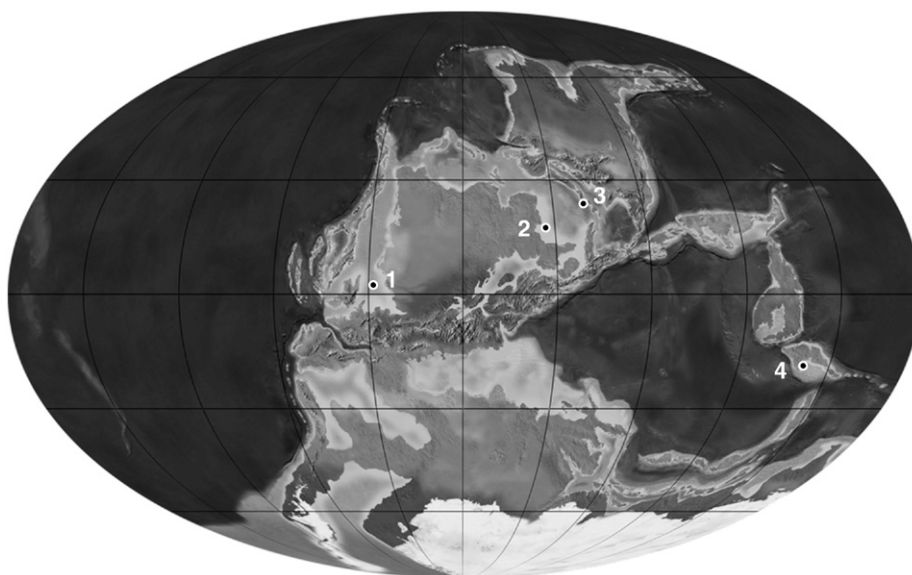


Fig. 1. Pennsylvanian palaeogeography at sea-level highstand (<http://jan.ucc.nau.edu/~rcb7/300moll.jpg>) and position of study areas: 1 – Kansas, 2 – Moscow, 3 – Urals, 4 – Yangtze.

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