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$\delta^{18}O$ and $\delta^{13}C$ of Permian brachiopods: A record of seawater evolution and continental glaciation

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Abstract

Two hundred sixty-four $\delta^{18}O$ and $\delta^{13}C$ values of Permian articulate brachiopod shells were analyzed and 81 of these values were characterized as well preserved and biostratigraphically well defined. These were then utilized for construction of baseline oxygen and carbon isotope curves for the Permian interval. In addition, 21 $\delta^{13}C$ whole rock values are reported for the Wordian and Capitanian.

The early Permian, Asselian to Artinskian, times are characterized by ~2.5‰ decrease in oxygen isotope values, from ~−0.7‰ to −3.3‰ (V-PDB). This is attributed to a ~ 4–7 °C increase in temperature in the Southern Urals, concomitant with the retreat of the Permo-Carboniferous ice sheets and return of the ^{18}O-depleted melt water into the oceans. The Late Permian samples from Iran (Jolfa at Kuh-e-Ali-Bashi) and China (Meishan) yield $\delta^{18}O$ values, and presumably temperatures, similar to those that followed the termination of the large-scale glaciation in the Lower Permian. In between, the upper Kungurian to Capitanian samples from the Delaware Basin (Guadalupe Mountains) are enriched in ^{18}O, at −1.5‰ to −3‰. We have no definitive explanation for these data, but tentatively suggest that the "anomaly" can potentially be a result of evaporative enrichment of seawater in ^{18}O, due to intracratonic arid setting of the basin. The ^{18}O-enriched nature of the Zechstein samples (−1.2‰ to +2.5‰), on the other hand, is in all probability a reflection of the high evaporation rates in the Zechstein sea.

The Permian interval is characterized by a relatively constant $\delta^{13}C$, at about 4‰. The exceptions are again the brachiopods from the Delaware Basin (Guadalupe Mountains), which show ~1.6‰ increase in the Guadalupian, to values of up to 5.9‰ in the Wordian. A tentative explanation, as in the case of oxygen, is based on the proposition that the semi-enclosed Delaware Basin was likely stratified, with sequestration of the ^{13}C-depleted carbon to the deeper water layers and a complementary ^{13}C enrichment in the upper oxygenated layer. The coeval open ocean water DIC may have been similar to that of the remainder of the Permian interval, at ~4‰, as indicated by whole rock carbonate samples from

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Oman, Sicily, and Iran. In the latest Permian, the trend mimics the well-known $\delta^{13}C$ drop at the Permian/Triassic boundary.

Keywords: Oxygen isotopes; Carbon isotopes; Permian; Brachiopods; Palaeoclimate

1. Introduction

The isotopic composition of carbon and oxygen in seawater has varied in the course of geologic history (Baertschi, 1957; Degens and Epstein, 1962; Weber, 1967; Veizer and Hoefs, 1976; Veizer et al., 1999). The changes in $\delta^{13}C$ are believed to have been triggered mostly by burial and re-oxidation of ^{12}C-enriched organic matter (Scholle and Arthur, 1980; Schidlowski and Aharon, 1992; Kump and Arthur, 1999), although the release of ^{13}C-depleted volcanic, "mantle" CO_2 into the ocean–atmosphere system (Renne et al., 1995), sudden methane discharges (Dickens et al., 1997), or an overturn of ^{12}C-enriched anoxic bottom waters (Knoll et al., 1996) may have played a role as well. Seawater $\delta^{18}O$ is controlled mainly by the waning and waxing of ^{16}O-enriched continental glaciers (Shackleton and Opdyke, 1973; Railsback, 1990), but larger variations on multimillion year time scales may have been related to variable degrees of interaction of seawater with the lithosphere (Gregory, 1991), likely driven by tectonic causes (Veizer et al., 1997, 1999; Veizer and Mackenzie, 2004; Wallmann, 2001, 2004).

In order to obtain the primary geochemical signal that would reflect seawater evolution, the studied samples should be free of any diagenetic and metamorphic overprint (Veizer, 1983a,b). Articulate brachiopod shells often serve as a suitable material that retains the carbon and oxygen isotopic compositions imparted by ancient seawater (Compston, 1960; Lowenstam, 1961; Popp et al., 1986; Veizer et al., 1986, 1999). This is because the low-Mg-calcite (LMC) of their shells is relatively resistant to diagenetic alteration. Nevertheless, even these are not always free of diagenetic overprint and the degree of alteration must be evaluated by optical and chemical techniques, such as standard optical, cathodoluminescence (CL) and scanning electron microscopy (SEM), and trace element analyses (e.g., Wadleigh and Veizer, 1992; Grossman et al., 1991; Bruckschen and Veizer, 1997; Mii et al., 1999). Furthermore, even if well preserved, not all marine organisms precipitate their shells in isotopic equilibrium with coeval seawater. This is the case, for example, for corals that usually produce ^{13}C- and ^{18}O-depleted skeletons (Wefer and Berger, 1991), due either to kinetic fractionation factors (McConnaughey, 1989a,b) or to a pH gradient between ambient water and intracellular fluid (Adkins et al., 2003). In brachiopod shells, the primary layers are usually depleted in ^{18}O and ^{13}C. In contrast, the secondary layers that were utilized for delineation of secular $\delta^{18}O$ and $\delta^{13}C$ trends for the Phanerozoic appear to have been formed in isotopic equilibrium with ambient seawater (Brand, 1989; Grossman et al., 1991; Brand et al., 2003). While Auclair et al. (2003) did observe in one intertidal specimen from NW Washington State deviations of several permils for both oxygen and carbon isotopes, the norm for the secondary brachiopod layers are discrepancies that are mostly within ± 1‰ range (Carpenter and Lohmann, 1995).

The Permian was a period of conspicuous geological and environmental changes. The supercontinent Pangea was at its culmination. It was surrounded on both sides by the Panthalassa Ocean and in the east incised by the Tethys. The latter, commencing with the Artinskian–Kungurian (in the westernmost part with the Roadian), was divided by continental fragments that split away from Gondwana into Palaeo- and Neotethys (Fig. 1). The Permo-Carboniferous glaciation tapered off during the Permian (Frakes et al., 1992; Crowell, 1995), and the biggest mass extinction in Earth's history occurred at the Permian–Triassic Boundary (PTB) (e.g., Schindewolf, 1953; Sepkoski, 1989; Kozur, 1998a). The Permian was characterized by widespread coal deposits in the Cathaysia Province (China) and in the southern Gondwana indicative of humid conditions, but also by coeval vast evaporitic sediments formed in arid conditions (Kozur, 1984). Floral provinces with humid and arid climates are often juxtaposed, with no separation by large seas or