Palaeogeography, Palaeoclimatology, Palaeoecology 326–328 (2012) 66–77

Contents lists available at SciVerse ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

Geochemical compositions of Neogene phosphatic brachiopods: Implications for ancient environmental and marine conditions

László Kocsis [a,*], Alfréd Dulai [b], Maria Aleksandra Bitner [c], Torsten Vennemann [a], Matthew Cooper [d]

[a] Institut de Minéralogie et Géochimie, Université de Lausanne, L'Anthropôle, CH-1015 Lausanne, Switzerland
[b] Department of Paleontology and Geology, Hungarian Natural History Museum, P.O. Box 137 H-1431, Budapest, Hungary
[c] Institute of Paleobiology, Polish Academy of Sciences, ul. Twarda 51/55, PL-00-818 Warszawa, Poland
[d] School of Ocean and Earth Science, University of Southampton, National Oceanography Centre Southampton, European Way, SO14 3ZH, UK

ARTICLE INFO

Article history:
Received 12 July 2011
Received in revised form 24 January 2012
Accepted 3 February 2012
Available online 12 February 2012

Keywords:
North Sea
Paratethys
Brachiopods
Phosphate
Isotopes
Palaeo-environment

ABSTRACT

Isotopic and trace element compositions of Miocene and Pliocene phosphatic brachiopods (Lingulidae and Discinidae) from southern North Sea, the Central Paratethys and the Atlantic coast of Europe were investigated in order to trace past environmental conditions and marine connections between the northern boreal and the southern subtropical–tropical marine basins. The North Sea genus *Glottidia* yielded low ε_{Nd} and high $\delta^{18}O_{PO4}$ values through the Mio-Pliocene indicating cold habitat temperature where the local seawater was dominated by the Atlantic Ocean. In contrast, the Middle Miocene Lingulidae and Discinidae of the Paratethys inhabited warm subtropical seawater with the possible influence of the Indian Ocean via the Mediterranean, as supported by their average ε_{Nd} value of −8.3. The combined geochemical data support a thermal and marine separation of the Paratethys from the North Sea with no direct connection or major exchange of water from the Miocene onwards.

The temperature in the Paratethys was very similar to that inferred from brachiopods from the Middle Miocene of western France, but the seawater ε_{Nd} value here is identical to that of contemporaneous Atlantic Ocean. A Late Miocene lingulid brachiopod from southern Portugal has a high $\delta^{18}O_{PO4}$, similar to the specimens investigated from the North Sea, reflecting either a deep water habitat or formation after the onset of major global cooling that resulted in an increased $\delta^{18}O$ value of seawater. The ε_{Nd} value of −8.4 for this site is compatible with an influence of Mediterranean outflow.

1. Introduction

Geochemical compositions of fossil biogenic apatite have been widely used to describe ancient marine environmental conditions. Oxygen isotope compositions of fish teeth are a reliable proxy for the temperature of the ambient water (e.g., Longinelli & Nuti, 1973; Kolodny et al., 1983; Pucéat et al., 2010), while their strontium and neodymium isotope ratios may help place constraints on the palaeo-oceanography (e.g., Staudigel et al., 1985; Elderfield & Pagett, 1986; Ingram, 1995; Vennemann & Hegner, 1998; Thomas et al., 2003; Martin & Scher, 2004; Pucéat et al., 2005; Kocsis et al., 2009).

A number of studies have also dealt with the geochemical compositions of both fossil and modern phosphatic brachiopods (Longinelli, 1966; Longinelli & Nuti, 1968; Lécuyer et al., 1996b, 1998; Wenzel et al., 2000; Rodland et al., 2003; Bassett et al., 2007). The Sr- and Nd-isotopic compositions of their shells may be used in a similar way as those of fossil fish remains to help interpret the palaeo-oceanography. However, the use of their oxygen isotopic composition as a palaeo-temperature proxy is not straightforward. While Lécuyer et al. (1996b) reported equilibrium fractionations between modern lingulid brachiopods and seawater, Rodland et al. (2003) showed variations as high as 4‰ in individual shells and attributed these to vital effects. In addition, Wenzel et al. (2000) pointed out that fossil shells have a higher susceptibility to diagenetic alteration compared to denser, enamel type biogenic apatite of fish teeth.

This study is focused on the geochemical composition of Miocene and Pliocene phosphatic brachiopods from the southern North Sea, the Central Paratethys, and the Atlantic coast of Europe. Fossils from these different palaeo-geographical regions allow us to investigate whether strontium and neodymium isotopic compositions of the brachiopods can give any characteristic geochemical information for these marine basins. These basins were linked by seaways at certain times during the Neogene (cf. Rögl, 1998), hence with the aid of these geochemical analyses connections could be further traced. Oxygen isotopic compositions of the brachiopods are also analyzed as a means of evaluating ancient living conditions and the impact of possible vital effects and/or diagenetic alteration are to be discussed in details.

* Corresponding author.
E-mail address: laszlo.kocsis@unil.ch (L. Kocsis).

0031-0182/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.palaeo.2012.02.004

1.1. Palaeo-geographical background

From the Early Oligocene the Tethyan seaway linking the Atlantic and the Indian Oceans began to close gradually due to the convergence of the European and African continental plates. In the south the Mediterranean Sea was formed, while in the north a large epicontinental sea, the Paratethys developed. It extended from the Rhône Basin via the North-Alpine Foreland Basin (NAFB) to the Central Paratethys (Vienna, Styrian, and Pannonian Basins, Carpathian foredeep) from where it extended further east into the Eastern Paratethys (Fig. 1). This epicontinental sea had a connection with the North Sea via the Rhine Graben during the Oligocene, and several intermittent links existed with the Mediterranean and the Indian Ocean during the Miocene (Fig. 1; Rögl, 1998; Kowalewski et al., 2002; Meulenkamp & Sissingh, 2003; Popov et al., 2004).

The North Sea maintained a northerly connection with the Atlantic Ocean during the entire Mio-Pliocene, although sea-level fluctuation and sometimes enhanced river input often influenced the local settings (Rasser et al., 2008). The different sub-basins of the Paratethys had variable conditions alternating between marine to brackish and freshwater environments. These circumstances and the existence of gateways toward the open sea depended on sea-level variation often relating to local tectonism. The youngest marine deposits in the NAFB occurred in the Lower Miocene, while in the Central Paratethys normal marine conditions ceased only after the late Middle Miocene. In the Eastern Paratethys these conditions prevailed till the latest Miocene (Rögl, 1998; Popov et al., 2004). At the end of the Miocene some of the sub-basins eventually filled up by sediments, others turned to large brackish or freshwater basins.

The complex palaeo-geographical and marine relationships among these basins have been investigated by neodymium isotopic ratios in foraminifera (Jacobs et al., 1996; Mühlstrasser, 2002; Kocsis et al., 2008), ostracods (Janz & Vennemann, 2005), phosphorites (Stille et al., 1996), and shark teeth (Vennemann & Hegner, 1998; Kocsis et al., 2009). While these studies focused on the Mediterranean and the Paratethys and their relative connections to the global oceans, our research extends this to the North Sea and the Atlantic coast of Europe with the aim of using the phosphatic brachiopods (Figs. 2–3) to trace possible links between these sub-basins.

1.2. Linguliform brachiopods

Linguliform brachiopods have a long geological history extending to the Early Paleozoic and two families, Lingulidae and Discinidae, still have modern representatives. They differ in ecology though: the Lingulidae live in vertical burrows in compact and stable sediments under the influence of moderate currents, while the Discinidae attach themselves to hard surfaces (Emig, 1997). Their shells are generally rare in the Miocene-Pliocene fossil records, often taken to indicate a low preservation potential (Emig, 1990), but locally they may be abundant and well-preserved.

Fossil Lingulidae shows apparent faunal provincialism: *Glottidia* is widespread in the North Sea region (Chuang, 1964), while *Lingula* occurs in the Central Paratethys (Emig & Bitner, 2005). The Discinidae, however, can be found in the North Sea, the Atlantic coast of France and in the Central Paratethys as well, and clear provincialism has not been observed at the genus level, although a taxonomical review is still required. Because all of these brachiopods belong to the order of Lingulida (Holmer & Popov, 2000) they are here referred to as lingulids.

The shells of lingulids are composed of prismatic layers of carbonate-fluorapatite (francolite) alternating with layers of chitinous organic matter (Iijima & Moriwaki, 1990; Williams et al., 1992, 2000; Cusack et al., 1997, 1999). In modern *Lingula*, *Glottidia* and *Discinisca* the basic mineral components are apatite granules up to 10 nm in size, with a chitino-proteinaceous coating (Williams et al., 1992, 2000; Cusack et al., 1999). The shell succession is characterized by a rhythmic set of laminae with two types of lamination—the baculate lamination in *Glottidia* and *Discinisca* and the virgose lamination in *Lingula* (Fig. 3, Williams et al., 1992, 2000).

The proportion of organic compounds can reach about 25–50% (Jope, 1965). Post-mortem the chitino-phosphate shells disintegrate due to rapid degradation of the organic matrix and within 2–3 weeks the valves may completely disappear from the sediment (Emig, 1990). Once buried in the sediment, hydrolysis of the organic matrix is the first diagenetic change noted, often coinciding with precipitation of secondary apatite or other minerals in the interstitial space, further stabilizing the original shell structure (e.g., Lucas & Prévôt, 1991; Kolodny et al., 1996). This process is often accompanied by trace element uptake from the ambient pore fluid (e.g., Lécuyer et al., 1998; Trueman & Tuross, 2002).

The post-mortem growth of apatite may change the bulk trace element and isotopic compositions of the original biogenic apatite (e.g., Kolodny et al., 1996; Lécuyer et al., 1998; Tütken et al., 2008). Consequently care must be taken with the interpretation of the Sr-isotopic ratios as palaeo-seawater proxies (e.g., Martin & Scher, 2004; Kocsis et al., 2007) or the $\delta^{18}O$ values as palaeo-thermometer (Kolodny et al., 1983; Lécuyer et al., 1996a).

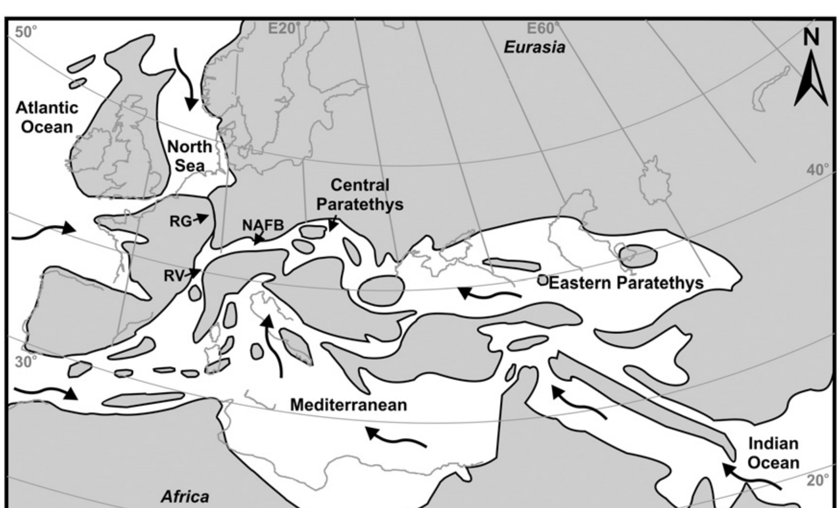

Fig. 1. Palaeo-geographic map of the Early-Middle Miocene marine basins between Eurasia and Africa and the possible gateways between the Atlantic and the Indian Oceans (adapted after Popov et al., 2004). The gray areas are correspondent to land, whereas white to sea. Abbreviations: NAFB—North Alpine Foreland Basin; RG—Rhine Graben; RV—Rhône Valley.