BASE-LiNE ESR-01
LITERATURE REVIEW

This project in divided in three main areas of investigation, all three very closely connected and dependent to one another, the order in which they are presented is not a priority/importance order, but rather a schematic overview.

The first part regards an introduction on brachiopods and their shells.

The second described part concerns the investigation area, the focus is on the remaniements of the Tethys Ocean, namely the Mediterranean Sea and the Paratethys, that started originating during the Eocene epoch.

The last part focuses on the proxies and new techniques to obtain stable isotopes and trace elements data from Brachiopods. In this part a new proxy will be tested and investigation on the general behaviour of Rare Earth Elements (REE) and oxygen and carbon stable isotopes on Brachiopods will be verified.

BRACHOIPODS

Brachiopods are divided into two main morphological categories, articulated and inarticulated (James et al. 1992). The toothed hinge and simple opening and closing muscle-system shells belong to the first group, while the untoothed hinge and complex muscle-system shells belong to the second one (Ruppert and Fox, 2004).

Normally, brachiopods are found to be sessile benthic marine invertebrates and mostly epifaunal (James et al. 1992). Brachiopods are world widely widespread in all modern ocean, ranging all depths and salinities (Ruppert and Fox 2004; Logan 2007; Zezina 2008; Brand et al. 2013). Generally, they tend to avoid locations with strong currents and waves and preferably dwell in low-light spaces of well-oxygenated normal salinity environments (Rudwick 1965; Fürsich and Hurst 1974; Emig 1987; Kowalewski et al. 2002).

The shell of articulated brachiopods is typically made up by two precipitated calcitic layers, occasionally, in some species, a third layer is also precipitated. The, outermost, primary layer is made of granular calcite, below the primary layer, a fibrous calcite secondary layer is present: the tertiary layer consist of prismatic calcite (Brand and Veizer 1980; Al-Aasm and Veizer 1982; Azmy et al. 1998, 2011; Brand et al. 2003, 2011, 2012, 2013; Parkinson et al. 2005). On the outside the shell is covered by the proteineacious periostracum which allows the ion exchange necessary for the calcite precipitation and cristallisation (James et al. 1992; Moore 1997). Brachiopods's secondary and tertiary layers only are proven to retain primary geochemical signatures in equilibrium with the ambient seawater (e.g., Lowenstam 1961; Carpenter and Lohmann 1995; Parkinson et al. 2005; Brand et al. 2013, 2015).

PARATETHYS

The Paratethys ocean came to existence after the Indian subcontinent and Africa started to move north/north-west during the Eocene; by the end of this period, the Indian ocean formed and in the western part of the Tethys ocean the Mediterranean Sea came in existence.

In the Early Oligocene the newly formed Paratethys is a west east oriented sea that has connection with the North Sea, the Polar Sea (trough the Turgai Strait) and the Mediterranean Sea (Rögl, 1999).

As in the Late Oligocene, the connection with the Polar Sea was lost due to the closure of the Turgai Strait.

Around 16 Ma, the Paratethys and the North Sea were not connecter anymore, and the only connection remaining with the Mediterranean Sea was trough the “Trans-Tethyan-Trench-Corridor” while the Eastern and Central Paratethys remained connected only by few narrow gateways.

The connection with other seas, both in the west and in the east, ceased by at the Badenian-Sarmatian boundary (12,7 Ma) due to the formation of the Himalayan and Alpine orogens, where the Central Paratethys became and enclosed water body known as Lake Pannon (Harzhauser and Piller 2007, ter Borgh et al 2014).

Kocsis et al (2009) on a study on the paleoceanography and climate of the Western and Central Paratethys observed that a sub-tropical to warm temperate climate was in place during the Early to Middle Miocene, with photic zone temperature ranging between 14 and 28 ºC. Regarding the paleoceanography, it has been shown that the inflow and input of other bodies of water was dominant in the Paratethys, meaning water exchange with the Indian Ocean was present during the Early-Middle Miocene, this setting has generally proven to follow the global climate trends.

ISOTOPES & REE

Oxygen and carbon stable isotopes have been widely used for paleoceaographical studies since the late 40s, when Urey (1947) described the fractionation of stable isotopes and theorised its importance for geoscientists.

Important example of the key uses for Oxygen isotopes come from papers from Zachos (2001), Lisieki and Raymo (2005), and the EPICA-EDM results (Oerter et al 2005). Although the vast importance of this tool for paleoclimatic reconstructions, the $\delta^{18}O$ of carbonates is usually derived from planktonic organisms, such as foraminifera, or bulk carbonate content to retrieve oceanic paleotemperature estimates and/or trends in the Earth climatic history. Stable carbon isotopes are, instead, interpreted to record biogeochemical changes in the carbon cycle (Oehlert and Swart 2014).

In this project we attempt to use Brachoipods to obtain $\delta^{18}O$ and $\delta^{13}C$ records of the Cenozoic of the Paratethys and Mediterranean Sea. This is a relatively novel approach in isotope geochemistry since only recently Uwe et al (2013, 2015) clarified that Brichiopods calcitic valves are deposited in equilibrium with the surrounding seawater and Zaky et al (2015) proposed a new sample processing protocol for acquiring this information without bumping into biased data due to the fact that Brachiopods primary calcite layers are not deposited in equilibrium.

Rare Earth Elements (REE) are widely used to obtain information on the earth’s past conditions (see Wright et al. 1984, 1987; Lécuyer et al. 1998, 2003, 2004; Reynard et al. 1999; Webb and Kamber 2000; Kemp and Trueman 2003; Trueman et al. 2006; Anderson et al. 2007; Garbelli et al. 2015). Their importance comes from their sensibility to water redox conditions, for example, well oxygenated waters are depleted in Ce (Elderfield and Sholkovitz 1987; de Baar et al. 1988; Sholkovitz et al. 1989, 1992; German et al. 1991; Haley et al. 2004).

Using brachiopods for REE analyses convenient because their shell’s secondary and tertiary layer are deposited in equilibrium with the surrounding seawater, the primary layer, on the contrary, does not. (e.g., Lowenstam 1961; Carpenter and Lohmann 1995; Parkinson et al. 2005; Brand et al. 2013, 2015). Because the primary layer’s non equilibrium, it’s important that strict sample preparation protocols have to be followed, in order to avoid biased results.

Zaky et al (2015) established new protocols for sample processing, the procedure is valid for recent and fossil shells, although for recent material an additional step is required. The “fossil” procedure consist in a physical removal of any external particles or organic fragments attached to the shell and its primary layer, subsequently it will be washed with HCl 10% until the calcite looks clean, follows water rinsing and air drying. The second procedure suggested by Zaky et al (2015) for biogenic calcite ads one more step at the above one, a 3-day immersion in H_2O_2 prior to the physical removal of particles.

With this two procedures, the obtained data should reflect more closely the original sea water concentrations of REE. Although Zaky et al (2015) state that post diagenetic alteration should be verified prior to the REE analyses.

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