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Preface

# New research on the development of high-resolution palaeoenvironmental proxies from geochemical properties of biogenic carbonates

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ABSTRACT

Geochemical signatures from biogenic carbonates are being increasingly employed as palaeoenvironmental proxies. In turn, many of these proxy archives including mollusc shells, corals, and otoliths have periodic growth structures, which allow the reconstruction of chronologically constrained records of palaeoenvironmental variability at unparalleled high temporal resolution. Studying the growth and chemistry of these periodic growth structures is known as sclerochronology. Biogenic hard parts accumulate in geological or archaeological deposits, and can be directly dated using radiometric and racemisation methods. They therefore offer the opportunity for high-resolution palaeoenvironmental reconstructions across many time intervals, all over the globe. Such data are important for several reasons: (1) understanding past climate and environmental change provides a means of contextualising current and future climate change and ecological disturbance; (2) high-resolution palaeoenvironmental records are essential for constraining, testing and validating global and regional numerical climate models; (3) palaeoenvironmental records from biogenic carbonates can provide an environmental framework from which to understand the behavioural changes and interactions of peoples with their environment. However, inter and intra-species differences in growth rate, physiology, and environmental response can cause variations in the chemical profiles of biogenic carbonates. Before geochemical data is employed for palaeoenvironmental reconstructions, it is thus necessary to examine modern specimens of the target species, or related taxa, to understand how geochemical variations are influenced by local environmental conditions, kinetic and vital effects. This allows the generation of quantitative and more reliable proxy records of environmental change.

This special issue brings together the latest research on palaeoenvironmental proxy development and validation in biogenic carbonates. It includes studies on marine, freshwater and estuarine organisms (molluscs, corals and echinoderms), and on traditional as well as novel geochemical proxies. The papers presented here include in situ field calibration studies, laboratory growth experiments as well as methodological studies into the effects of sampling and pre-treatment. The geographical scope is broad, encompassing both the northern and southern hemispheres including South Africa, South America, Australia, Asia, the Mediterranean Sea and the North Atlantic.



## 1. Palaeoenvironmental records from biogenic carbonate archives

Climate and environmental change is an increasingly pressing issue in today's world, yet instrumental records of past climate are short, rarely stretching back beyond 1860 CE (Jones et al., 2001, 2009). The analysis of palaeoenvironmental proxies, preserved in various natural archives, enables the reconstruction of climate and environmental conditions prior to the instrumental record. The development of a broad range of proxy records of climatic and environmental change is crucially important for understanding patterns of past climate and environmental change at various spatial and temporal scales (IPCC, 2013). Robust, quantitative and high-resolution palaeoclimate and palaeoenvironmental data from varied regions of the globe are needed to provide a framework of past changes, to form baselines for environmental monitoring, and provide data for numerical simulations that will allow climate modellers to better predict anthropogenic impacts on the natural climate system (McCarroll, 2010; Schmidt et al., 2014; IPCC, 2013).

It is becoming increasingly evident that understanding past climate and environmental change at high-resolution timescales (annual to sub-annual) is critical both for unravelling the complexities of the Earth system as a whole and for evaluating the relationship between past climate and environmental changes and human behaviour (Luterbacher et al., 2004; Denton et al., 2005). Seasonality in particular is of fundamental importance in this respect, yet few archives can capture the full range of seasonal variation (Denton et al., 2005; Ferguson

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et al., 2011; Prendergast et al., 2016a). Many Quaternary environmental archives such as marine sediment cores are limited in their geographic extent and temporal resolution. In fact, the majority of high-resolution climate archives such as speleothems, tree rings, and ice cores are terrestrial (e.g. Abram et al., 2013; Orland et al., 2014; Wong and Breecker, 2015; McCarroll and Loader, 2004). With the exception of coralline red algae, annually and better-resolved and internally temporally well-constrained palaeoenvironmental archives from aquatic ecosystems outside of the tropics are rare (Wanamaker et al., 2011).

Biogenic carbonates are widely distributed in marine, estuarine, freshwater, and terrestrial environments. They are abundant from the tropics to the poles and occur at different water depths. The use of biogenic carbonates as palaeoenvironmental archives is based on the fact that carbonate secreting organisms generally accurately record environmental conditions in their hard parts. Therefore, the chemical properties of these hard parts record changes in the organism's environment during growth (Epstein et al., 1951; Wefer and Berger, 1991; Lécuyer et al., 2004). The palaeoenvironmental proxies utilised from these archives include stable isotopes as well as trace and minor elements. Furthermore, growth rate and microstructure can provide data on environmental conditions during growth (Füllenbach et al., 2014; Milano et al., 2016).

Many organisms deposit their carbonate hard parts sequentially, resulting in incremental growth structures that can provide time-series of palaeoenvironmental change. The study of the structure and chemistry of the incrementally deposited hard parts of organisms is known as sclerochronology. This field has expanded exponentially in the past few decades (see Schöne and Surge, 2005; Gröcke and Gillikin, 2008; Oschmann, 2009; Wanamaker et al., 2011; Schöne and Gillikin, 2013; Butler and Schöne, 2017 for recent overviews). Commonly utilised incrementally deposited biogenic carbonates include corals (e.g. Gagan et al., 2000; Cobb et al., 2003, 2013; Tierney et al., 2015), bivalves (e.g. Goodwin et al., 2003; Grossman and Ku, 1986; Schöne et al., 2004, 2005a, 2005c; Versteegh et al., 2012; Reynolds et al. 2016), gastropods (e.g. Mannino et al., 2003, 2008; Burman and Passe, 2008; Wang et al., 2012; Prendergast et al., 2013; Gutiérrez-Zugasti et al., 2015), coralline algae (e.g. Halfar et al., 2008, 2011; Kamenos et al., 2008; Hetzinger et al., 2009, 2011) and fish otoliths (e.g. Müller et al., 2015; Surge and Walker, 2005; Disspain et al., 2011). Such archives have the potential to provide robust, high-resolution palaeoenvironmental records from almost every geographic region. The time span and resolution that can be obtained for climate records from sequentially deposited biogenic carbonates depends upon on the sampling method used, and the growth rates and longevity of the organism (Schöne, 2008). Physical and chemical analyses of the annual, and in some cases, fortnightly, daily, and even tidal growth increments allow the reconstruction of chronologically constrained records of palaeoenvironmental variability at unparalleled high temporal resolutions. Long-lived organisms such as the bivalve *Arctica islandica* are useful for creating absolutely dated stacked chronologies via cross-dating, where the individual histories of several shells can be aligned chronologically based on overlaps in their periods of shell growth to reconstruct longer time-series of environmental change (e.g., Witbaard et al., 1997; Marchitto et al., 2000; Schöne et al., 2003; Butler et al., 2009b; Helama and Hood, 2011; Reynolds et al., 2016). Analysis of chemical proxies within these cross-dated archives has allowed the reconstruction of centuries-long and even millennia-long continual high-resolution palaeoenvironmental records (e.g. Schöne et al., 2003; Wanamaker et al., 2008; Black et al., 2009; Butler et al., 2009a; Reynolds et al. 2016). Banded carbonates of shorter-lived, faster growing organisms such as intertidal bivalves and gastropods, and otoliths are useful for obtaining ultra-high resolution snapshots of palaeoenvironmental change, allowing sub-seasonally resolved records of the amplitude of the seasonal cycle (Schöne et al., 2007; Mannino et al. 2008; Prendergast et al., 2013).

Biogenic carbonates accumulate in geological or archaeological deposits, and can be directly dated using methods such as radiocarbon (e.g. Magnani et al., 2007; Butler et al., 2009a; Reimer, 2015; Bosch et al., 2015b), U-Th series (e.g. Magnani et al. 2007; Rowe et al., 2015), or amino acid racemisation (e.g. Murray-Wallace et al., 2005; Demarchi et al., 2015). Mollusc shells and fish otoliths in particular are routinely preserved in the archaeological record. Many archaeological sites contain freshwater, marine, terrestrial and estuarine mollusc shells, and freshwater, marine, and estuarine otoliths likely to be refuse from foraging and fishing activities (Andrus, 2011; Colonese et al., 2011; Prendergast and Stevens, 2014; Disspain et al., 2016; Twaddle et al., 2016). They can potentially provide records of palaeoenvironmental change stretching over tens of thousands of years (see Andrus, 2011; Prendergast and Stevens, 2014; Leng and Lewis, 2016; Thomas, 2015; Twaddle et al., 2016 for recent reviews). This is especially important in coastal regions where sea level changes may have obscured coastal records of human habitation and environmental change (Gutiérrez-Zugasti et al., 2016). Importantly, food-species molluscs and otoliths preserved in archaeological sites can provide local palaeoenvironmental records that can be directly linked both spatially and temporally to records of human habitation and behaviour. This is crucial for generating robust data on human-environment interaction (Prendergast and Stevens, 2014; Prendergast et al., 2016b). Furthermore, studying the geochemical composition of the most recently formed increment allows the season in which the organism died to be determined. When this is applied to archaeological food remains such as molluscs and otoliths, it allows the reconstruction of ancient foraging patterns. These data can be combined with other archaeological data to obtain a more complete picture of site use patterns (e.g. Mannino et al., 2007; Burchell et al., 2013; Jew and Fitzpatrick, 2015; Prendergast et al., 2016a; Hausmann and Meredith-Williams, 2016).

As with any living creature, the life cycles of carbonate-secreting organisms are complex. It is becoming increasingly evident that inter and intra-species differences in growth rates, physiology, and environmental responses can cause variations in the chemical profiles of biogenic carbonates (Schöne, 2008). In some species, the crystallisation process may be mediated by physiology (Wada and Fujinuki, 1976) and any attempt to understand an organism's growth cycles, physiology and habitat preferences must be made before growth patterns and geochemistry can be interpreted with confidence (Schöne, 2008). Before geochemical analysis is employed for palaeoenvironmental reconstruction, it is therefore necessary to examine modern populations of the proxy-bearing species, or related taxa, to understand how geochemical variations are influenced by local environmental conditions. This allows any offsets between the environmental signal and the carbonate geochemistry to be identified, and allows the generation of more quantitative and reliable records of environmental change. This special issue focuses on recent advances in the development and calibration of geochemical proxies from incrementally-deposited biogenic carbonates.

## 2. The papers in this special issue

This special issue brings together eleven papers reflecting a diverse array of the latest research on palaeoenvironmental proxy development and validation in biogenic carbonate palaeoenvironmental archives. The scientific works herein are at the cutting edge of this fast-growing field. Many offer the first calibrations of new high-resolution palaeoenvironmental proxies. Methodologically, this special issue encompasses both stable isotope approaches as well as trace element geochemistry. Taxonomically, the organisms investigated include molluscs (bivalves and gastropods), corals and echinoderms. Some of the papers concern more traditional proxies such as bivalve stable isotopes and coral trace elements, whilst others offer more novel applications including echinoid spine and mollusc operculum geochemistry. The papers cover both tropical and temperate regions in both hemispheres. The archives include marine, freshwater and estuarine organisms and the research approaches include in situ field calibration studies, laboratory growth experiments as well as methodological studies into the effects

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