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The geochemistry of deep-sea coral skeletons: A review of vital effects and applications for palaeoceanography

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A R T I C L E I N F O

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A B S T R A C T

Deep-sea corals were discovered over a century ago, but it is only over recent years that focused efforts have been made to explore the history of the oceans using the geochemistry of their skeletal remains. They offer a promising archive of past oceanic environments given their global distribution, layered growth patterns, longevity and preservation as well as our ability to date them using radiometric techniques. This paper provides an overview of the current state-of-the-art in terms of geochemical approaches to using deep-sea coral skeletons to explore the history of the ocean. Deep-sea coral skeletons have a wide array of morphologies (e.g. solitary cup corals, branching colonial corals) and materials (calcite, aragonite and proteins). As such their biomineralization strategies are diverse, leading to complex geochemistry within coral skeletons. Notwithstanding these complications, progress has been made on developing methods for reconstructing the oceanographic environment in the past using trace elements and isotopic methods. Promising approaches within certain coral groups include clumped isotopes and Mg/Li for temperature reconstructions, boron isotopes and radiocarbon for carbon cycling, εNd, and radiocarbon for circulation studies and $\delta^{15}N$, P/Ca and Ba/Ca for nutrient tracer studies. Likewise there is now a range of techniques for dating deep-sea corals skeletons (e.g. U-series, radiocarbon), and determining their growth rates (e.g. radiocarbon and ^{210}Pb). Dating studies on historic coral populations in the Atlantic, Southern Ocean and Pacific point to climate and environmental changes being dominant controls on coral populations over millennial and orbital timescales. This paper provides a review of a range of successes and promising approaches. It also highlights areas in which further research would likely provide new insights into biomineralization, palaeoceanography and distribution of past coral populations.

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1. Introduction

With ongoing changes to Earth's climate there is a need to understand how the ocean, land, and climate interact, particularly on decadal to centennial time scales. Whilst direct observations of ocean changes are being carried out, for example by the Ocean Observatories Initiative, the instrumental record of climate is sporadic and does not capture the full range of oceanographic conditions. As an example, Bryden et al. (2005) interpreted a series of observations across the Atlantic taken over five decades as indicative of a substantial slow down in Meridional Overturning related to global warming (Bryden et al., 2005). Further investigations suggested that the results may have been skewed by capturing a period of decreased circulation within the natural variability (Cunningham et al., 2007). In addition, mounting paleoceanographic evidence indicates that the ocean can exist in at least two very different circulation states, for example during the last glacial maximum (LGM, ~20,000 years ago) and during

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abrupt climate events of the last glacial and deglaciation (Boyle and Keigwin, 1987; Curry and Oppo, 2005). Traditional paleoceanographic archives of the deep ocean (sediments) have provided a wealth of information relating to the past ocean, but they are only rarely preserved with sufficient time resolution to address decadal-scale questions. However, the geochemistry of deep-sea coral skeletons may provide a way to address this gap.

Cairns (2007) defined corals as 'Animals in the cnidarian classes Anthozoa and Hydrozoa that produce either calcium carbonate (aragonitic or calcitic) secretions resulting in a continuous skeleton or as numerous, usually microscopic, individual sclerites, or that have a black, horn-like, proteinaceous axis'. As such, corals exhibit a vast range of morphologies and life habitats making a comprehensive review of their geochemistry a challenging task. In fact there is little known about many deep-water corals. In this review paper we focus the discussion predominantly on scleractinian corals where most work has been carried out thus far, but we also include comparable studies of the longevity and geochemistry of other corals, where available.

A particular advantage of (some) deep-sea corals as climate archives is that the skeletons can be accurately dated using radiometric techniques. Such dating allows coral-based records to be compared directly to records from other parts of the climate system without relying on stratigraphic correlations. The lack of stratigraphic order can also be a disadvantage because measurements must to be performed on each and every coral individual to screen the age and/or growth rates of samples. As a consequence, work on deep-sea corals has yielded a number of new developments of radiometric dating tools e.g. Douville et al. (2010), Longworth et al. (2013) and McIntyre et al. (2011). To reconstruct the corals' marine environment considerable efforts have been focused on developing proxies that reflect past environments (Case et al., 2010; Thiagarajan et al., 2011). Ideally, such information may yield quantitative in situ records of local environmental conditions over the lifetime of that coral. Some proxy approaches such as radiocarbon reconstructions appear to be relatively 'successful' e.g. Adkins et al. (2002), whereas others, such as $\delta^{18}O$, have proven more complex e.g. Smith et al. (2002). Corals, like other marine organisms, manipulate the chemistry of seawater as they build their skeletons (Tambutte et al., 2011). The chemical composition of the skeleton is therefore controlled by two main factors: the external environment and biological activity, commonly referred to as 'vital' effects. In deep-sea corals, these 'vital effects' may dominate the environmental controls. For example for oxygen isotopes ($\delta^{18}O$) or trace metal ratios (e.g. Mg/Ca) that are typically used as temperature proxies in other marine organisms the internal variability has been shown to be greater than the predicted variation from external forcing (Adkins et al., 2003; Case et al., 2010; Cohen and Gaetani, 2006; Gagnon et al., 2007; Meibom et al., 2008; Rollion-Bard et al., 2010, 2003; Smith et al., 2002; Smith et al., 2000; Weber, 1973). Other geochemical parameters do not seem to be significantly overprinted by 'vital' effects, including neodymium (Nd, van de Flierdt et al., 2010) and uranium (U) isotopes (Robinson and Adkins, 2004), radiocarbon, and Δ_{47} (the clumped isotopes of C and O in carbonates, Thiagarajan et al., 2011). Despite the challenges, we will show later in this review how the interplay between proxy development and vital effects has led to progress in understanding coral biomineralisation so that skeletal chemistry can be used to make reconstructions of the past ocean.

The geochemistry of deep-sea corals therefore has the potential to address outstanding questions relating to the role of ocean circulation in a changing Earth climate system and to examine the effects of climate change on cold-water coral habitats and biodiversity. Investigations of the recent past (centuries to millennia) may provide a clearer picture of the extent of anthropogenic influences in the ocean. Records of the past 25,000 years and beyond may provide information on ocean circulation during times of major oceanic reorganization. However even those proxies which appear to be relatively straightforward to interpret have not yet been fully exploited. Limiting factors are the existence of only a few collections of appropriate coral archive material, as well as the fact that some geochemical methods (e.g. clumped isotopes) are limited to a small number of labs (Thiagarajan et al., 2011).

In the following sections we review the progress that has been made using deep-sea coral skeletons to reconstruct paleoclimate. We start by reviewing the methods that have been used for dating corals and for determining their growth rates. We then move on to describe a range of geochemical approaches that have been investigated in deep-sea corals, their biomineralisation and their potential for making paleoceanographic reconstructions.

2. Dating and growth rates

Some coral genera, including the black coral *Leiopathes* live for thousands of years (Roark et al., 2009), providing the potential to produce a high-resolution deep-ocean record from a single live-collected organism (Fig. 1). Individual carbonate corals do not appear to have such great longevity, However their skeletons can be preserved, in a non-lithified state, on the seafloor, or within sedimentary sequences for hundreds of thousands or even millions of years (Fig. 1) (Frank et al., 2011; Kano et al., 2007; Robinson et al., 2007). Analyzing the geochemistry of multiple carbonate coral individuals offers the potential to produce long records at high temporal resolution. Accurate and precise dates and growth rates are therefore required to take full advantage of deep-sea coral paleoceanographic archives.

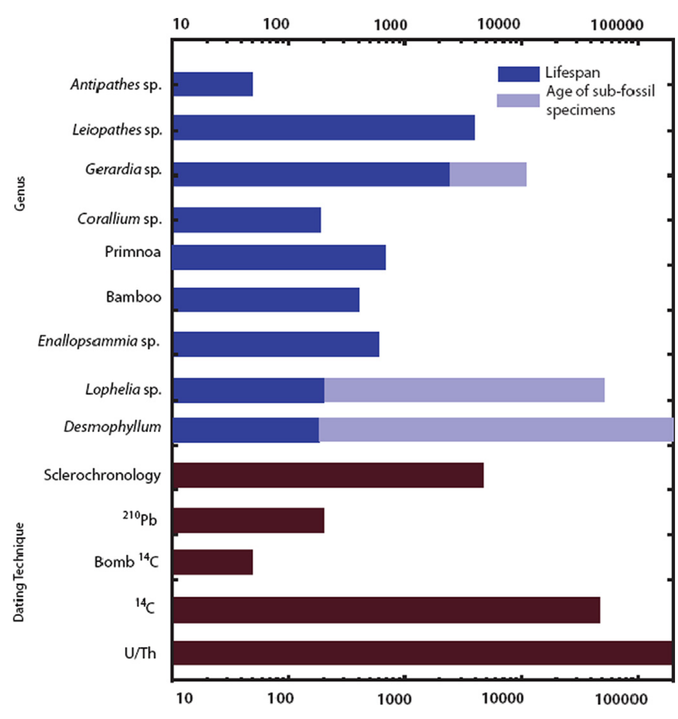

Fig. 1. Lifespan (years) of several deep-sea corals, and the relative age span of different dating techniques used in chronology studies. Dark purple denotes the lifespan of an individual coral, whilst the light purple denotes the maximum age range of sub-fossil/fossil skeletal material. The brown bars indicate the ages over which different dating methods can be used. After Prouty et al. (2013). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

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