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Constraining calcium isotope fractionation ($\delta^{44/40}Ca$) in modern and fossil scleractinian coral skeleton

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ABSTRACT

The present study investigates the influence of environmental (temperature, salinity) and biological (growth rate, inter-generic variations) parameters on calcium isotope fractionation ($\delta^{44/40}Ca$) in scleractinian coral skeleton to better constrain this record. Previous studies focused on the $\delta^{44/40}Ca$ record in different marine organisms to reconstruct seawater composition or temperature, but only few studies investigated corals.
This study presents measurements performed on modern corals from natural environments (from the Maldives for modern and from Tahiti for fossil corals) as well as from laboratory cultures (Centre Scientifique de Monaco). Measurements on *Porites* sp., *Acropora* sp., *Montipora verrucosa* and *Stylophora pistillata* allow constraining inter-generic variability.
Our results show that the fractionation of $\delta^{44/40}Ca$ ranges from 0.6 to 0.1‰, independent of the genus or the environmental conditions. No significant relationship between the rate of calcification and $\delta^{44/40}Ca$ was found. The weak temperature dependence reported in earlier studies is most probably not the only parameter that is responsible for the fractionation. Indeed, sub-seasonal temperature variations reconstructed by $\delta^{18}O$ and Sr/Ca ratio using a multi-proxy approach, are not mirrored in the coral's $\delta^{44/40}Ca$ variations. The intergeneric variability and intrageneric variability among the studied samples are weak except for *S. pistillata*, which shows calcium isotopic values increasing with salinity. The variability between samples cultured at a salinity of 40 is higher than those cultured at a salinity of 36 for this species.
The present study reveals a strong biological control of the skeletal calcium isotope composition by the polyp and a weak influence of environmental factors, specifically temperature and salinity (except for *S. pistillata*). Vital effects have to be investigated in situ to better constrain their influence on the calcium isotopic signal. If vital effects could be extracted from the isotopic signal, the calcium isotopic composition of coral skeletons could provide reliable information on the calcium composition and budget in ocean.

1. Introduction

Calcium is an essential element in many geological and biological processes (see review in DePaolo, 2004). Calcium isotopic fractionation ($\delta^{44/40}Ca$) was studied in various marine organisms including foraminifera (Gussone et al., 2003; Griffith et al., 2008; Gussone et al., 2009; Hippler et al., 2009; Gussone et al., 2010), coccoliths (Gussone et al., 2007; Langer et al., 2007), rudists (Immenhauser et al., 2005), brachiopods (von Allmen et al., 2010), dinoflagellate (Gussone et al., 2010) and bivalves (Heinemann et al., 2008). These studies revealed a significant relationship between calcium isotopic fractionation and temperature (Nägler et al., 2000; Gussone et al., 2003), mineralogy (Gussone et al., 2005) and inter-generic differences (Gussone et al., 2006, 2007). These studies on biogenic calcite or aragonite were extended to experimental precipitates (e.g. Lemarchand et al., 2004; Tang et al., 2008). Differences in calcium isotopic composition between inorganic and biogenic precipitates were reported (Gussone et al., 2006). Calcium isotopic fractionation was used to reconstruct seawater composition and calcium balance in ocean through time (De La Rocha and DePaolo, 2000) but some uncertainties remain. Some studies argue for disequilibrium between outputs and inputs (Zhu and MacDougall, 1998), whereas other studies suggest a balanced budget (e.g. Schmitt et al., 2003; Fantle and DePaolo, 2005). Some modeling

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studies have proposed that variations of $\delta^{44/40}Ca$ are influenced by secular variations in seawater composition, specifically by shifts from aragonitic to calcitic seas, or carbonate precipitation (Farkas et al., 2007a,b). Thus, many uncertainties about calcium isotopic fractionation in biogenic carbonates remain.

Zooxanthellate scleractinian corals are widely used to reconstruct paleoenvironmental changes (e.g. Weber and Woodhead, 1970; Swart, 1983; Gagan et al., 2000; Felis and Pätzold, 2003; Corrège, 2006): the oxygen isotopic composition of the skeleton is a proxy for sea surface temperature (SST) and seawater isotopic composition ($\delta^{18}O_{sw}$) (e.g. Cole et al., 1993; Linsley et al., 1994; Quinn et al., 1998; Felis et al., 2009); the carbon isotopic composition is used to understand coral physiology ($\delta^{13}C$: e.g. Felis et al., 1998; Heikoop et al., 2000; Juillet-Leclerc and Reynaud, 2010); in addition, boron isotopic composition appears to be an indicator for pH (e.g. Hönisch et al., 2004; Reynaud et al., 2004; Pelejero et al., 2005; Taubner et al., 2010). However the calcium isotopic composition of corals, particularly with respect to interspecific variations and influences of environmental parameters is poorly constrained (Halicz et al., 1999; Chang et al., 2004; Böhm et al., 2006).

Furthermore, coral skeletons are prone to diagenetic alteration (McGregor and Gagan, 2003; Allison et al., 2007; Hathorne et al., 2011). Thus, along with potential vital effects that could affect the isotopic signals recorded in the skeleton, a careful screening for alteration using techniques such as microscopy, powder X-ray diffraction (XRD) and laser ablation ICP-MS is required prior to any analysis or data interpretation (Hathorne et al., 2011; Felis et al., 2012). The evaluation of vital effects requires a detailed knowledge of polyp biology and biomechanics including calcification (Cohen and McConnaughey, 2003; Allemand et al., 2004; Tambutté et al., 2011), calcium pathway through the organism (Wright and Marshall, 1991; Allemand et al., 2011), growth rate and other parameters that may influence the isotopic fractionation in the skeleton. Processes involved in coral skeleton calcification are still under debate and there is no consensus regarding the ion pathway from seawater to calcification area (Tambutté et al., 1996; Gaetani et al., 2011; Tambutté et al., 2011). The understanding and quantification of biomineralization require discriminating the influence of environmental factors.

The present study focuses on the biological and environmental parameters that are fundamental in interpreting calcium isotopic signals in coral skeletons, specifically (1) linear extension rate and inter- and intra-generic variations; and (2) sea surface temperature (SST) and sea surface salinity (SSS). The interpretation is based on a systematic investigation of these parameters using coral sample sets from various locations, different ages and genera.

2. Material and methods

2.1. Fossil corals from Tahiti

The fossil coral material was recovered by the Integrated Ocean Drilling Program (IODP) Expedition 310 off Tahiti, French Polynesia, in the central tropical South Pacific Ocean (Fig. 1) (Camoin et al., 2007). The modern sea surface temperature mean is 27.5 ± 0.2 °C and varies between 26.2 °C (August) and 28.8 °C (March). The modern sea surface salinity mean is around 36 [1982–1995. Salinity and temperature data derived from Integrated Global Ocean Services System (IGOSS) Products bulletin; http://iridl.ldeo.columbia.edu/SOURCES/.IGOSS/; Asami et al., 2009]. The massive *Porites* sp. coral investigated in the present study (310-M0018A-19R-1W 29–45) was recovered from 115 m below present sea level (33 m below sea floor) at the outer shelf of Maraa located on the south side of the island of Tahiti (Hole M0018A; 17°46.0124′S, 149°32.8433′W, Fig. 1). X-radiography of the slabbed coral revealed skeletal density banding with no evidence for diagenetic cements (Fig. 2). Furthermore, XRD analyses confirmed that the coral skeleton in all samples is pristine (see Deschamps et al., 2012; Felis et al., 2012). Using a 0.8 mm diameter drill bit, samples were obtained from the coral slab by continuous spot-sampling along the major growth axis, following a single fan of corallites.

2.2. Modern corals from the Maldives

Modern corals from natural environment were collected on 2010 in Maghoodoo Island, the Maldives (Faafu, Nilandhoo atoll, 3°04′49°76″N; 72°57′55°98″E; Fig. 1), northern Indian Ocean. Modern sea surface temperature varies between 28 °C and 31 °C (2005–2011 data: area average time series 72°E–73°E, 3°N–3°N) (MTMO_SST_9km.CR, Modis Terra, http://disc.sci.gsfc.nasa.gov/giovanni/overview/index.html). Monthly SST was lowest in December–January and highest in April–

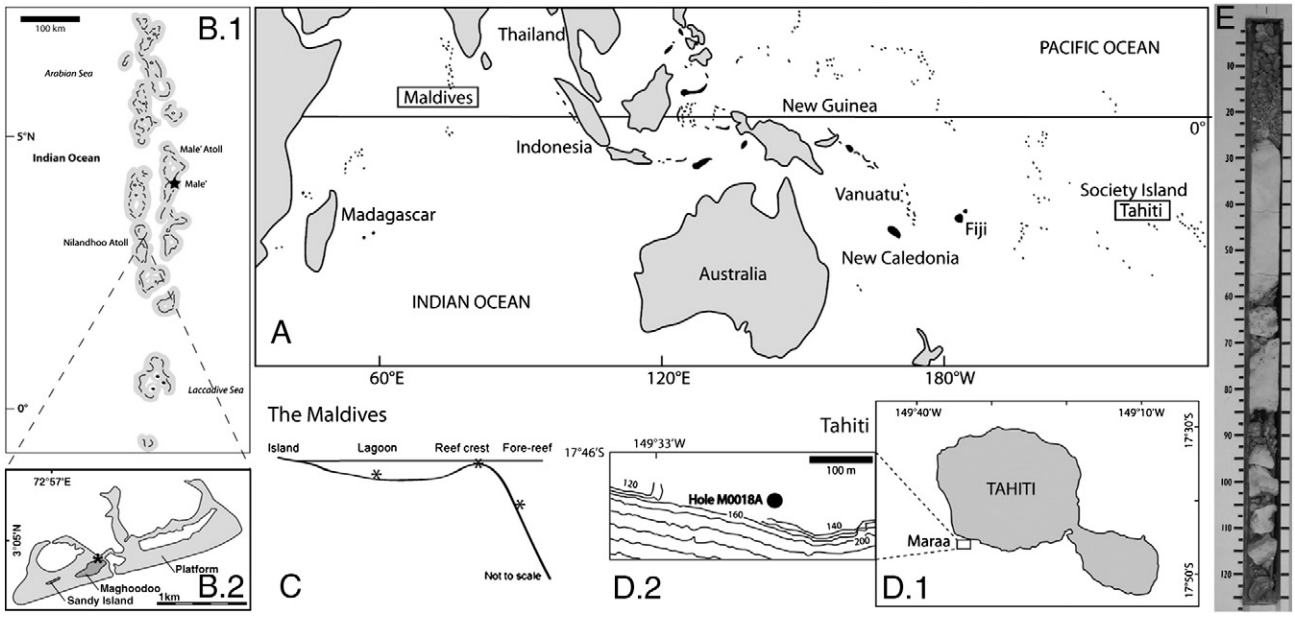

Fig 1. Geographic location of the samples studied (A.): The Maldives (B.1), Maghoodoo Island (B.2), along with the sampled transect (C.) and Tahiti (D.1) along with the location of IODP Hole M0018A (D.2, E) wherein coral samples originated from.