Chemical Geology 381 (2014) 223–233

Contents lists available at ScienceDirect

Chemical Geology

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

# Oxygen and carbon isotope fractionation in calcitic deep-sea corals: Implications for paleotemperature reconstruction

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ARTICLE INFO

*Article history:*
Received 17 June 2013
Received in revised form 8 May 2014
Accepted 11 May 2014
Available online 20 May 2014

Editor: Michael E. Böttcher

*Keywords:*
Calcite–water fractionation
Oxygen isotope fractionation
"Lines" method
Deep-sea coral
Paleotemperature proxy
Biomineralization

ABSTRACT

Inhabiting areas of the ocean where paleoenvironmental records are sparse, deep-sea corals represent valuable yet largely untapped Holocene records of intermediate and deep ocean variability. $\delta^{18}O$ and $\delta^{13}C$ were analyzed in nine live-collected deep-sea gorgonian corals (Isididae and Coralliidae) in order to further develop the "lines" paleotemperature method. Least squares linear regression analysis for full lifespan $\delta^{18}O$ vs. $\delta^{13}C$ (corrected for $\delta^{18}O_{water}$ and $\delta^{13}C_{DIC}$) was utilized to yield equations of the form $y = mx + b$. $\delta^{18}O$ and intercept values were found to be a function of temperature, and to approximate calcite $\delta^{18}O$ equilibrium. The corals in this study extend the previously reported calibration (Hill et al., 2011) over a broader range of temperatures from 5 °C to 11.2 °C. When combined with the data from Hill et al. (2011), a new expression for the relationship between the $\delta^{18}O_{intercept}$ value and temperature is proposed:

$$T(^{\circ}C) = -4.12 \pm 0.38\left(\delta^{18}O_{intercept}\right) + 12.33 \pm 0.75\ \left(R^2 = 0.90, \text{p value} < 0.0001\right).$$

Error estimates are ±0.7 °C for corals living at cold temperatures (2 °C), ±1.4 °C in warmer waters (11 °C), and ±0.5 °C at the mean water temperature of the data set (4.6 °C). The first multi-specimen verification of the "lines" method was performed on three co-located bamboo (Isididae) corals and found to give nearly coincident $\delta^{18}O$ intercepts. Detailed intraspecimen sampling reveals $\delta^{18}O$ and $\delta^{13}C$ isotopic variability within coeval portions of the skeleton. In one specimen, "lines" method analysis was utilized on multiple samples taken from the same temporal increment of the skeleton, yielding multiple $\delta^{18}O$ intercepts. Calculated temperatures using the calibration proposed here describe a temperature range of 7.9 to 10.3 °C, which approaches the temperature range of 11.1 ± 0.7 °C at the coral collection location.

## 1. Introduction

Oxygen isotope records from carbonate minerals are a cornerstone of paleotemperature reconstruction, initiated when the theoretical and inorganic experimental work of McCrea (1950) demonstrated the temperature dependency of oxygen isotope partitioning between inorganic carbonates and water. Epstein et al. (1953) arrived at the same empirical conclusion using biological carbonates. These experimental results validated theoretical calculations (Bigeleisen and Mayer, 1947; Urey, 1947) and paved the way for the production of temperature records from a variety of carbonate-secreting organisms (Weber and Woodhead, 1972; Druffel et al., 1990). Foraminifera and shallow hermatypic scleractinian corals have been the workhorse organisms for oceanographic paleotemperature reconstructions and detailed data syntheses now document long-term ocean conditions (Zachos et al., 2001) as well as modern tropical oceanic variability (Cole et al., 1993; Urban et al., 2000; Cobb et al., 2003).

Deep-sea corals represent another valuable archive of paleoenvironmental conditions due to their cosmopolitan distribution within the global ocean, presence over a large range of depths and longevity. Carbonate deep-sea coral have lifespans on the order of centuries, and fossil deep-sea coral are recorded for at least the last 225,000 years (Robinson et al., 2007; Thiagarajan et al., 2013). Deep-sea corals have successfully been used to reconstruct ocean ventilation (Adkins et al., 1998; Frank et al., 2004; Eltgroth et al., 2006) and surface productivity signals (Sherwood et al., 2005). Emiliani et al. (1978) and McConnaughey (1989a) recognized that deep-sea corals have significant skeletal "vital effects" that invalidate the classic $\delta^{18}O$ paleotemperature method laid out by McCrea (1950) and Epstein et al. (1953). Instead of a constant offset from environmental $\delta^{18}O$ equilibrium, deep-sea corals

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http://dx.doi.org/10.1016/j.chemgeo.2014.05.008
0009-2541/

exhibit strong linear correlations between $\delta^{18}O$ and $\delta^{13}C$, often with variability exceeding several per mil within any one individual that lives in a relatively temperature-invariant environment. To date, three methods have been proposed to circumvent these "vital effects" and extract paleotemperature information from deep-sea corals. The "lines" method (Smith et al., 2000; Hill et al., 2011), a clumped-isotope method (Thiagarajan et al., 2011), and the Rayleigh-based multi-element method (Gaetani et al., 2011) are all undergoing experimental calibration and evaluation. This study focuses on the $\delta^{13}C$ and $\delta^{18}O$ characteristics of Isididae and Coralliidae gorgonian deep-sea coral and their implication for the "lines" paleotemperature method.

While scleractinian deep-sea corals produce an aragonitic skeleton, gorgonian deep-sea corals (Anthozoa: Gorgonacea) secrete calcium carbonate in the form of calcite (Allemand et al., 1994; Noe and Dullo, 2006; Vielzeuf et al., 2008). *Corallium* sp. (Anthozoa: Gorgonacea: Coralliidae) corals produce an uninterrupted calcitic skeleton, whereas the structure of bamboo coral (Anthozoa: Gorgonacea: Isididae) includes a calcitic internode as well as a proteinaceous gorgonin node (Fig. 1). The nodes of bamboo coral record the carbon isotopic signature of surface produced organic matter, while the carbon source for calcitic internodes is the *in situ* total dissolved inorganic carbon (DIC) at the coral growth site (Roark et al., 2005). This allows environmental reconstructions of both surface and deep water conditions within one individual coral. Skeletal calcite in Isididae and Coralliidae exhibit concentric alternating light and dark growth rings, much like tree rings. Growth in branching deep-sea corals is dendritic to arborescent and both vertical and radial. Bamboo corals typically have radial growth rates of 10–150 μm year$^{-1}$ and longevities on the order of a few hundred years (Roark et al., 2005; Noe and Dullo, 2006; Noe et al., 2008; Andrews et al., 2009; Sherwood and Edinger, 2009; Hill et al., 2011). The radial growth rate and longevity of *Corallium secundum* specimens were determined in Roark et al. (2006) to be ~170 μm year$^{-1}$ and 67 to 71 years, respectively. Gorgonian corals are found at water depths of less than 100 to greater than 4000 m water depth (Roark et al., 2005) and are pan-Pacific (Etnoyer and Morgan, 2003; Noe et al., 2008).

Smith et al. (2000) proposed a method for extracting paleotemperatures from aragonitic scleractinian deep-sea corals that utilizes regression analysis of $\delta^{18}O$ vs. $\delta^{13}C$ values over the lifetime of the coral. They calibrate a method that uses the $\delta^{18}O$ value of the coral at $\delta^{13}C_{coral} = \delta^{13}C_{DIC}$ and find a linear correlation between this value and temperature. Their empirical calibration (when corrected for $\delta^{18}O_{water}$ and $\delta^{13}C_{DIC}$) is:

$$T(^{\circ}C) = -4.0\left(\delta^{18}O_{intercept}\right) + 19.88 \tag{1}$$

which they note is similar to the biogenic aragonite temperature equation developed by Grossman and Ku (1986):

$$T(^{\circ}C) = -4.34\left(\delta^{18}O_{aragonite} - \delta^{18}O_{water}\right) + 20.6. \tag{2}$$

The Smith et al. (2000) method proposes that by utilizing $\delta^{18}O$ vs. $\delta^{13}C$ regression analysis over the lifetime of the coral, the aragonite $\delta^{18}O$ equilibrium value for a individual coral can be defined. Their conclusion that regression analysis of coral $\delta^{18}O$ vs. $\delta^{13}C$ (when $\delta^{18}O_{water}$ and $\delta^{13}C_{DIC}$ are known) over the lifetime of a coral yields accurate average temperature to within 0.35 °C at cold temperatures (1 °C) and to within 1.0 °C at warm temperatures (28 °C), is a significant yet largely unexplored finding.

Hill et al. (2011) explored this method in calcitic live-collected Isidids and found that $\delta^{18}O$ intercepts standardized for $\delta^{18}O_{water}$ and $\delta^{13}C_{DIC}$ yielded inaccurate temperatures using the Smith et al. (2000) calibration. Following the same method as Smith et al. (2000), Hill et al. (2011) developed a new "lines" calibration for calcitic bamboo corals using eight samples collected from the Gulf of Alaska, California, and Florida that span a temperature range of 2 to 5 °C. The relationship between $\delta^{18}O$ intercept and temperature (corrected for $\delta^{18}O_{water}$ and $\delta^{13}C_{DIC}$) for their eight specimens is described by:

$$T(^{\circ}C) = -2.09\left(\delta^{18}O\ \text{intercept}\right) + 8.25. \tag{3}$$

In this paper, we present full lifespan $\delta^{18}O$ vs. $\delta^{13}C$ regression data for nine live-collected deep-sea gorgonian corals and apply "lines" method analyses. Fidelity of the "lines" paleotemperature method was explored in three live-collected bamboo specimens that lived at the same time and experienced very similar environmental conditions. The exploration of time-series potential from sequential growth intervals within a single coral is done through detailed intra-specimen $\delta^{18}O$ and $\delta^{13}C$ sampling.

## 2. Materials and methods

### 2.1. Materials

Nine specimens of gorgonian deep-sea coral (Table 1) were analyzed for calcite oxygen and carbon isotopic composition. All specimens were collected alive by deep-sea submersible diving on Warwick Seamount, Gulf of Alaska (DSRV Alvin, 2002), and the Hawaiian Islands (DSRV Pisces V, 2007). The nine corals belong to the families Isididae and

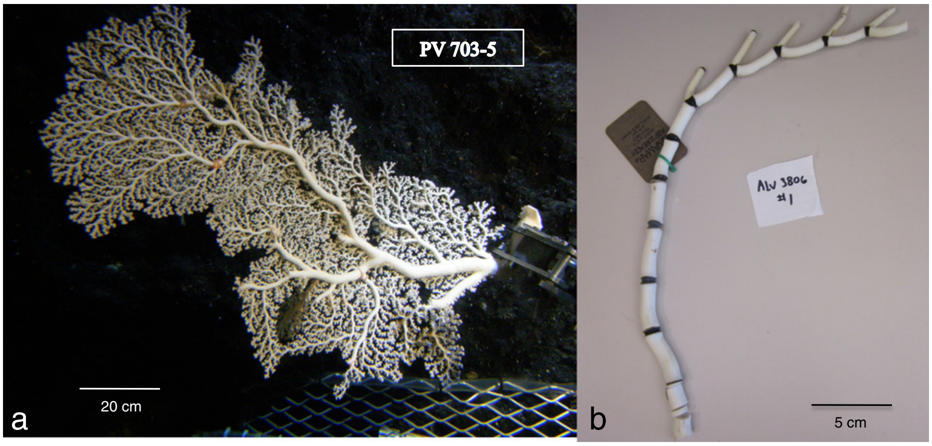

**Fig. 1.** a) PV 703-5 as it is being collected, scale is an approximate. b) ALV 3806-1. Disk cut at bottom was used for this study. High-Mg calcitic internodes are clearly separated from each other by gorgonin nodes.