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The Suess effect in Fiji coral $\delta^{13}C$ and its potential as a tracer of anthropogenic CO_2 uptake

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ABSTRACT

In the context of increasing anthropogenic CO_2 emissions, determining the rate of oceanic CO_2 uptake is of high interest. Centennial-scale changes in $\delta^{13}C$ of the surface water dissolved inorganic carbon (DIC) reservoir have been shown to be influenced by the carbon isotopic composition of atmospheric CO_2. However, the availability of direct oceanic $\delta^{13}C$ measurements is limited and methods for reconstructing past $\delta^{13}C$ variability of the oceanic DIC are needed. Geochemical reconstructions of DIC variability can help in understanding how the ocean has reacted to historical changes in the carbon cycle. This study explores the potential of using temporal variations in $\delta^{13}C$ measured in five Fijian *Porites* corals for reconstructing oceanic $\delta^{13}C$ variability. A centennial-scale decreasing $\delta^{13}C$ trend is observed in these Fiji corals. Other studies have linked similar decreasing $\delta^{13}C$ trends to anthropogenic changes in the atmospheric carbon reservoir (the "^{13}C Suess effect"). We conclude that solar irradiance is the factor influencing the $\delta^{13}C$ cycle on a seasonal scale, however it is not responsible for the centennial-scale decreasing $\delta^{13}C$ trend. In addition, variations in skeletal extension rate are not found to account for centennial-scale $\delta^{13}C$ variability in these corals. Rather, we found that water depth at which a Fijian *Porites* colony calcifies influences both $\delta^{13}C$ and extension rate mean values. The water depth-$\delta^{13}C$ relationship induces a dampening effect on the centennial-scale decreasing $\delta^{13}C$ trend. We removed this "water depth effect" from the $\delta^{13}C$ composite, resulting in a truer representation of $\delta^{13}C$ variability of the Fiji surface water DIC ($\delta^{13}C_{Fiji-DIC}$). The centennial-scale trend in this Fiji coral composite $\delta^{13}C_{Fiji-DIC}$ time-series shares similarities with atmospheric $\delta^{13}C_{CO_2}$, implicating the ^{13}C Suess effect as the source of the this coral $\delta^{13}C$ trend. Additionally, our study finds that the $\delta^{13}C$ variability between the atmosphere and the ocean in this region is not synchronous; the coral $\delta^{13}C$ response is delayed by ~10 years. This agrees with the previously established model of isotopic disequilibrium between atmospheric $\delta^{13}C_{CO_2}$ and oceanic surface water DIC.

1. Introduction

Many massive scleractinian corals are known to be high-quality archives for paleoclimate reconstruction due to their capacity to incorporate geochemical tracers into their aragonite skeletons (see Druffel, 1997; Corrège, 2006; Pandolfi, 2011 for reviews). Various proxies, such as skeletal Sr/Ca and $\delta^{18}O$ have been shown to be accurate tracers of water temperature and $\delta^{18}O_{sw}$ at many sites (Corrège, 2006 for a review). However, because of the influence of both kinetic and metabolic effects, the interpretation of the carbon isotopic composition ($\delta^{13}C$) of coral skeleton is more complex (McConnaughey, 1989a, 1989b; Grottoli and Wellington, 1999; Grottoli, 2000). The kinetic effect is a physical process occurring during the incorporation of dissolved inorganic carbon (DIC) inside the coral's aragonite skeleton (McConnaughey, 1989b). Kinetic fractionation results from discrimination against heavy

isotopes of both C and O during the hydration and hydroxylation of CO_2 (McConnaughey, 1989b). This effect produces a simultaneous depletion of ^{13}C and ^{18}O in coral skeleton relative to the composition of ambient seawater (McConnaughey, 1986, 1989b). Metabolic fractionation induces additional changes in the skeletal $\delta^{13}C$ due to the processes of photosynthesis and respiration (coral/algae symbiotic system) (McConnaughey, 1989a; Grottoli and Wellington, 1999; Grottoli, 2000). These metabolic effects are controlled by external environmental factors, which indirectly affect coral $\delta^{13}C$.

In addition to the influence of metabolic and kinetic effects, decadal- and centennial-scale changes in $\delta^{13}C$ of the surface water DIC are reflected in coral $\delta^{13}C$ records (Swart et al., 1996a,b; Quinn et al., 1998; Linsley et al., 1999, 2000; Asami et al., 2005; Wei et al., 2009; Swart et al., 2010). These changes in the isotopic composition of the surface water DIC are influenced by the carbon isotopic composition of atmospheric CO_2 (Druffel and Benavides, 1986). A solid understanding of the relationship between atmospheric CO_2 and changes in the DIC is needed to refine oceanic CO_2 uptake dynamics, which is vital in the context of ongoing global change. Monitoring of $\delta^{13}C$ in surface water DIC

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has only recently begun (Quay et al., 1992), thus coral-derived $\delta^{13}C$ data, could provide a means to reconstruct centennial-scale surface water DIC variability after a thorough assessment of all factors affecting mean annual $\delta^{13}C$.

Many studies have reported a secular-scale decreasing trend in coral $\delta^{13}C$ over the 20th century that has been attributed to the addition of ^{13}C-depleted CO_2 into the atmosphere by the burning of fossil fuels and deforestation, and the subsequent influx of this ^{13}C-depleted CO^2 into the ocean (Keeling et al., 1980; Swart et al., 1996a,b; Quinn et al., 1998; Linsley et al., 1999; Asami et al., 2005; Wei et al., 2009; Swart et al., 2010). In this study we explore intracolonial $\delta^{13}C$ variability using a network of coral cores from Fiji (~17° S,~180° W). The generation of a coral composite $\delta^{13}C$ reconstruction permits the extraction of a clearer signal of regional $\delta^{13}C$ variability, which is used to evaluate the isotopic variability of Fiji surface water DIC over time. This will provide a better look at possible factors responsible for oceanic $\delta^{13}C$ variability.

2. Materials and methods

2.1. Coral collection and sampling

Five coral cores from different regions of Fiji were utilized for this study (see Table 1). Linsley et al. (2004, 2006, 2008) and Dassié (2012) provide detailed descriptions of these cores and sampling locations. The coral cores were cut into ~7-mm-thick slabs at the University at Albany-SUNY with a modified tile saw. The slabs were X-rayed with an HP cabinet X-ray system at 35 kV for 90 s, then the X-ray negatives were scanned to generate X-ray positives. Density bands and growth axes were visible on the X-ray positives, which allowed us to determine the sampling tracks and to identify signs of diagenesis. Slabs were cleaned in an ultrasonic bath of deionized water for 30 min. Coral cores FVB1, 16F and FVB2 were also cleaned with a high-energy (500 W, 20 kHz) probe sonicator in a deionized water bath, for approximately 10 min on each slab face. The dried slabs were sampled using a low-speed micro-drill with a 1-mm-round diamond drill bit along the maximum growth axis in tracks (U-shaped groves) parallel to corallite traces, as identified in X-ray positives. A ~3-mm-deep by ~3-mm-wide groove was excavated at 1 mm increments.

2.2. Stable isotope analysis

Isotopic analyses followed the procedures summarized in Linsley et al. (2000, 2004, 2006, 2008). Approximately 100 μg of coral powder per sample was dissolved in ~100% H_3PO_4 at 90 °C in a Multi-Prep sample preparation device, and the generated CO_2 gas was analyzed on a Micromass Optima gas-source-triple-collector mass spectrometer at the University at Albany. For the first 14 years of growth, every 1 mm sample (200 samples) was analyzed, and

below this depth every other 1 mm sample was analyzed. Analysis of every other 1 mm sample resulted in a resolution of about 6 to 7 samples per year. Replicate samples were analyzed every 8 samples (every 16 samples after 200 mm). The average difference between duplicate $\delta^{13}C$ analyses of 735 samples (for all cores) was 0.066‰. Samples of international standard NBS-19 were interspersed every ~10 samples. The standard deviation of 1,039 NBS-19 standards analyzed for $\delta^{13}C$ was ± 0.016‰.

2.3. Chronology

The annual character of coral density banding (see Lough and Barnes, 1989; Barnes and Lough, 1993 for reviews) has proven useful at many sites for developing an accurate coral chronology (Knutson et al., 1972). Density bands for the corals in this study are not always distinct, therefore counting the number of growth bands is ineffective for making an accurate chronology. However, the clear annual cycle (~8 to 15 mm·yr^{-1}) in the $\delta^{18}O$ data from Fiji *Porites* allows for the construction of an accurate down-core chronology (see Linsley et al., 2004, 2006). The lightest (most negative) $\delta^{18}O$ value in each seasonal cycle was attributed to the warmest month of the year and the heaviest (most positive) value to the coldest. Linsley et al. (2004, 2006) established chronologies for cores 1F and AB, whereas Dassié (2012) established chronologies for FVB1, 16F, and FVB2. This method has been verified by Sr/Ca measurements on coral core 1F (Linsley et al., 2004).

2.4. Skeletal extension rate

Skeletal extension rates were determined by counting the number of millimeters between two consecutive $\delta^{18}O$ minima (~two consecutive Januarys in each $\delta^{18}O$ record). The error associated with this method is ± 1 mm for the top-most (youngest) 200 samples and ± 2 mm below that depth when every other 1-mm sample were analyzed.

3. Results and discussion

The Fiji $\delta^{13}C$ records (except for FVB2, which will be discussed in further detail in Section 3.3) have a secular long-term trend toward increasingly depleted $\delta^{13}C$ values towards the present (Fig. 1). Identifying the cause of this $\delta^{13}C$ trend is the main focus of this study.

3.1. Seasonal $\delta^{13}C$ variability

All $\delta^{13}C$ coral records presented here have a discernible seasonal cycle (Fig. 1A), in which lower $\delta^{13}C$ values are observed during austral winter months and higher $\delta^{13}C$ values during austral summer months. When comparing monthly $\delta^{13}C$ and $\delta^{18}O$ variability, the two signals are not always in phase (e.g. Fig. 1B). The seasonal solar irradiance

Table 1
Description of the coral cores used in this study, AB, 1F, FVB1, 16F and FVB2.

Core ID	Location	Latitude longitude	Water depth[a] (m)	Ext. rate[b] (mm/yr) and standard deviation	Mean $\delta^{13}C$[b] (‰) and standard deviation
1F	Savusavu Bay	16°49′S 179°14′W	10	12 (2.1)	−1.9 (0.24)
AB	Savusavu Bay	16°49′S 179°14′W	10	11 (2.6)	−1.4 (0.59)
FVB1	Vanua Balavu	17°20.1′S 178°56.7′W	6.0	13 (3.0)	−1.5 (0.3)
16F	Aïwa Island	18°19.21′S 178°43.01′W	3.5	15 (3.8)	−0.93 (0.36)
FVB2	Vanua Balavu	17°20.5′S 178°55.7′W	1.0	16 (4.6)	−0.50 (0.32)

[a] Water depth at top of coral colony.
[b] Values established from annual averaged data from the same common period (1905–1997).