Palaeogeography, Palaeoclimatology, Palaeoecology 370 (2013) 30–40

Contents lists available at SciVerse ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

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

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

Emilie P. Dassié [a,b,*], Gavin M. Lemley [a], Braddock K. Linsley [b]

[a] Department of Atmospheric and Environmental Sciences, University at Albany, State University of New York, 1400 Washington Avenue, Albany, NY 12222, USA
[b] Lamont–Doherty Earth Observatory of Columbia University, 61 Route 9w, P.O. Box 1000 Palisades, NY 10964, USA

ARTICLE INFO

Article history:
Received 14 May 2012
Received in revised form 13 November 2012
Accepted 17 November 2012
Available online 27 November 2012

Keywords:
Coral
Carbon isotope
CO_2
Suess effect
Dissolved inorganic carbon
Fiji
Water depth
Skeletal extension rate

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 ($\delta^{13}C_{Fiji\text{-}DIC}$). The centennial-scale trend in this Fiji coral composite $\delta^{13}C_{Fiji\text{-}DIC}$ 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

* Corresponding author at: Lamont-Doherty Earth Observatory of Columbia University, 61 Route 9w, P.O. Box 1000 Palisades, NY 10964, USA. Tel.: +1 518 210 6702.
E-mail address: edassie@ldeo.columbia.edu (E.P. Dassié).

0031-0182/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.palaeo.2012.11.012

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 $mm \cdot yr^{-1}$) 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).

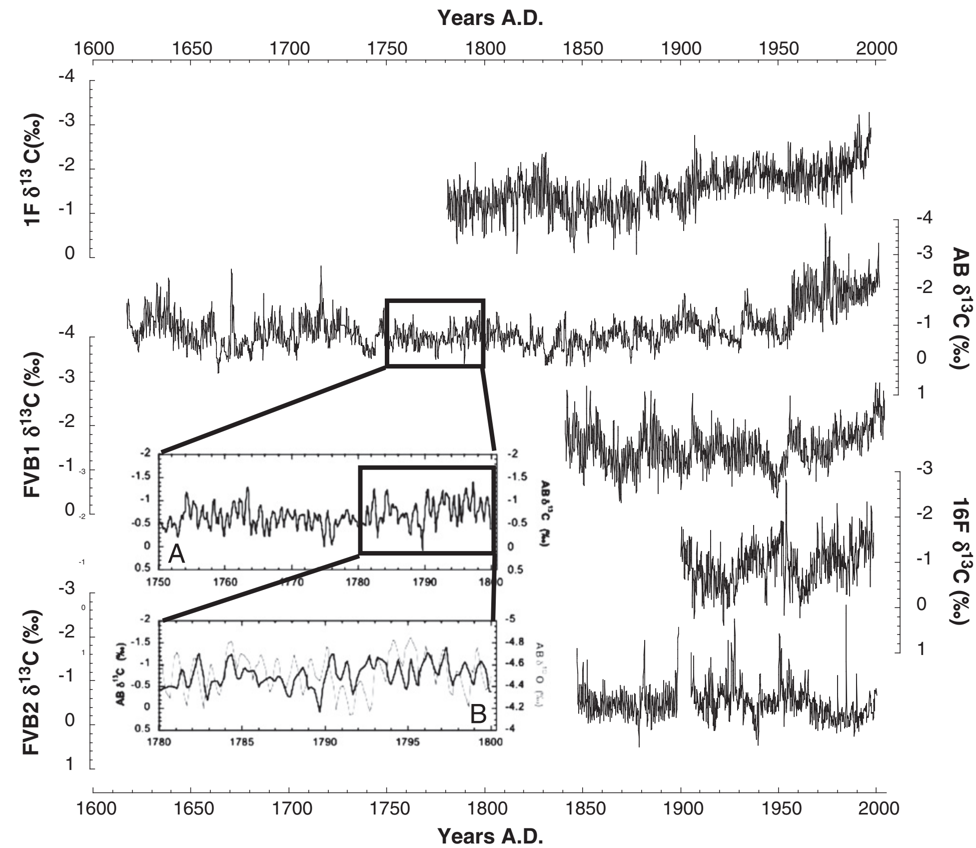

Fig. 1. Monthly resolution of Fiji coral $\delta^{13}C$ data in ‰ from cores 1F, AB, FVB1, 16F and FVB2. Magnified box A. shows core AB from 1750 to 1800 for a clearer view of the seasonal variability. Magnified box B. shows core AB $\delta^{13}C$ (black line) and $\delta^{18}O$ (light grey line) from 1780 to 1800.

(SI) cycle precedes the sea surface temperature (SST) maximum by 1 to 2 months for most of Earth's surface. In our Fiji $\delta^{13}C$ records, no significant relationship or consistent time lag is observed between $\delta^{18}O$ and $\delta^{13}C$ time series (e.g. Fig. 1B). Thus the seasonal SST cycle does not seem to be the factor causing seasonal $\delta^{13}C$ variability. This finding is in agreement with Romanek et al. (1992), who concluded that $\delta^{13}C$ in biogenic carbonate is independent of SST from 10 to 40 °C. Other studies conclude that increases in photosynthetic activity are also linked to increases in coral skeletal $\delta^{13}C$ (Weber and Woodhead, 1970; Swart, 1983; McConnaughey, 1989a; Allison et al., 1996; Grottoli, 1999, 2000; Grottoli and Wellington, 1999; Omata et al., 2008). Therefore, the seasonal SI cycle could be indirectly responsible for the seasonal cycle observed in $\delta^{13}C$ records by influencing photosynthetic activity (Swart et al., 1996b; Reynaud-Vaganay et al., 2001; Shimamura et al., 2008).

3.2. Water depth influences on coral $\delta^{13}C$ and extension rate

Fiji coral cores were collected at different water depths, ranging from 1.5 to 10 m (Table 1), which were measured from the top of

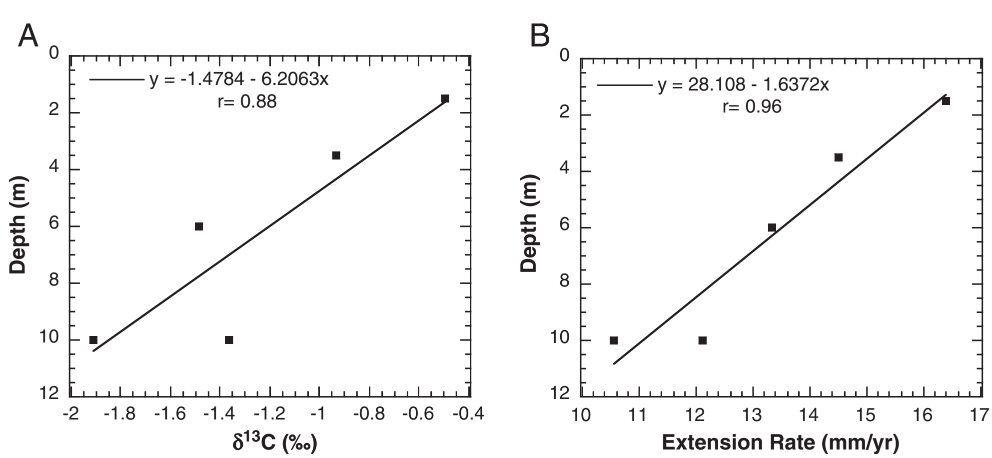

Fig. 2. Regression equations and their correlation coefficients (r) between annual average coral $\delta^{13}C$ (over the common time period, 1905–1997) and coral collection depth (A), and between coral extension rate and coral collection depth (B).

each coral colony growth surface to the ocean surface. For the time period common to all coral records (1905–1997), an offset in the mean value (bulk value) is present between the different coral $\delta^{13}C$ records. For the same common time period, the mean $\delta^{13}C$ values are −1.9‰ for 1F, −1.4‰ for AB, −1.5‰ for FVB1, −0.93‰ for 16F, and −0.5‰ for FVB2 (Table 1).

Individual coral skeletal $\delta^{13}C$ bulk data (averaged over the common time period, 1905–1997) were plotted against their respective water depths (Fig. 2A). A negative linear regression ($r^2=-0.77$) between water depth and $\delta^{13}C$ is observed ($p<0.01$, using a bootstrap resampling method with 1000 resamples). Corals growing deeper in the water column have lower (more negative) mean $\delta^{13}C$ values than corals growing at shallower water depths. The relationship between water depth and $\delta^{13}C$ implies that water depth is the main factor controlling mean $\delta^{13}C$ values in these corals, as previously reported by Weber and Woodhead (1970, 1971). The amount of photosynthetic activity by symbiotic zooxanthellae varies with the amount of light; light attenuation with increasing water depth results in reduced photosynthetic activity, as demonstrated by McCloskey and Muscatine (1984) and Grottoli (1999). It has been established that skeletal $\delta^{13}C$ increases with increasing photosynthetic activity (Weber and Woodhead, 1970; Swart, 1983; McConnaughey, 1989a). This water depth-$\delta^{13}C$ relationship is consistent with other published studies (Weber et al., 1976; Fairbanks and Dodge, 1979; Swart and Coleman, 1980; McConnaughey, 1989a; Leder et al., 1991; Grottoli, 1999; Grottoli and Wellington, 1999; Grottoli, 2000).

An insignificant correlation is present between $\delta^{18}O$ and water depth ($r^2=0.013$ with $p>0.05$, using a bootstrap resampling method with 1000 resamples). This suggests that the observed $\delta^{13}C$-water depth relationship in these corals is primarily related to metabolic, rather than kinetic factors, the latter of which would have simultaneously affected both $\delta^{18}O$ and $\delta^{13}C$ values. Grottoli (1999) and Grottoli and Wellington (1999) published similar findings for corals from similar water depths.

Additionally, a distinct relationship is present between mean skeletal extension rate (SER) and water depth (Fig. 2B). For the common time period, the mean SER is 12 $mm\cdot yr^{-1}$ for 1F, 11 $mm\cdot yr^{-1}$ for AB, 13 $mm\cdot yr^{-1}$ for FVB1, 15 $mm\cdot yr^{-1}$ for 16F, and 16 $mm\cdot yr^{-1}$ for FVB2 (Table 1). Corals residing at deeper water depths exhibit lower SERs (Fig. 2b). This linear relationship ($r^2=0.92$; $p<0.01$, using a boot strap resampling method with 1000 resamples) has been previously described by Felis et al. (1998), Grottoli (1999), Rosenfeld et al. (2003), and Omata et al. (2005) for *Porites* at other sites. This is a light-dependent relationship; light attenuation increases with water depth, resulting in a decrease in SER. A decrease in photosynthetic activity reduces the amount of carbon available for the coral to grow (McCloskey and Muscatine, 1984; Grottoli, 1999). Another possible cause of this relationship could involve coral morphological changes with water depth (Grottoli, 1999), which is beyond the scope of this study.

Coral cores 1F and AB were collected from colonies residing at the same water depth, however their respective mean SER and mean $\delta^{13}C$ values are slightly different. The difference between the mean $\delta^{13}C$ and mean SER of AB and 1F could be used to set the regression error for both $\delta^{13}C$- and SER-water depth relationships. It is worth noting that this offset might be due to microenvironmental (Pandolfi, 2011 for a review) or genetic differences between the two colonies (Forsman et al., 2009), which are also beyond the scope of this study.

3.3. $\delta^{13}C$ and coral extension rate

The different $\delta^{13}C$ time series were centered by subtracting their mean values for the common time period (1997–1905) in order to facilitate a comparison between them. This process removed the influences of both water depth and colony-specific disparities on the mean values of the $\delta^{13}C$ records (Section 3.2). Annual averages of the coral $\delta^{13}C$ data (arithmetic mean of the monthly data) were compared to their respective SER values (Fig. 3). SER and $\delta^{13}C$ are negatively correlated (Fig. 3); when SER increases, $\delta^{13}C$ decreases. This suggests that SER and $\delta^{13}C$ are influenced by a common factor. The correlation coefficients between SER and $\delta^{13}C$ are −0.20 ($p<0.05$) for 1F, −0.61 ($p<0.01$) for AB, −0.41 ($p<0.01$) for FVB1, −0.22 ($p<0.05$) for 16F, and −0.44 ($p<0.01$) for FVB2, with a degree of freedom (df) of 90 ($df=n-2$). The significance of the correlation coefficients was determined using the Pearson Product–moment correlation coefficient table, and will be used for the remainder of this report.

During the mid-20th century, the depletion of skeletal $\delta^{13}C$ in all cores begin to accelerate, while their respective SERs remain generally constant (Fig. 3). The onset of the trend in the $\delta^{13}C$ records might have reduced its correlation with SER. A slight increasing trend is present in the SER records; this trend is a result of the corals' cumulative growth. As the coral colonies grow toward the surface, an increase in light intensity leads to an increase in photosynthetic activity, which leads to increase in extension rate (see Section 3.2) (see Huston, 1985; Heiss et al., 1993; Hoogenboom et al., 2006 for reviews).

Both SER and $\delta^{13}C$ values for coral core FVB2 present a peculiar pattern beginning around 1960 (Fig. 3). A decreasing trend is observed in all the other four Fiji coral records, whereas FVB2 mean $\delta^{13}C$ undergoes a 0.2‰ increase between the pre-1960 and post-1960 periods. Additionally, there is a decreasing trend in SER values from 1960 to present ($r=-0.85$; $df=38$; $p<0.01$). SER varies from 32 $mm\cdot yr^{-1}$ to 12 $mm\cdot yr^{-1}$ with a mean of 17 $mm\cdot yr^{-1}$ for the older portion of the record, whereas the younger portion of the record presents a general decreasing trend going from an average of 18 $mm\cdot yr^{-1}$ around 1960 to an average of 7 $mm\cdot yr^{-1}$ for the most recent part of the record. Coral FVB2 grew in relatively shallow water (1 m water depth at low tide) and the top of the colony was partially dead. Coral reefs live near their upper thermal tolerance limits (Coles et al., 1976) as well as their ultraviolet (UV) radiation limits, and generally do not tolerate conditions outside of the normal (average) range (Glynn, 1996; Hoegh-Guldberg, 1999). Incidences of coral bleaching have been associated with warmer-than-normal sea surface temperature (SST) conditions (e.g. Glynn, 1984; Goreau et al., 1993; Hoegh-Guldberg and Salvat, 1995; Winter et al., 1998). Prolonged exposure to increased SSTs (even for a short period) can reduce coral growth rates (Jokiel and Coles, 1977, 1990; Coles and Jokiel, 1978; Glynn, 1993, 1996; Meesters and Bak, 1993) and leave the skeleton significantly enriched in $\delta^{13}C$ (Allison et al., 1996). Light plays a major role in providing the energy that drives photosynthesis in zooxanthellae (Chalker et al., 1988). UV radiation has been reported to have destructive effects on zooxanthelae activity (Jokiel, 1980; Fisk and Done, 1985; Harriott, 1985; Oliver, 1985; Goenaga et al., 1988; Lesser et al., 1990; Gleason and Wellington, 1993) and may result in decreased growth rates (Lesser, 1996). Brown (1997) concluded that a combination of elevated temperature and high irradiance is a likely cause of coral bleaching in shallow waters. McGregor et al. (2011) pointed out that microatoll types of corals (reef-flat corals) might have a stronger resistance to changes in SST and solar irradiance. The coral colony from which core FVB2 was collected did not have a flat surface, and its extreme shallow-water environment of the core likely caused the colony to undergo bleaching and partial mortality, affecting both its SER and $\delta^{13}C$ values for the top portion.

Previous studies have described an increase in SER following an increase in SST (Nie et al., 1997; Lough and Barnes, 2000; Bessat and Buigues, 2001). However, no specific relationship between SER and SST was observed in this study. One reason could be related to the error associated with the method used for determining SER, which is not as precise as the gamma densitometry method (Chalker and Barnes, 1990) used in the aforementioned studies. Another reason for not finding a relationship between SST and skeletal $\delta^{13}C$ could be due to the small interannual SST cycle at Fiji. Lough and Barnes (2000) found that an SST increase of 1 °C resulted in a 3.1 mm increase in *Porites* SER, and similarly, Nie et al. (1997) found a 1.5 mm increase per 0.5 °C increase. The mean interannual SST amplitude at Fiji is

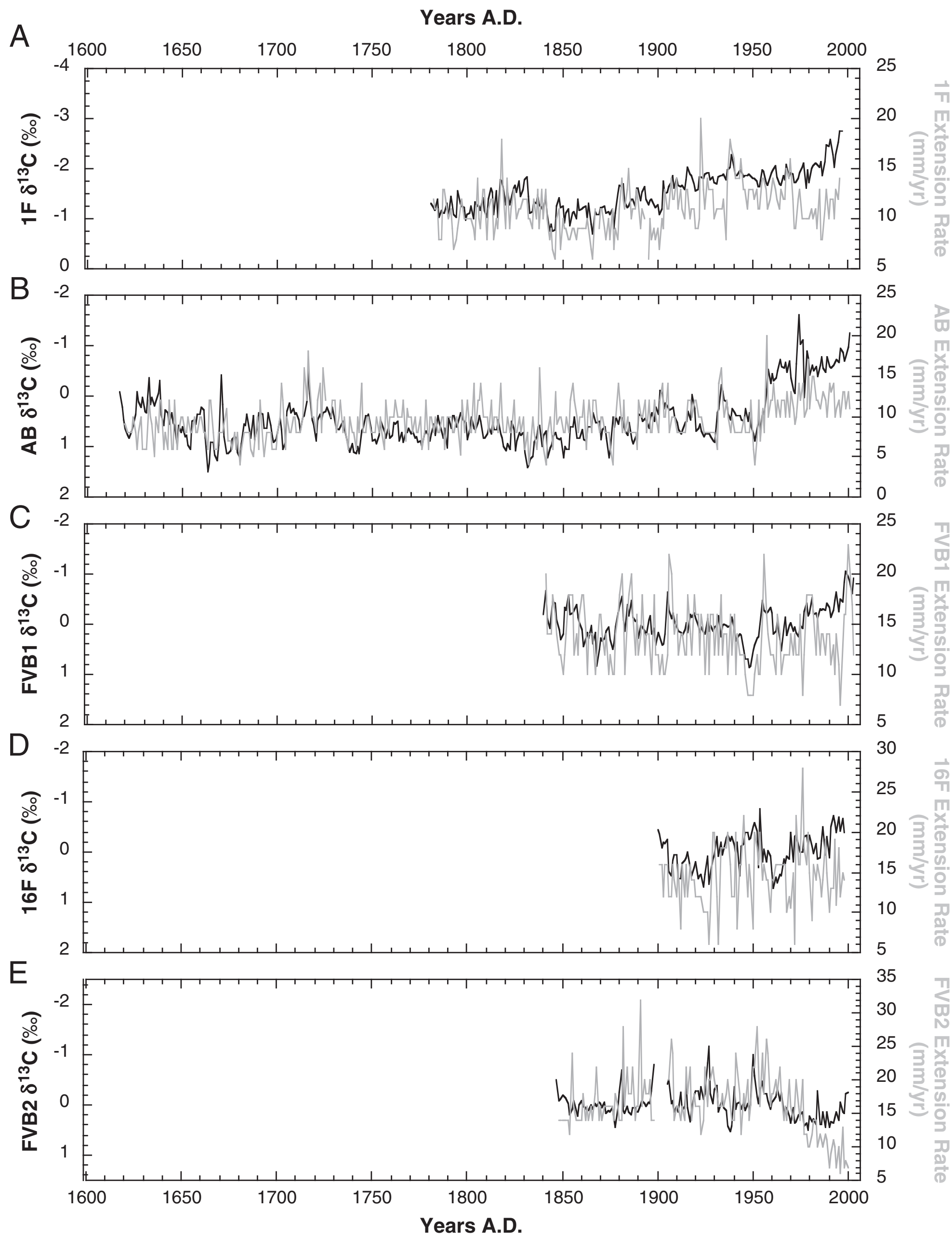

Fig. 3. Centered coral $\delta^{13}C$ data (black lines) from the five Fiji coral cores 1F (A), AB (B), FVB1 (C), 16F (D), and FVB2 (E), and their respective extension rates in millimeters per year (gray lines).

~0.26 °C (Smith et al., 2008). Following Lough and Barnes' study, this would imply an interannual SER variability of ~0.8 mm. This calculated 0.8 mm variability falls within the range of error associated with our SER measurements. The interannual SST range at Fiji is likely too small to cause any significant variability in SER.

3.4. $\delta^{13}C$ composite and long term variability

3.4.1. Composite

The creation of a composite record is a method traditionally utilized in tree ring studies. Previous coral-based studies have stressed the idea of using a network of coral records at multiple sites (Tudhope et al., 1995; Gagan et al., 1998; Linsley et al., 1999, 2006, 2008; Lough, 2004; Delong et al., 2007; Dassié, 2012). A coral core composite is likely to reflect regional-scale variability and filter out site-specific influences. In this study, a $\delta^{13}C$ composite was created by averaging the $\delta^{13}C$ records (centered data) from the four coral cores: 1F, AB, FVB1, and 16F (Fig. 4). Centering the data provides the benefit of removing the water depth influence on the individual coral $\delta^{13}C$ records. Section 3.3 discussed the peculiar pattern in FVB2 $\delta^{13}C$ starting around 1960 when both its skeletal $\delta^{13}C$ and SER values begin decreasing, in disagreement with the other four Fiji coral records. An anomalous pattern was also observed in FVB2 $\delta^{18}O$ values (Dassié, 2012). The shallowness of the coral colony (1 m water depth) likely caused the colony to bleach and partially die. Therefore FVB2 $\delta^{13}C$ data were not included in the composite.

The $\delta^{13}C$ composite only includes years where there are two or more records present; therefore it spans from 1781 to 2001 (Fig. 4). The confidence level of the composite (gray dotted lines in Fig. 4) takes into account the number of records used. For each year, the standard deviation between each core was determined, which was then divided by the

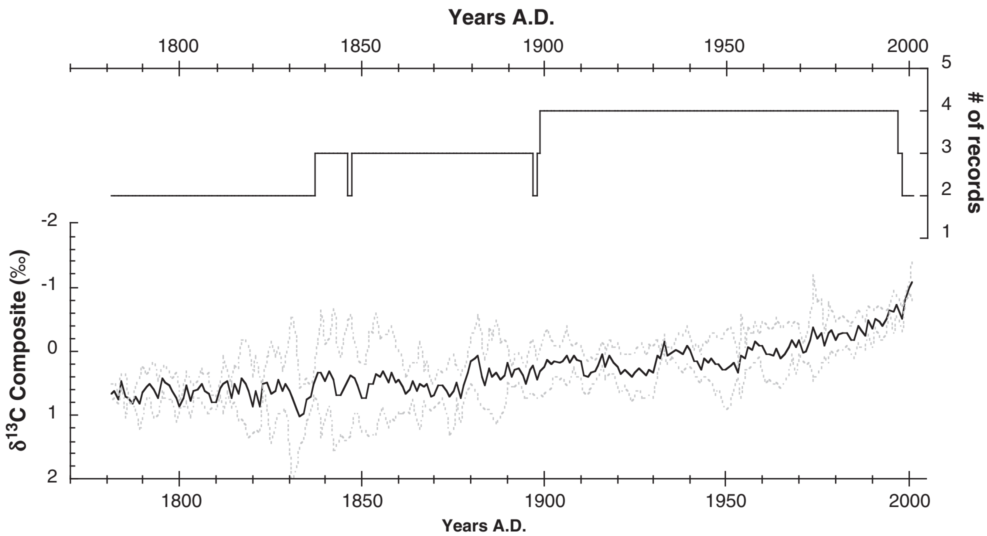

Fig. 4. Top panel: number of coral records included in the Fiji coral core composite. Bottom panel: centered annual averaged Fiji coral $\delta^{13}C$ composite (solid black line) and its 95% confidence interval (dotted gray line).

square root of the sample size (number of coral cores used to create the composite). The confidence level was computed at 95%.

For the entire length of the record, the coral $\delta^{13}C$ composite presents a general trend toward increasingly depleted $\delta^{13}C$ values ($r=-0.87$; df = 219; $p<0.01$). This accelerating decrease exceeds the limits of the confidence interval for the composite $\delta^{13}C$ (Fig. 4) and translates to a decreasing rate of ~0.0052‰·yr^{-1} (~1.2‰ decrease over a 221-year period). Other studies on the Pacific Ocean have reported long-term decreasing trends in coral $\delta^{13}C$ data (Quinn et al., 1998; Linsley et al., 1999; Stephans et al., 2004; Asami et al., 2005; Wei et al., 2009 and Swart et al., 2010 for a compilation). The magnitudes of the trends from these studies are summarized and compared with the values from this study in Table 2. The magnitude of decrease in $\delta^{13}C$ observed in the Fiji corals is similar to that found by other studies that sampled *Porites* sp. from the Pacific Ocean (Table 2). These inter-site similarities suggest that the coral $\delta^{13}C$ composite reflects regional, and not just local DIC variability. The rate of the $\delta^{13}C$ decrease becomes higher during the 1960–1990 period (−0.014‰·yr^{-1}; $r^2=0.65$, df = 28, $p<0.01$), compared to a rate of −0.0062‰·yr^{-1} ($r^2=0.58$, df = 88, $p<0.01$) for the 1900–1990 period. The rate of coral $\delta^{13}C$ decrease is therefore accelerating with time, which aligns with the conclusion of Swart et al. (2010). However, rates of decrease for the Fiji composite are higher than the rate found by Swart et al. (2010) for their Pacific Ocean compilation (−0.0066‰·yr^{-1} for the 1960–1999 period and −0.0027‰·yr^{-1} for the 1900–1990 period). Fiji is located in the South Pacific Convergence Zone (SPCZ), which is an area of high wind that is favorable to a high rate of gas exchange between the atmosphere and the ocean (Wanninkhof and McGillis, 1999; Nightingale et al., 2000). Moreover, the Revelle factor, which is an indicator of the buffering capacity of seawater (Revelle and Suess, 1957; Zeebe and Wolf-Gladrow, 2001), is not constant through the Pacific Ocean (see Sabine et al., 2004 Fig. 3). These factors suggest that the rate of $\delta^{13}C$ decrease is location-dependent.

3.4.2. Solar irradiance influence

With the understanding that SI and $\delta^{13}C$ are positively correlated (relationship determined at seasonal time scale — Section 3.1) a long term decreasing trend in the SI data would be expected. The release of human-made aerosol particles into the atmosphere enhances light scattering and absorption, inducing a large reduction of SI reaching Earth's surface (Ramanathan et al., 2001). This global dimming effect has been recorded by instrumental data around the world during the 1950–1990 period (Ramanathan et al., 2001; Liepert, 2002; Liepert et al., 2004; and Wild et al., 2005), making this reduction in SI a possible cause for the centennial scale $\delta^{13}C$ decrease observed in the coral skeleton. Peaks of aerosols are found near their source of production (Ramanathan et al., 2001), thus since the Fiji archipelago is not located near any major industrial sites, this dimming effect should not be a significant factor in Fiji. Moreover, no significant decrease in SI is observed during the late 20th century, and the global dimming effect fades after 1985 (Wild et al., 2005). Furthermore, coral extension rates, which are indirectly related to SI via photosynthesis (Sections 3.2 and 3.2) do not present any sign of change ~1950. Additionally, various global-scale SI reconstructions show a slight increasing trend over the last several centuries (Wang et al., 2005; Schmidt et al., 2011). Therefore, we conclude that the observed long-term decrease in coral $\delta^{13}C$ cannot be attributed to SI variability.

3.4.3. Cumulative-growth influence

Section 3.2 discusses how skeletal $\delta^{13}C$ decreases with increasing water depth. If water depth influences long-term skeletal $\delta^{13}C$ variability, $\delta^{13}C$ is expected to undergo an increase as the coral grows toward the surface (decrease of water depth). However, Fiji coral $\delta^{13}C$ undergoes a long-term decrease (Fig. 4). Therefore the variation in water depth due to cumulative coral growth could not be responsible for the long-term decreasing $\delta^{13}C$ trend. The water depth effect on $\delta^{13}C$

Table 2
A comparison of the coral $\delta^{13}C$ magnitude over common time periods, between the Fiji coral $\delta^{13}C$ composite and other published studies.

Publication	Region	Period	Coral species	Change in $\delta^{13}C$	Change in Fiji composite $\delta^{13}C$ change[a]
Wei et al., 2009	Great Barrier Reef (SW Pacific)	1807–1997	*Porites* sp.	~−1.1	~−1.3
Asami et al., 2005	Guam (SW Pacific)	1950–2000	*Porites lobata*	~−0.80	~−0.90
Linsley et al., 1999	Clippteron Atoll (E Pacific)	1970–1994	*Porites lobata*	~−0.40	~−0.50
Stephans et al., 2004	New Caledonia (SW Pacific)	1967–1992	*Porites lutea*	~−0.38	~−0.34

[a] Change in Fiji composite $\delta^{13}C$ for the coinciding time period (third column).

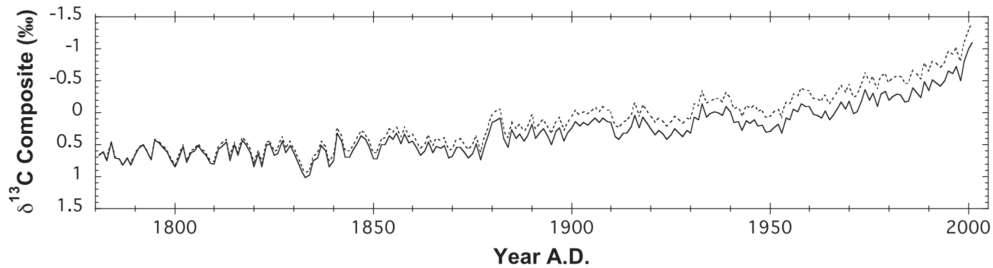

Fig. 5. Centered annual averaged coral $\delta^{13}C$ composite (solid black line) and $\delta^{13}C_{Fiji\text{-}DIC}$ (dotted black line) created from centered annual averaged coral $\delta^{13}C$ composite with the influence of cumulative growth removed.

(Fig. 2) opposes the observed decreasing trend, since a decrease in water depth is linked to an increase in $\delta^{13}C$. In order to make the composite more reflective of the regional DIC, this cumulative growth influence on the composite $\delta^{13}C$ record was calculated and removed. The average cumulative growth of all four coral cores from the entire length of the coral composite record (1781–2001) was determined to be ~2.5 m. Using the equation of $\delta^{13}C$ vs. water depth (Fig. 2), the total variation in $\delta^{13}C$ resulting from a water depth change of 2.5 m was calculated. A fraction of this value was annually incorporated from 1781 to 2001 (Fig. 5 dotted line), which caused the slope of the $\delta^{13}C$ vs. time relationship to increase, resulting in a higher rate of coral $\delta^{13}C$ depletion. The rate of decrease of $\delta^{13}C$ minus the cumulative growth influence is similar to the rate of $\delta^{13}C$ decrease of the DIC as recorded by ship measurements in the Pacific Ocean (Kroopnick et al., 1977; Gruber et al., 1999; Quay et al., 2003) (Table 3). These results suggest that removing the water depth influence on the coral $\delta^{13}C$ composite results in a truer representation of regional surface water DIC $\delta^{13}C$ variability. The Fiji composite $\delta^{13}C$ time series minus the cumulative growth influence will be referred as $\delta^{13}C_{Fiji\text{-}DIC}$ for the remainder of this report. There is no known upwelling near our study sites in Fiji, therefore $\delta^{13}C$ of the surface water DIC (and thus $\delta^{13}C_{Fiji\text{-}DIC}$) should principally vary as a function of atmospheric $\delta^{13}C_{CO_2}$.

3.4.4. ^{13}C Suess effect influence

The continuous increase in atmospheric CO_2 concentration since the early 19th century has been attributed to human activities (deforestation, agricultural practices, and the combustion of fossil fuels; see IPCC 4th Assessment Report for a review). This anthropogenic CO_2 is depleted in ^{13}C; therefore the $^{13}C/^{12}C$ ratio ($\delta^{13}C$) of the atmospheric carbon reservoir is decreasing as the atmospheric CO_2 concentration continues to increase. The ocean is one of the main global sinks of anthropogenic CO_2 emissions (Quay et al., 1992), consequently, the last two-centuries of atmospheric $\delta^{13}C$ depletion, termed "the ^{13}C Suess effect", is reflected in $\delta^{13}C$ of the oceanic DIC reservoir.

The Fiji $\delta^{13}C$ composite time series minus the cumulative growth influence ($\delta^{13}C_{Fiji\text{-}DIC}$) has a long-term decreasing trend, with a rate of ~0.0066‰$\cdot yr^{-1}$ (~1.5‰ decrease over a 221-year period). This decrease, present in many other published coral studies (Nozaki et al., 1978; 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) is attributable to the oceanic ^{13}C Suess effect.

The low-frequency variability of the $\delta^{13}C_{Fiji\text{-}DIC}$ record (frequencies inferior to 100 years) was extracted using singular spectrum analysis (SSA) software. A detailed description of this technique and its paleoclimate application is explained by Vautard and Ghil (1989), and Vautard et al. (1992). E. Cook from the Lamont–Doherty Earth Observatory wrote the SSA program used in this study. The extracted low frequency variability and its first derivative are plotted in Fig. 6. The depletion of $\delta^{13}C_{Fiji\text{-}DIC}$ is not constant through time, but presents periods of acceleration and deceleration. The earliest part of the record undergoes a steady depletion until ~1825, when it begins to accelerate, reaching a maximum around 1880. For the next ~40 years (1880 to 1920) the depletion decelerates before accelerating again, reaching an unprecedented rate (in comparison to the last 200 years) around 1995.

The atmospheric $\delta^{13}C_{CO_2}$ and atmospheric CO_2 concentration data (obtained from Antarctic ice core and firn samples by Francey et al., 1999) are compared to the $\delta^{13}C_{Fiji\text{-}DIC}$ long-term trend (Fig. 7). The $\delta^{13}C_{Fiji\text{-}DIC}$ time series presents similarities with the atmospheric $\delta^{13}C_{CO_2}$ record and the reconstructed atmospheric CO_2 concentration time series.

The atmospheric $\delta^{13}C_{CO_2}$ time series is discontinuous, therefore the raw atmospheric $\delta^{13}C_{CO_2}$ data had to be linearly interpolated into annual data (using the ARAND software package by Howell et al., 2006) prior to extracting the low frequency signal and calculating its first derivative (using the same methods as for $\delta^{13}C_{Fiji\text{-}DIC}$). The magnitudes of the coral $\delta^{13}C$ and atmospheric $\delta^{13}C_{CO_2}$ decreasing trends (Fig. 8) are approximately the same (~1.5‰). The decelerating period (1880–1920) observed in the first derivative of $\delta^{13}C_{Fiji\text{-}DIC}$ is not present in the 1st derivative of the atmospheric $\delta^{13}C_{CO_2}$ record (Fig. 8), however a halt in acceleration of the atmospheric $\delta^{13}C_{CO_2}$ depletion rate appears to precede the deceleration in $\delta^{13}C_{Fiji\text{-}DIC}$ depletion. This slowing of the atmospheric $\delta^{13}C_{CO_2}$ depletion may have resulted in the deceleration of $\delta^{13}C_{Fiji\text{-}DIC}$ depletion and/or some local factors may have affected the variability of the $\delta^{13}C$ DIC (see Pandolfi, 2011 for a review).

The atmospheric $\delta^{13}C_{CO_2}$ depletion begins to accelerate in the early to mid-20th century, followed by an acceleration of $\delta^{13}C_{Fiji\text{-}DIC}$ depletion (Fig. 8). The depletion observed between 1960 and 1990 in atmospheric $\delta^{13}C_{CO_2}$ (ice core data; Francey et al., 1999), is -0.030‰$\cdot yr^{-1}$ ($r^2 = 0.98$, df = 28, $p < 0.01$). This rate is close to the -0.023 to -0.029‰$\cdot yr^{-1}$ range found by Keeling (2005) from direct measurements of atmospheric $\delta^{13}C_{CO_2}$ at Manua Loa. The $\delta^{13}C_{Fiji\text{-}DIC}$ depletion for the same time period is -0.015‰$\cdot yr^{-1}$ ($r^2 = 0.69$, df = 28, $p < 0.01$), which is ~50% of the atmospheric $\delta^{13}C$ depletion found by Francey et al. (1999) and ~52% to

Table 3
A comparison of the coral $\delta^{13}C$ depletion over common time periods, between the Fiji coral $\delta^{13}C$ composite, minus the depth influence ($\delta^{13}C_{Fiji\text{-}DIC}$), and published values of measured $\delta^{13}C$ of the dissolved inorganic carbon (DIC).

Publication	Period	Region	Change in $\delta^{13}C$ of DIC	Change in $\delta^{13}C_{Fiji\text{-}DIC}$[a]
Kroopnick et al., 1977	1970–1993	Pacific Ocean	−0.39‰	~−0.30‰
Gruber et al., 1999	~1980–1990	Tropical Pacific	−0.15 ± 0.06‰	~−0.19‰
Quay et al., 2003	~1970s–1990s	Pacific (60°S–55°N)	−0.16 ± 0.02‰/decade	~−0.14‰/decade

[a] Change in $\delta^{13}C_{Fiji\text{-}DIC}$ for the coinciding time period (third column).

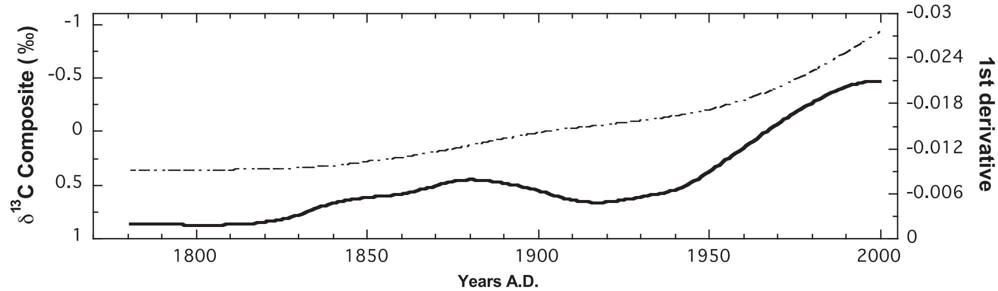

Fig. 6. The extracted low frequency (frequencies less than 100 years) of the Fiji composite δ^{13}C time series minus the cumulative growth influence ($\delta^{13}C_{Fiji\text{-}DIC}$) (dashed black) and its first derivative (black).

65% of the atmospheric δ^{13}C depletion determined by Keeling (2005). This difference in depletion between atmospheric $\delta^{13}C_{CO_2}$ and surface water DIC ($\delta^{13}C_{Fiji\text{-}DIC}$) is similar to what Böhm et al. (1996) found using Sclerosponges from the Coral Sea. They determined that 50% to 65% of the atmospheric $\delta^{13}C_{CO_2}$ decrease is observed in the surface water DIC δ^{13}C of the Coral Sea. Quay et al. (2003) found similar results; they determined that the decrease in δ^{13}C of the DIC per decade represents about 70% of the measured atmospheric $\delta^{13}C_{CO_2}$ depletion over the 1970–1990 period.

The increase in the rate of atmospheric $\delta^{13}C_{CO_2}$ depletion around the early-mid 20th century precedes the increase in coral $\delta^{13}C_{Fiji\text{-}DIC}$ depletion (Figs. 7 and 8). The $\delta^{13}C_{Fiji\text{-}DIC}$ depletion from 1970 to 2000 is 0.023‰·yr^{-1}, which is within the range of atmospheric $\delta^{13}C_{CO_2}$ depletion for the 1960–1990 period presented by Keeling (2005). This finding suggests that the $\delta^{13}C_{Fiji\text{-}DIC}$ depletion lags that of atmospheric $\delta^{13}C_{CO_2}$ by ~10 years. The correlation coefficient between atmospheric $\delta^{13}C_{CO_2}$ and $\delta^{13}C_{Fiji\text{-}DIC}$ increases when the data are offset by 10 years (from $r^2=0.64$ to $r^2=0.72$ (df = 28; $p<0.01$)). This is in agreement with the established model of isotopic disequilibrium between atmospheric $\delta^{13}C_{CO_2}$ and oceanic surface water DIC being on the order of 10 years (Broecker et al., 1980; Walker and Kasting, 1992).

The recent development of an oceanic δ^{13}C database, including measurements made during the World Ocean Circulation Experiment and the Ocean Atmosphere Carbon Exchange Study programs allowed Quay et al. (2003) to estimate a global oceanic δ^{13}C surface change of -0.16 ± 0.2‰ per decade for the 1970–1990 period (-0.18 ± 0.5‰ per decade for the Pacific Ocean). Prior to the work of Quay et al. (2003), studies using the change in δ^{13}C of the DIC to estimate the rate of anthropogenic CO_2 uptake by the oceans (Quay et al., 1992, 2003; Bacastow et al., 1996; Heimann and Maier-Reimer, 1996) faced uncertainties in their calculations due to a lack of oceanic δ^{13}C measurements. Using the ocean-wide CO_2 uptake rate of -0.16‰ per decade, Quay et al. (2003) estimated that ~1.5 ± 0.6 Gt C yr^{-1} entered the global ocean over the period 1970–1990. The rate of $\delta^{13}C_{Fiji\text{-}DIC}$ depletion we observed over the same period (~-0.19‰ per decade) is close to the Pacific Ocean $\delta^{13}C_{DIC}$ rate as determined by Quay et al. (2003), however the rate of $\delta^{13}C_{Fiji\text{-}DIC}$ depletion increases with time as discussed above. This increase leads us to conclude that the rate of oceanic CO_2 uptake might have correspondingly increased. Similar reconstructions of past δ^{13}C variability of the DIC using corals at other sites could help in determining the spatial and temporal patterns of past oceanic CO_2 uptake, and could potentially be used as a baseline for ocean model simulations.

4. Conclusion

This study highlights the inter-colony reproducibility of coral skeletal δ^{13}C, as well as the benefits of establishing a coral δ^{13}C composite record. Whereas solar irradiance seems to be the factor influencing the seasonal cycle in coral skeletal δ^{13}C, we conclude that it cannot be responsible for the long term decreasing δ^{13}C trend. Additionally, coral skeletal extension rate variability does not account for the long-term change in coral δ^{13}C, since extension rate is relatively constant with time and does not change significantly after ~1950 A.D. However, the water depth at which a coral colony is living influences both δ^{13}C and extension rate mean values. Corals growing deeper in

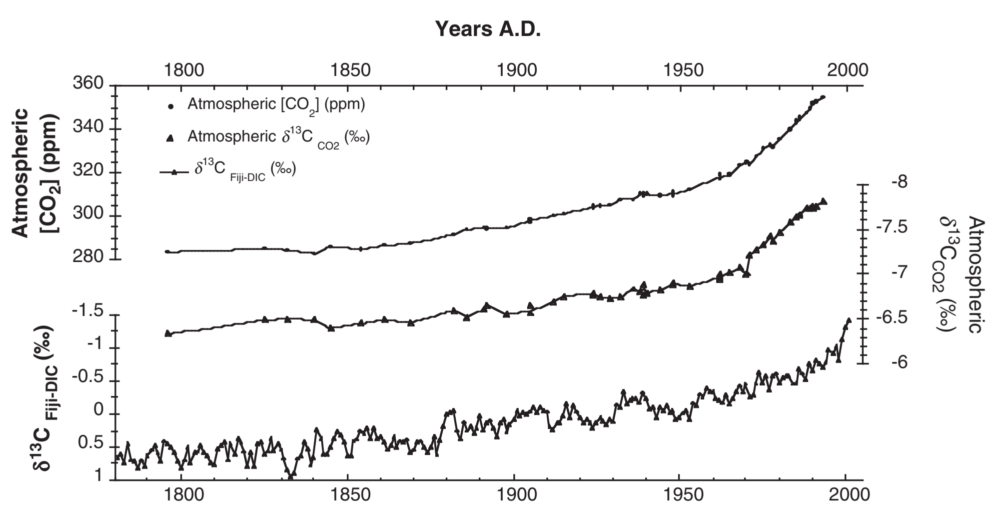

Fig. 7. Fiji composite δ^{13}C time series minus the cumulative growth influence ($\delta^{13}C_{Fiji\text{-}DIC}$) (bottom), reconstructed atmospheric $\delta^{13}C_{CO_2}$ (middle) and reconstructed atmospheric CO_2 concentration (top) time series. Atmospheric $\delta^{13}C_{CO_2}$ and atmospheric CO_2 concentration data are obtained from Antarctic ice core and firn samples (Francey et al., 1999).

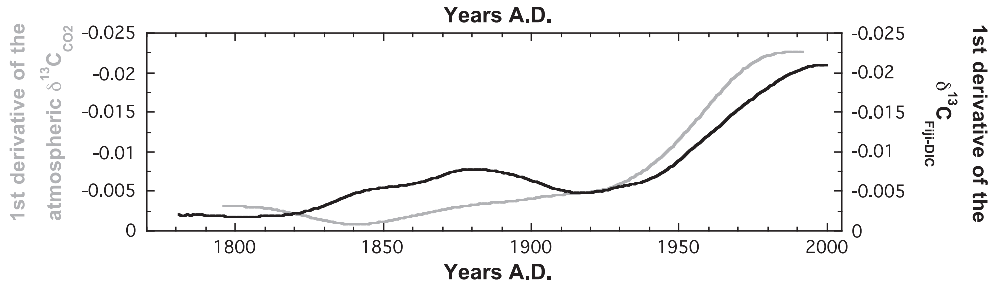

Fig. 8. The first derivative of the Fiji composite $\delta^{13}C$ time series minus the cumulative growth influence ($\delta^{13}C_{Fiji\text{-}DIC}$) (black) and the first derivative of the atmospheric $\delta^{13}C_{CO_2}$ (Francey et al., 1999) (gray). The first derivatives were made from the extracted low frequency (inferior to 100 years) variability of both records.

the water column present lower mean $\delta^{13}C$ values and lower mean extension rates than corals growing at shallower water depths.

The Fiji $\delta^{13}C$ coral composite was created by averaging the four centered coral records: AB, 1F, FVB1, and 16F. Centering the data provides the benefit of removing the water depth influence on the individual coral records residing at different water depths. A separate type of water depth influence results from a decrease in water depth as the top of the colony grows toward the surface, which induces a cumulative dampening effect on the long-term decreasing $\delta^{13}C$ trend. This influence was removed from the $\delta^{13}C$ composite, creating a refined $\delta^{13}C$ Fiji composite ($\delta^{13}C_{Fiji\text{-}DIC}$), which resulted in a truer representation of $\delta^{13}C$ variability of the Fiji surface water DIC. The oceanic ^{13}C Suess effect has high spatial variability (Quay et al., 1992), but the coral record composite utilized for this study provides a regional view of $\delta^{13}C$ variability of the DIC around Fiji, as proven by its similarities with measured $\delta^{13}C_{DIC}$ (Kroopnick et al., 1977; Gruber et al., 1999; Quay et al., 2003).

The long-term $\delta^{13}C_{Fiji\text{-}DIC}$ signal becomes increasingly depleted toward the present. Similarities between atmospheric $\delta^{13}C_{CO_2}$ and $\delta^{13}C_{Fiji\text{-}DIC}$ records suggest that the increase in isotopically-light atmospheric CO_2 is reflected in surface water DIC, which is in turn reflected in Fiji coral $\delta^{13}C$. $\delta^{13}C_{Fiji\text{-}DIC}$ variability is not synchronous with atmospheric $\delta^{13}C_{CO_2}$variability. For a common time period, only ~50% of the atmospheric $\delta^{13}C_{CO_2}$variability is represented in the $\delta^{13}C_{Fiji\text{-}DIC}$; $\delta^{13}C_{Fiji\text{-}DIC}$ response to atmospheric $\delta^{13}C_{CO_2}$ depletion is delayed by ~10 years. These relationships provide a means to study the dynamics of CO_2 uptake at a given site (Quay et al., 1992; Bacastow et al., 1996; Heimann and Maier-Reimer, 1996).

In the context of increasing anthropogenic CO_2 emissions, the rate of oceanic CO_2 uptake might be strongly enhanced, especially in certain regions of the oceans. The lack of direct oceanic $\delta^{13}C_{DIC}$ measurements raises the need for further understanding of past surface water $\delta^{13}C_{DIC}$ variability. Reconstructions such as the coral skeletal $\delta^{13}C$ data presented in this report may serve as invaluable resources for determining more accurate budget estimates of oceanic CO_2 uptake.

Acknowledgments

For coral core FVB1 and FVB2 collection, we thank the following persons and organizations: Saimone Tuilaucala (Director of Fisheries) and Aisake Batibasaga (Principal Research Officer) of the Government of Fiji, Ministry of Fisheries and Forests, for supporting this research program; Jennifer Caselle, David Mucciarone, Tom Potts, Stephan Bagnato, Ove Hoegh-Guldberg, and the J. M. Cousteau Resort in Savusavu (Fiji) for the assistance in the field sampling. For coral core 16F collection, we thank the following persons and organizations: Guy Cabioch, leader of the Paleofiji cruise. The officers and crew of IRD R/V Alis: Guy Cabioch, Yvan Joël Orempüller and Stéphanie Reynaud-Vaganay for their assistance in coral drilling. We would like to acknowledge the work of Stephen S. Howe for the acquisition of the $\delta^{13}C$ data. The National Oceanic and Atmospheric Administration's CCDD Paleoclimate Program provided major funding to Braddock K. Linsley for this research.

References

Allison, N., Tudhope, A., Fallick, A., 1996. Factors influencing the stable carbon and oxygen isotopic composition of *Porites lutea* coral skeletons from Phuket, South Thailand. Coral Reefs 15 (1), 43–57.

Asami, R., Yamada, T., Iryu, Y., Quinn, T.M., Meyer, C.P., Paulay, G., 2005. Interannual and decadal variability of the Western Pacific Sea surface condition for the years 1787–2000: reconstruction based on stable isotope record from a Guam coral. Journal of Geophysical Research, Oceans 110 (C5) (13 pp.).

Bacastow, R.B., Keeling, C.D., Lueker, T.J., Wahlen, M., Mook, W.G., 1996. The ^{13}C Suess effect in the world surface oceans and its implications for oceanic uptake of CO_2: analysis of observations at Bermuda. Global Biogeochemical Cycles 10 (2), 335–346. http://dx.doi.org/10.1029/96GB00192.

Barnes, D.J., Lough, J.M., 1993. On the nature and causes of density banding in massive coral skeletons. Journal of Experimental Marine Biology and Ecology 167 (1), 91–108. http://dx.doi.org/10.1016/0022-0981(93)90186-R.

Bessat, F., Buigues, D., 2001. Two centuries of variation in coral growth in a massive *Porites* colony from Moorea (French Polynesia): a response of ocean–atmosphere variability from south central Pacific. Palaeogeography, Palaeoclimatology, Palaeoecology 175 (1–4), 381–392. http://dx.doi.org/10.1016/S0031-0182(01)00381-9.

Böhm, F., Joachimski, M.M., Lehnert, H., Morgenroth, G., Kretschmer, W., Vacelet, J., Dullo, W., 1996. Carbon isotope records from extant Caribbean and South Pacific sponges: evolution of $\delta^{13}C$ in surface water DIC. Earth and Planetary Science Letters 139 (1–2), 291–303.

Broecker, W.S., Peng, T.H., Takahashi, T., 1980. A strategy for the use of bomb-produced radiocarbon as a tracer for the transport of fossil fuel CO_2 into the deep-sea source regions. Earth and Planetary Science Letters 49 (2), 463–468. http://dx.doi.org/10.1016/0012-821X(80)90087-4.

Brown, B., 1997. Coral bleaching: causes and consequences. Coral Reefs 16 (5), 129–138.

Chalker, B.E., Barnes, D.J., 1990. Gamma densitometry for the measurement of skeletal density. Coral Reefs 9 (1), 11–23. http://dx.doi.org/10.1007/BF00686717.

Chalker, B.E., Barnes, D.J., Dunlap, W.C., Jokiel, P.L., 1988. Light and reef-building corals. Interdisciplinary Science Reviews 13 (3), 222–237. http://dx.doi.org/10.1179/030801888789798510.

Coles, S.L., Jokiel, P.L., 1978. Synergistic effects of temperature, salinity and light on the hermatypic coral *Montipora verrucosa*. Marine Biology 49 (3), 187–195. http://dx.doi.org/10.1007/BF00391130.

Coles, S.L., Jokiel, P.L., Lewis, C.R., 1976. Thermal tolerance in tropical versus subtropical Pacific reef corals. Pacific Science 30 (2), 159–166.

Corrège, T., 2006. Sea surface temperature and salinity reconstruction from coral geochemical tracers. Palaeogeography, Palaeoclimatology, Palaeoecology 232 (2–4), 408–428. http://dx.doi.org/10.1016/j.palaeo.2005.10.014.

Dassié, E.P., 2012. Assessing the reproducibility of coral oxygen and carbon isotope time series from Fiji and Tonga and their application to the reconstruction of South Pacific Convergence Zone movements since the mid-1800s. (Doctoral dissertation). Department of Atmospheric and Environmental Sciences, State University of New York at Albany.

DeLong, K.L., Quinn, T.M., Taylor, F.W., 2007. Reconstructing twentieth-century sea surface temperature variability in the southwest Pacific: a replication study using multiple coral Sr/Ca records from New Caledonia. Paleoceanography 22 (4). http://dx.doi.org/10.1029/2007PA001444.

Druffel, E.R., 1997. Geochemistry of corals: proxies of past ocean chemistry, ocean circulation, and climate. Proceedings of the National Academy of Sciences of the United States of America 94 (16), 8354–8361.

Druffel, E.R.M., Benavides, L.M., 1986. Input of excess CO^2 to the surface ocean based on $^{13}C/^{12}C$ ratios in a banded Jamaican sclerosponge. Nature 321 (6065), 58–61. http://dx.doi.org/10.1038/321058a0.

Fairbanks, R.G., Dodge, R.E., 1979. Annual periodicity of the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios in the coral *Montastrea annularis*. Geochimica et Cosmochimica Acta 43 (7), 1009–1020.

Felis, T., Patzold, J., Loya, Y., Wefer, G., 1998. Vertical water mass mixing and plankton blooms recorded in skeletal stable carbon isotopes of a Red Sea coral. Journal of Geophysical Research, Oceans 103 (C13), 30731–30739. http://dx.doi.org/10.1029/98JC02711.

Fisk, D., Done, T., 1985. Taxonomic and bathymetric patterns of bleaching in corals, Myrmidon Reef (Queensland). Proceedings of The Fifth International Coral Reef Congress.

Forsman, Z.H., Barshis, D.J., Hunter, C.L., Toonen, R.J., 2009. Shape-shifting corals: molecular markers show morphology is evolutionarily plastic in Porites. BMC Evolutionary Biology 9, 45. http://dx.doi.org/10.1186/1471-2148-9-45.

Francey, R.J., Allison, C.E., Etheridge, D.M., Trudinger, C.M., Enting, I.G., Leuenberger, M., Langenfelds, R.L., Michel, E., Steele, L.P., 1999. A 1000-year high precision record of $\delta^{13}C$ in atmospheric CO_2. Tellus 51B (2), 170–193. http://dx.doi.org/10.1034/j.1600-0889.1999.t01-1-00005.x.

Gagan, M., Ayliffe, L., Hopley, D., Cali, J., Mortimer, G., Chappell, J., McCulloch, M., Head, M., 1998. Temperature and surface-ocean water balance of the mid-holocene tropical Western Pacific. Science 279 (5353), 1014–1018.

Gleason, D.F., Wellington, G.M., 1993. Ultraviolet radiation and coral bleaching. Nature 365 (6449), 836–838. http://dx.doi.org/10.1038/365836a0.

Glynn, P.W., 1984. Widespread coral mortality and the 1982–83 El Niño warming event. Environmental Conservation 11 (02), 133–146. http://dx.doi.org/10.1017/S0376892900013825.

Glynn, P., 1993. Coral reef bleaching: ecological perspectives. Coral Reefs 12 (1) (17 pp.).

Glynn, P.W., 1996. Coral reef bleaching: facts, hypotheses and implications. Global Change Biology 2 (6), 495–509. http://dx.doi.org/10.1111/j.1365-2486.1996.tb00063.x.

Goenaga, C., Vincente, V., Armstrong, R., 1988. Aposymbiosis in Puerto Rican zooxanthellate cnidarians. Proceedings of the Association of Island Marine Laboratories of the Caribbean 21, 49.

Goreau, T.J., Hayes, R.L., Clark, J.W., Basla, D.J., Robertson, C.N., 1993. Elevated sea surface temperatures correlate with Caribbean coral reef bleaching. In: Geyer, R.A. (Ed.), A Global Warming Forum: Scientific. Economic and Legal Overview. CRC Press, Boca Raton, FL, pp. 225–255.

Grottoli, A., 1999. Variability of stable isotopes and maximum linear extension in reef-coral skeletons at Kaneohe Bay, Hawaii. Marine Biology 135 (3), 437–449. http://dx.doi.org/10.1007/s002270050644.

Grottoli, A., 2000. Stable carbon isotopes ($\delta^{13}C$) in coral skeletons. Oceanography 13 (2), 93–97.

Grottoli, A., Wellington, G., 1999. Effect of light and zooplankton on skeletal $\delta^{13}C$ values in the eastern Pacific corals *Pavona clavus* and *Pavona gigantea*. Coral Reefs 18 (1), 29–41. http://dx.doi.org/10.1007/s003380050150.

Gruber, N., Keeling, C.D., Bacastow, R.B., Guenther, P.R., Lueker, T.J., Wahlen, M., Meijer, H.A.J., Mook, W.G., Stocker, T.F., 1999. Spatiotemporal patterns of carbon-13 in the global surface oceans and the oceanic Suess effect. Global Biogeochemical Cycles 13 (2), 307–336. http://dx.doi.org/10.1029/1999GB900019.

Harriott, V.J., 1985. Mortality rates of scleractinian corals before and during a mass bleaching event. Marine Ecology Progress Series 21, 81–88.

Heimann, M., Maier-Reimer, E., 1996. On the relations between the oceanic uptake of CO_2 and its carbon isotopes. Global Biogeochemical Cycles 10 (1), 89–110. http://dx.doi.org/10.1029/95GB03191.

Heiss, G., Dullo, W.-C., Reijmer, J., 1993. Short- and long-term growth history of massive *Porties* sp. from Aqaba (Red Sea). Senckenbergiana maritima 23 (4–6), 135–141.

Hoegh-Guldberg, O., 1999. Climate change, coral bleaching and the future of the world's coral reefs. Marine and Freshwater Research 50 (8), 839–866. http://dx.doi.org/10.1071/MF99078.

Hoegh-Guldberg, O., Salvat, B., 1995. Periodic mass-bleaching and elevated sea temperatures: bleaching of outer reef slope communities in Moorea, French Polynesia. Marine Ecology Progress Series 121, 181–190.

Hoogenboom, M., Anthony, K., Connolly, S., 2006. Energetic cost of photoinhibition in corals. Marine Ecology Progress Series 313, 1–12.

Howell, P., Pisias, N., Ballance, J., Baughman, J., Ochs, L., 2006. ARAND Time-Series Analysis Software. Brown University, Providence RI.

Huston, M., 1985. Variation in coral growth rates with depth at Discovery Bay, Jamaica. Coral Reefs 4 (1), 19–25. http://dx.doi.org/10.1007/BF00302200.

Jokiel, P.L., 1980. Solar ultraviolet radiation and coral reef epifauna. Science (New York, N.Y.) 207 (4435), 1069–1071. http://dx.doi.org/10.1126/science.207.4435.1069.

Jokiel, P.L., Coles, S.L., 1977. Effects of temperature on the mortality and growth of Hawaiian reef corals. Marine Biology 43 (3), 201–208. http://dx.doi.org/10.1007/BF00402312.

Jokiel, P.L., Coles, S.L., 1990. Response of Hawaiian and other Indo-Pacific reef corals to elevated temperature. Coral Reefs 8 (4), 155–162. http://dx.doi.org/10.1007/BF00265006.

Keeling, R.F., 2005. Comment on "The Ocean Sink for Anthropogenic CO_2". Science 308 (5729), 1743. http://dx.doi.org/10.1126/science.1109620.

Keeling, C.D., Bacastow, R.B., Tans, P.P., 1980. Predicted shift in the $^{13}C/^{12}C$ ratio of atmospheric carbon dioxide. Geophysical Research Letters 7 (7), 505–508.

Knutson, D.W., Buddemeier, R.W., Smith, S.V., 1972. Coral chronometers: seasonal growth bands in reef corals. Science 177 (4045), 270–272. http://dx.doi.org/10.1126/science.177.4045.270.

Kroopnick, P.M., Margolis, S.V., Wong, C.S., 1977. δ13C variations in marine carbonate sediments as indicators of the CO2 balance between the atmosphere and oceans. In: Andersen, R.N., Malahoff, A. (Eds.), The Fate of Fossil Fuel CO2 in the Oceans. Plenum, New York, NY, pp. 295–321.

Leder, J.J., Szmant, A.M., Swart, P.K., 1991. The effect of prolonged "bleaching" on skeletal banding and stable isotopic composition in *Montastrea annularis*. Coral Reefs 10 (1), 19–27.

Lesser, M.P., 1996. Elevated temperatures and ultraviolet radiation cause oxidative stress and inhibit photosynthesis on symbiotic dinoflagellates. Limnology and Oceanography 41 (2), 271–283.

Lesser, M.P., Stochaj, W.R., Tapley, D.W., Shick, J.M., 1990. Bleaching in coral reef anthozoans: effects of irradiance, ultraviolet radiation, and temperature on the activities of protective enzymes against active oxygen. Coral Reefs 8 (4), 225–232.

Liepert, B.G., 2002. Observed reductions of surface solar radiation at sites in the United States and worldwide from 1961 to 1990. Geophysical Research Letters 29 (10), 1–4. http://dx.doi.org/10.1029/2002GL014910.

Liepert, B.G., Feichter, J., Lohman, U., Roeckner, E., 2004. Can aerosols spin down the water cycle in a warmer and moister world? Geophysical Research Letters 31 (6), 2–5. http://dx.doi.org/10.1029/2003GL019060.

Linsley, B.K., Messier, R., Dunbar, R.B., 1999. Assessing between-colony oxygen isotope variability in the coral *Porites lobata* at Clipperton Atoll. Coral Reefs 18 (1), 13–27. http://dx.doi.org/10.1007/s003380050148.

Linsley, B.K., Wellington, G.M., Schrag, D.P., 2000. Decadal sea surface temperature variability in the subtropical South Pacific from 1726 to 1997 A.D. Science 290 (5494), 1145–1148. http://dx.doi.org/10.1126/science.290.5494.1145.

Linsley, B., Wellington, G.M., Schrag, D.P., Ren, L., Salinger, M.J., Tudhope, A.W., 2004. Geochemical evidence from corals for changes in the amplitude and spatial pattern of South Pacific interdecadal climate variability over the last 300 years. Climate Dynamics 22 (1), 1–11. http://dx.doi.org/10.1007/s00382-003-0364-y.

Linsley, B.K., Kaplan, A., Gouriou, Y., Salinger, J., DeMenocal, P.B., Wellington, G.M., Howe, S.S., 2006. Tracking the extent of the South Pacific Convergence Zone since the early 1600s. Geochemistry, Geophysics, Geosystems 7 (Q05003). http://dx.doi.org/10.1029/2005GC001115 (15 pp.).

Linsley, B.K., Zhang, P., Kaplan, A., Howe, S.S., Wellington, G.M., 2008. Interdecadal-decadal climate variability from multicoral oxygen isotope records in the South Pacific Convergence Zone region since 1650 AD. Paleoceanography 23 (PA2219) (16 pp.).

Lough, J.M., 2004. A strategy to improve the contribution of coral data to high-resolution paleoclimatology. Palaeogeography, Palaeoclimatology, Palaeoecology 204 (1–2), 115–143. http://dx.doi.org/10.1016/S0031-0182(03)00727-2.

Lough, J.M., Barnes, D.J., 1989. Possible relationships between environmental variables and skeletal density in a coral colony from the central Great Barrier Reef. Journal of Experimental Marine Biology and Ecology 134 (3), 221–241. http://dx.doi.org/10.1016/0022-0981(89)90071-3.

Lough, J., Barnes, D., 2000. Environmental controls on growth of the massive coral *Porites*. Journal of Experimental Marine Biology and Ecology 245 (2), 225–243.

McCloskey, L., Muscatine, L., 1984. Production and respiration in the Red Sea Coral *Stylophora pistillata* as a function of depth. Proceedings of the Royal Society of London Series B 222 (1227), 215–230.

McConnaughey, T.A., 1986. Oxygen and carbon isotope disequilibria in Galapagos corals: isotopic thermometry and calcification physiology. (Doctoral dissertation). University of Washington.

McConnaughey, T., 1989a. ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I. Patterns. Geochimica et Cosmochimica Acta 53 (1), 151–162. http://dx.doi.org/10.1016/0016-7037(89)90282-2.

McConnaughey, T., 1989b. ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: II. In vitro simulation of kinetic isotope effects. Geochimica et Cosmochimica Acta 53 (1), 163–171.

McGregor, H.V., Fischer, M.J., Gagan, M.K., Fink, D., Woodroffe, C.D., 2011. Environmental control of the oxygen isotope composition of *Porites* coral microatolls. Geochimica et Cosmochimica Acta 75 (14), 3930–3944. http://dx.doi.org/10.1016/j.gca.2011.04.017.

Meesters, E.H., Bak, R.P.M., 1993. Effects of coral bleaching on tissue regeneration and colony survival. Marine Ecology Progress Series 96, 189–198.

Nie, B., Chen, T., Liang, M., Wang, Y., Zhong, J., Zhu, Y., 1997. Relationship between coral growth rate and sea surface temperature in the northern part of South China Sea during the past 100 a. Science in China Series D: Earth Sciences 40 (2), 173–182.

Nightingale, P.D., Malin, G., Law, C.S., Watson, A.J., Liss, P.S., Liddicoat, M.I., Boutin, J., Upstill-Goddard, R.C., 2000. In situ evaluation of air–sea gas exchange parameterizations using novel conservative and volatile tracers. Global Biogeochemical Cycles 14 (1), 373–387. http://dx.doi.org/10.1029/1999GB900091.

Nozaki, Y., Rye, D., Turekian, K., Dodge, R.E., 1978. A 200 year record of carbon-13 and carbon-14 variations in a Bermuda coral. Geophysical Research 5 (10), 825.

Oliver, J., 1985. Recurrent seasonal bleaching and mortality of corals on the Great Barrier Reef. Proceedings of the 5th International Coral Reef Congress 4, 201–206.

Omata, T., Suzuki, A., Kawahat, H., Okamoto, M., 2005. Annual fluctuation in the stable carbon isotope ratio of coral skeletons: the relative intensities of kinetic and metabolic isotope effects. Geochimica et Cosmochimica Acta 69 (12), 3007–3016. http://dx.doi.org/10.1016/j.gca.2004.12.018.

Omata, T., Suzuki, A., Sato, T., Minoshima, K., Nomaru, E., Murakami, A., Murayama, S., Kawahata, H., Maruyama, T., 2008. Effect of photosynthetic light dosage on carbon isotope composition in the coral skeleton: long-term culture of *Porites* spp. Journal of Geophysical Research 113 (G02014). http://dx.doi.org/10.1029/2007JG000431 (15 pp.).

Pandolfi, J.M., 2011. The paleoecology of coral reefs. Coral Reefs: An Ecosystem in Transition 13–24. http://dx.doi.org/10.1007/978-94-007-0114-4_2.

Quay, P.D., Tilbrook, B., Wong, C.S., 1992. Oceanic uptake of fossil fuel CO_2: carbon-13 evidence. Science 256 (5053), 74–79.

Quay, P., Sonnerup, R., Westby, T., Stutsman, J., McNichol, A., 2003. Changes in the $^{13}C/^{12}C$ of dissolved inorganic carbon in the ocean as a tracer of anthropogenic CO_2 uptake. Global Biogeochemical Cycles 17 (1004). http://dx.doi.org/10.1029/2001GB001817 (20 pp.).

Quinn, T.M., Crowley, T.J., Taylor, F.W., Henin, C., Joannot, P., Join, Y., 1998. A multicentury stable isotope record from a New Caledonia coral: interannual and decadal sea surface temperature variability in the southwest Pacific since 1657 A.D. Paleoceanography 13 (4), 412. http://dx.doi.org/10.1029/98PA00401.

Ramanathan, V., Crutzen, P.J., Kiehl, J.T., Rosenfeld, D., 2001. Aerosols, climate, and the hydrological cycle. Science 294 (5549), 2119–2124. http://dx.doi.org/10.1126/science.1064034.

Revelle, R., Suess, H., 1957. Carbon dioxide exchange between atmosphere and ocean and the question of an increase in CO_2 during the past decades. Tellus 9, 18–27.

Reynaud-Vaganay, S., Juillet-Leclerc, A., Jaubert, J., Gattuso, J., 2001. Effect of light on skeletal $\delta^{13}C$ and $\delta^{18}O$, and interaction with photosynthesis, respiration and calcification in two zooxanthellate scleractinian corals. Palaeogeography, Palaeoclimatology, Palaeoecology 175 (1–4), 393–404. http://dx.doi.org/10.1016/S0031-0182(01)00382-0.

Romanek, C., Grossman, E., Morse, J., 1992. Carbon isotopic fractionation in synthetic aragonite and calcite: effects of temperature and precipitation rate. Geochimica et Cosmochimica Acta 56 (1), 419–430. http://dx.doi.org/10.1016/0016-7037(92)90142-6.

Rosenfeld, M., Yam, R., Shemesh, a., Loya, Y., 2003. Implication of water depth on stable isotope composition and skeletal density banding patterns in a *Porites lutea* colony: results from a long-term translocation experiment. Coral Reefs 22 (4), 337–345. http://dx.doi.org/10.1007/s00338-003-0333-2.

Sabine, C.L., et al., 2004. The oceanic sink for anthropogenic CO_2. Science (New York, N.Y.) 305 (5682), 367–371. http://dx.doi.org/10.1126/science.1097403.

Schmidt, G.A., et al., 2011. Climate forcing reconstructions for use in PMIP simulations of the last millennium (v1.0). Geoscientific Model Development 4 (1). http://dx.doi.org/10.5194/gmd-4-33-2011.

Shimamura, M., Hyeong, K., Watanabe, T., Irino, T., Yoo, C., Kim, W., 2008. Opposed trend of skeletal carbon isotopic ratios found in two different coral species collected from the same site: genus-dependent responses. Proceedings of the 11th International Coral Reef Symposium, Ft. Lauderdale, Florida, pp. 87–91.

Smith, T.M., Reynolds, R.W., Peterson, T.C., Lawrimore, J., 2008. Improvements to NOAA's historical merged land–ocean surface temperature analysis (1880–2006). Journal of Climate 21 (10), 2283–2296. http://dx.doi.org/10.1175/2007JCLI2100.1.

Stephans, C.L., Quinn, T., Taylor, F., Corrège, T., 2004. Assessing the reproducibility of coral-based climate records. Geophysical Research Letters 31 (L18210). http://dx.doi.org/10.1029/2004GL020343 (4 pp.).

Swart, P.K., 1983. Carbon and oxygen isotope fractionation in scleractinian corals: a review. Earth-Science Reviews 19 (1), 51–80.

Swart, P.K., Coleman, M.L., 1980. Isotopic data for scleractinian corals explain their palaeotemperature uncertainties. Nature 283, 557–559.

Swart, P.K., Dodge, R.E., Hudson, P.E., 1996a. A 240-year stable oxygen and carbon isotopic record in a coral from South Florida; implications for the prediction of precipitation in southern Florida. Palaios 11 (4), 362–375.

Swart, P.K., Healy, G.F., Dodge, R.E., Kramer, P., Hudson, J.H., Halley, R.B., Robblee, M.B., 1996b. The stable oxygen and carbon isotopic record from a coral growing in Florida Bay: a 160 year record of climatic and anthropogenic influence. Palaeogeography, Palaeoclimatology, Palaeoecology 123 (1–4), 219–237. http://dx.doi.org/10.1016/0031-0182(95)00078-X.

Swart, P.K., Greer, L., Rosenheim, B.E., Moses, C.S., Waite, A.J., Winter, A., Dodge, R.E., Helmle, K., 2010. The ^{13}C Suess effect in scleractinian corals mirror changes in the anthropogenic CO_2 inventory of the surface oceans. Geophysical Research Letters 37 (L05604). http://dx.doi.org/10.1029/2009GL041397 (5 pp.).

Tudhope, A.W., Shimmield, G.B., Chilcott, C.P., Jebb, M., Fallick, A.E., Dalgleish, A.N., 1995. Recent changes in climate in the far western equatorial Pacific and their relationship to the Southern Oscillation; oxygen isotope records from massive corals, Papua New Guinea. Earth and Planetary Science Letters 136 (3–4), 575–590.

Vautard, R., Ghil, M., 1989. Singular spectrum analysis in nonlinear dynamics, with applications to paleoclimatic time series. Physica D: Nonlinear Phenomena 35 (3), 395–424. http://dx.doi.org/10.1016/0167-2789(89)90077-8.

Vautard, R., Yiou, P., Ghil, M., 1992. Singular-spectrum analysis: a toolkit for short, noisy chaotic signals. Physica D: Nonlinear Phenomena 58 (1–4), 95–126. http://dx.doi.org/10.1016/0167-2789(92)90103-T.

Walker, J.C., Kasting, J.F., 1992. Effects of fuel and forest conservation on future levels of atmospheric carbon dioxide. Palaeogeography, Palaeoclimatology, Palaeoecology 97 (1902), 151–189.

Wang, Y., Lean, J., Sheeley, N.J., 2005. Modeling the Sun's Magnetic Field and Irradiance since 1713. The Astrophysical Journal 625 (1), 522–538.

Wanninkhof, R., McGillis, W.R., 1999. A cubic relationship between air-sea CO_2 exchange and wind speed. Geophysical Research Letters 26 (13), 1889. http://dx.doi.org/10.1029/1999GL900363.

Weber, J.N., Woodhead, P.M.J., 1970. Carbon and oxygen isotope fractionation in the skeletal carbonate of reef-building corals. Chemical Geology 6, 93–117. http://dx.doi.org/10.1016/0009-2541(70)90009-4.

Weber, J.N., Woodhead, P.M.J., 1971. Diurnal variations in the isotopic composition of dissolved inorganic carbon in seawater from coral reef environments. Geochimica et Cosmochimica Acta 35 (9), 891–902.

Weber, J.N., Deines, P., Weber, P.H., Baker, P.A., 1976. Depth related changes in the $^{13}C/^{12}C$ ratio of skeletal carbonate deposited by the Caribbean reef-frame building coral *Montastrea annularis*: further implications of a model for stable isotope fractionation by scleractinian corals. Geochimica et Cosmochimica Acta 40 (1), 31–39. http://dx.doi.org/10.1016/0016-7037(76)90191-5.

Wei, G., McCulloch, M.T., Mortimer, G., Deng, W., Xie, L., 2009. Evidence for ocean acidification in the Great Barrier Reef of Australia. Geochimica et Cosmochimica Acta 73 (8), 2332–2346. http://dx.doi.org/10.1016/j.gca.2009.02.009.

Wild, M., Gilgen, H., Roesch, A., Ohmura, A., Long, C.N., Dutton, E.G., Forgan, B., Kallis, A., Russak, V., Tsvetkov, A., 2005. From dimming to brightening: decadal changes in solar radiation at Earth's surface. Science 308 (5723), 847–850. http://dx.doi.org/10.1126/science.1103215.

Winter, A., Appeldoorn, R.S., Bruckner, A., Williams Jr., E.H., Goenaga, C., 1998. Sea surface temperatures and coral reef bleaching off La Parguera, Puerto Rico (northeastern Caribbean Sea). Coral Reefs 17 (4), 377–382. http://dx.doi.org/10.1007/s003380050143.

Zeebe, R., Wolf-Gladrow, D., 2001. CO_2 in Seawater: Equilibrium, Kinetics, Isotopes. Elsevier Science B.V., Amsterdam.