Clim. Past Discuss., 10, 1783–1798, 2014
www.clim-past-discuss.net/10/1783/2014/
doi:10.5194/cpd-10-1783-2014

Climate of the Past
Discussions
Open Access

Evidence for the non-influence of salinity variability on the coral Sr / Ca paleothermometer

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Received: 21 March 2014 – Accepted: 27 March 2014 – Published: 14 April 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

The influence of salinity in the incorporation of trace elements in the skeleton of calcareous organisms is still poorly known. Studies on foraminiferal Mg / Ca thermometry have suggested a bias due to Sea Surface Salinity (SSS) variations, leading to potential erroneous estimation of Mg / Ca-based Sea Surface Temperature (SST). Culture experiments seem to indicate that in three coral species (not including the widely used *Porites* genus), salinity does not influence the Sr / Ca thermometer. In this study, we test the salinity effect on coral Sr / Ca-based SST reconstructions at monthly and interannual timescales in open-ocean environmental conditions, using a large spatial compilation of published coral data (mainly based on the *Porites* genus) originating from the Western Pacific Ocean, the Atlantic Ocean, the Indian Ocean, the China Sea and the Red Sea and adding a new Eastern Pacific coral Sr / Ca record from the Clipperton atoll.

We use simple and multiple regressions between Sr / Ca on one hand and SST and SSS on the other hand at the various sites. We find no evidence for a salinity bias on the Sr / Ca SST proxy for the two studied timescales. This study reinforces the use of coral Sr / Ca as a reliable paleothermometer.

1 Introduction

Massive scleractinian corals have been extensively used in the past three decades as source of environmental information for the tropical belt, at different time scales (from weekly to multi-annual). The hermatypic *Porites* genus is one of the most suitable coral to reconstruct past oceanic parameters such as sea surface temperature (SST) and qualitative estimates of sea surface salinity (SSS). *Porites* corals have a wide distribution area, a strong resistance to breakage and erosion, a potential to be accurately dated by U/Th and seasonal banding allowing the establishment of a reliable

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chronology (Knutson et al., 1972; Barnes and Lough, 1993; Cobb et al., 2003b; Corrège, 2006; Helmle and Dodge, 2011).

Among the different geochemical tracers integrated in the aragonitic skeleton of corals, the Sr/Ca ratio is usually regarded as the most robust and straightforward to reconstruct past SST changes (Smith et al., 1979; Beck et al., 1992; Alibert et McCulloch, 1997; Corrège, 2006; Linsley et al., 2006; Delong et al., 2012). Sr^{2+} ions substitute for Ca^{2+} ions in aragonite depending on temperature and are therefore strongly bound to the crystal lattice (Amiel et al., 1973; Mitsuguchi et al., 2001; Watanabe et al., 2001; Allison et al., 2001; Finch et al., 2003), limiting diagenetic effects.

However, correlation of the Sr/Ca proxy with instrumental SST is never optimal, suggesting the probable influence of others factors. Intrinsic effects known as "vital effects" could be due to zooxanthelae photosynthetic activity (Cohen et al., 2002), growth rate variations (de Villier et al., 1995; Alibert and McCulloch, 1997; Mitsuguchi et al., 2003; Goodkin et al., 2007), and other biologically controlled processes. Recently, a study showed that skeletogenesis within the living tissue layer could attenuate the temperature-sensitivity of Sr/Ca, over-estimating the SST reconstruction (Gagan et al., 2012). Environmental factors such as spatial and temporal variations of the seawater Sr/Ca ratio could also influence coral Sr/Ca records (de Villier et al., 1994, 1995; Sun et al., 2005).

However, one of the main questions surrounding the use of Sr/Ca as a thermometer is whether salinity has an influence on this tracer. More generally, the influence of salinity in the incorporation of trace elements in the skeleton of calcareous organisms is still highly debated. Studies on foraminiferal Mg/Ca thermometry have shown a bias due to salinity variations, leading to an erroneous estimation of Mg/Ca-based SST (Mathien-Blard and Bassinot, 2009; Arbuszewski et al., 2010; Hönisch et al., 2013). Coupled measurements of Sr/Ca and δ^{18}O in coral samples have been used to estimate past variations in seawater isotopic composition (δ^{18}Osw) (McCulloch et al., 1994; Gagan et al., 1998). Since δ^{18}Osw and SSS are affected by the same processes in the tropics (the precipitation to evaporation ratio, and vertical and horizontal advection), the

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combination of Sr/Ca and δ^{18}O measurements in corals can theoretically provide information on SST and qualitative SSS changes through time (Gagan et al., 1998; Ren et al., 2003; Cahyarini et al., 2008). It is therefore necessary to prove that salinity does not influence the Sr/Ca thermometer in the first place. Earlier studies investigated the effect of fluvial discharges (i.e. locally decreasing the SSS) and found no measurable influence on the Sr/Ca-SST calibration (Alibert et al., 2003; Fallon et al., 2003), despite the fact that riverine inputs can also change the Sr/Ca ratio of seawater. These studies however were rather local and did not encompass a large salinity range. A recent in-vitro study (Pretet et al., 2013) found no effect of salinity (in the range 36–40) on Sr/Ca, but the authors did not use the *Porites* genus.

Until recently, testing potential salinity bias on coral Sr/Ca thermometry was difficult because most coral Sr/Ca records originated from the Western Pacific Ocean, a region characterised by a weak seasonal to interannual SSS range (34–35.3 psu) (Delcroix et al., 1996). Several coral Sr/Ca records (mostly generated from *Porites*) are now available in other regions such as the Atlantic Ocean, the Indian Ocean, the China Sea and the Red Sea, encompassing a much wider salinity range (∼ 7 psu). In addition we extend the spatial coverage of available Sr/Ca data by presenting the first Eastern Pacific coral record from the Clipperton atoll (Fig. 1).

Thus, all this material calls for a more complete investigation, and in the present paper, we test the potential influence of salinity on the coral Sr/Ca paleothermometer in multiple open-ocean conditions at monthly and interannual timescales.

2 Material and method

2.1 Clipperton record

In February 2005, a sampling expedition led by the Institut de Recherche pour le Développement France (IRD) collected a 1.94 m length *Porites* core labelled CL3.

The CL3 core was slabbed (1 cm) with a circular saw along the main growth axis to allow the sampling of continuous corallites. The two first slabs (44 cm length) were cleaned with deionized water in an ultrasonic bath for 10 min and then dried at room temperature for 24 h. Micro-sampling of CL3 slabs was conducted with a computer controlled three axis positioning system and a micro-drill at 1.5 mm increments to obtain a near-monthly resolution.

The Sr/Ca record from the CL3 (Fig. S1) was generated on a VARIAN Ultramass® ICP MS (Inductively Coupled Plasma Mass Spectrometer) at the IRD centre in Bondy (France), following the method developed by Le Cornec and Corrège (1997). Powdered carbonate samples (~ 1 mg) were dissolved in 8 mL of 2 % nitric acid with a target concentration of ~ 40 ppm for Ca and ~ 0.8 ppm for Sr. Concentrations of Sr and Ca were determined by isotopic dilution using internal standards of ^{89}Y and ^{45}Sc, respectively with measurement uncertainties of less than 1 % (Le Cornec and Corrège, 1997). An in-house coral standard was repeatedly measured ($n = 82$) achieving a relative standard deviation of ±0.05 mmol mol^{-1} (1σ). The chronology is based on peak matching between Sr/Ca and instrumental SST. The monthly Sr/Ca data were linearly interpolated (12 points year^{-1}) using the AnalySeries software (Paillard et al., 1996).

2.2 Coral database

Fourteen Sr/Ca records (twelve from *Porites*, one from *Siderastrea* and one from *Montastraea*) from coral cores covering different time intervals within the last 3 decades (record length from 5 to 25 years) were compiled using the NOAA paleoclimatology database (http://www.ncdc.noaa.gov/data-access/paleoclimatology-data) (Table S1 and Fig. 1). Among those fifteen records, one is located in the Eastern Pacific ocean, four in the Central Pacific Ocean, four in the Western Pacific ocean, two in the Western Atlantic Ocean (*Siderastrea* and *Montastraea*), two in the southwestern Indian Ocean, one in the South China Sea and one in the Northern Red Sea (Fig. 1). Time resolution of these records is monthly except for the Red Sea and the Indian

Ocean records (bimonthly) and for one coral from the Central Pacific (Rarotonga, 8 points year^{-1}).

2.3 Processing of data

When trying to relate Sr/Ca to SST, a site-specific calibration is usually necessary to obtain the best-possible fit between the two variables (see Corrège 2006 for a compilation of published calibrations). This approach yields variable calibration slopes, indicating that the effect of other factors (growth rate, zooxanthelae activity . . .) might be locally incorporated in the process. To enable us to investigate the influence of other factors on the Sr/Ca in corals, we used a unique Sr/Ca-SST calibration that we applied to each coral record. The calibration used corresponds to the average of 38 linear regressions compiled by Corrège, 2006 ($SST = -0.0607 \times Sr/Ca + 10.553$; thereafter C06). Moreover, in order to have a consistent instrumental reference, we chose to perform the Sr/Ca-SST calibrations using the OISST monthly product (version 2, Reynolds et al., 2002) for all Sr/Ca records. The OISST product blends instrumental data from different sources and is regularly updated. Use of other SST products does not change our main conclusions. For each coral Sr/Ca record, we used the closest SST grid point (Table S2) in the OISST dataset.

Each Sr/Ca record was converted to SST ($T_{Sr/Ca}$) using the average C06 calibration. We then subtracted the instrumental SST (SST_I) from the $T_{Sr/Ca}$ at monthly and interannual resolution to obtain residual temperatures (ΔT). Residual temperatures were then linearly regressed against the SODA SSS product (version 2.2.4, Carton and Giese, 2008) at monthly (Fig. 2 and Table S1) and interannual resolution (using a 25, 17 or 13-point Hanning filter depending on the record time resolution, i.e. 12, 8 or 6 months respectively) (Table S1). The different correlations between ΔT and SSS are characterized by the coefficient of determination (R^2) and the corresponding Student's t test (p) (Table S1). We did not apply any filter to the Red Sea record due to its short time interval (5 years). As with SST, we used the closest SSS grid point (Table S2) for each location. We also performed a multiple linear regression (MLR) between the

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Sr/Ca record and two explanatory variables, i.e. SST_I and SSS at monthly and interannual resolution. This MLR regression was then used to recalculate theoretical Sr/Ca from instrumental SSS and SST, which we compared with the original Sr/Ca record at monthly resolution (Fig. 3a). A similar approach was used with a simple linear regression (SLR) between the Sr/Ca record and the SST (Fig. 3b).

3 Results and discussion

One of the main advantages of corals records is their ability to provide high temporal resolution paleorecords (typically from monthly to multi-annual resolution) (Corrège, 2006). To assess the potential effect of SSS on coral Sr/Ca at monthly resolution, we first investigated each individual records. We observe no significant correlation between ΔT and SSS at monthly resolution for any of the records (Table S1). We then grouped the data (Fig. 2) and, a weak but significant trend ($R^2 = 0.1$; p value< 0.01) appears in ΔT over the investigated salinity range (~ 7 psu). This trend is uniquely forced by the scarce Red Sea data, and disappears when these data are omitted. Our conclusion is thus that the documented trend is too weak to be reliably interpreted as a salinity effect.

To put our results in perspective with other trace elements studies on calcareous organisms, we show similar results considering the salinity effect on Mg/Ca in foraminifera (Fig. 2, inset). As mentioned previously, studies on foraminiferal Mg/Ca thermometry have shown a bias due to salinity variations, leading to an erroneous estimation of Mg/Ca-based SST (Mathien-Blard and Bassinot, 2009; Arbuszewski et al., 2010). A strong correlation is found by these authors ($R^2 = 0.76$ and $R^2 = 0.77$ respectively) between residual Mg/Ca temperature ($\Delta T = T_{Mg/Ca} - T_{isotopic}$, where $T_{isotopic}$ is calculated taking into account the oxygen isotopic composition of sea water) and SSS. However, a recent study showed that the large salinity sensitivity inferred from some sub-tropical Atlantic foraminifera with elevated Mg/Ca values (Arbuszewski et al., 2010) could be overestimated (Hönisch et al., 2013). Therefore, we only show the

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Mg/Ca-based ΔT from Mathien-Blard and Bassinot (2009) to compare with our Sr/Ca-based ΔT (Fig. 2, inset). This comparison highlights the important ΔT magnitude difference between foraminifera and corals. Indeed, foraminifera ΔT represent a smaller range ($\Delta T \sim \pm 4\,^{\circ}$C) (Fig. 2, inset) than the coral ΔT ($\Delta T \sim \pm 10\,^{\circ}$C). The reasons for this different behaviour could be biologic and/or mineralogic, but it is beyond the scope of the present study to determine them.

In order to reinforce our preliminary conclusion based on the ΔT approach, we investigated whether Sr/Ca variability could be better explained by two variables (i.e. SST and SSS) than by SST. The coefficient of determination between the SST-SSS-derived Sr/Ca and the original Sr/Ca is lower ($R^2 = 0.28$; p value< 0.01; Fig. 3a) than the coefficient of determination between the SST-derived Sr/Ca and the original Sr/Ca ($R^2 = 0.39$; p value < 0.01; Fig. 3b). In other words, Sr/Ca is better explained by SST only without the need to introduce SSS as a forcing agent. These results clearly confirmed our preliminary conclusion. We see no evidence for a salinity bias on the Sr/Ca paleothermometer at monthly resolution.

Reef-building corals are mainly present in the tropical belt, a region affected by different climate modes (from seasonal to multi-decadal). One of the most studied modes is the El-Niño Southern Oscillation (ENSO) that operates in the interannual band (typically 2 to 7 years) in the Pacific Ocean (Philander, 1990). The instrumental SST record being relatively short in the Pacific Ocean, corals have been used to extend it over the past several centuries and beyond to study the time evolution of ENSO (Cobb et al., 2003a; Nurhati et al., 2010; DeLong et al., 2012). In order to eliminate the seasonal cycle and to highlight ENSO in a proxy or instrumental record, a high-pass filter is traditionally applied. In the case of monthly resolved records, a 25 month Hanning filter is used (Blackman and Tukey, 1958). At the ENSO time scale most filtered records give similar result to the unfiltered one and no correlation between ΔT and SSS is found (Table S1). However, records from Christmas Island, Madagascar and the Gulf of Mexico (*Montastraea*) present a weak but significant relationship between ΔT and salinity variability ($R^2 = 0.37$, $R^2 = 0.34$, $R^2 = 0.33$ respectively) (Table S1). The reason of this

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correlation is unclear but could be due to a coupling between salinity and temperature variations at the interannual timescale. The Christmas Island and Gulf of Mexico instrumental SSS and SST present a low but significant correlation ($r = -0.28$; $p < 0.01$ and $r = -0.56$; $p < 0.01$ respectively) whereas the Madagascar SSS and SST are uncorrelated ($r = -0.25$; $p > 0.01$). Without the generation of further Sr/Ca records at these sites, we cannot conclude whether the Madagascar correlation is fortuitous or due to a yet unidentified cause. Comparison between the two regressions (SST-SSS-derived Sr/Ca vs. original Sr/Ca record and SST-derived Sr/Ca vs. original Sr/Ca record) shows the same results that those obtained with the monthly resolution dataset. The coefficient of determination between the SST-SSS-derived Sr/Ca and the original Sr/Ca is lower ($R^2 = 0.25$; p value < 0.01) than the coefficient of determination between the SST-derived Sr/Ca and the original Sr/Ca ($R^2 = 0.39$; p value < 0.01). Overall, it appears that even at the interannual timescale, salinity has no obvious influence on the Sr-based paleothermometer in corals.

The coral results are in agreement with previous laboratory investigations from Zhong and Mucci (1989). They showed that synthetic aragonite precipitation in seawater solutions of various salinity (from 5 to 44 psu) indicates that the Sr^{2+} incorporation is unaffected by salinity variations. Our results are also in agreement with the recently published work of Pretet et al. (2013) who investigated the effect of salinity on the skeletal chemistry of cultured corals *Acropora* sp., *Montipora verrucosa* and *Stylophora pistillata*.

4 Conclusions

To strengthen our confidence in palaeo SST tracers, we have to test for potential biases. Studies on foraminiferal Mg/Ca thermometry have suggested a bias due to SSS variations, leading to potential erroneous estimation of Mg/Ca-based SST. In the present study, we investigated a possible salinity effect on coral Sr/Ca-based SST reconstructions at monthly and interannual timescales, in open-ocean environmental

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conditions, using a large spatial compilation of published and new coral data (mainly based on the Porites genus). We find no evidence for a salinity perturbation of the Sr/Ca thermometer in corals in open-ocean conditions (in agreement with the coastal studies of Alibert et al., 2003 and Fallon et al., 2003, and the in-vitro study of Pretet et al., 2013), reinforcing our confidence in this tracer. Further work should include culture experiments with the Porites genus, although its slow growth rate has so far hampered its use in-vitro.

Supplementary material related to this article is available online at http://www.clim-past-discuss.net/10/1783/2014/cpd-10-1783-2014-supplement.pdf.

Acknowledgements. The authors would like to thanks Antoine Grémare, Bruno Malaizé and Thibaut Caley for their comments and statistical advices. This research was funded by the CNRS INSU LEFE-EVE, through the Imago program "VADE RETRO" awarded to Thierry Corrège.

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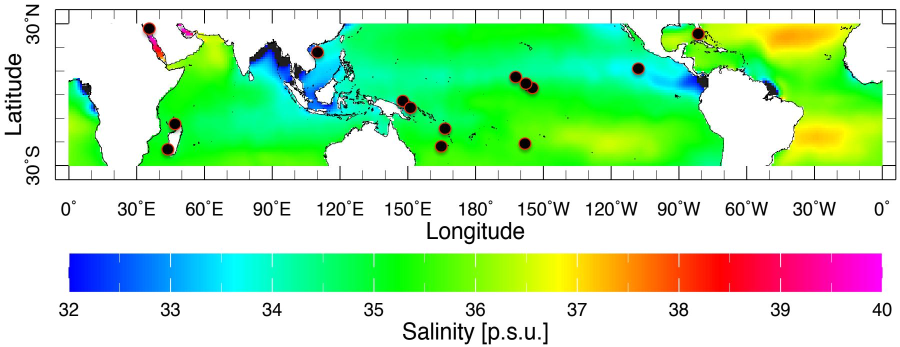

Fig. 1. Study sites plotted over an annual averaged salinity map (Antonov et al., 2006). Coral records location are shown as red circles.

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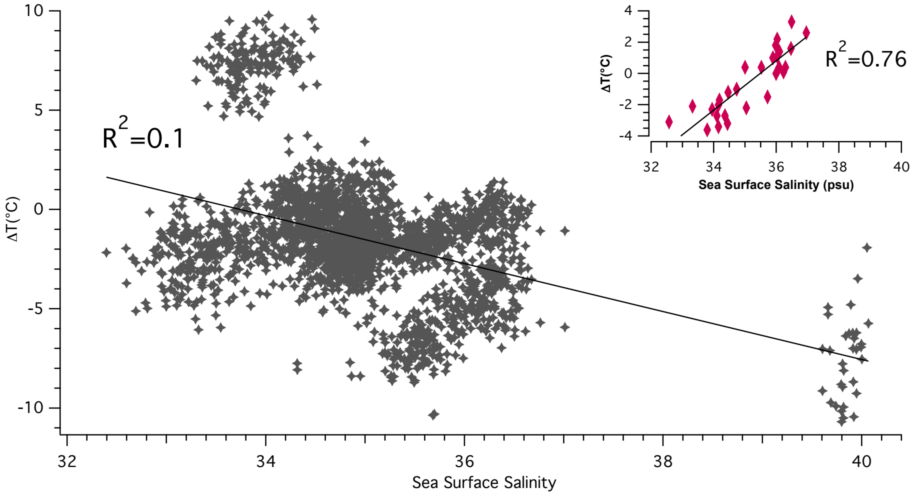

Fig. 2. $\Delta T (= T_{Sr/Ca} - T_I)$ plotted against salinity (SODA SSS v2.2.4, Carton and Giese, 2008) at monthly resolution for all coral data. Inset: $\Delta T (= T_{Mg/Ca} - T_{iso})$ plotted against atlas-derived sea surface salinities (Antonov et al., 2006) adapted from Mathien-Blard and Bassinot (2009).

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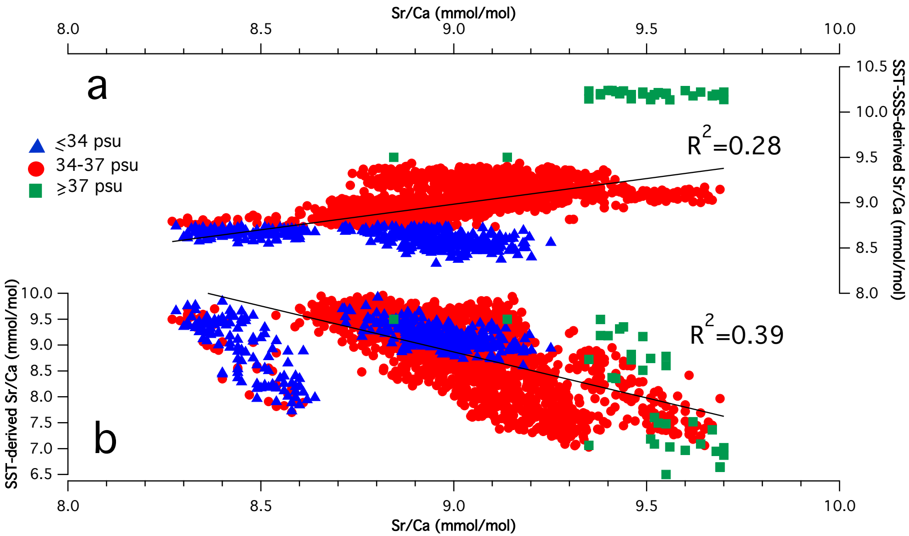

Fig. 3. (a) SST-SSS-derived Sr/Ca obtained from a Multiple Linear Regression (MLR) plotted against the original Sr/Ca record. **(b)** SST-derived Sr/Ca obtained from a Simple Linear Regression (SLR) plotted against the original Sr/Ca record. Data are grouped in 3 groups relative to their correspondant salinity (blue triangles for the data ≤ 34 psu, red circles for the data between 34 and 37 psu and green squares for the data ≥ 37 psu).

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