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Sea-surface temperature reconstruction from trace elements variations of tropical coralline red algae

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ABSTRACT

We used laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) to obtain high-resolution variations of the Mg/Ca, Sr/Ca and Li/Ca composition of free-living forms (i.e. rhodoliths) of the coralline red algal species *Sporolithon durum* in order to test their potential to archive seawater temperature information. A monitoring experiment was conducted based on alizarin red S (ARS) staining of rhodoliths specimens collected in various locations across a ~1 km^2 rhodolith bed in the vicinity of Nouméa, New Caledonia, where *in situ* temperature (IST) variations were recorded for 22 months between November 2009 and August 2011. A >45-year comparison of Mg and trace elements with sea-surface temperature (SST) was established from the analysis of 5 different branches belonging to three of the largest (7.4–8.5 cm in diameter) rhodolith specimens observed at the site. Consistent mean Mg/Ca, Sr/Ca and Li/Ca concentrations and seasonal patterns are found for the rhodoliths' last living years (2009–2011) across 43 branches and for the full 1963–2008 period across the 5 branches. Average elemental concentrations (Mg/Ca: 0.31 ± 0.04 mol/mol; Sr/Ca: 3.5 ± 0.4 mmol/mol and Li/Ca: 0.08 ± 0.02 mmol/mol) fall within range of those found in the literature. Individual element variations show good reproducibility between records and Mg/Ca, Sr/Ca and Li/Ca co-vary systematically. Combined records of Mg/Ca, Sr/Ca and Li/Ca are highly correlated with the IST monthly pattern for the 2009–2011 period ($0.82 < r < 0.91$; $p < 0.001$) and with local variations of monthly SST for the 1963–2008 period ($0.65 < r < 0.85$; $p < 0.001$), with Mg/Ca systematically being the best fit to monthly seawater temperature variations. Inter-annual Mg/Ca anomalies show significant correlation with the Oceanic Nino Index (ONI), indicating that *S. durum* rhodoliths also have the capacity to record the regional climate pattern in the tropical Pacific. Finally, consistent variations between the combined Mg/Ca record in *S. durum* rhodoliths and one Sr/Ca record of a *Porites* sp. coral from the same site, as well as a similar relationship with local SST at both monthly and interannual scales, suggest that *S. durum* rhodoliths have the potential to compare favourably with corals in terms of SST reconstruction.

1. Introduction

Coralline red algae are globally-distributed calcareous marine organisms that deposit a high-magnesium calcite skeleton during growth (e.g. Adey and MacIntyre, 1973; Bosence, 1983b). They occur either as attached forms on hard bottoms or as free-living nodules (i.e. rhodoliths) on unstable substrata (Steneck, 1986) where they can develop into thick crusts or nodules up to 20 cm in diameter (Adey and MacIntyre, 1973; Littler et al., 1991; Frantz et al., 2005). Coralline algae generally exhibit slow growth rates (0.015–2.17 mm/yr – Foster, 2001; Blake and Maggs, 2003; Böhm et al., 1978) and individual organisms can live for more than 800 years (Halfar et al., 2007). This places coralline red algae among the oldest living shallow-water calcifiers (Frantz et al., 2005). As they grow, environmental information may be recorded in their calcite skeletons, including their annual growth pattern, which comprises alternating small cells and heavily calcified cell walls generally produced in winter, and longer cells with less calcified cell walls typically produced in summer (e.g. Halfar et al., 2008; Kamenos and Law, 2010). This commonly appears as paired clear and dark bands on visual examination of sectioned coralline red algae skeletons (Kamenos et al., 2008; Burdett et al., 2010; Kamenos and Law, 2010).

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Providing high-resolution archives is crucial to improve our understanding of climate variability at the seasonal and interannual timescales worldwide. In this endeavour, a number a recent studies have focussed on the climate information that is contained in coralline red algae, both within their growth increment variations and in the geochemical composition of their skeleton (e.g. Halfar et al., 2000). These endeavours have provided critical decadal to century-length reconstructions of environmental parameters, mainly for the northern hemisphere high latitudes (Halfar et al., 2007, 2008, 2011; Hetzinger et al., 2009, 2011; Kamenos, 2010; Chan et al., 2011; Williams et al., 2011). Particularly, the variation in Mg composition of coralline red algae with seawater temperature has proved the most promising tool for palaeo-environmental reconstructions (Halfar et al., 2000; Kamenos et al., 2008; Hetzinger et al., 2009, 2011; Kamenos, 2010). Sr/Ca records in coralline red algae are scarce but have also been shown to present significant, positive correlations with temperature for various high-latitude species (Kamenos et al., 2008; Hetzinger et al., 2011).

Sporolithon durum is widely distributed in oceanic shallow waters, from tropical to temperate-cold environments (e.g. Townsend et al., 1995; Womersley, 1996; Goldberg and Heine, 2008; Basso et al., 2009). It has been reported to live for several decades (Goldberg and Heine, 2008; Darrenougue et al., 2013) and can display annual increments in its growth pattern (Darrenougue et al., 2013), however environmental reconstructions are yet to be generated for this species.

Here, we assess the potential for Mg and trace elements variations in *S. durum* rhodoliths to be used for sea-surface temperature (SST) reconstruction in a tropical environment. This is aimed at confirming the potentiality of coralline red algae as reliable palaeoclimate archives where other proxies (e.g. corals) are absent or unusable. We have used laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) to measure Mg/Ca, Sr/Ca and Li/Ca variations at a monthly to sub-monthly resolution. The results were compared to solution ICPMS and ICP atomic emission spectrometry (ICP-AES) measurements on the same samples to assess the accuracy of the LA-ICPMS calibration. Variations of the studied elements were compared to instrumental records of both *in situ* temperature (IST) and local SST. The Oceanic Nino Index (ONI) was used to investigate the potential of interannual Mg/Ca anomalies in *S. durum* to record regional scale climate pattern. In addition, an evaluation of Mg/Ca in coralline algae as a tool for SST reconstruction was tested against the Sr/Ca record of a *Porites* sp. coral from the same site.

2. Material and methods

2.1. Study site and rhodoliths collection

New Caledonia is a group of islands located in the western tropical Pacific Ocean, ~1000 km offshore Australia. The 8000-km^2 barrier reef on the west side of the main island defines one of the largest lagoons in the world, with an area of 23,400 km^2 (Dandonneau et al., 1981; Labrosse et al., 2000). The typical annual pattern of climate in New Caledonia alternates between a warm and wet austral summer season (Jan–Mar) and a cooler and humid winter season (Jul–Sep). Dry conditions are generally observed in spring (Oct–Dec) and autumn (Apr–Jun). The interannual climatic variations are closely related to the El Niño Southern Oscillation (ENSO) pattern, with cooler and drier conditions during periods of El Niño whereas La Niña periods are generally responsible for warmer temperatures and heavier rainfall (Nicet and Delcroix, 2000).

The Ricaudy Reef (22°18′57″S; 166°27′26″E) is one of the fringing coral reefs that borders Nouméa, the most populated city in New Caledonia (Fig. 1). Ricaudy Reef is located at the southern end of the Sainte Marie Bay in the southwest region of New Caledonia, where seawater within the lagoon is subject to episodic freshwater inputs from the nearby Coulée River (e.g. Fernandez et al., 2006).

All samples studied here were collected at 4–5 m depth by hand using SCUBA from a rhodolith bed that covers ~1 km^2 on the edge of the Ricaudy Reef. The rhodolith samples are monospecific, of ellipsoidal shape and present a degree IV branching structure (according to the classification in Bosence, 1983a).

A small number of rhodolith samples, representative of the size range observed within the bed (~4–8 cm in diameter), were selected for marking and monitoring in February 2011. These specimens were stained onshore for a period of 48 h using alizarin red S (ARS), at a concentration of 7.5 mg/l in seawater taken from the Ricaudy Reef (adapted from Payri, 1997). They were then returned to Ricaudy reef and placed in a ~1 × 1 m^2 mesh enclosure within their natural environment, where they were left to grow for 28 weeks before being retrieved at the end of August 2011. The IST was recorded hourly for the entire period using a TinyTag TG-4100 Aquatic 2 data logger, that had been attached to the enclosure since November 2009.

For longer-term environmental reconstruction, three rhodoliths were collected in October 2009 (for the BSA specimen) and February 2011 (for the MSA and SSA specimens; note that BSA, MSA and SSA are catalogue numbers for the studied rhodolith branches). These specimens were selected for being some of the largest nodules within the bed (7.4–8.5 cm in diameter for SSA and MSA, respectively).

2.2. Mg and trace elements analyses

Rhodoliths were dried and impregnated into araldite resin before being cut into ~5-mm thick sections, parallel to their long axis (Fig. 2A). After polishing and ultrasonic cleaning, the thick sections were oven-dried (40 °C) prior to LA-ICPMS analyses and/or sampling for solution ICPMS and ICP-AES analyses.

43 different rhodolith branches in which the alizarin stain was clearly marked (Fig. 2B), were analysed by LA-ICPMS along with five different branches belonging to the samples BSA (3 branches), SSA and MSA (1 branch each) which were also analysed by solution ICPMS and ICP-AES.

LA-ICPMS analyses were conducted using an ArF excimer laser (193 nm wavelength) and in-house built ANU HelEx laser ablation cell in combination with a Varian 820 ICPMS, at the Research School of Earth Sciences (RSES) of the Australian National University (ANU). The laser ablation sampling was performed using a spot diameter of 42 μm, laser fluence of ~5 J/cm^2 and a pulse rate of 10 Hz. The laser was scanned across pre-defined tracks following the main growth axis along the branches at a speed of 5 μm/s. The ICPMS was set to time-resolved analysis mode using 1 point-per-peak on each of the isotopes ^{7}Li, ^{24}Mg, ^{25}Mg, ^{43}Ca and ^{88}Sr, and different dwell times that resulted in a total integration time of ~1 s per measurement cycle. The same analysis protocol was applied to each run and comprised a pre-analysis ablation to remove surface contamination, and 60 s bracketing measurements of standard materials and background levels before and after the sample acquisition, which typically lasted about 7 min for analyses of the last living years and about 2 h for the longer-term analyses. The data reduction procedure followed that described in Longerich et al. (1996), with ^{43}Ca used as an internal standard to correct for variation in ablation yield. The bracketing background levels were extrapolated to correct for drift in instrumental background noise. The standard deviation of the measured background was used to determine detection limits (defined here as 3σ of the background