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A record of mining and industrial activities in New Caledonia based on trace elements in rhodolith-forming coralline red algae

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Abstract

We investigate the ability of coralline red algae to record historical nickel mining activity that occurred between the early 1960s and 1981 in the Coulée River watershed, southwest New Caledonia. Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) was used to determine high-resolution (sub-annual) variations of trace metal ratios (Mn/Ca, Fe/Ca, Ni/Ca and Co/Ca) in three ~45 years old, free-living forms of the rhodolith coralline red alga *Sporolithon durum* from Ricaudy Reef in the inner lagoon of New Caledonia, 15 km from the Coulée River mouth. We find increased Mn/Ca and Fe/Ca ratio values track the intensity of mining in the Coulée River catchment whereas Ni/Ca ratio values appear more sensitive to the ore type (saprolite versus laterite) that were targeted during two separate stages of mining activity. Mn/Ca, Fe/Ca and Ni/Ca decrease following the cessation of mining in 1981, but did not reach current values until more than 10 years after that date. Surprisingly, Co/Ca variations do not correlate with mining activity but rather increase steadily through the record period. We argue this relates to nickel refining and smelting activity over the past half century. Our results further suggest that the local, inter-annual rainfall variability may influence the metal concentrations recorded in the rhodoliths during the period of intense mining activity, but the link between metal uptake and rainfall is not entirely clear for the entire growth period of the rhodoliths.

HIGHLIGHTS

1. Metal concentrations (Mn/Ca, Fe/Ca, Ni/Ca and Co/Ca) were measured by LA-ICPMS along several branches of rhodoliths formed from 1963 to 2009 in Le Lagon in New Caledonia

2. It was possible to determine annual variations on several branches of the same specimen, through a combination of radiocarbon dates and Mg/Ca related to winter SST lows.
3. Analyses reveal broad changes in the release of metals to Le Lagon coinciding with changes in mining activity (Nickel extraction from the regolith) within the catchment the River Coulée that fed into Le Lagon.
4. Rhodoliths can be used as environmental indicators of metal pollution as indicated in the Fe, Mn and Ni composition of rhodoliths and, therefore, help identify conditions that existed before anthropogenic activities.

1. Introduction

Rhodoliths are free-living forms of coralline red algae that are globally distributed in the shallow-water oceans from the tropics to the poles (Foster, 2001). Coralline red algae play a significant role as carbonate reef builders (e.g. Freiwald and Heinrich, 1994; Steneck et al., 2003), although they grow by secretion of high-Mg calcite at a relatively slow rates that vary from 0.015 to more than 1 mm.y⁻¹ (Foster, 2001), depending on species and environmental factors. Their slow growth rates, combined with the thick crusts that they generally form (often >10 cm, see e.g. Bosence, 1983b), offer the potential to retrieve specimens that have grown continuously for many decades, and in the case of encrusting algal crust up to centuries (e.g. Frantz et al., 2005; Halfar et al., 2007).

Coralline red algae have attracted the interest of the palaeoclimate community due to their potential to act as archives of environmental change, through variations in the growth rate and geochemical composition of their high-Mg calcite skeletons. In particular, Mg/Ca variations in different species have been shown to correlate with *in situ* and regional sea surface temperature (SST) (e.g. Halfar et al., 2000; Kamenos et al., 2008, 2009; Hetzinger et al., 2009; 2011; Halfar et al. 2011; Darrenougue et al., 2014). $\delta^{18}\text{O}$, Sr/Ca and U/Ca variations have also been linked to oceanic temperature (Halfar et al., 2000; 2007; 2008; Kamenos et al., 2008; Hetzinger et al., 2011; Williams et al. 2014), whereas Ba/Ca variations has been linked to salinity changes in the Northwest Pacific (Chan et al., 2011; Hertzinger et al. 2013; and discussion in Adey et al., 2013) Note that all these studies, apart from the ones by Darrenougue et al. (2014) for tropical New Caledonia and Sletten et al. (2017a,b) from the tropical Gulf of Panama), deal with the cold Arctic and to a lesser extent temperate environments. Changing ocean conditions and circulation have also been shown to be recorded in coralline red algae through variations of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ (Halfar et al., 2007; Williams et al., 2011; Frantz et al., 2000). Hertzinger et al. (2012) showed also that the record of Mg/Ca in encrusting coralline algae in the Bering Sea do correlate well with the North Atlantic Oscillation, thus providing

information on past sea-level pressure during the late boreal winter. Growth rate and calcification pattern studies have supported environmental reconstructions of temperature and cloud cover (e.g. Halfar et al., 201a, b; Burdett et al., 2011). In addition, several investigations (Kamenos et al. 2008; Burdett et al. 2015) identified the significant role of coralline algae that host associated bacteria in producing volatile components such as dimethylsulphoioipropionate (DMSP); this clearly contributes to the marine sulphur cycle. This is also followed by the work of Attard et al. (2015) which shows the important contribution of live coralline algal beds to enhancing oxygen in shallow water habitats.

Finally, more recently, growth experiments were conducted to identify how coralline red algae respond to changes in seawater pH as a result of ocean acidification and $p\text{CO}_2$ changes. These studies were conducted on crustose rhodoliths in high latitude and cold water regions, and, as yet, similar work has to be done in warmer and tropical regions where rhodoliths also abound. The current findings suggest that the examination of the Mg-O bond in coralline algae may inform on $p\text{CO}_2$ changes through time in the environment in which the rhodoliths grew, and more particularly for comparison for before and after the anthropogenic addition of atmospheric CO_2 (Pauly et al., 2015; Kamenos et al., 2013; Kamenos et al., 2016).

Anthropogenic input of carbon, nutrients and toxins into the oceans *via* terrestrial runoff is of concern for the sustainability of marine biota. Numerous studies have explored the use of various types of marine organisms to monitor changes in such anthropogenic inputs (e.g. Fichez et al., 2005; Silva et al., 2006). However, only a handful of “biomonitors” are able record such changes with high resolution (subannual) over extended periods of time (decades to centuries). Corals are the most widely used archives of environmental pollution in the tropical waters (e.g. Fallon et al., 2002; McCulloch et al., 2003; David, 2003; Alibert et al., 2003). Adding coralline red algae to the toolbox of high-resolution bio-monitors of anthropogenic impact could extend the geographical range over which studies can be conducted into the extra-tropical and high-latitude regions, as well as broaden the use of coralline red algae as a high-resolution archive of environmental conditions.

In this study, we analysed three rhodolith specimens of the species *Sporolithon durum* to assess their ability to record historical industrial mining activities in southwest New Caledonia. Two papers already dealt with the same rhodolith specimens, one assessing growth and chronologies (specimen BSA; see Darrenougue et al., 2013) and the other on the use of various metals, and in particular the uptake of Mg in the carbonate lattice, as a proxy for sea-surface temperatures (SST) spanning 45 years (also specimen BSA; see Darrenougue et al., 2014) This record was compared against a *Porites* scleractinian coral that grew nearby the rhodoliths and also provided a SST (Montaggioni et al., 2006) with good correlation (r : 0.72; see Darrenougue et al., 2014). A high-resolution record of trace metal (Mn/Ca, Fe/Ca, Ni/Ca and Co/Ca)

variation extending over more than 45 years was obtained along five rhodolith branches from the same specimens mentioned above, using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). We assess the reproducibility of the metal/Ca records along five different rhodolith branches and investigate the pathways leading to the incorporation of these metals into the rhodolith structure. This paper is the first of its kind that shows how rhodoliths can be successfully used to detect environmental pollution through time.

2. Study site and associated mining activities

New Caledonia is located in the South West Pacific, near the tropic of Capricorn, about 1500 km east of Australia (Fig. 1). The main island is ringed by the world's second largest barrier reef. It encloses a lagoon of $\sim 23,400$ km² and is up to 50 m deep (Labrosse et al., 2000). The Ricaudy Reef is adjacent to one of the most populated area of Nouméa, the capital city of the main island and is located at the southern end of Sainte Marie Bay (Figure VII-1). An approximately 3-m deep, 500-m wide channel connects the Sainte Marie Bay to the Boulari Bay, which is under the direct influence of terrigenous input transported by the Coulée River (as shown by Fernandez et al., 2006). Fernandez et al. (2006) demonstrated that, as a consequence of its direct connection to the Boulari Bay, the Sainte Marie Bay receives a significant input of material from the Coulée River. Discharge from the Coulée River is closely linked to seasonal variations in local rainfall and displays a torrential-type of hydrological regime. During dry periods, the Coulée River has reduced discharge ($1\text{--}3$ m³.s⁻¹) and carries a minimal sediment load, whereas during intense rainfall events, discharge can be more than a hundred times higher (e.g. ~ 850 m³.s⁻¹ during cyclone Erica in 2003; Alric, 2009) and river waters are then loaded with sediment eroded from the catchment (Fernandez et al., 2006). The Coulée River catchment rises up to about 500 m above sea level (Alric, 2009) and the steep slopes of the upper watershed have promoted the intense weathering of the magnesium-silicate-rich peridotite bedrock and the development Ni-rich laterite and saprolite ore deposits (Trescases, 1975). Erosion of these weathered profiles results in the transport of particles with high transition metal (Ni, Co, Cr, Fe, Mn) concentrations into the lagoon.

Ni-ore extraction is the main economic resource in New Caledonia, which ranks as the 3rd largest Ni producer in the world. In addition to Ni-ores, mining activities also focus on Co, Cr and Mn extraction using open-cast mining methods that involve an initial deforestation, followed by removal of surficial regolith layers to uncover the exploitable saprolite and enriched laterite profiles. This leads to drastic changes in the natural landscape and leaves the

mined sites exposed to the direct influence of erosion and weathering (Labrosse, 2000; Fernandez et al., 2006).

Mining in the Coulée River watershed started at the beginning of the 20th century with a relatively small scale Ni-extraction occurring from 1904 to 1965, during which ~64,000 tons of Ni were produced (P. Maurizot, *pers. comm.*). Large-scale industrial mining followed, and resulted in the extraction of more than five times the pre-mechanisation production of Ni (~362,000 tons) between 1966 and 1980. Mining activities in the Coulée region ceased in 1981 and since that time, despite attempts at landscape rehabilitation, significant erosion and weathering of the original mining sites have continued to supply silica- and metal-enriched material to the Coulée River (e.g. Fernandez et al., 2006).

FIGURE 1 ABOUT HERE

3. Material and methods

3.1. Rhodolith collection and studied specimens

Three rhodolith specimens formed by the coralline red algal species *Sporolithon durum* (Family Sporolithaceae) were the subjects of detailed study. These rhodoliths were collected from 4-5 m water depth by SCUBA divers on the edge of the Ricaudy Reef (22°18'57"S; 166°27'26"E), New Caledonia, in October 2009 (rhodolith BSA) and February 2011 (rhodoliths MSA and SSA). *Sporolithon durum* is the most abundant rhodolith species in this low-slope, somewhat sheltered environment, reaching concentrations >50 individuals m⁻² and often entirely covering the substrate. All three rhodoliths collected for analysis are spheroidal in shape and are larger than the average rhodolith size at the site, with long axis lengths of 8.1 cm (BSA), 8.5 cm (MSA) and 7.4 cm (SSA). They have thick and very dense branching structures (degree IV in the classification of Bosence, 1983a) that are typical of most *S. durum* at the site (Fig. 2). Of interest is that no dolomite was detected in our *S. durum* specimens in contrast to the crustose coralline alga, *Hydrolithon onkodes* studied by Nash et al. (2009) and that were collected on the Great Barrier Reef offshore northeastern Australia. This is a rather important observation, otherwise it could affect previous interpretation of past SST reconstructions using our specimens (see Darrenougue et al., 2014).

FIGURE 2 ABOUT HERE

The three rhodoliths specimens were oven dried (40°C) before being set in hard resin (araldite) blocks and sectioned along their long axes using a diamond rock saw. This procedure preserves the dense and fragile branch network during sawing. Polished thick sections (2-5 mm-thick) were then cut parallel to each rhodolith's long axis-short axis plane to obtain transverse branch sections for analysis (Fig. 2).

The transverse sections reveal each rhodolith to be monospecific and to have grown continuously over its entire lifetime (as evidenced by the absence of growth discontinuities or hiatuses along branches otherwise indicated by the presence of green algae bands). Growth increments can be clearly seen with the naked eye as well as on high-definition digital images of the samples (see figs. 2, 3 and 6 in Darrenougue et al. (2013)). Reproductive structures (conceptacles) could not be seen by either method and are considered not to be present in any of the studied rhodoliths.

Prior to laser ablation and solution ICPMS analyses, the thick sections were ultrasonicated in Milli-Q water to remove any material that had been redeposited in the pores of the skeleton structure during the cutting process. The sections were then dried in an oven at 40°C overnight.

3.2. LA-ICPMS analysis

Three separate, continuous branches were selected for detailed analysis on the BSA specimen: two branches aligned along the long axis on opposing sides of the nodule (BSA1 and BSA3) and one branch along the short axis (BSA2). Due to the complex three-dimensional structure of the rhodoliths, the cutting procedure did not expose a continuous branch sections from the centre to the edges of either of the MSA and SSA specimens. In these cases, analyses of adjacent branches from the long axes were combined to obtain a complete record of the coralline algae's living period (Fig. 2). This was already carried out successfully in the previous work of Darrenougue et al. (2014) using Mg/Ca bands on the same rhodolith branches.

LA-ICPMS analyses were carried out at the Research School of Earth Sciences (RSES) of the Australian National University (ANU) using a ANU Helex laser ablation system ($\lambda=193$ nm) connected to a Varian 820 ICPMS. For a full description of instrumentation and its analysis capabilities, including the optimization of sampling yields and spatial resolution via ablation in a helium atmosphere and design aspects of the ablation cell the reader is referred to Eggins et al. (1998, 2003). Complete or partial sections of the rhodoliths were placed into the sample holder that enabled the entire length of the targeted branches to be measured using a laser scanning procedure in a single analytical run. This involved defining and cleaning the analysis tracks by pre-ablating the sample surface prior to analysis in order to remove possible surface

contaminants introduced during sectioning. Analyses were conducted using a 42- μm -diameter laser spot, with an applied energy density of 5 $\text{J}\cdot\text{cm}^{-2}$ and laser repetition rate of 10 Hz, which was scanned at 5 $\mu\text{m}\cdot\text{s}^{-1}$ from the centre to the edge of the rhodolith following the growth axis of the branch. This ablation sampling procedure resulted in a trough <20 μm -deep in the rhodolith's skeleton. The analyte isotopes ^{24}Mg , ^{25}Mg , ^{43}Ca , ^{55}Mn , ^{57}Fe , ^{59}Co and ^{60}Ni were measured repeatedly using a peak hopping routine that gave a total integration time of about 1 s for each measurement cycle. The data reduction method followed Longerich et al. (1996), using NIST SRM 612 glass for external calibration with GeoReM preferred concentration values (after Jochum et al., 2011) and ^{43}Ca as the internal standard to correct for laser sampling yield. Typical detection limits (3σ of the background) were $\text{Ca}=0.02\%$ w.w $^{-1}$, $\text{Mn}=0.5\ \mu\text{g}\cdot\text{g}^{-1}$, $\text{Fe}=5\ \mu\text{g}\cdot\text{g}^{-1}$, $\text{Co}=0.3\ \mu\text{g}\cdot\text{g}^{-1}$ and $\text{Ni}=1\ \mu\text{g}\cdot\text{g}^{-1}$. Results are presented as element/Ca molar ratios in the supplementary section to be made available on the journal's website (e.g. Mn/Ca , Fe/Ca – $\mu\text{mol}\cdot\text{mol}^{-1}$). Background count rates with laser off were determined and the NIST SRM 612 glass analysed before and after every rhodolith branch scan and used to correct for any instrument drift during the analytical run. The combination of the laser ablation speed and ICPMS integration time produces a nominal spatial increment of $\sim 5\ \mu\text{m}$ per data point. These data were subsequently averaged over 6 measurement cycles to realise a final spatial resolution of $\sim 30\ \mu\text{m}$, that corresponds to monthly to sub-monthly growth intervals given a typical extension rate of $0.6\ \text{mm}\cdot\text{yr}^{-1}$ for the specimens analysed.

3.3. Solution ICPMS analysis

Approximately 1 mg samples of calcite powder were hand drilled along the long axes of the BSA and MSA nodule, in order to closely match the LA-ICPMS sampling strategy. These samples were weighed and dissolved in ultrapure 2% HNO_3 to 1000x dilution for solution ICPMS analysis. The same elements were measured using identical mass spectrometer settings as used for LA-ICPMS analysis. Four standard solutions, prepared from "AccuTrace" reference standard solutions (National Institute of Standards and Technology), were used to generate calibration curves, and a solution of pure 2% HNO_3 was used as a blank. Internal standards were also used. Three calibration curves were established, before, mid-way and at the end the analytical run to correct for instrumental drift. Repeats of a single sample and blanks were measured throughout the run to assess the analytical reproducibility and the detection limits (3σ of the blanks, $n=6$) for each element which were as follows: $\text{Ca}=59\ \mu\text{g}\cdot\text{g}^{-1}$, $\text{Mn}=49\ \text{ng}\cdot\text{g}^{-1}$, $\text{Fe}=16\ \mu\text{g}\cdot\text{g}^{-1}$, $\text{Ni}=85\ \text{ng}\cdot\text{g}^{-1}$, $\text{Co}=8\ \text{ng}\cdot\text{g}^{-1}$. All measured analyte concentrations in the samples were at least 17 times higher than the corresponding detection limit, and the analytical reproducibility (1σ) was 1.8% (Ca), 0.9% (Mn), 3.6% (Fe), 2.8% (Ni) and 3.9% (Co).

3.3. Chronology based on Radiocarbon dating, seasonal Mg/Ca cycles, and annual band counting

The chronologies on the different analysed branches were established using a combination of radiocarbon dating, and counting of seasonal growth bands and seasonal Mg/Ca cycles. This was already achieved in a previous paper that dealt with the same branches of the same rhodolith discussed herewith (see Darrenougue et al., 2013). In summary, for rhodolith BSA that is discussed in the present paper, two branches were radiocarbon dated: from a long branch, 10 samples, 10 mg each, were dated, and from a short branch, another 10 samples, also 10 mg each, were dated. Radiocarbon dating was carried out using the single stage accelerator mass spectrometer (SSAMS) at RSES, ANU (see Fallon et al., 2010; Darrenougue et al., 2013). The original results obtained in percent Modern Carbon [pMC] were calibrated against a pMC curve obtained by Fallon et al. (2003) from Vanuatu following the atomic bomb curve from the 1950s. This was carried out as both Vanuatu and New Caledonia are both located in the northwestern edge of the South Pacific Gyre that is likely to produce similar trend in ^{14}C enrichment after the atomic tests. Because the samples used for dating were somewhat large, Darrenougue et al. (2013) estimated that the uncertainty for every date was close to one to two years. In addition, Darrenougue et al. (2013), using the determination of seasonal Mg/Ca cycles along each rhodolith branch, related the low points in Mg/Ca cycle (that relate to the coolest months) to anchor points with the coolest months of successive years in SST. This enabled to determine a good annual chronology for the studied rhodolith branches. In addition, a plot of the annual extension rates calculated for the rhodolith branches are already presented in Darrenougue et al. (2013, Fig. 9, Tables 2-3; see also Supplement 1 linked to that publication). Both latter methods gave concordant results, as found in previous studies of other species of coralline red algae (e.g. Hetzinger et al., 2009; 2011; Burdett et al., 2010; Gamboa et al., 2010). We used an easily identifiable match between overlapping Mg/Ca cycles from different branches of the MSA and SSA specimens to construct a single master Mg/Ca record for each rhodolith specimen. The resulting chronologies for each branch were employed with the data analysis software AnalySeries (Paillard et al., 1996) to convert the LA-ICPMS results to a common temporal scale with monthly resolution.

4. Results

4.1. Trace elements records

4.1.1. Solution ICPMS results and comparison with LA-ICPMS results

Variations in the concentrations of Mn, Fe, Ni and Co determined by solution ICPMS are consistent with variations in respective metal/Ca ratio values determined by LA-ICPMS analysis for the same branch parts of the BSA and MSA rhodoliths (Fig. 3).

Comparison between the elemental concentrations obtained by solution ICPMS and by LA-ICPMS (calculated assuming constant Ca concentration for every sample and using the average Ca concentration value obtained from solution ICPMS measurements) shows very similar results for Mn and Co. It was then possible to assign absolute element concentrations to the Mn/Ca and Co/Ca values reported in Fig. 3. The absolute Mn concentration in *S. durum* ranges from 5-10 $\mu\text{g.g}^{-1}$ for the youngest part of the branches, to 11-34 $\mu\text{g.g}^{-1}$ for the oldest part. Co concentrations vary from 0.4 to 1.0 $\mu\text{g.g}^{-1}$ for the 2000s period to 0.2-0.4 $\mu\text{g.g}^{-1}$ for the older parts. Solution ICPMS, Fe and Ni analyses appear to be affected by relatively high levels of interference resulting in slightly higher apparent bulk concentrations compared to values obtained using LA-ICPMS. The concentrations of Fe along the rhodolith branches range from 48 to 77 (1.5 to 2) $\mu\text{g.g}^{-1}$ for the 2011-early 1980s period, and for Ni they range between 30 to 350 (2 to 5) $\mu\text{g.g}^{-1}$ in the early 1960's to mid 1970's period.

FIGURE 3 ABOUT HERE

4.1.2. LA-ICPMS results

The trace elements concentrations measured by LA-ICPMS for the five rhodolith branches are presented in Fig. 4. The chronology applied to each branch and used to convert distances along the laser tracks to calendar years is also shown in that figure at the top of each plot. The reproducibility of the profiles was tested by running two parallel tracks only a few mm apart under the same experimental conditions along the BSA2 branch (Figure 5). A close match is observed for each elemental ratio (Mn/Ca, Fe/Ca, Ni/Ca and Co/Ca) measured along the two parallel tracks ($0.77 < r < 0.83$; $p < 0.0001$). The resulting record for the BSA2 branch which is presented in Figure 3 represents the average of the two parallel tracks.

FIGURE 4 ABOUT HERE

The patterns of Mn/Ca, Fe/Ca and Ni/Ca variation are broadly consistent between the different rhodolith profiles, and show two distinct compositional regions that are separated by a transition zone (Fig. 4). The first region corresponds to the eldest portion of the branches, from the approximately 1963 until the mid-1970s. The second region corresponds to the youngest parts of the branches, from the early 1980s until the time of rhodolith collection, viz, 2009 [BSA specimen] and 2011 [MSA/SA specimen]. The metal/Ca ratios vary from one specimen to another. For the three branches of the BSA rhodolith, Mn/Ca values average $14.4 \mu\text{mol.mol}^{-1}$, and a similar value is obtained for the SSA sample ($13.6 \mu\text{mol.mol}^{-1}$). However, the average Mn/Ca value for the MSA rhodolith is significantly higher at $29.9 \mu\text{mol.mol}^{-1}$. In the oldest parts of each branch, Mn/Ca concentrations increase by between 2.0 and 4.8 times (BSA2 and SSA, respectively), reaching values of 31.3 to $85.8 \mu\text{mol.mol}^{-1}$ in the BSA and MSA specimens, respectively (Fig. 4). Fe/Ca concentrations vary from 0.14 (BSA) to 0.27 (MSA) mmol.mol^{-1} for the early 1980s to collection period, and from 0.3 to $0.78 \text{ mmol.mol}^{-1}$ for the oldest parts, corresponding to a 1.9 to 3.6 times increase (BSA2 and SSA, respectively). In the most recent part of the branches, Ni/Ca values range from 3.9 to $5.6 \mu\text{mol.mol}^{-1}$ in all records, and increase by a factor of 1.3 to 3.0 (SSA and BSA3, respectively) to 5.7 to $9.9 \mu\text{mol.mol}^{-1}$ within the bottom parts of the branches. The Co/Ca concentration ranges from 0.7 to $3.1 \mu\text{mol.mol}^{-1}$ with the highest values (1.4 to $3.1 \mu\text{mol.mol}^{-1}$) generally occurring during the 2000s and the lowest (0.7 to $0.9 \mu\text{mol.mol}^{-1}$) in the older parts of the branches. There is a significant decrease (1.4 to 3.6 times) towards the earlier parts of the records (i.e. early 1960s).

FIGURE 5 ABOUT HERE

Despite differences in metal concentrations between branches, each element displays a similar overall pattern of variation with time. Moreover, Mn/Ca and Fe/Ca variation are strongly coupled in each profile and, to some extent Ni/Ca also follows a similar pattern of variation. For these metals, the early 1960s to mid 1970s period of each branch displays high-frequency variations that are higher in amplitude than for the youngest parts of the records. For most branches, a slight decrease in Mn/Ca and Fe/Ca occurs from the early to late 1960s. For the early 1980s to the 2011 period, each branch exhibits generally constant low values with sporadic, high-frequency peaks. The amplitude of these peaks is typically greater for Mn/Ca than for Fe/Ca and is the least pronounced for the Ni/Ca signals.

The Co/Ca variation pattern, with the absence of higher Co/Ca values in the oldest part of the analysed branches in addition to an increase in concentrations towards the youngest part of the records, differ drastically from what is seen for the Mn/Ca, Fe/Ca and Ni/Ca variations.

4.2. Trace element profile reproducibility

The reproducibility of trace elements in the rhodoliths skeleton is based on monthly data for each LA-ICPMS record and was tested at three different scales: intra-branch, intra-rhodolith and inter-rhodolith. The distribution of trace elements within a single rhodolith branch is compared long two parallel LA-ICPMS profiles of the BSA2 branch (Fig. 5). The variability between different branches of the same rhodolith is assessed using the profiles obtained for three branches from the BSA specimen. The reproducibility between rhodoliths is based on the average compositional profiles obtained from the BSA, MSA and SSA rhodoliths. Correlation coefficients for the four ratios (Mn/Ca, Fe/Ca, Ni/Ca and Co/Ca) are based on the monthly data for the 1963-2009 period and are presented in Table 1.

Within the BSA2 branch, Mn/Ca and Fe/Ca variations follow very similar patterns and show a high degree of reproducibility ($r=0.82$ and $r=0.83$, respectively; $p<0.0001$), that is slightly greater than that obtained between Ni/Ca and Co/Ca profiles ($r=0.77$; $p<0.0001$, for both).

TABLE 1 ABOUT HERE

The reproducibility of metal/Ca profiles between branches of the same rhodolith is generally much weaker. Mn/Ca and Fe/Ca in different branches display correlation coefficients that range from $r=0.28$ to $r=0.63$. The lowest correlation coefficients occur between the two branches that are perpendicular to each other, and correspond to the long (BSA1) and short growth axes (BSA2). Nevertheless, these correlation coefficients are significant at the 95% confidence interval ($r=0.28$ for Mn/Ca and $r=0.41$ for Fe/Ca). Correlation coefficients for Ni/Ca within the three branches of the BSA rhodolith range from $r=0.42$ to $r=0.61$ and are also statistically significant. This contrasts with the correlation coefficients obtained for Co/Ca, which are not statistically significant, except in for the BSA2-BSA3 branch comparison which is only weakly significant ($r=0.21$; $p<0.05$). For an explanation, refer to the discussion section below.

For the between rhodolith comparison, both Mn/Ca and Fe/Ca display good reproducibility ($0.62<r<0.70$ for Mn/Ca and $0.74<r<0.83$ for Fe/Ca; $p<0.0001$). Ni/Ca variations are more weakly correlated ($0.43<r<0.59$; $p<0.0001$) as found for the intra-specimen comparison. In the case of Co/Ca, the profiles from SSA and MSA are in good agreement ($r=0.60$; $p<0.0001$) but, when compared with the BSA profiles, the reproducibility is weak, although still significant at the 95% confidence interval (Table 1).

5. Discussion

5.1. Trace metal variability and incorporation into the rhodoliths

The agreement between the trace element profiles along parallel tracks on the same branch indicates Mn, Fe, Ni and Co are consistently incorporated into the rhodoliths at the branch scale. However, some variability is observed between records of different branches from the same rhodolith at different time scales. Nevertheless, consistency of the results give us some confidence in our results and interpretation.

Within an individual rhodolith, the greatest difference occurs between the long and short axes of growth profiles (particularly for Mn/Ca and Fe/Ca). This might be due to a combination of physical parameters. The surface sediments in the Sainte Marie Bay are enriched in trace metals (Dalto et al., 2006; Debenay and Fernandez, 2009) such that significant diffusive fluxes from the sediments to the water column are likely to occur (see Grenz et al., 2010), with dissolved metal concentrations decreasing very rapidly across the water-sediment interface where rhodoliths live. It is therefore possible that different parts of a rhodolith are exposed to seawater with very different metal concentrations, and resulting in the variability recorded in different profiles within the same rhodolith. Any overturning of the rhodoliths would further contribute to such variability within rhodoliths.

Dissolution or recrystallisation processes are unlikely to contribute significantly to the metal concentration variability evidenced by back scattered electron images of different parts of branches that show consistent and apparently unmodified cell structures from the margin to the centre of the studied rhodoliths (Fig. 6). One cause of this variability may be linked to the uncertainties with the age model, which is determined for each branch individually. Indeed, the linear interpolation of the trace-element signals between every summer and winter peak would result in a mismatch in the monthly data across branches when the sub-annual extension rates differ. It is important also to stress that Mg/Ca values are lower in the eldest part of the record, but these are not caused by partial dissolution/alteration nor diagenesis as the SST trends calculated from the Mg/Ca in the rhodolith branches match well with the progressive SST (local) instrumental records (refer to Fig. 9 in Darrenougue et al., 2014).

FIGURE 6 ABOUT HERE

Already, in the New Caledonian lagoon, oxygen and nutrient fluxes from the sediments to the overlying water are spatially highly variable (Grenz et al., 2010), and this could explain

some of the inter-rhodolith heterogeneity. Fish feeding and grazing activities, which can resuspend sediment locally in reefal environments (Yahel et al., 2002), may also contribute to variable amounts of available trace metals in the water column across the rhodolith bed. However, it is uncertain for how long this occurs and, therefore, may not even show up in the record of the rhodoliths. In addition, rhodoliths can roll around during storm activity and also be moved by bioturbators such as fish and large invertebrates (refer to Marrack, 1999 for evidence in the Gulf of California) and, consequently, parts of the rhodoliths in contact with the sea-floor sediment may stop growing during that period.

For different rhodoliths, an active role of the alga in the incorporation of trace metals might explain some of the observed variability. Table 2 presents an estimate of the distribution coefficients (K_D) of the corresponding divalent cations (Mn^{2+} , Fe^{2+} , Ni^{2+} and Co^{2+}) into the high-Mg calcite of rhodoliths based on seawater analyses conducted by Moreton et al. (2009) near Anse Vata. In order to establish the K_D for our rhodoliths, we only used the average Mn/Ca, Fe/Ca, Ni/Ca and Co/Ca concentrations (in $\mu mol.mol^{-1}$) in the 'modern' portion of the rhodolith (see Table 2). Note that Ca concentration value was calculated as the average of 9 solution ICPMS measurements of seawater samples collected bi-monthly at the Ricaudy Reef between October 2009 and February 2011 (unpublished data). Published K_D values for Mn^{2+} , Fe^{2+} , Ni^{2+} and Co^{2+} for abiotic calcite are also displayed for comparison. Although the absence of any symbiont-mediated feeding process in coralline red algae (as it is the case, for example, in corals through zooxanthellae - e.g. Harland and Nganro, 1990; Harland et al., 1990; Fallon et al., 2002) eliminates a potential source of biological intervention in the metal incorporation into the rhodoliths, the K_D for Fe in the rhodoliths is ~ 100 times higher than for abiotic calcite (Table 2) and indicates a strong contribution of the coralline red alga in the uptake of Fe from the dissolved phase of seawater. It is important to note that the K_D values analysed here for the rhodoliths are only an indication of what may be happening at the site and are subject to various sources of uncertainty. Indeed, trace metal concentrations in seawater used here were not measured exactly at the Ricaudy Reef but at the Anse Vata Bay, a few kilometres from the rhodolith bed (Moreton et al., 2009). Due to the high spatial variability of trace metal concentrations in the SW lagoon of New Caledonia (Migon et al., 2007), this can have a significant effect on the actual K_D value calculated for the study site. Also, considering that the water-sediment boundary layer is enriched in trace metals would result in lower K_D values than calculated here. The rapid average extension rate of *S. durum* (Darrenougue et al., 2013) is another factor that may influence to some extent the K_D values in the rhodoliths (Rimstidt et al., 1998). Therefore, although a vital effect in Fe incorporation seems to be suggested by our results, a more reliable quantification of the distribution coefficients of Mn^{2+} , Ni^{2+} and Co^{2+} in *S. durum* rhodoliths, potentially using culture experiments, is needed to better understand the

role of this phenomenon considering for the variability between and within rhodoliths, rhodoliths are particularly good at recording significant changes in environmental metal concentrations with high temporal resolution.

TABLE 2 ABOUT HERE

FIGURE 7 ABOUT HERE

The significance of the living component of the *S. durum* rhodoliths in the Co distribution is illustrated by the decrease in Co/Ca concentration in the outermost part of the MSA branch after H₂O₂ treatment (Fig. 7). This indicates that approximately 60% of Co in the modern part of the branch was bound to actual or remnants of organic matter, which is a potential source of variability for Co/Ca distribution between rhodolith branches as well as rhodolith specimens. H₂O₂ treatment had no significant effect on the average Mn/Ca, Fe/Ca and Ni/Ca concentrations along the MSA branch (Fig. 7), suggesting that these elements are not controlled by organic matter distribution in the rhodoliths and are likely to be incorporated in the calcite structure.

In summary, variations of Mn/Ca, Fe/Ca, Ni/Ca and Co/Ca concentrations in *S. durum* rhodoliths are subject to various sources of uncertainties that would affect the monthly-resolution data. Therefore, although the reproducibility of monthly data at every level (from a single branch to inter-rhodolith) is statistically significant at the 95% confidence interval (except for two Co/Ca profiles), for the purpose of environmental studies, it seems more reasonable to average the records of several rhodolith branches and to focus on the annual to inter-annual resolution patterns of metal variations.

5.2. Rhodoliths as a proxy for mining activities: Mn/Ca, Fe/Ca and Ni/Ca

Fig. 8 compares metal variations in the rhodoliths with the intensity of the mining activities for the period 1965-2008, specifically with the total extracted material and Ni concentration of the extracted material from the Coulée River watershed. Inter-annual changes in rainfall for Nouméa city are also shown for the same period. The average Mn/Ca and Fe/Ca variations can be seen to closely follow each other and to broadly track the intensity of mining production from the Coulée River watershed for the 1965-1981 period. Ni/Ca variations show a similar pattern but the relationship to the mining production curve is less clear, especially during the early phase of mining. These differences in the behaviour of Mn/Ca and Fe/Ca on the one hand and Ni/Ca on the other can be explained by the change in ore type during the two main principal stages of nickel mining activity in the Coulée region. These are as follows:

(1) Prior to the 1960s, small-scale mining activities in the Coulée region (and elsewhere in New Caledonia) targeted saprolite formations as they contain thin layers of garnierite bearing ore with very high Ni concentrations, of up to 37% (Trescases, 1975; P. Maurizot, *pers. comm*), and low Mn and Fe concentrations. The initial phase of larger-scale industrial mining in the Coulée basin (1960-1970), continued to target the saprolites but as their availability decreased, as indicated by the decrease in percentage of Ni extracted relative to the total amount of extracted material (Fig. 8), mining transitioned to laterite formations with lower Ni concentrations (1-2% w.w⁻¹) and higher concentrations of Fe and Mn (Baltzer and Trescases, 1971; Trescases, 1975). This transition is matched in the geochemical composition of the rhodoliths over the 1960-1970 period, where Mn/Ca and Fe/Ca increase with the overall amount of extracted material (and extracted laterite ore) and Ni/Ca concentrations drop with the decrease in saprolite excavation (Fig. 8).

(2) Laterites were mined following the peak of mining activity (late 1960s-early 1970s), as indicated by the low percentage of Ni in the extracted material. This period corresponds to the highest Mn/Ca and Fe/Ca values in the rhodoliths as well as lower, but still elevated Ni/Ca concentrations. From this time on, Mn/Ca, Fe/Ca and Ni/Ca show similar trends in accordance with the laterite-derived erosion products entering the lagoon.

FIGURE 8 ABOUT HERE

The fact that Ni/Ca concentrations in the rhodoliths during the peak of mining activities (and thus, the peak of overall Ni extraction) are lower than for the onset of the industrial mining at the site over the 1960-1970 period illustrates the complex behaviour of nickel in this particular type of environment. In addition, the transition from saprolite to laterite extraction in the highlands of New Caledonia implies different amounts of Ni being released aqueously within the ambient environment and subsequently transported fluvially (see Ambatsian et al., 1997). During the weathering of the coarse-grained saprolite formations, significant amounts of dissolved Ni can be exported as Ni tends to behave as a “satellite” element of the very soluble Mg and Si (Trescases, 1975). In contrast, in the fine-grained laterite formations, Ni is mostly bound to Fe oxides and to a lesser extent Mn oxides and is less soluble. Accordingly, the dominant mode of Ni transport from the laterites to the lagoon is *via* eroded particles during heavy rainfall events (Baltzer and Trescases, 1971; Ambatsian et al., 1997). Hence, although the amount of Ni entering the lagoon would have been higher during the peak of mining activity and laterite extraction, it may be that Ni may have been more readily ‘available’ in the

saprolites (making it more available for co-precipitation with carbonates) and this would explain the higher Ni/Ca concentrations observed in the rhodoliths during the first stage of industrial mining rather than the peak period. Furthermore, what could be interpreted as pseudo-annual “cyclicity” can be observed in the average Ni/Ca record for the 1965-1970 period and might reflect the seasonal weathering/erosion of the exposed saprolites associated with the seasonally contrasted precipitation regime in the region.

After mining activity ceased in 1981, rhodolith Mn/Ca, Fe/Ca and Ni/Ca ratios continued to display elevated but decreasing values relative to today. This suggests weathering and erosion of the mining sites continued to supply enhanced metal fluxes to the lagoon. However, metal concentrations in the rhodoliths decreased rapidly within the first few years following the cessation of mining, and then more gradually, reflecting decreased susceptibility of the original mining sites to erosion/weathering with time. Present-day Mn/Ca, Fe/Ca and Ni/Ca concentrations in the rhodoliths were reached in the early 1990s, more than 10 years after the mining activities stopped.

5.3. The case of cobalt

Surprisingly, Co/Ca does not follow the mining activity pattern although it has been shown to be generally closely related to Mn in laterite formations (Trescases, 1975; Ambatsian et al., 1997). One explanation might be that Co is highly concentrated only in transitional absolane formations that are located between the saprolites and laterites (Trescases, 1975). Moreover, absolane formations are not present everywhere in the region (P. Maurizot and J-M Fernandez, *pers comm.*) and may not have been extracted during mining activities in the Coulée watershed. As a consequence, no enrichment occurred in dissolved Co entering the Bay where it could be recorded by the rhodoliths, but we cannot disprove this phenomenon.

Another potential explanation for the absence of any Co/Ca enrichment in the rhodoliths during the industrial mining period might be found in the way Co is assimilated by *S. durum*. We showed that a significant part of the Co is bound to organic matter in the surface layers of the organisms. These outermost layers display a pinkish to brownish colour (see Figs. 2, 6), most likely due to the presence of pigments possessed by the coralline red algae. This colouration disappears in older parts of the skeleton, suggesting these pigments have decayed and are no longer present. This interpretation is supported by Co/Ca variations below the first few millimetres of the MSA branch remaining very similar after H₂O₂ treatment to remove organic matter (Fig. 7). The progressive increase of Co/Ca values during the last decade of record in the rhodoliths (Fig. 4) can be explained in a variety of ways. For example, Dalto et al. (2006) showed that Co is abundant in the surface sediments of the Boulari/Sainte Marie Bays with a decreasing gradient in Co concentration from the Coulée River mouth outward into the

lagoon, thus indicating that a significant contribution of the Co reaching the Recaudy Reef site originates from the Coulée River watershed. Another potential source of Co to the Ricaudy Reef site is the proximity of the major nickel-smelting factory (SLN – Société Le Nickel). Macholz (1982) measured the highest atmosphere concentrations of Co adjacent to a nickel refinery in Wales and demonstrated that Co was a by-product of Ni-smelting. Salmon et al. (1978) also reported enrichment in Co in the atmosphere around industrial sites compared to rural areas. It follows that continued expansion of nickel production in New Caledonia has been associated with an increasing source of Co to the atmosphere over the last decades.

In conclusion, even although Co/Ca variations in the rhodoliths do not seem to record the historical mining activity in the Coulée region, they may be recording the industrial expansion of nickel refining activity and/or vehicle exhausts from the city of Nouméa.

5.2. Metal records and the local rainfall pattern

Variation in local, inter-annual rainfall cannot be linked to some of the variation observed in rhodolith metal contents, especially during the period of mining activity (Fig. 7). Although an increase in excavated laterite material is likely to be the main driver in the rise of Mn/Ca and Fe/Ca between 1963 and 1969, the period from 1965 to 1968 was also associated with elevated rainfall over Nouméa, and likely enhanced erosion within the Coulée watershed. A subsequent decrease in rainfall during the period 1969 to 1971, may consequently account for a decrease in rhodolith metal contents. Although the mining production continued to increase during this time of low precipitation, a slight decrease is recorded in the Mn/Ca and Fe/Ca concentrations, suggesting a possible reduced supply of dissolved Mn and Fe to the lagoon. Higher Mn/Ca and Fe/Ca values in subsequent years may reflect both higher rainfall and a period of very active mining, but it is not possible to distinguish between both effects.

After mining stopped, Mn/Ca and Fe/Ca concentrations in the rhodoliths decreased steeply and the influence of local rainfall is more difficult to discern in the rhodolith metal records, with exception of a slight increase in Mn/Ca, Fe/Ca and Co/Ca between 1986 and 1990 that corresponds to a period of elevated precipitation. The Mn/Ca values for the period preceding 1990 appears to follow the broad precipitation changes, but this is not entirely consistent for the earlier part of the record as, for example, the two obvious Mn/Ca peaks seen during the period of 1978 and 1980 do not match with high rainfall records. Finally, the inter-annual rainfall pattern shows no clear correlation with the rhodolith metal concentrations after 1993.

6. Conclusion

The observed variability of trace metals, both in absolute concentrations and in the LA-ICPMS profiles makes the use of monthly resolution data from a single *S. durum* rhodolith

branch unreliable for obtaining environmental information. However, considering broad variations of averaged trace metals profiles enables us to record historical mining activities in the Coulée region of New Caledonia. Increased Mn/Ca and Fe/Ca concentrations reflect the intensity of the mining activity from 1965 to 1977, while Ni/Ca variations appear sensitive to the type of excavated material (Ni-rich saprolites versus relatively Ni-poor laterites). Concentrations in Mn/Ca, Fe/Ca and Ni/Ca steeply decrease in the rhodoliths after the cessation of mining. However, present-day values are not reached until 1993, indicating a response-time of the system of more than ten years. We found that Co/Ca in the rhodoliths is not associated with mining activity but, instead, a slight steady increase over the last decade may be related to atmospheric pollution from the smelter adjacent to the city of Nouméa where nickel ore is being processed, but we have no way of verifying this assumption..

We also suggest that trace metal variations in *S. durum*, especially Mn/Ca and Fe/Ca, may be sensitive, to some extent, to local rainfall variability. However, further work is required to establish why this sensitivity only appears when metal concentrations in the rhodoliths are relatively high. Studies at sites more prone to have a quicker rainfall/metal concentration response (e.g. closer to a river mouth) would be critical to assess this characteristic.

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ACCEPTED MANUSCRIPT

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FIGURE AND TABLE CAPTIONS

Fig. 1. Map of the studied area showing the Ricaudy Reef (star) in New Caledonia, offshore the city of Nouméa and the extent of the Coulée River watershed (dashed line).

Fig. 2. Photographs of the rhodolith samples studied. Top-left: Whole rhodoliths after collection from the Ricaudy Reef. Note the high branch density. Top-right and bottom: photos of transverse sections across the BSA, MSA and SSA rhodoliths (refer to text for more information on terminology). The dashed lines display the laser ablation tracks. The dark colouration surrounding the branches represents empty space or organic stains that are not derived from the coralline red algae.

Fig. 3. Comparison and calibration plots between metal concentration data obtained from solution ICPMS and elemental molar ratios over Ca recorded by LA-ICPMS for Mn, Fe, Ni and Co from the BSA and MSA rhodoliths. Solution ICPMS data points represent individual samples drilled along different branches for each rhodolith (dots). LA-ICPMS values (squares) were obtained by averaging the record corresponding to the same distance interval as the solution ICPMS samples for each rhodolith. For the BSA individual, the LA-ICPMS values were obtained from the average signal of the 3 branches analysed for that same rhodolith. Vertical error bars for the LA-ICPMS data points corresponds to 2σ for any particular distance interval. Vertical error bars for the solution ICPMS data points are too small to be displayed. Note that absolute concentrations displayed here for Fe and Ni are derived from the LA-ICPMS results and do not correspond to the solution ICPMS results (see text for details).

Fig. 4. LA-ICPMS records of Mn/Ca, Fe/Ca, Ni/Ca and Co/Ca variations obtained along 5 different branches of 3 individual rhodoliths. Original, raw data have been smoothed with a 6-points average and are represented on the bottom axes of each profile against distance from the outside (most recent) layer of the branches. The chronology for each branch is also displayed above each plot and permits the correlation of the original distances with any particular year. Note the varying annual growth rates recorded for each profile. The BSA2 record and some parts of the SSA record correspond to the average signal of two parallel tracks (for BSA2) and parts of two overlapping branches (for SSA).

Fig. 5. LA-ICPMS record of two parallel tracks measured along the same rhodolith branch (BSA2) for Mn/Ca, Fe/Ca, Ni/Ca and Co/Ca. Distance goes from the top (most recent) layer towards the bottom (oldest part) of the branch. Correlation coefficients for each profile show the reproducibility of the results.

Fig. 6. Light microscope (left) and back-scattered electron (BSE) (right) images of different parts of a branch for the BSA specimen from the youngest portion of the branch (top) to the oldest part of the rhodolith (bottom), with an intermediate step in between (middle). Note the similar cell structure and alignment for each of the three parts of the branch, suggesting that no major dissolution/recrystallisation process occurred.

Fig. 7. LA-ICPMS record of Mn/Ca, Fe/Ca, Ni/Ca and Co/Ca from two parallel tracks carried out along the same rhodolith branch (MSA1). Grey records are before the 15% H₂O₂ treatment aimed at removing the organic matter from the branch, and the coloured records are after the 15% H₂O₂ treatment was applied. Correlation coefficients for each profile show the reproducibility of the results.

Fig. 8. Variations in average Mn/Ca, Fe/Ca, Ni/Ca and Co/Ca for the 1963-2008 period compared to annual total mining production and percentage of nickel extracted over the total amount of material extracted in the Coulée area between 1961 and 1981 (data from the Direction des Mines et de l'Energie de Nouvelle Calédonie – DIMENC) and 3-years smoothed rainfall anomaly over Nouméa from 1961 (monthly data obtained from Météo France). The average metal variations (thick lines) were obtained using the mean of monthly-resolved values for each branch analysed with LA-ICPMS. The shaded area surrounding the average signals is $2\sigma_M$ (std err) for each mean value. The different stages of mining activity in the Coulée region are separated by the vertical dotted lines.

Table 1. Correlation matrix of the reproducibility of metal variations based on monthly data from a single branch to an inter-rhodolith scale. All coefficients are significant for a 95% confidence interval, except for values followed by an asterisk. Note that for the inter-branch and inter-rhodoliths scales, all

available matching years between two records are considered. The data were not detrended prior to correlation.

Table 2. Left: Average Mn/Ca, Fe/Ca, Ni/Ca and Co/Ca concentrations (in $\mu\text{mol.mol}^{-1}$) in the modern part of the rhodoliths (1993-2008, except for Co: 2008-2005) and the corresponding concentrations in seawater calculated from the data in Moreton et al. (2009) for the Anse Vata site. Right: Distribution coefficients (K_D) for the divalent cations Mn^{2+} , Fe^{2+} , Ni^{2+} and Co^{2+} calculated for the rhodoliths as $K_D = \text{Rhodolith conc.} / \text{Seawater conc.}$, compared to corresponding published K_D' values for calcite (Mn^{2+} : Mucci, 1988; Pingitore et al., 1988; Fe^{2+} : Dromgoole and Walter, 1989; Ni^{2+} : Rimstidt et al., 1998; Co^{2+} :

Table 1

r	Mn/Ca		Fe/Ca		Ni/Ca		Co/Ca	
<i>Single branch</i>	BSA2b		BSA2b		BSA2b		BSA2b	
BSA2a	0.82		0.83		0.77		0.77	
<i>Single rhodolith</i>	BSA1	BSA2	BSA1	BSA2	BSA1	BSA2	BSA1	BSA2
BSA2	0.32		0.41		0.61		0.10*	
BSA3	0.47	0.51	0.60	0.63	0.55	0.43	0.12*	0.21
<i>Inter-rhodoliths</i>	SSA	BSA	SSA	BSA	SSA	BSA	SSA	BSA
BSA	0.69		0.74		0.59		0.22	
MSA	0.70	0.62	0.82	0.78	0.43	0.56	0.66	0.32

Table 2

	Rhodolith concentration ($\mu\text{mol.mol}^{-1}$)	Seawater concentration ($\mu\text{mol.mol}^{-1}$)		K_D rhodoliths	K_D' calcite
Mn/Ca	15	2.29	Mn^{2+}	7	13-17
Fe/Ca	153	0.34	Fe^{2+}	450	4
Ni/Ca	4.1	1.62	Ni^{2+}	2.5	0.2
Co/Ca	1.8	0.065	Co^{2+}	28	8

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8