ARTICLE IN PRESS

Chemical Geology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Chemical Geology

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

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

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ARTICLE INFO

Editor: K Johannesson

Keywords:
CCA
Sporolithon durum
Laser ablation
Metals
Pollution

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 > 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.

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 Henrich, 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 > 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., 2008a, 2008b, 2009; Hetzinger et al., 2009, 2011; Halfar et al., 2011a, 2011b; Darrenougue et al., 2014). δ^{18}O, Sr/Ca and U/Ca variations have also been linked to oceanic temperature (Halfar et al., 2000, 2007, 2008; Kamenos et al., 2008a, 2008b; 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; Hetzinger 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, 2017b) 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 δ^{18}O, δ^{13}C and Δ^{14}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., 2011a, 2011b; Burdett et al., 2011). In addition, several

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https://doi.org/10.1016/j.chemgeo.2018.05.014
Received 18 February 2018; Received in revised form 2 May 2018; Accepted 8 May 2018
0009-2541/

investigations (Kamenos et al., 2008a, 2008b; Burdett et al., 2015) identified the significant role of coralline algae that host associated bacteria in producing volatile components such as dimethylsulfphoiopropionate (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 contribition of live coral 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 pCO_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 rhodoloths also abound. The current findings suggest that the examination of the Mg—O bond in coralline algae may inform on pCO_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 > 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 rhololiths 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 ~23,400 km^2 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 (Fig. 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 (1–3 $m^3 \cdot s^{-1}$) and carries a minimal sediment load, whereas during intense rainfall events, discharge can be more than a hundred times higher (e.g. ~850 $m^3 \cdot s^{-1}$ 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 et al., 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).

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 to 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. (2011) and that were collecte 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).

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' long axis-short axis