



## Distribution of sulphur and magnesium in the red coral

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### ABSTRACT

The concentrations of major and trace elements were measured in red coral skeletons (*Corallium rubrum*) by electron microprobe (EMP), isotope dilution inductively coupled mass spectrometry (ID-ICPMS) and laser ablation-ICPMS (LA-ICPMS). The average composition (in mg/kg or ppm) is as follows: Ca:  $356300 \pm 3200$ , Mg:  $29500 \pm 2400$ , Sr:  $2600 \pm 250$ , S:  $3100 \pm 400$ , Na:  $4200 \pm 500$ , K:  $140 \pm 20$ , P:  $140 \pm 40$ , B:  $28 \pm 4$ , Ba:  $9 \pm 1$ , Fe:  $8 \pm 3$ , Li:  $4 \pm 1$ , Mn:  $1 \pm 0.5$ , Pb:  $0.5 \pm 0.3$ , U:  $0.08 \pm 0.05$ . In terms of Mg, the compositions of the red coral skeletons range from 9 to 15 mol%  $\text{MgCO}_3$  with a mean value of  $12 \pm 1\%$ . Concentrations of sulphur are high (approx. 3000 ppm) and among the highest reported in biogenic calcites. EMP maps (Mg and S) and organic matter (OM) staining show a regular alternation of 100–200  $\mu\text{m}$  wide annual growth rings. Combination of these results with a previous study (Marschal et al., 2004) suggests that Mg-rich rings form during the period spring to early fall, while S-rich rings form immediately after (late autumn and winter). Elemental mapping by EMP shows an unexpected anticorrelation between S and Mg confirmed by LA-ICPMS. This anticorrelation is ascribed to the concomitant presence of S in the organic matter and the anticorrelation between Mg and OM in the skeleton. However, mass balance constraints indicate that in the skeleton sulphur is probably present both as organo-sulphur and structurally substituted sulphur. The studied samples of red coral were collected at various locations and different depths (8–73 m) where the temperature of the sea water was monitored for long periods of time. Although overall decreases of the Mg/Ca and Sr/Ca are observed as a function of depth (and temperature), the use of these ratios as an indication of the sea water temperature (SWT) seems difficult. In addition, a single colony that grew in an area where the temperature was monitored for 30 years did not register the measured increase of SWT of about 1 °C. However, Mg and OM distributions inside skeletons could be good indicators of variations of growth rates on decadal time scales and anomalous ‘summer suffering’ events that could be associated with periods of unusually high SWT conditions. The red coral is thus an example of how growth dynamics (and not temperature alone) affects the chemistry of biominerals.

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### 1. Introduction

Biominerals display characteristic physical, morphological and chemical hierarchical patterns at length scales from the nanometer to the centimeter (Lowenstam and Weiner, 1989; Mann, 2001). Physical

patterns comprise the nature of the polymorph involved in the biomineral construction, variations in the crystallographic arrangement of modular units within the structure and periodic variations of density and porous space distribution. Morphological patterns are related to the shape of the organism, the shapes of the various constituting units, the shape of the pores and the morphology of growth fronts. Chemical patterns include variations in major and trace element concentrations, stable and radiogenic isotope ratios, and organic matter concentrations and compositions. The physical and morphological patterns often display self-similar characteristics; they are important to understand the origin of the mechanical properties of biominerals, the dynamics of biomineral growth, and to find new routes to synthesize

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new materials. On the other hand, periodic chemical patterns are essential to understand how biominerals which are adaptive complex systems respond to cyclic biological or environmental forcings. In addition, they represent important clues to understand the principles of bio-assisted crystal growth.

Biominerals are composite materials associating an inorganic part (crystalline or amorphous), organic matter and porous spaces. As a result, it can be difficult to determine whether an element from the bulk composition is associated with the organic, inorganic part or both, with important consequences on the interpretation of underlying processes. This is the case of magnesium, and more so of sulphur which is classically observed as a trace element in biogenic carbonates (Lorenz and Bender, 1980; Blake and Peacor, 1981; Busenberg and Plummer, 1985; Rosenberg and Hughes, 1991; Dauphin and Cuif, 1999; Vander Putten et al., 2000; Cuif et al., 2003; England et al., 2007; Hermans, 2010).

In this article, we present a study of the chemical composition of red coral skeletons (*Corallium rubrum*). It complements previous works on the physical and crystallographic organization of the skeleton (Grillo et al., 1993; Vielzeuf et al., 2008, 2010). A comprehensive review of the multi-disciplinary researches carried out on the red coral of the Mediterranean (ecology, biology, management, trade, history) will be found in the proceedings of the international workshop on red coral science (Bussoletti et al., 2010). The studied samples were collected at various places in the Mediterranean, at different depths where long-term instrumental records of seawater temperature exist. The concentrations and the spatial distribution of major (Ca and Mg) and trace elements (Li, B, Na, Al, P, S, K, Cr, Mn, Fe, Zn, Rb, Sr, Ba, Pb, Bi, U) were determined. Elemental correlations are presented and the relationships between chemical patterns, distribution of organic matter, and sea water temperature are discussed.

## 2. Materials and methods

### 2.1. Biological samples and long time series of sea water temperature

Most of the studied red coral colonies come from the rocky coast near Marseille (France) and the Medes Islands (Spain). Colonies from Corsica (France) and Cap de Creus (Spain) were also studied (Fig. 1). Pieces of axial skeletons were analyzed by isotope dilution inductively coupled mass spectrometry (ID-ICPMS). On the other hand, axial skeleton sections (Fig. 2) were mounted in epoxy and polished for electron microprobe (EMP) elemental mapping and chemical analyses, laser ablation inductively coupled mass spectrometry (LA-ICPMS) analyses, and backscattered electron (BSE) imaging. Polished sections of axial skeleton perpendicular to the axis (Fig. 2) and still surrounded by the dried organic tissues containing sclerites (grains of Mg calcite) were also prepared for EMP imaging.

Long term temperature series are scarce for the coastal waters of the NW Mediterranean. The longest series come from the Medes Islands (NE Spain). Weekly temperature measurements were initiated in 1973 and cover a large range of depth levels (0–80 m depth) (Pascual et al., 1995; Salat and Pascual, 2002; Calvo et al., 2011). Likewise, bi-weekly temperature measurements at different depth levels (0–60 m) are available since 1994 for the bay of Marseille (SOMLIT, Service d'Observation, Institut Pytheas UMS 3470). High resolution temperature series (hourly records) have also been acquired since 1998 in the Marseille area, NW Corsica (France) and in the Medes Islands (NE Spain) using autonomous temperature recorders (Stowaway Tidbits). For more information on high resolution temperature series see Bensoussan et al. (2010) and [www.t-mednet.org](http://www.t-mednet.org). These recorders were located within benthic communities where red coral colonies develop. Thus, coral samples that grew under known temperature conditions for long durations can be studied to explore their potential as proxies for seawater temperature.

### 2.2. Analytical and preparation methods

In order to obtain comprehensive chemical information on the red coral skeleton, various techniques with complementary capabilities were used. EMP provides good spatial resolution and allows accurate surface mapping of Ca, Mg, S, Sr, Na, and P. On the other hand, LA-ICPMS has better sensitivity and precision than EMP for minor and trace elements (like Sr, Ba, Li, B). Finally, ID-ICPMS provides high precision measurements for selected metal/calcium ratios on bulk samples.

#### 2.2.1. ID-ICPMS

Isotope dilution-ICPMS analyses were carried out in the Division of Geological and Planetary Sciences at Caltech. For these analyses, red coral branches (5 to 8 mm in diameter) were sub-sampled transversely into pieces, each containing a complete circular section of the branch. The 15–20 mg sub-samples were cleaned prior to analysis. For the cleaning process, samples were separately sonicated and rinsed in trace metal clean water four times over 30 min; sonicated in dilute (~2%) sodium hypochlorite for 2 h (with one exchange of sodium hypochlorite after 1 h); followed by another 30 min of sonication and rinsing with clean water. The samples were then dried in a flow bench prior to grinding in a clean mortar and pestle. Portions of the powders (0.2–1 mg each) were dissolved in trace metal clean nitric acid and analyzed for Mg/Ca and Sr/Ca by an isotope dilution method on a Neptune multi-collector ICPMS. The process involves a mixed element spike, an adaptation of the method described by Fernandez et al. (2011). Repeated measurements of two consistency standards during the analysis were used to assess precision, reported as the 2 sigma std. deviation of more than 4 replicates. A reference standard was made from a dissolved red coral and another from dissolved scleractinian (aragonite) deep-sea coral. For both standards, the relative Sr/Ca reproducibility was better than 0.1%, while Mg/Ca reproducibility was better than 0.4%. For a typical red-coral sample, this analytical precision corresponds to  $\pm 0.003$  mmol/mol Sr/Ca and  $\pm 0.5$  mmol/mol Mg/Ca. The average Sr/Ca and Mg/Ca of the scleractinian deep-sea coral consistency standard matches the long-term mean for this standard, as measured by our lab over more than two years.

#### 2.2.2. LA-ICPMS

Trace element concentrations in several spots within two red coral skeleton samples (Medes1 and Riou-73) were determined using laser ablation inductively coupled mass spectrometry (LA-ICPMS) at ETH Zürich. The LA-ICPMS system combines a 193 nm ArF Excimer laser with an ELAN 6100 ICPMS. Details of the instrument and analytical technique are given elsewhere (Günther et al., 1997; Klemme et al., 2005). In this article, some emphasis will be put on sulphur. It is worth noting that the quantification of sulphur with LA-ICPMS remains problematic for several reasons (Guillong et al., 2008). A specific approach to overcome these difficulties developed by the Zurich group has been applied here (Guillong et al., 2008). For the present study, the diameter of the laser beam was set to 40  $\mu\text{m}$ . For each analysis, the gas background was measured for 30 s and the signals for the samples were acquired for 10–30 s. The carrier gas used was 1 L/min helium, which was mixed with 0.75 L/min argon in front of the ICP. Calcium was used as internal standard and its concentration was determined independently by EMP for each sample; internal variations of calcium content within each sample were not taken into account. The NIST SRM 610 glass was used as external reference material (Jochum et al., 2011). The two samples used for the LA-ICPMS measurements (Medes 1 – 20 analyses and Riou73 – 16 analyses) were collected at depth of 28 m and 73 m, respectively to illustrate two contrasted annual sea water temperature (SWT) regimes.

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