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Reproducibility of *Clathromorphum compactum* coralline algal Mg/Ca ratios and comparison to high-resolution sea surface temperature data

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Abstract

The potential of crustose coralline algae as high-resolution archives of past ocean variability in mid- to high-latitudes has only recently been recognized. Few comparisons of coralline algal proxies, such as temperature-dependent algal magnesium to calcium (Mg/Ca) ratios, with *in situ*-measured surface ocean data exist, even rarer are well replicated records from individual sites. We present Mg/Ca records from nine coralline algal specimens (*Clathromorphum compactum*) from a single site in the Gulf of Maine, North Atlantic. Sections from algal mounds were analyzed using Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) yielding individual Mg/Ca records of up to 30 years in length. We first test intra- and inter-sample signal replication and show that algal Mg/Ca ratios are reproducible along several transects within individual sample specimens and between different samples from the same study site. In addition, LA-ICP-MS-derived Mg/Ca ratios are compared to electron microprobe (EMP) analyzed data on the longest-lived specimens and were found to be statistically commensurable. Second, we evaluate whether relationships between algal-based SST reconstructions and *in situ* temperature data can be improved by averaging Mg/Ca records from multiple algal specimens (intersample averages). We found that intersample averages yield stronger relationships to sea surface temperature (SST) data than Mg/Ca records derived from individual samples alone. Thus, Mg/Ca-based paleotemperature reconstructions from coralline algae can benefit from using multiple samples per site, and can expand temperature proxy precision from seasonal to monthly.

Keywords: Coralline algae; Sea surface temperature; Calibration; Paleotemperature

1. INTRODUCTION

While global-mean surface temperature has unequivocally risen over the instrumental record (IPCC, 2013), the observed warming is spatially heterogenous, with the near-surface temperatures of the Northern Hemisphere higher latitudes warming at rates double that of lower latitudes - a phenomenon known as *Arctic amplification*

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(Serreze et al., 2009). In recent decades northern North Atlantic climate and ocean variability have experienced rapidly changing conditions, with most prominent surface warming occurring in the northeastern Canadian region and Greenland (Ding et al., 2014). These trends have already started altering ecosystems as well as human behavior and may even influence the large-scale atmospheric circulation beyond the Arctic (Cohen et al., 2014). A better understanding of the internal processes driving natural variability in higher latitude surface temperatures and the amount of overprint by anthropogenic activities are essential to improving the prediction of future evolution of climate.

Hence, it is necessary to resolve year-to-year temperature variability during the past centuries, i.e. prior to the industrial revolution, when humans started impacting climate and ocean chemistry by the emission of fossil fuels. Our ability to understand processes driving Arctic and Subarctic climate variability depends upon time series of environmental parameters including reanalysis datasets, model output and reconstructions from environmental archives. However, reanalysis data and model output of Arctic climate change are limited in temporal and spatial extent (Zhang and Walsh, 2006) and climate models significantly underestimate recent surface warming, especially in high latitudes (Boé et al., 2009). The major reason is lack of data and the short duration of satellite records generally not extending beyond the late 1970s. Very little is known about the natural variability of Subarctic to Arctic North Atlantic surface ocean temperature and freshwater dynamics on longer time scales prior to satellite measurements. Typically, reconstructions are achieved by using (so-called) proxy archives, for example tree rings or ice cores on land or corals in the tropical ocean (Wanamaker et al., 2011). High-resolution proxy-based climate reconstructions of decadal to centennial length are often derived from long-lived marine biota such as corals and bivalve molluscs (Schöne et al., 2005; Hetzinger et al., 2010; Wanamaker et al., 2011; Cahyarini et al., 2014; Mallela et al., 2015; Mette et al., 2016; Reynolds et al., 2016; Sagar et al., 2016; von Reumont et al., 2016). However, most high-resolution proxy-based paleoclimate research has concentrated on low-latitude tropical oceans, while mid- and high-latitude marine regions have received less attention, despite their importance in the global climate system.

Long-lived coralline algae that grow attached to the seafloor have emerged as novel mid- and high-latitude paleoclimate archives (Halfar et al., 2007; Halfar et al., 2008; Gamboa et al., 2010; Hetzinger et al., 2012). The genus *Clathromorphum* Foslie, 1898 (Hapalidiales, Rhodophyta), a coralline red alga, has been shown to be well suited as a new climate recorder because it is (1) widely distributed in the extratropical Atlantic and Pacific, (2) has a multi-century lifespan, and (3) displays annual growth increments (similar to tree rings) in a high-Mg calcite skeleton. The species *Clathromorphum compactum* (Kjellmann) Foslie (1898) forms thick carbonate crusts on rocky bottoms in the sublittoral spanning from the northwestern Atlantic through the Arctic Ocean (Adey et al., 2008; Adey et al., 2013; Adey et al., 2015). Slow growth rates (<50–500 μm/year) and clear annual banding permit the development of sub-annually resolved reconstructions that are known to exceed a millennium in long-lived specimens in Subarctic and Arctic environments (Adey, 1965; Moberly, 1968). *Clathromorphum compactum* is particularly abundant along the temperate and subarctic eastern Canadian coastline (Adey, 1965; Adey and Steneck, 2001). It occurs in summer water temperatures <15 °C, and winter temperatures of <2–3°C, and occurs from 1 to 40 m water depth reaching maximum abundance around 10–20 m (Adey, 1966). *Clathromorphum compactum* thrives at summer water temperatures of 5–10 °C.

A number of studies have examined various aspects of the chemical and physical structure of coralline algae in order to reconstruct past changes in large-scale climate patterns affecting the North Pacific and North Atlantic Oceans (Gamboa et al., 2010; Halfar et al., 2000, 2007, 2011a, 2011b, 2013; Hetzinger et al., 2011, 2012; Williams et al., 2011, 2014). The foundation for the above studies was provided by *in situ* field calibration experiments confirming that algal geochemistry provides a reliable indication of SST (Halfar et al., 2008). Previous studies on coralline algae (Moberly, 1968; Halfar et al., 2000) and other biogenic carbonates (Mitsuguchi et al., 1996) have revealed that areas of high Mg values within the skeleton typically occur during the period of main growth in summer and hence are interpreted to correspond to summer values. This relationship was also confirmed for the genus *Clathromorphum* (Halfar et al., 2000; Halfar et al., 2008). Algal Mg/Ca element ratios have been shown to be excellent proxies for ocean temperatures (Hetzinger et al., 2009). Other trace elements within the algal skeleton (U/Ca, Sr/Ca, Ba/Ca, and Li/Ca) have also been examined (Chan et al., 2011; Hetzinger et al., 2011; Hetzinger et al., 2013; Caragnano et al., 2014). Previously, reproducibility of LA-ICP-MS trace element profiles was evaluated in deep-water corals (e.g. Sinclair et al., 2005; Sinclair et al., 2011). However, well replicated proxy records, especially comparisons between records from multiple algal samples from the same site are rare (Williams et al., 2014; Ng et al., 2016; Caragnano et al., 2017). Furthermore, only few comparisons between coralline algal proxies, such as temperature-dependent algal Mg/Ca ratios, and *in situ*-measured surface ocean data are available (Halfar et al., 2008; Kamenos et al., 2008).

Here we present high-resolution Mg/Ca ratio transects measured on several specimens of attached-living encrusting coralline algae (*Clathromorphum compactum*) from a single site and water depth (10 m) in the Gulf of Maine. First, we examine whether trace Mg/Ca ratios measured in multiple coralline algal specimens are reproducible within each sample and between different samples from the same study site. Then, we compare method-to-method reproducibility by using records analyzed with the LA-ICP-MS and electron microprobe techniques. Finally, we examine the relationship between algal Mg/Ca ratios and *in situ* seawater temperature measurements/observations, testing whether relationships between the algal paleotemperature proxy and SST can be improved by averaging Mg/Ca records from multiple algal specimens (intersample averages).