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Calcite-filled borings in the most recently deposited skeleton in live-collected *Porites* (Scleractinia): Implications for trace element archives

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Abstract

Skeletons of the scleractinian coral *Porites* are widely utilized as archives of geochemical proxies for, among other things, sea surface temperature in paleoclimate studies. Here, we document live-collected *Porites lobata* specimens wherein as much as 60% of the most recently deposited skeletal aragonite, i.e., the part of the skeleton that projects into the layer of living polyps and thus is still in direct contact with living coral tissue, has been bored and replaced by calcite cement. Calcite and aragonite were identified in situ using Raman microspectroscopy. The boring-filling calcite cement has significantly different trace element ratios ($Sr/Ca_{(mmol/mol)} = 6.3 \pm 1.4$; $Mg/Ca_{(mmol/mol)} = 12.0 \pm 5.1$) than the host coral skeletal aragonite ($Sr/Ca_{(mmol/mol)} = 9.9 \pm 1.3$; $Mg/Ca_{(mmol/mol)} = 4.5 \pm 2.3$). The borings appear to have been excavated by a coccoid cyanobacterium that dissolved aragonite at one end and induced calcite precipitation at the other end as it migrated through the coral skeleton. Boring activity and cement precipitation occurred concomitantly with coral skeleton growth, thus replacing skeletal aragonite that was only days to weeks old in some cases. Although the cement-filled borings were observed in only ~20% of sampled corals, their occurrence in some of the most recently produced coral skeleton suggests that any corallum could contain such cements, irrespective of the coral's subsequent diagenetic history. In other words, pristine skeletal aragonite was not preserved in parts of some corals for even a few weeks. Although not well documented in coral skeletons, microbes that concomitantly excavate carbonate while inducing cement precipitation in their borings may be common in the ubiquitous communities that carry out micritization of carbonate grains in shallow carbonate settings. Thus, such phenomena may be widespread, and failure to recognize even very small quantities of early cement-filled borings in corals used for paleoclimate studies could compromise high resolution paleotemperature reconstructions. The inability to predict the occurrence of cement-filled borings in coralla combined with the difficulty in recognizing them on polished blocks highlights the great care that must be taken in vetting samples both for bulk and microanalysis of geochemistry.

1. INTRODUCTION

The geochemistry of scleractinian coral skeletons is increasingly applied to the study of paleoclimate (e.g., Beck et al., 1992; de Villiers et al., 1995; Mitsuguchi et al., 1996; Marshall and McCulloch, 2002; Cobb et al., 2003; Fallon et al., 2003; McGregor and Gagan, 2003; Linsley et al., 2004; Lough, 2004; Yu et al., 2005; Corrège, 2006), coastal run-off and pollution (e.g., Naqvi et al., 1996; Fallon et al., 2002; Alibert et al., 2003; McCulloch et al., 2003; Sinclair and McCulloch, 2004; Sinclair, 2005; Lewis et al., 2007), ocean up-welling (Shen et al., 1987; Lea et al., 1989; Fallon et al., 1999), and even marine productivity (Wyndham et al., 2004). Techniques such as laser ablation-inductively

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coupled plasma-mass spectrometry (LA-ICP-MS) (e.g., Sinclair et al., 1998; Fallon et al., 1999; McCulloch et al., 2003; Runnalls and Coleman, 2003; Sinclair and McCulloch, 2004) and ion microprobe (Allison and Tudhope, 1992; Allison, 1996a; Cohen et al., 2001, 2002; Meibom et al., 2003; Rollion-Bard et al., 2003a,b; Meibom et al., 2007) are allowing geochemical sampling at increasing levels of spatial resolution with the hope for increased, subannual (Cohen et al., 2001; Watanabe et al., 2001b; Gill et al., 2006) to even sub-daily temporal resolution (Meibom et al., 2007). However, the use of coral skeletons as temporal archives for geochemical proxies requires that coral skeletons preserve trace element and isotopic ratios that reflect the ambient conditions of the seawater in which the skeleton was precipitated. Although evidence increasingly suggests that trace element and stable isotope distributions within coral skeletons are heterogeneous at very fine scales and are affected by poorly understood vital effects (Cohen et al., 2002; Marshall, 2002; Meibom et al., 2003, 2004, 2006, 2007; Rollion-Bard et al., 2003a,b; Allison et al., 2005; Shirai et al., 2005; Sinclair, 2005; Stolarski and Mazur, 2005; Gaetani and Cohen, 2006; Sinclair and Risk, 2006), coral skeletons can provide useful palaeoenvironmental proxies where original trace element and stable isotope inventories have not been altered by subsequent diagenesis. Although coral skeletons are routinely vetted prior to analysis to check for diagenetic alteration, such as recrystallization of skeletal aragonite to calcite (e.g., Enmar et al., 2000; McGregor and Gagan, 2003; Quinn and Taylor, 2006), it is generally assumed that coral skeleton that has not been exposed to freshwater (meteoric) diagenesis, especially in live-collected corals, should retain reliable marine trace element inventories.

Early marine aragonite cement that precipitates syntaxially on coral aragonite surfaces in seawater (e.g., Potthast, 1992) has the potential to disturb important geochemical proxies in coral skeletons, because the cement generally has higher Sr and lower Mg content than the biogenic aragonite of the coral skeleton (Dauphin et al., 1990; Enmar et al., 2000; Quinn and Taylor, 2006). However, such cement can be avoided by not sampling the margins or surfaces of internal structures (e.g., walls and septa) within the coral skeleton (i.e., the corallum). Cements precipitated in microborings within the coral skeleton are more problematic and in rare cases include calcite with very different Sr/Ca and Mg/Ca ratios than the host aragonite (Houck et al., 1975; Macintyre and Towe, 1976). In this paper we investigate early diagenetic calcite cements that completely occlude microbial borings in live-collected samples of *Porites lobata*. The borings occur within the most recently formed parts of the coral skeletons, i.e., those parts that are contained within the uppermost part of the corallum that is still occupied by living coral polyps (Fig. 1, Fig. 2A). Skeleton in this region of living polyps is theoretically the most pristine skeleton possible, because it is still in direct contact with living coral tissue, and its surfaces are still potentially undergoing active biomineralization beneath the calicoblastic epithelium of the coral. Although microborings are well known in scleractinian coral skeletons (Duerden, 1902; Risk et al., 1987; Le Campion-Alsumard et al., 1995a,b; Allison, 1996b; Bentis et al., 2000; Golubic et al., 2005), the rapidity with which borings can be excavated and occluded by cement may not have been adequately appreciated. Inclusion of even small traces of such cements in a geochemical analysis may greatly alter Sr/Ca, Mg/Ca and other potential elemental and isotopic ratios that are commonly used for, among other things, paleothermometry (Allison, 1996b). Forming so rapidly after initial secretion of the coral skeleton, boring-filling cements could potentially occur in any sample of coral skeleton, irrespective of its subsequent diagenetic history.

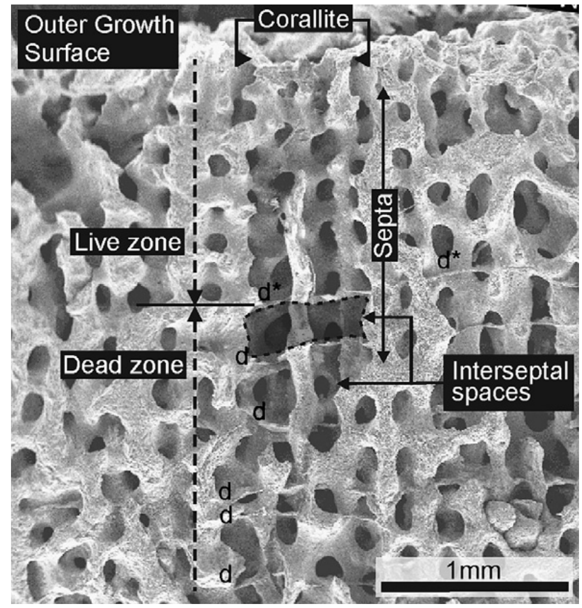

Fig. 1. Scanning electron microscope images of *Porites lobata* corallum cut with a diamond saw. Longitudinal section of the upper part of coral skeleton showing the different vertical (e.g., septa) and horizontal (e.g., dissepiments, d) skeletal elements. Living coral polyps occupied the part of the skeleton above the last deposited dissepiment (d*). The area below the last formed dissepiment is 'dead' skeleton containing empty cavities abandoned by the coral polyp during upward growth.

Fig. 2. Backscattered scanning electron microscope images of polished and etched surfaces of *Porites lobata* showing cement-filled microborings. (A) Transverse section similar in orientation to sample shown in Fig. 1 showing the area occupied by the coral polyp above the last formed dissepiment (d*). Box shows position of Fig. 2B. Scale bar = 1 mm. (B and C) The growth tip of a septum containing calcite-filled microborings within micrometers of the growth surface. Scale bar = 100 μm. (C) Magnified section of Fig. 2B showing that some borings at the tip of the septum remain fully or partially empty. Scale bar = 50 μm. (D) Microborings are irregularly distributed but mostly concentrated near central regions of skeletal elements and oriented more or less in the growth direction of the coral. Scale bar = 100 μm. (E) Cement-filled borings occupy 60% of the skeletal volume in this longitudinal section. Scale bar = 100 μm.