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The role of skeletal micro-architecture in diagenesis and dating of *Acropora palmata*

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Abstract

Past variations in global sea-level reflect continental ice volume, a crucial factor for understanding the Earth's climate system. The Caribbean coral *Acropora palmata* typically forms dense stands in very shallow water and therefore fossil samples mark past sea-level. Uranium-series methods are commonly used to establish a chronology for fossil coral reefs, but are compromised by post mortem diagenetic changes to coral skeleton. Current screening approaches are unable to identify all altered samples, whilst models that attempt to correct for 'open-system' behaviour are not applicable across all diagenetic scenarios. In order to better understand how U-series geochemistry varies spatially with respect to diagenetic textures, we examine these aspects in relation to skeletal micro-structure and intra-crystalline amino acids, comparing an unaltered modern coral with a fossil *A. palmata* colony containing zones of diagenetic alteration (secondary overgrowth of aragonite, calcite cement and dissolution features). We demonstrate that the process of skeletogenesis in *A. palmata* causes heterogeneity in porosity, which can account for the observed spatial distribution of diagenetic features; this in turn explains the spatially-systematic trends in U-series geochemistry and consequently, U-series age. We propose a scenario that emphasises the importance of through-flow of meteoric waters, invoking both U-loss and absorption of mobilised U and Th daughter isotopes. We recommend selective sampling of low porosity *A. palmata* skeleton to obtain the most reliable U-series ages. We demonstrate that intra-crystalline amino acid racemisation (AAR) can be applied as a relative dating tool in Pleistocene *A. palmata* samples that have suffered heavy dissolution and are therefore unsuitable for U-series analyses. Based on relatively high intra-crystalline concentrations and appropriate racemisation rates, glutamic acid and valine are most suited to dating mid-late Pleistocene *A. palmata*. Significantly, the best-preserved material in the fossil specimen yields a U-series age of 165 ± 8 ka, recording a paleo sea-level of -35 ± 7 msl during the MIS 6.5 interstadial on Barbados.

Keywords: Coral; U-series dating; Amino acid racemisation; Diagenesis; Skeletogenesis; Sea-level; MIS 6.5

1. INTRODUCTION

The elk horn coral *Acropora palmata* is a useful proxy for past sea-level because it has a very limited depth range, with dense stands developing in or just below the breaker

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zone (Lighty et al., 1982), and was common in Quaternary fossil reefs of the Caribbean. Sea-level reconstructions based on fossils require a robust chronology, and U-series dating provides the most precise approach for Quaternary corals (as reviewed in Stirling and Andersen, 2009). The most commonly used U-series dating technique assumes that decay of the ^{238}U parent nuclide into its longest-lived intermediate radioactive daughter nuclides, ^{234}U and ^{230}Th, occurs within a closed system. This assumption is often compromised by diagenetic alteration of the aragonitic skeleton (e.g. Hamelin et al., 1991). Diagenesis can involve loss of mineral (dissolution) and preferential leaching of certain elements (e.g. Schroeder, 1969; Hendy et al., 2007), addition of new material (cementation) of the same or different mineralogy (e.g. Nothdurft and Webb, 2009), and/or replacement of primary material (e.g. Scherer, 1974; Cusack et al., 2008). The rigidity and porosity of coral skeletons increases susceptibility to diagenesis by promoting fluid circulation (e.g. Constantz, 1986; Dullo, 1987). *A. palmata* is particularly susceptible to these diagenetic changes and the consequent occurrence of inaccurate U-series ages has led to a preference for other, apparently less sensitive, species (e.g. Stirling et al., 1995, 1998; Andersen et al., 2008). The advantage of using *A. palmata*, for this study is twofold: (1) the potential to improve reliable dating capabilities of this coral species given its superiority as a sea-level marker compared to most other coral species and (2) the susceptibility to diagenesis, together with the characteristic internal variability in *A. palmata* microstructure, make this species an excellent candidate for investigating the general open-system U-series systematics that can affect all corals during diagenetic alteration.

Current techniques used to screen altered material prior to U-series isotopic analysis cannot identify all samples exhibiting open-system behaviour (e.g. Bar-Matthews et al., 1993; Fruijtier et al., 2000; Scholz et al., 2007; Andersen et al., 2008). Consequently, various 'post-analytical' methods, such as comparing decay-corrected $^{234}U/^{238}U$ in fossil corals to that of modern counterparts, have been used to identify compromised samples (e.g. Hamelin et al., 1991; Gallup et al., 1994; Stirling et al., 1995). Further attempts to obtain reliable U-series ages from fossil corals have steered towards modelling and correcting for open-system behaviour (e.g. Thompson et al., 2003). Typically, open-system U-series corrections are based solely on post-analytical geochemical observations (e.g. Thompson et al., 2003; Villemant and Feuillet, 2003; Scholz et al., 2004; Potter et al., 2004), rather than linking physical evidence of subtle diagenetic changes to the U-series system. In part, this dichotomy is a consequence of *a priori* rejection of samples with visible alteration, but sub-sampling across coevally deposited skeletal material within single diagenetically altered colonies can help isolate geochemical imprints from diagenesis (Henderson et al., 1993; Scholz and Mangini, 2007; Scholz et al., 2007; Shen et al., 2008; Andersen et al., 2010a; Obert et al., 2016), thereby improving the screening of material and enhancing the capacity for model age corrections. In addition, initial screening could include a secondary dating technique such as amino acid racemisation (AAR), to improve sample selection for U-series dating of fossil corals (Hendy et al., 2012). Recent improvements in analysis and sample preparation (e.g. Kaufman and Manley, 1998; Penkman et al., 2008) mean a re-assessment of the diagenetic sensitivity and geochronological potential of AAR in Quaternary coral, last explored by Wehmiller et al. (1976), is timely.

In this study we test the influence of coral skeletogenesis and a range of diagenetic processes on U-series geochemistry and AAR by comparing a modern and a fossil diagenetically-altered *A. palmata* colony to isolate primary micro-structural, organic (intra-crystalline amino acids) and isotopic (U-series) variability from secondary diagenetic features. We provide evidence that heterogeneity in porosity within an individual colony localises diagenetic processes, promoting spatially-systematic trends in geochemistry, with particular relevance to retrieving robust ages from *A. palmata*. By examining U-series and AAR systematics at the millimetre-scale within the fossil colony, we identify 'pristine' areas of coral skeleton in order to derive a more robust U-series age. Significantly, these results indicate that the fossil *A. palmata* colony grew during Marine Isotope Stage (MIS) 6.5, a warmer sub-stage within the MIS 6 glacial that coincided with a prominent peak in Northern Hemisphere insolation (Berger, 1978). Previous sea-level, and therefore ice-volume, estimates during this complex but climatically important interstadial indicate only a moderate sea-level high-stand compared with interglacial levels (Scholz et al., 2007; Grant et al., 2014). The duration is also uncertain (Bard et al., 2002; Thompson and Goldstein, 2005; Scholz et al., 2007). We use the data derived from the fossil *A. palmata* sample to constrain the timing and amplitude of sea-level during MIS 6.5.

2. MATERIALS AND METHODS

2.1. Coral samples

The fossil *A. palmata* sample (U6-11 K3243) was selected because it displayed spatial variability in microstructure and diagenetic alteration. It was collected in growth position at 9.8 m above current sea-level from the "Gully" sample site at Foul Bay (13°5′30″ N, 59°26′54″ W) SE coast of Barbados, between Salt Cave Point and Deebles Point (Schellmann and Radtke, 2004a; Fig. 1). Electron spin resonance (ESR) dates from *A. palmata* colonies in the same reef sequence range between 182 ± 18 and 232 ± 27 ka (Schellmann and Radtke, 2004a). A 10 mm thick slice (150 × 120 mm diameter) cut perpendicular to growth was sectioned into four transects (Fig. 2a); three of these were cut into 16 contiguous sub-samples (~6 × 9 × 10 mm) for SEM, U-series and AAR analysis (transects A–C respectively), whilst four thin sections were prepared from the fourth transect (transect D).

The modern *A. palmata* colony came from the University of Bristol's collection (collected live by Dr. Tom Thompson, Jamaica, 1974). Transverse slices were cut (Fig. 2b) from the growing tip, middle and base of the colony branch (Fig. 2c–e respectively). The central axial region (i.e. minus protruding radial corallites) was sub-sampled from the top slice, and transects were