



Diagenetic effects on uranium isotope fractionation in carbonate sediments from the Bahamas

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Abstract

Uranium isotope variations ($\delta^{238}\text{U}$) recorded in sedimentary carbonate rocks are a promising new proxy for the extent of oceanic anoxia through geological time. However, the effects of diagenetic alteration on the U isotopic composition in carbonate sediments, which are crucial to understand the accurate reconstruction of marine $\delta^{238}\text{U}$, are currently poorly constrained. Here we examine the effects of the aragonite-to-calcite transition in the Pleistocene Key Largo Limestone of South Florida, and assess the effects of vadose meteoric, phreatic meteoric, and phreatic marine diagenesis on U isotope fractionation in carbonate sediments from the Bahamas Transect, including the well-studied Clino, Unda, and ODP Site 1006 drill cores.

Our results suggest that early diagenetic processes in Bahamas carbonate sediments fractionate U isotopes by an average of $0.27 \pm 0.14\text{‰}$ (1 SD) heavier than contemporaneous seawater. Downcore variations of $\delta^{238}\text{U}$ in slope and basin sediments display little, if any, correlation with U concentration and common geochemical indicators of diagenesis ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, Mn/Sr, Mg/Ca, Sr/Ca), enrichments of redox-sensitive elements, or rare earth elements anomalies. We propose two possible mechanisms to interpret the positive change in the $\delta^{238}\text{U}$ during carbonate diagenesis: authigenic enrichment of isotopically positive U(IV) in carbonates and preferential incorporation of isotopically positive aqueous U(VI) species into carbonates. These processes likely operate during early (syndepositional) diagenesis on the banktop. Further diagenesis during deeper burial is limited by the low solubility of U(IV) under reducing pore water conditions.

The early diagenetic behavior of U isotopes in Bahamas carbonate sediments is likely broadly representative of carbonate diagenesis in the geological past. We suggest that the mean diagenetic offset determined in this study be applied when reconstructing seawater $\delta^{238}\text{U}$ from ancient carbonates. Furthermore, early diagenesis induces significant statistical variability in sediment $\delta^{238}\text{U}$ values, pointing to the need for large, high resolution data sets in order to average out stochastic variations in individual bulk sediment samples.

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1. INTRODUCTION

The development of new paleoredox proxies which can be applied to sedimentary carbonates offers significant advantages over more traditional proxies established for black shales (e.g., [Algeo and Maynard, 2004](#); [Algeo and Rowe, 2011](#); [Pufahl and Hiatt, 2012](#)). Whereas black shale deposition is often confined to relatively rare marginal basins leading to a spatially- and temporally intermittent record, the ubiquitous and often-continuous deposition of sedimentary carbonate rocks along passive continental margins offers the potential for long, continuous records of past ocean redox conditions. Such records would directly complement the well-established Phanerozoic records of carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ and therefore provide important insights into the links between tectonics, climate, nutrient cycling, and atmospheric and ocean redox conditions ([Morse and Mackenzie, 1990](#); [Jacobsen and Kaufman, 1999](#); [Veizer et al., 1999](#); [Shields and Veizer, 2002](#)).

Among a range of prospective carbonate paleoredox proxies, which includes redox sensitive elements ([Huang et al., 2009](#); [Chun et al., 2010](#)), I/Ca ([Lu et al., 2010](#); [Zhou et al., 2014, 2015](#)), and $\delta^{53}\text{Cr}$ ([Frei et al., 2011, 2013](#); [Holmden et al., 2016](#); [Wang et al., 2016a, 2016b](#); [Gilleaudeau et al., 2016](#); [D'Arcy et al., 2017](#)), uranium isotopes ($\delta^{238}\text{U}$) are uniquely capable of integrating global average paleoredox conditions. The $\delta^{238}\text{U}$ value of seawater changes due to isotope fractionation between oxidized U (VI) and reduced U(IV), which results in the preferential removal of ^{238}U to sediments under anoxic conditions, leaving residual seawater ^{238}U -depleted ([Weyer et al., 2008](#); [Basu et al., 2014](#); [Wang et al., 2015](#); [Stirling et al., 2015](#); [Stylo et al., 2015](#); [Andersen et al., 2017](#)). Because of the long residence time of U in seawater (~ 400 kya), the $\delta^{238}\text{U}$ of the open ocean is uniform, and thus $\delta^{238}\text{U}$ of seawater—and potentially of carbonates that precipitate from it—offers a globally averaged record of ocean redox conditions ([Dunk et al., 2002](#); [Romaniello et al., 2013](#); [Tissot and Dauphas, 2015](#)). This technique has already seen growing application to ancient carbonate sediments including the late Cambrian SPICE event and the Permo-Triassic and End-Triassic mass extinction events ([Brennecke et al., 2011](#); [Dahl et al., 2014](#); [Azmy et al., 2015](#); [Lau et al., 2016, 2017](#); [Elrick et al., 2017](#); [Jost et al., 2017](#)).

A significant challenge in applying the $\delta^{238}\text{U}$ proxy to carbonates is understanding the potential impact of syndepositional and post-depositional diagenesis in these permeable sediments. The potential impact of carbonate diagenesis on a wide range of geochemical proxies is well-known (e.g., $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, I/Ca, $\delta^{11}\text{B}$; [Swart, 2015](#); [Stewart et al., 2015](#); [Hardisty et al., 2017](#)). $\delta^{238}\text{U}$ is no exception. Although modern primary biogenic carbonates record $\delta^{238}\text{U}$ values close to seawater, [Romaniello et al. \(2013\)](#) found that $\delta^{238}\text{U}$ in modern banktop carbonate sediments from the Bahamas are 0.2–0.4‰ more positive than seawater, due to reductive authigenic enrichments of U from sulfide-rich pore water. Similarly, [Hood et al. \(2016\)](#) found large variations of $\delta^{238}\text{U}$ in samples of different carbonate microfacies with varying degrees of diagenetic alteration

from the Cryogenian Balcanoona reef complex in South Australia.

The goal of this project was to systematically explore the impact of early diagenesis on bulk-sediment $\delta^{238}\text{U}$ values in well-characterized modern settings. Because the $\delta^{238}\text{U}$ of seawater has been nearly constant over the Cenozoic, the initial $\delta^{238}\text{U}$ value of these sediments can be assumed to be close to modern seawater ([Romaniello et al., 2013](#); [Wang et al., 2016a, 2016b](#); [Chen et al., 2016](#)). During early diagenesis, carbonate dissolution and recrystallization typically results in mineralogy transformations, loss of the endogenous U and incorporation of the exogenous U into the secondary carbonate precipitates, and changes in pore water chemistry (e.g., Ca^{2+} , Mg^{2+} , and CO_3^{2-} concentrations). Pervasive recrystallization of metastable aragonite and replacement by calcite is one of the most important early diagenetic transitions, especially given that the partition coefficients for U into calcite are much lower than those for aragonite, resulting in the preferential loss of U from recrystallized sediments ([Reeder et al., 2000, 2001](#); [Chen et al., 2016](#)).

In order to explore U isotope fractionation during the reaction of aragonite to calcite during meteoric diagenesis, we measured $\delta^{238}\text{U}$ along a transect of an *Orbicella annularis* (previously named as *Montastrea annularis*) coral head from the Pleistocene Key Largo Limestone, South Florida ([Gill et al., 2008](#)). Additional alteration of carbonate sediments occurs in a number of settings, including further meteoritic diagenesis due to changes in sea level and exposure of sediments to freshwater, and phreatic marine diagenesis. These more aggressive diagenetic regimes can result in extensive recrystallization of carbonates, including replacement of sedimentary fabrics and dolomitization of sediments, as well as potential exchange of U with exogenous diagenetic fluids. To examine the effect of these different diagenetic processes, we measured $\delta^{238}\text{U}$ variations in the extremely well-characterized Bahamas carbonate transect, including samples from the Unda, Clino and Site 1006 (ODP, Leg 166) drill cores. We used fluid-rock interaction modeling to set our observations into a theoretical context, and combine these empirical and theoretical results to draw broader conclusions about how to identify and correct for the most likely patterns of $\delta^{238}\text{U}$ diagenetic alteration in ancient sediments.

2. SAMPLES

2.1. Key Largo limestone samples

The *Orbicella annularis* coral head KL1 from the Pleistocene Key Largo Limestone, provides a simple case study of U isotope fractionation during aragonite-to-calcite alteration resulting from meteoric diagenesis ([Gill et al., 2008](#)). The corals which now form the Key Largo Limestone grew on the Florida platform during Marine Isotope Stage 5e (MIS 5, Eemian interglacial period, 119–124 ka), when sea-level was 6–9 m higher than present ([Broecker and Thurber, 1965](#); [Hoffmeister and Multer, 1968](#)). Due to falling sea level, these coral skeletons were continuously exposed to meteoric fluids for the past ~ 100 ky

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