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ScienceDirect

Geochimica et Cosmochimica Acta 242 (2018) 233–265

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Controls of eustasy and diagenesis on the $^{238}U/^{235}U$ of carbonates and evolution of the seawater ($^{234}U/^{238}U$) during the last 1.4 Myr

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Received 19 January 2018; accepted in revised form 10 August 2018; Available online 23 August 2018

Abstract

Using a leaching protocol designed for the study of U isotopes in recent carbonates, we measured the U isotope composition, both $^{238}U/^{235}U$ and $^{234}U/^{238}U$, of modern and ancient corals (n = 6), a limestone and a dolostone, as well as 43 shallow-water carbonate sediments from the ODP Leg 166 Site 1009 drill core, on the slope of the Bahamas platform. Although bulk corals record the seawater $\delta^{238}U$ value within ±0.02‰, differences of up to 0.30‰ in the $\delta^{238}U$ of individual leachates suggest a control of the coral structure and a more positive $^{238}U/^{235}U$ ratio in the centers of calcification.

The drill core $\delta^{238}U$ data shows that the $^{238}U/^{235}U$ ratio of shallow-water carbonates is controlled mainly by (1) variations in sea-level through the mixing of different amounts of platform-derived sediments (with $\delta^{238}U$ ~0.50–0.60‰ heavier than seawater) and pelagic sediments (with seawater-like $\delta^{238}U$ values), (2) authigenic U enrichment via pore-water circulation and U reduction both on the platform and down to ~5 m below the surface (mbsf) after deposition of the sediment, and, to a lesser extent, by (3) early diagenetic processes (*i.e.*, carbonate dissolution and/or recrystallization) during sediment burial. The global effect of these processes leaves the $\delta^{238}U$ values of shallow-water carbonates offset relative to that of seawater by $\Delta_{\text{Carbonates-SW}} = +0.24 \pm 0.06$‰ (95% CI, including all samples). This shift can be used in seawater paleoredox reconstructions based on carbonates deposited on shallow-water platform, shelf and slope environments (*i.e.*, most of the carbonate sedimentary record prior to the Mesozoic) to account for the average effect of carbonate diagenesis. Assuming that the $^{238}U/^{235}U$ ratio of carbonate platform sediments directly records the seawater $^{238}U/^{235}U$ ratio would underestimate the extent of ocean-seafloor anoxia by at least a factor 10. The rapid fluctuations in $\delta^{238}U$ values due to sea-level changes (i) is a factor that should be considered before interpreting $\delta^{238}U$ variations as reflecting changes in oceanic paleoredox conditions and (ii) reinforces the need for statistically meaningful data sets.

The $\delta(^{234}U)$ data suggest that the ($^{234}U/^{238}U$) ratio of the seawater has remained within ~20‰ of the modern seawater value during the last 1–1.4 Myr. Furthermore, we find that small-scale (1–15‰) variations in seawater $\delta(^{234}U)$ mirror sea-level changes during the penultimate glacial-interglacial period (~140 to ~200 ka), thus confirming the record of lower $\delta(^{234}U)_{SW}$ during periods of low sea-level stand and expanding it to at least the last two glacial-interglacial events (*i.e.*,

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https://doi.org/10.1016/j.gca.2018.08.022

~0.23 Ma). Such fluctuations in $\delta(^{234}U)_{initial}$ values should be taken into account when screening carbonate sediments U-Th ages on the basis of the initial ($^{234}U/^{238}U$) ratios of the samples.

Keywords: Shallow-water carbonate; Bahamas; ODP drill core; U isotopes; Sea-level variations; Diagenesis

1. INTRODUCTION AND BACKGROUND

Reconstructions of Earth's ancient atmosphere-ocean redox conditions rely on proxies such as the survival of redox-sensitive detrital minerals (Ramdohr, 1958; Rasmussen and Buick, 1999), variations in the elemental abundance of redox-sensitive elements (*e.g.*, Mo, Re, U; Anbar et al., 2007; Partin et al., 2013a, 2013b; Scott et al., 2008), or variations in the isotopic composition of traditional stable isotopes (*e.g.*, S, C, N; Holland, 2006). Since the mid-2000s, the so-called 'non-traditional' stable isotope systems (*e.g.*, Cr, Fe, Mo, U) have emerged as powerful tracers of both high- and low-temperature geochemical processes (reviewed in Teng et al., 2017). Of particular interest for paleoredox studies is the $^{238}U/^{235}U$ ratio, which has the potential to track the global extent of oceanic anoxia (*e.g.*, Weyer et al., 2008; Tissot and Dauphas, 2015).

Uranium has three naturally occurring isotopes: primordial ^{238}U and ^{235}U ($t_{1/2} = 4468$ Myr and 704 Myr, respectively, Jaffey et al., 1971), and the shorter-lived ^{234}U ($t_{1/2} = 245{,}620$ yr, Cheng et al., 2013), which is part of the decay chain of ^{238}U. In terrestrial surface environments, U exists in two main oxidation states: soluble U^{6+} that behaves conservatively in the modern ocean (*i.e.*, U concentration varies linearly with salinity, Ku et al., 1977; Owens et al., 2011), and insoluble U^{4+}. Because the mean oceanic residence time of U (~400 kyr; Ku et al., 1977) is much longer than the global ocean mixing time (1–2 kyr), the salinity-normalized seawater composition is homogeneous with regards to both U concentrations ($[U]_{SW} = 3.22 \pm 0.06$ ng/g, for a salinity of 35 g/L, Chen et al., 1986) and U isotopes ($\delta^{238}U_{SW} = -0.39 \pm 0.02‰$, Tissot and Dauphas, 2015; $\delta(^{234}U)_{SW} = 144.9 \pm 0.4‰$, Chen et al., 1986; Chutcharavan et al., 2018) (see Eqs. (1) and (2), for δ-notations). The seawater U concentration and isotopic composition at any given time is thus the balance between U input to the ocean, mainly from rivers, and U removal, mostly into biogenic carbonates, anoxic/euxinic sediments and suboxic/hypoxic sediments (*i.e.*, oxygen-minimum zones in continental margin settings with high primary productivity; *e.g.*, Dunk et al., 2002; Tissot and Dauphas, 2015).

In the ocean, $\delta(^{234}U)$ and $\delta^{238}U$ values are controlled by different processes, making uranium a two-facetted system. On the one hand, the evolution of the seawater $^{234}U/^{238}U$ through time both holds clues into continental weathering and affects U-Th ages. Indeed, alpha-recoil during ^{238}U decay and preferential leaching of ^{234}U over lattice-bound ^{238}U lead to ^{234}U excesses in rivers and marine sediment pore-waters, which are eventually transferred to the oceans (*e.g.*, Chabaux et al., 2003). This results in a modern $\delta(^{234}U)_{SW}$ value of ~145‰ (*e.g.*, Ku et al., 1977; Chen et al., 1986; Andersen et al., 2010). As removal of U from the homogenized ocean into sediments and during hydrothermal alteration does not significantly fractionate ^{234}U and ^{238}U, changes in $\delta(^{234}U)_{SW}$ predominantly reflects changes in the source ^{234}U fluxes to the ocean (*e.g.*, Henderson, 2002). To reconstruct $\delta(^{234}U)_{SW}$ through time, carbonates, and particularly corals, are predominantly used. These samples can faithfully record the ambient seawater $^{234}U/^{238}U$ ratio at formation time (*e.g.*, Chutcharavan et al., 2018), and thus provide a way of concomitantly dating the carbonate using U-Th and accessing the $\delta(^{234}U)_{SW}$ at the time of formation (*e.g.*, Edwards et al., 2003). As even minimal sample alteration can, however, lead to large and mostly positive shifts in the $^{234}U/^{238}U$ of carbonates (*e.g.*, Bard et al., 1991; Hamelin et al., 1991; Gallup et al., 1994; Stirling et al., 1995), disentangling changes in the seawater $^{234}U/^{238}U$ from minor open-system behavior is far from straightforward, and past works concluded to a constant $\delta(^{234}U)_{SW}$ throughout the late Quaternary (Bard et al., 1991; Hamelin et al., 1991; Gallup et al., 1994). A growing body of evidence subsequently suggested a 1–15‰ lowering of $\delta(^{234}U)_{SW}$ in times of lower than modern sea-level stand during the last glacial-interglacial period. Establishing the magnitude and timing of these variations and understanding their origins is the focus of intense research (*e.g.*, Robinson et al., 2004; Esat and Yokoyama, 2006; Andersen et al., 2007; Esat and Yokoyama, 2010; Chen et al., 2016a; Chutcharavan et al., 2018; Arendt et al., 2018).

On the other hand, the evolution of the seawater $^{238}U/^{235}U$ through time provides a direct record of the global oceanic redox history. Indeed, and unlike the parent-daughter pair of isotopes (^{234}U and ^{238}U), the two long-lived isotopes of U (^{235}U and ^{238}U) are not significantly fractionated during weathering and transport to the ocean (*e.g.*, Wang et al., 2015; Tissot and Dauphas, 2015) and $\delta^{238}U_{SW}$ is mainly controlled by isotopic fractionation during U removal into sedimentary sinks. While the isotopic fractionation factors ($\Delta_{Sink\text{-}SW}$) associated with U removal into most sinks are relatively small ($|\Delta_{Sink\text{-}SW}| \leq 0.25‰$), nuclear field shift effects (Bigeleisen, 1996; Schauble, 2007; Abe et al., 2008) impart larger isotopic fractionation ($\Delta_{Anoxic/euxinic\text{-}SW} \sim +0.60‰$) during U removal into anoxic/euxinic sediments (*e.g.*, Andersen et al., 2014), leaving the seawater isotopically lighter than the riverine discharge. This fractionation forms the basis of the $^{238}U/^{235}U$ paleoredox proxy: during periods of extensive anoxia, U sequestration into anoxic/euxinic sediments will drive the $\delta^{238}U_{SW}$ towards lower (^{238}U-depleted) values.

Initially, $^{238}U/^{235}U$ paleoredox reconstructions focused on black shales (Montoya-Pino et al., 2010; Asael et al., 2013; Kendall et al., 2013; Kendall et al., 2015) in part because of their high U content and common occurrence