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ScienceDirect
Geochimica et Cosmochimica Acta 190 (2016) 332–346
Geochimica et Cosmochimica Acta
www.elsevier.com/locate/gca

Intra- and inter-annual uranium concentration variability in a Belizean stalagmite controlled by prior aragonite precipitation: A new tool for reconstructing hydro-climate using aragonitic speleothems

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Received 15 February 2016; accepted in revised form 30 June 2016; available online 9 July 2016

Abstract

Aragonitic speleothems are increasingly utilised as palaeoclimate archives due to their amenability to high precision U–Th dating. Proxy records from fast-growing aragonitic stalagmites, precisely dated to annual timescales, can allow investigation of climatic events occurring on annual or even sub-annual timescales with minimal chronological uncertainty. However, the behaviour of many trace elements, such as uranium, in aragonitic speleothems has not thus far been as well constrained as in calcitic speleothems. Here, we use uranium concentration shifts measured across primary calcite-to-aragonite mineralogical transitions in speleothems to calculate the distribution coefficient of uranium in aragonitic speleothems (derived $D_U = 3.74 \pm 1.13$). Because our calculated D_U is considerably above 1 increased prior aragonite precipitation due to increased karst water residence time should strongly control stalagmite aragonite U/Ca values. Consequently, uranium concentrations in aragonitic speleothems should act as excellent proxies for effective rainfall.

We test this using a high-resolution ICP-MS derived trace element dataset from a Belizean stalagmite. YOK-G is an aragonitic stalagmite from Yok Balum cave in Belize with an extremely robust monthly-resolved chronology built using annual $\delta^{13}C$ cycles. We interpret seasonal U/Ca variations in YOK-G as reflecting changes in the amount and seasonality of prior aragonite precipitation driven by variable rainfall amounts. The U/Ca record strongly suggests that modern drying has occurred in Belize, and that this drying was primarily caused by a reduction in wet season rainfall. This is consistent with published stable isotope data from YOK-G also very strongly suggesting modern rainfall reductions, previously interpreted as the result of southward ITCZ displacement. Our results strongly suggest that U/Ca values in aragonitic speleothems are excellent proxies for rainfall variability. This new tool, combined with the exceptional chronological control characteristic

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http://dx.doi.org/10.1016/j.gca.2016.06.037

of aragonitic stalagmites and the high spatial resolution afforded by modern microanalytical techniques, should facilitate the construction of new exquisitely resolved rainfall records, providing rare insights into seasonality changes as well as long-term changes in local recharge conditions.

Keywords: Speleothem; Trace elements; Prior aragonite precipitation; Uranium; Seasonality; Belize

1. INTRODUCTION

Speleothems are invaluable continental palaeoclimate archives that are amenable to precise and accurate U–Th dating, and can yield high-resolution proxy records. Speleothem-based climate reconstructions are particularly useful for reconstructing effective rainfall, and can provide diverse information about rainfall, including moisture source and trajectory, rainfall amount, seasonality, and karst residence time (Fairchild et al., 2006). Well-established stable isotope proxies retain each of these variables to varying degrees in different stalagmites. Disentangling these effects in a given sample is challenging, with individual proxies such as $\delta^{18}O$ or $\delta^{13}C$ potentially reflecting multiple climatological and environmental factors in a single proxy record. Therefore, considering multi-proxy approaches when attempting to reconstruct effective rainfall from speleothem records is critical. Trace element proxies for prior carbonate precipitation and/or residence time reflect the volume of water infiltrating through the karst and can help deconvolve these separate signals. In calcite speleothems, the most commonly used trace element proxy for prior calcite precipitation (PCP) is Mg/Ca (Fairchild and Treble, 2009), due to its abundance and strong partitioning between fluid and solid phases (Fairchild et al., 2000). Other element ratios such as Sr/Ca or Ba/Ca also produce complementary information about hydrology (McDonald et al., 2007). In addition, sulphate concentrations in speleothems have been used as tracers of volcanic or anthropogenic inputs to the karst system (Frisia et al., 2005; Wynn et al., 2008, 2010, 2014; Borsato et al., 2015). Elements that are less water soluble or less easily incorporated into the calcite crystal lattice, although utilised more rarely, are useful proxies for volcanic or anthropogenic inputs into the karst system (Jamieson et al., 2015) or as chronological markers of seasonal flushing of associated organic material (Borsato et al., 2007; Hartland et al., 2012). Similar mechanisms control trace elements in aragonitic speleothems, although the differing crystal structure of aragonite compared to that of calcite means that elements are incorporated differently between the two minerals. Aragonitic speleothems are particularly useful in palaeoclimatic research because their generally high uranium content allows very high U–Th dating precision (Kennett et al., 2012; Woodhead et al., 2012; Denniston et al., 2013). Despite this potential, the relative scarcity of published aragonitic stalagmite trace element records (Finch et al., 2003; Wassenburg, 2013; Tan et al., 2014) means that trace element partitioning behaviour into their structure remains poorly understood. Research constraining uncertainties in elemental behaviour in aragonitic stalagmite is therefore crucial.

1.1. Prior aragonite precipitation

Prior calcite precipitation is a significant control on dripwater element concentrations before trace element incorporation in speleothems (Fairchild et al., 2000, 2001; Fairchild and Treble, 2009; Treble et al., 2015). Precipitation of calcium carbonate up-flow from the speleothem may affect the ratios of various trace elements to calcium in dripwaters (and thus speleothems) depending on the value of their distribution coefficients. This mechanism controls a significant proportion of variability in water-soluble alkaline earth metal concentrations due to their abundance and predictable behaviour. PCP is not a primary control on other elemental variations due to the dominance of other processes such as supply, transport, and/or growth/crystal structure dependencies for incorporation, for example pH (Wynn et al., 2014) or growth rate (Fairchild et al., 2001). Far less is known about the effects of prior aragonite precipitation (PAP) on speleothem geochemistry. However, PAP probably significantly influences speleothem geochemistry in environments where aragonite precipitation is favoured, though currently very few studies have considered PAP controls on speleothem geochemistry. Fairchild and Treble (2009) discussed the potential of PAP as an influence on Sr/Ca, but concluded that it would have a minimal effect on strontium concentrations. Wassenburg et al. (2012) highlighted the potential for PAP to increase dripwater Mg/Ca, and a lack of PCP as an explanation for the decoupling of Sr, Mg and Ba within speleothem aragonite. Wassenburg et al. (2013) identified PAP from monitored dripwaters by observing a negative correlation between Ca and Sr concentrations. These studies established PAP as a process that can affect dripwater and/or speleothem trace element ratios, but did not propose a diagnostic elemental proxy for PAP. The potential of PAP to function as an important hydrologically mediated control on speleothem geochemistry merits further consideration, especially considering that the differing crystal structure of aragonite compared to calcite may favour the incorporation of elements with larger ionic radii, thereby providing proxies for environmental changes that are not available in calcite speleothems. One element incorporated in greater concentrations in aragonite because of the aforementioned reasons is uranium, which is mostly incorporated as $UO_2(CO_3)_3$ (Reeder et al., 2000) and readily substitutes for Ca within the aragonite crystal structure but less so in that of calcite.