



Dripwater organic matter and trace element geochemistry in a semi-arid karst environment: Implications for speleothem paleoclimatology

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Abstract

A series of four short-term infiltration experiments which revealed hydrochemical responses relevant to semi-arid karst environments were carried out above Cathedral Cave, Wellington, New South Wales (NSW), Australia. Dripwater samples were collected at two sites for trace element and organic matter analysis. Organic matter was characterised using fluorescence and interpreted using a PARAFAC model. Three components were isolated that represented unprocessed, soil-derived humic-like and fulvic-like material, processed humic/fulvic-like material and tryptophan-like fluorescence. Principal Component Analysis (PCA) performed on the entire dataset comprising trace element concentrations and PARAFAC scores revealed two dominant components that were identified as soil and limestone bedrock. The soil component was assigned based on significant contributions from the PARAFAC scores and additionally included Ba, Cu, Ni and Mg. The bedrock component included the expected elements of Ca, Mg and Sr as well as Si. The same elemental behaviour was observed in recent stalagmite growth collected from the site. Our experiments demonstrate that existing paleoclimate interpretations of speleothem Mg and Sr, developed in regions of positive water balance, are not readily applicable to water limited environments. We provide a new interpretation of trace element signatures unique to speleothems from water limited karst environments.

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1. INTRODUCTION

Trace elements are preserved in speleothem calcite and are increasingly used either in chronology (where trace elements vary rhythmically; [Smith et al., 2009](#)) or as a paleoclimate proxy ([Sundqvist et al., 2013](#); [Wassenburg et al., 2013](#)). Trace elements can derive directly from precipitation; from

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biogeochemical reactions between recharge and trace elements associated with organic matter, colloids, clays and bedrock clasts within the overlying soil; and from biogeochemical reactions between infiltration water and trace elements associated primarily with the limestone bedrock overlying the cave (Fairchild et al., 2000; Fairchild and Treble, 2009; Tremaine and Froelich, 2013). Therefore trace element composition of waters infiltrating into a cave can be a product of many processes which include metal-organic matter binding (Borsato et al., 2007; Hartland et al., 2012), soil cation exchange, incongruent and congruent dissolution of bedrock and soil clasts (Hansen and Postma, 1995), and the amount of prior calcite precipitation (PCP). Variable soil water residence times (related to climatic conditions) and degrees of mixing between recently infiltrated precipitation, existing older soil water, and vadose zone water may lead to variable elemental compositions for elements that are released by kinetically controlled reactions, such as weathering of primary silicate minerals (Appelo and Postma, 2005). Regardless, the trace element distribution in speleothem deposits will be related to the infiltration water geochemistry and further modified during calcite precipitation. For full reviews, we refer the reader to Fairchild and Treble (2009), Fairchild and Baker (2012), and Tremaine and Froelich (2013).

Trace elements have been widely investigated in speleothem paleoclimatology because they can give insights in the multitude of processes that determine infiltration. However they have yielded quantifiable paleoclimate proxies in only a limited number of cases. The majority of research has focussed on Mediterranean, temperate and alpine climatic regions, where mean annual precipitation (P) is typically greater than mean annual evapotranspiration (ET). Pioneering initial research by Roberts et al. (1998) demonstrated annual variability in Sr/Ca, Mg/Ca and Ba/Ca in a temperate climate Scottish speleothem. Fairchild et al. (2000) demonstrated that variations in water availability, which control the extent of prior calcite precipitation (PCP) and incongruent dissolution of bedrock could be the primary controls on speleothem Sr/Ca and Mg/Ca, and this has been recently demonstrated through the investigation of many diverse sites by Tremaine and Froelich (2013). In drier conditions, there is longer water residence time in the epikarst leading to decreased drip rates and enhanced CO_2 degassing. This system results in higher Mg/Ca and Sr/Ca ratios than those found in congruent dissolution of limestone due to preferential removal of Ca (Tremaine and Froelich, 2013). Organic matter associated trace elements have also been recognised which include, P, Cu, Pb, Zn and Y (Borsato et al., 2007), and have been associated with infiltration events that mobilise soil organic matter and colloids (Hartland et al., 2012). Where trace element variations occur regularly, such as in climate regions with strong seasonality, high resolution (sub-annual) analysis of these trace elements in speleothems provides an annual chronology (Smith et al., 2009), which has been successfully used to provide high precision records of past climate (for example, Sundqvist et al., 2013).

Although karst infiltration water trace element geochemistry increasingly is well understood, the majority of research has been undertaken in temperate to alpine environments, where on average mean annual $P > ET$. In these environments, soil organic matter is relatively abundant, soil geochemistry is primarily controlled by weathering of the underlying bedrock, and infiltration and associated speleothem deposition can be considered to be relatively continuous (Fairchild and Baker, 2012). These conditions contrast those in more arid environments: where $P < ET$, soil organic matter may be limited and the soil is poor in nutrients such as phosphorus. In these regions evaporation processes dominate over infiltration, leading to salt accumulation within the soil profile (McDonald et al., 2007). With increasing aridity, aeolian processes and dust deposition becomes an increasingly important contributor to the soil geochemical profile (Greene et al., 2009). Soil trace element geochemistry therefore depends on the interplay between the extent of soil salinisation (controlled by ET), the proximity of potential dust sources, a site climatology that permits dust transport and deposition, the soil organic matter content and character, and the bedrock geochemistry. Infiltration events are irregular, often without an annual frequency. Consequently speleothem deposition, and thus trace elemental composition, can be considered to be episodic rather than seasonal. In a pioneering study in SE Australia, McDonald et al. (2007) presented 5-yr of trace metal data from cave dripwater and noted a more complex response of dripwater Mg/Ca, Sr/Ca and Ba/Ca to climate than observed in temperate regions. More recently, Frisia et al. (2012) demonstrated that the P record preserved in Australian speleothems could be both a function of within-cave microbial processes as well as soil-derived infiltration. However, despite these two studies, review of available literature indicate that karst infiltration processes in arid and semi-arid zones are rarely investigated and thus require further research.

In this paper we present the results of an infiltration experiment performed at the Wellington Caves, NSW, Australia. We undertook an artificial infiltration experiment to better understand the trace element geochemistry of dripwaters in semi-arid climate regions where $P < ET$. We believe that this is the first such experiment undertaken to understand karst dripwater trace element composition. Furthermore, water sampling comprised both inorganic elements (trace metals) and dissolved organic matter analysis by fluorescence, permitting the investigation of the association of organic matter with trace elements. Our results are relevant to the interpretation of speleothem trace element records from any arid or semi-arid regions where infiltration events are infrequent and evaporation dominates the soil water balance. This of course includes modern day semi-arid and arid climate regions, as well as regions which have experienced past aridity in the Quaternary or older time periods. Our results will therefore facilitate the interpretation of speleothem trace element records from regions such as Israel (Bar-Matthews et al., 1991), Yemen (Van Rangelbergh et al., 2013), Turkey (Siklós et al., 2009) and Morocco (Wassenburg et al., 2013), as well as from Australia (McDonald et al., 2007).

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