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High-resolution trace element and stable/radiogenic isotope profiles of late Pleistocene to Holocene speleothems from Dim Cave, SW Turkey

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ABSTRACT

Multiple climate-sensitive trace element/Ca and stable isotope (O and C) profiles derived from Dim Cave speleothems (S-SW Turkey) provide evidence of climatic changes and define a series of palaeohydrological conditions for the period ~10–90 kyr. Dim Cave speleothem Mg/Ca, Sr/Ca, U/Ca, Ba/Ca, and Y/Ca ratios demonstrate similar patterns over glacial–interglacial scales, in agreement with $\delta^{18}O$ and $\delta^{13}C$ records. Three episodes of more positive moisture balance (71–63 kyr, 51–40 kyr, and 18–10 kyr) were observed based on Y/Ca (and to a lesser extent Zr/Ca), $^{87}Sr/^{86}Sr$ ratios, calcite micromorphology, and growth rates. Increasing concentrations of Y, Zr (and U) and elevated $^{87}Sr/^{86}Sr$ ratios are attributed to enhanced levels of terrestrial input during these periods. Correlations between $\delta^{13}C$, $\delta^{18}O$ and Mg/Ca during 40–18 kyr (corresponding with the lowest growth rate of ~0.8 mm/kyr), 63–51, and 80–71 kyr (relatively low growth rates), as well as co-varying and enhanced Mg/Ca, Sr/Ca, and to a lesser extent Ba/Ca, ratios point to the prior calcite precipitation, wall rock interaction, and preferential dolomite dissolution over calcite in the host dolomitic limestone during these periods. This relationship suggests that water–rock interactions are maximised during episodes of slower drip rates of water through the karst under drier conditions. Chondrite-normalised rare earth element and yttrium (REY) patterns of the stalagmites reveal seawater signatures closely linked to the dolomitic limestone. Excluding the aragonite formation during ~80–75 kyr, which is an autogenic effect, trace element/Ca ratios appear to respond to millennial scale global cooling periods such as Heinrich events.

1. Introduction

Geochemical records derived from speleothems are becoming significantly more important in constraining past climatic conditions (Bar-Matthews, 2014; Fairchild et al., 2006). Together with stable/radiogenic isotope data, trace element/Ca (TE/Ca) ratios (e.g., Mg/Ca, Sr/Ca, and U/Ca) can be used to define and refine climate-driven palaeohydrological variability, including the extent of soil–fluid–rock interactions and exotic terrestrial inputs into cave systems (e.g., riverine input or aeolian dust) (e.g., Ayalon et al., 1999; Bar-Matthews et al., 1996, 2003; Fairchild et al., 2000; Fairchild and Treble, 2009; Frumkin et al., 2000; Goede and Vogel, 1991; Goede et al., 1998; Griffiths et al., 2010; Hellstrom and Mcculloch, 2000). High-resolution, continuous records with precise chronological control give the opportunity to investigate the interplay between various environmental and climate-sensitive proxies that have been preserved by terrestrial cave deposits (Rowe et al., 2012; Jex et al., 2011; Fairchild and Treble, 2009; Fleitmann et al., 2009; Wang et al., 2001; Zhao et al., 2001). Changes in climate and particularly precipitation over annual to centennial timescales have always been important for the ancient civilizations of the Eastern Mediterranean (EM) (e.g., Bar-Matthews and Ayalon, 2011; Robinson et al., 2006; Roberts et al., 2011; Frumkin et al., 2011). Research suggests that decreases in rainfall-driven water availability during the Holocene (after ~7000 cal BP) in this region (Bar-Matthews, 2014; Vaks et al., 2003; Tzedakis, 2007; Jalut et al., 2009), was one of the main reasons for the decline and/or collapse of some former civilizations (e.g., decline of Ottoman Empire in the preindustrial era, the collapse of Uruk society in Mesopotamia, transition from chalcolithic to the early Bronze Age, societal collapse of the Late Bronze Age; Dean et al., 2015; Kaniewski et al., 2012; Staubwasser and Weiss, 2006; Roberts et al., 2011). Therefore, climatic archives revealing past variability of rainfall regimes are of great importance for society.

Trace element variations within speleothems have been investigated in many experimental and cave monitoring studies (e.g., Bar-Matthews et al., 1999; Fairchild et al., 2000; Fairchild and Treble, 2009; Murray, 1954), underlining their potential as an independent qualitative palaeoenvironmental proxy. The transmission of the trace elements into the karst host rock is based on the geochemical behaviour of the

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trace elements (i.e., partitioning coefficients of individual elements between host rock, seepage water and speleothems; Morse and Bender, 1990) in the overlying soil and unsaturated epikarst zones, and hydrological processes affecting the infiltration of surface and soil waters (Roberts et al., 1998; Fairchild et al., 2001; Fairchild and Treble, 2009). Moreover, the differential dissolution of host rock calcite and dolomite controlled by rainfall and pathway-driven residence times can cause considerable variation in trace element chemistry of the waters (Fairchild et al., 1994, 2000). The Mg/Ca ratio, in particular, has been used to determine temperature-related partitioning at the water–calcite interface (Gascoyne, 1983) and also effective precipitation (i.e., precipitation minus evapotranspiration) that controls the dripping rate and hence the residence time of the seepage water (Fairchild and Treble, 2009; Roberts et al., 1998; Gascoyne, 1983; Hellstrom and Mcculloch, 2000). For example, drier conditions limit the seepage rates, maximizing the water–soil–rock interactions, leading to incongruent dolomite dissolution relative to calcite in solution, and hence yield higher Mg/Ca in cave waters and speleothems (Roberts et al., 1998; Fairchild et al., 2000).

In addition to Mg/Ca, Sr/Ca and Ba/Ca ratios are also used as proxies for palaeo-aridity, although increasing Sr/Ca may also reflect input from additional sources such as terrestrial aeolian dust and sea salt in near-coastal sites (Goede et al., 1998). Drier conditions also promote CO_2 degassing during the infiltration of seepage waters and result in "upstream" or prior calcite precipitation (PCP) along the flow path (e.g., in the epikarst or on the cave roof) removing Ca^{+2} and ^{12}C from the solution, and leading to elevated Mg/Ca, Sr, Ba/Ca, and $\delta^{13}C$ in speleothems (Huang et al., 2001; Fairchild and Treble, 2009; Johnson et al., 2006; Regattieri et al., 2014). Zr/Ca, U/Ca, and Y/Ca can also be used as indicators of both relative aridity and the degree of exotic terrestrial input (e.g., from leached felsic or other types of silicate rocks), though this is best achieved in conjunction with cave monitoring data and other proxies (e.g., stable isotope data) showing similar trends. Overall, the host and basement rock compositions play a vital role in sourcing the trace element inventory of the drip waters and speleothems (Belli et al., 2013; Fairchild and Treble, 2009).

As with most of the global speleothem-based studies, regional studies in the EM focus primarily on stable isotope ($\delta^{18}O$ and $\delta^{13}C$) variations (e.g., Bar-Matthews et al., 2003; Fleitmann et al., 2009; Bar-Matthews et al., 1999) to reconstruct the palaeo-rainfall, palaeotemperature, and palaeo-vegetation styles. In this region, the climate system is complex as it is located at the boundary between the northern hemisphere westerlies and the sub-tropical high pressure belt (Türkeş,

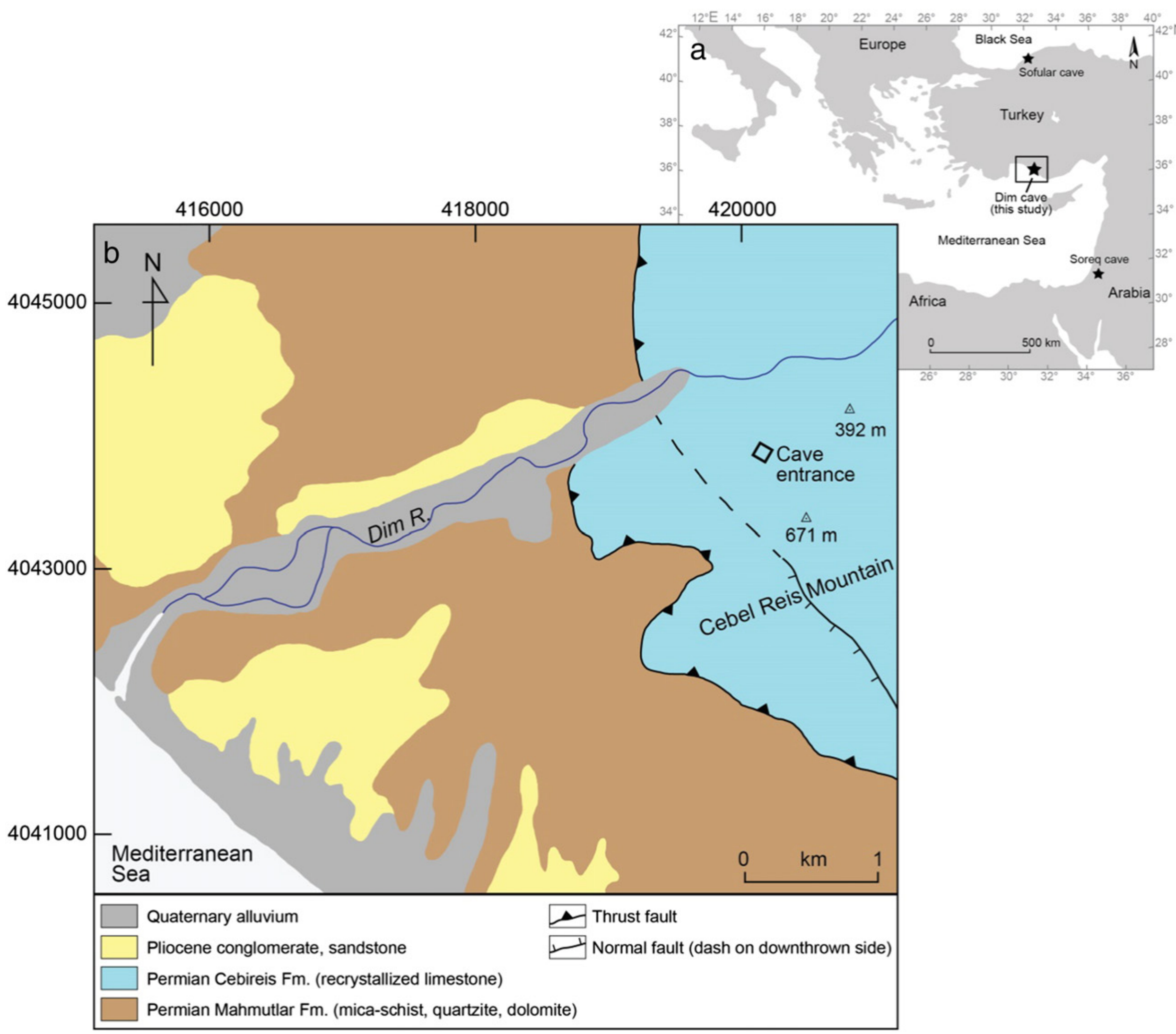

Fig. 1. Location **(a)** and geological map **(b)** of the Dim Cave (232 m a.s.l.) and its surroundings (modified from Gündalı et al., 1989). Permian dolomitic limestone (Cebireis Fm) hosts the Dim Cave (Ünal-İmer et al., 2015), see Table S3 (online) for trace element concentration of the host limestone.