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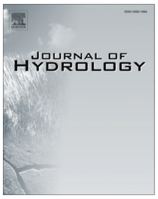

Research papers

Controls on dripwater chemistry of Oregon Caves National Monument, northwestern United States

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ABSTRACT

Cave dripwater chemistry of Oregon Caves National Monument (OCNM) was studied, where the parameters pH, total alkalinity, calcium, magnesium, strontium, sodium and barium were analyzed at quasi-monthly intervals from 2005 to 2007. Different statistical analyses have been used to investigate the variability of the chemical parameters in the different sites in the OCNM cave system. The dripwater varies in response to seasonal changes in rainfall. The drip rates range from zero in summer to continuous flow in winter, closely following the rainfall intensity. Spatial variations of dripwater chemistry, which is nonlinearly related to dripwater discharge likely, reflect the chemical composition of bedrock and overlying soil, and the residence time of the ground water within the aquifer. The residence time of infiltrated water in bedrock cracks control the dissolution carbonate bedrock, reprecipitation of calcium carbonate and the degree of saturation of dripwater with respect to calcium carbonate minerals. Spatiotemporal fluctuations of dripwater Mg/Ca and Sr/Ca ratios are controlled by dissolution of carbonate bedrock and the degree of calcite reprecipitation in bedrock cracks. This suggests that trace elements in speleothem deposits at the OCNM may serve as paleoclimatological proxies for precipitation, if interpreted within the context of understanding local bedrock chemistry.

1. Introduction

Interactions between rain, soil, and bedrock produce a variety of biogeochemical signals in cave dripwaters including $\delta^{18}O$ and δD from rain, traces of organic matter, $\delta^{13}C$ of total dissolved CO_2 and elements such as calcium, magnesium, strontium. Dripwater properties depend on the surrounding environmental conditions and on the dissolution and precipitation processes in the karst system (Fairchild et al., 2000, 2006; Toran and Roman, 2006; Borsato et al., 2015; Casteel and Banner, 2015; Zeng et al., 2015). Studies of limestone caves identified seasonal variations in ionic concentrations of dripwaters (Baker et al., 2000; Drever, 1982; Musgrove and Banner, 2004; Day and Henderson, 2013). For example, total dissolved ion concentrations in dripwaters were observed to correlate with soil CO_2 seasonal variations (Mayer, 1999) because higher levels of soil CO_2 increase carbonate mineral dissolution. The composition of the host rock also strongly influences the water composition (Motyka et al., 2005; Smart et al., 1986; Tooth and Fairchild, 2003). Dripwaters with high concentrations of calcium and bicarbonate are mainly produced from calcitic bedrock while waters with high concentrations of calcium, magnesium, bicarbonate, and sulfate are produced from dolomitic bedrock with pyrite (Chalmin et al., 2007; Bar-Matthews et al., 1991; Frisia et al., 2002; Wu et al., 2015). The variation in physical and chemical properties of dripwater may be incorporated and preserved in speleothem deposits, and these changes have been used to infer paleoclimate and paleoenvironmental conditions in the caves where speleothem deposits were formed (McDermott, 2004; Fairchild et al., 2006; Johnson et al., 2006; McDonald et al., 2007; Lachniet 2009, Steponaitis et al., 2015). The physicochemical characteristics of the drip waters can help in understanding the processes that affect the formation of stalagmites and carbon, hydrogen and oxygen isotopic composition (McDonald et al., 2007; Lambert and Aharon, 2011).

Drip water rates change seasonally and vary from slow and irregular to fast and continuous (Baker and Brunsdon, 2003; Baker et al., 2000; Fernández-Cortés et al., 2007). The drip water rates in the Oregon Caves National Monumeent (OCNM) also vary seasonally and range from slow to no drip at shallow rooms to fast and constant drip at the deeper rooms (Schubert 2007). The control of drip water rate and room locality (i.e., shallow vs depth) on the

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drip water chemistry has not been fully investigated. Therefore, the objectives of this work were to: (1) characterize the geochemistry and the saturation states of the waters with respect to carbonate minerals and (2) investigate the possible factors that control dripwater chemistry and their potential influence on the chemical composition of speleothems from shallow (slow dripwater rate) and deep (fast dripwater rate) rooms. Here, we analyze dripwaters from the OCNM in southwestern Oregon of the USA.

2. Study area and sampling sites

The OCNM is located in the Klamath Mountains, southwestern Oregon (42° 05′ 53″ N, 123° 24′ 26″ W, altitude ~ 1220 m) (Fig. 1). The modern vegetation above the cave is dominated by *Pseudotsuga menziesii* (Douglas fir) and *Abies concolor* (white fir). The plants are mainly of C-3 type vegetation. Soils overlying the OCNM are from various bedrock lithologies including granites and serpentinites. The bedrock in the OCNM cave system belongs to the Paleozoic-Triassic Applegate Group, consisting of metavolcanics and metasediments (Irwin, 1966; Barnes et al., 1996). The OCNM was formed in a faulted and folded marble lens, and was carved by meteoric waters that have percolated through the overlying soil and bedrock (Barnes et al., 1996; Vacco et al., 2005; Schubert, 2007).

The measured temperature deep inside the cave is approximately constant through the year at 8.8 ± 0.7 °C. The monthly-average temperature outside the cave ranges from ~19 °C in summer to ~6.5 °C in winter (Schubert, 2007). Precipitation falls mostly as rain in the fall and spring and as snow in winter, but is virtually absent in summer (Taylor and Hannan, 1999). Water entering the cave is derived from local snowmelt and rainfall (Salinas, 2003; Ersek et al., 2010). Rainfall events activate dripwater sites within hours to days in the upper part of the cave, although water also may take months to years to reach the cave through cracks parallel to the orientation of the bedrock structure (Roth, 2005). While upper parts of the cave dry out by the end of summer, deeper parts remain wet throughout the year (Schubert, 2007).

3. Methodology

3.1. Sampling

Dripwater samples were collected at four sites within the OCNM cave system (Fig. 1) at quasi-monthly intervals from January 2005 to July 2007. We collected the water samples manually and used a stopwatch to count the number of drips/minute. We did this 3 times and averaged the number. Precipitation data were obtained from a weather station installed outside the cave. Collection sites were situated in the the Kings and Queens Throne Room (KQR, ~14 ms subsurface), Imagination Room (IR, ~18 m subsurface), the Miller's Chapel Room (MR, ~30 m subsurface), and from two sites in the Shower Room (SR1 and SR2, ~51 m subsurface). All water samples were collected into dark amber glass bottles with airtight screw-cap seals and plastic vapor barriers which were acid-washed, rinsed with deionized water purified with Milli-Q Plus Water System (Millipore) prior to use. Nitric acid was added to each sample to achieve pH ~ 1.0 (Cenci and Martin, 2004).

The samples were subsequently stored in a refrigerator for 1–12 months before analysis, where the pH and total alkalinity measurements were performed during the first 2–3 months of the sample collection. The analyses of trace and major elements were conducted 3–6 months later.

3.2. Chemical analyses

The bottles were carefully sealed to ensure that they remain gas-tight to prevent any atmospheric gas exchange. We divided

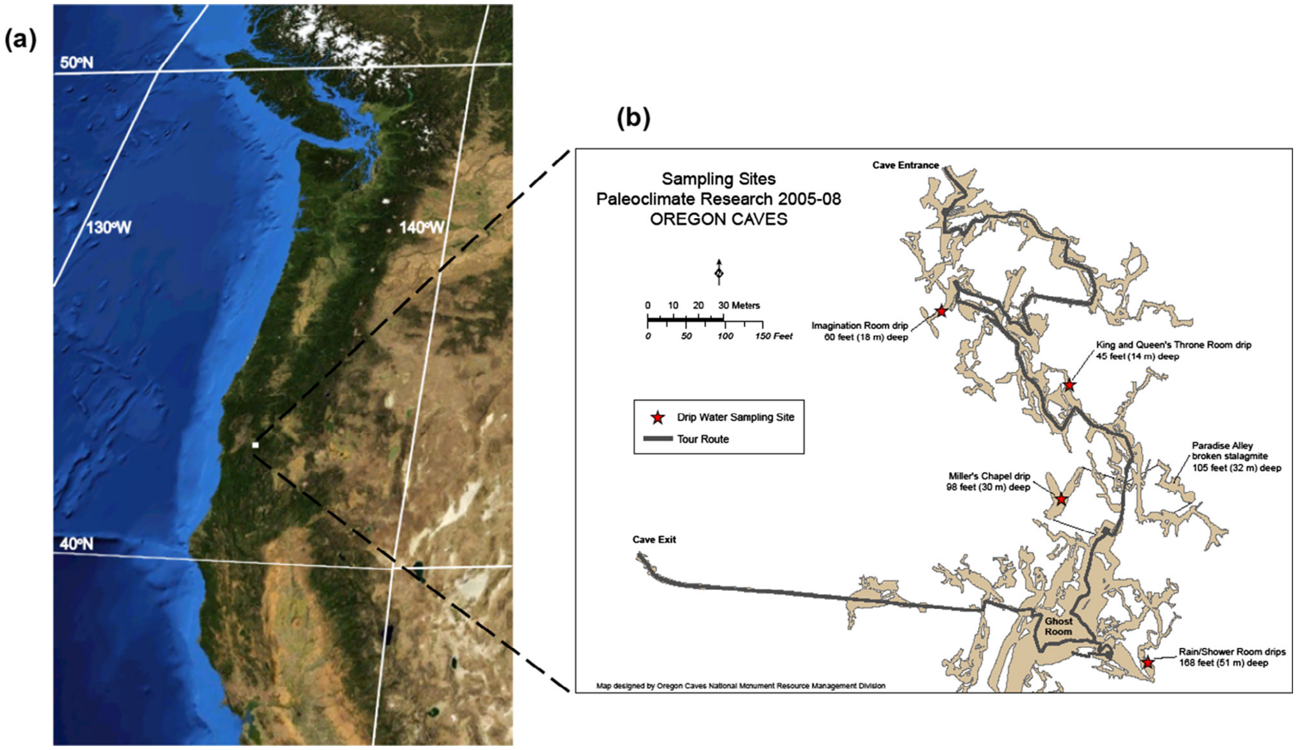

Fig. 1. Map showing the locations of (a) Oregon Caves National Monument (OCNM), which is located in the Klamath Mountains, western the United States of America and (b) the water sampling sites in the OCNM caves.