

# Were fossil spring-associated carbonates near Zaca Lake, Santa Barbara, California deposited under an ambient or thermal regime?



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## ABSTRACT

A previously undescribed succession of currently-inactive spring-associated carbonates located near Zaca Lake, Southern California, was investigated in order to determine the nature of deposition (ambient temperature or hydrothermal water, as both are found within the region). The carbonate deposits are up to ~1 m thick and formed discontinuously for over 200 m in a narrow valley between two ridges that drain Miocene Monterey Formation bedrock. Depositional facies along the presently dry fluvial path include barrage deposits, narrow fluvial channels, and cascade deposits. The carbonates are mesoscopically banded and contain ubiquitous micro- to macrophyte calcite encrusted fabrics. All of the depositional facies contain alternating bands (~0.05 mm to 5 mm thick) of dark brown and light brown isopachous calcite; the dark brown bands are composed of dense isopachous bladed calcite, whereas the light brown bands are composed of bundles of calcite tubules interpreted as the biosignature of the desmid microalgae *Oocardium stratum*. Oxygen isotope thermometry utilizing modern water  $\delta^{18}\text{O}$  values from the piped spring reveal depositional water temperature estimates that collectively range from ~11 to 16 °C. Stable isotope carbon values exhibit a mean  $\delta^{13}\text{C}$  value of  $-9.01 \pm 0.62\%$  ( $1\sigma$ ,  $n = 27$ ). Our petrographic and geochemical data demonstrate that (1) inactive carbonates were likely sourced from ambient temperature water with a strong soil-zone  $\delta^{13}\text{C}$  signal, (2) the *Oocardium* calcite biosignature can be used to infer depositional temperature and flow conditions, and (3) the occurrence of extensive carbonates (especially the presence of a perched cascade deposit) indicate the carbonates formed when conditions were much wetter.

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## 1. Introduction

Terrestrial carbonates that form via spring activity are sensitive to the environment in which they form, potentially serving as valuable archives of hydrology, water chemistry, biology and climate of their local depositional setting (Chafetz et al., 1991; Fouke et al., 2000; Pentecost, 2005; Andrews, 2006; Cremaschi et al., 2010; Sanders et al., 2011). Spring-associated carbonate deposits are commonly classified based on the temperature and origin of the carrier  $\text{CO}_2$  of the water from which they are sourced (e.g., Ford and Pedley, 1996). The term travertine refers to carbonate deposits that form from high-temperature spring water, where the  $\text{CO}_2$  is sourced from hydrothermal fluids, whereas the term tufa has been assigned to ambient temperature carbonate spring precipitates, where the  $\text{CO}_2$  is sourced from the local soils and the atmosphere (Ford and Pedley, 1996). Their distinct hydrologic origins thereby provide different information on the environmental setting of deposits that are no longer active. The presence of travertine, for example, has implications for nearby hydrothermal/volcanic activity (Hancock et al., 1999; Fouke et al., 2000), whereas

the groundwater-fed nature of tufa deposits results in a strong influence by local climate (Andrews, 2006).

In order to accurately interpret depositional information from a given fossil/inactive terrestrial carbonate succession, we must first determine the hydrologic regime under which the carbonates formed (ambient temperature, thermal, or a mix of thermal and ambient water). Degree of lithification, macrophyte encrustations, and organic carbon content allow travertine to be distinguished from tufa (Ford and Pedley, 1996; Minissale et al., 2002; Gandin and Capezuoli, 2008; Capezuoli et al., 2014). However, poor textural preservation, similar sedimentological facies, and interlayering/mixing of tufa and travertine in sites where (1) hydrothermally sourced waters cool with extensive lateral transport and/or (2) where thermal and ambient waters from the same site mix to produce interlayering facies of travertine and tufa (e.g., Capezuoli et al., 2008; Pedley, 2009) may complicate our ability to fully decipher depositional information from fossil/inactive deposits. For these reasons, geochemical analyses (e.g., stable isotopes) are often used to infer the hydrologic nature of inactive spring carbonates (Confiantini et al., 1968; Szulc and Cwizewicz, 1989; Guo et al., 1996; Minissale et al., 2002; Andrews and Brasier, 2005; Kele et al., 2008). Nonetheless, terrestrial carbonates are highly susceptible to recrystallization, possibly compromising geochemical signatures and thus primary structures are desirable.

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A potential complementary approach to verify the hydrology of deposition is to examine the micromorphology of the deposit. It is well-established that microorganisms can contribute to the formation and alteration of terrestrial spring carbonates (Freytet and Verrecchia, 1998; Riding, 2000; Golubić et al., 2008; Pedley, 2009; Arp et al., 2010; Manzo et al., 2012). Much of the focus on terrestrial carbonates has been on the interplay between the physicochemical and biological mechanisms that contribute to carbonate precipitation. Active carbonate-depositing springs serve as natural laboratories where we can study the extent to which microorganisms might influence the precipitation of carbonates and other minerals. By examining mineral phases/structures associated with specific taxa (e.g., Freytet and Plet, 1996; Freytet and Verrecchia, 1998), we may be able to constrain environmental signals from dormant/inactive deposits presuming they have not yet become diagenetically altered beyond recognition. Here we combine a multiscale facies approach (sensu Shapiro, 2000) with analyses of stable isotopes to determine the depositional regime (ambient or thermal) of previously undescribed fossil/inactive spring carbonates located in Santa Barbara County, Southern California as both cold springs and hot springs have been reported in the surrounding area (USGS, 1995).

## 2. Geological and environmental context of study site

Spring-derived carbonate deposits are located about 2 km upstream of Zaca Lake in Santa Barbara County, California, USA (Fig. 1). In 1911 a natural spring was boxed and piped to provide water for consumption (Fig. 1B) such that carbonate deposition downstream has not been observed in the modern. Carbonates crop out discontinuously for over 200 m along the stream grade bed of a narrow valley that is bound by two ridges composed of the carbonate-rich Miocene Monterey Formation (Hall, 1981). The ridges define the relatively small catchment that drains into Zaca Lake, one of only a few naturally-occurring lakes in Southern California.

Two distinct units of spring-related carbonate growth have been observed. The first spring carbonate succession, the focus of the majority of the work described here, was deposited discontinuously for approximately 200 m along the stream grade bed of the valley (Fig. 1B). The

width of the spring carbonate transect varies from about 1 m to approximately the width of the valley floor (~15 m) and ranges in thickness from 0 to about 1 m. A second carbonate unit (approximately 15 m in lateral extent and ~2 m thick) occurs perched upon the slope of the north ridge about 10 m above the modern stream grade bed (Fig. 1B). The ages of the carbonate units are unknown, but we assume a relatively young age (possibly late Quaternary) based on the geomorphic position of the deposits within the valley system.

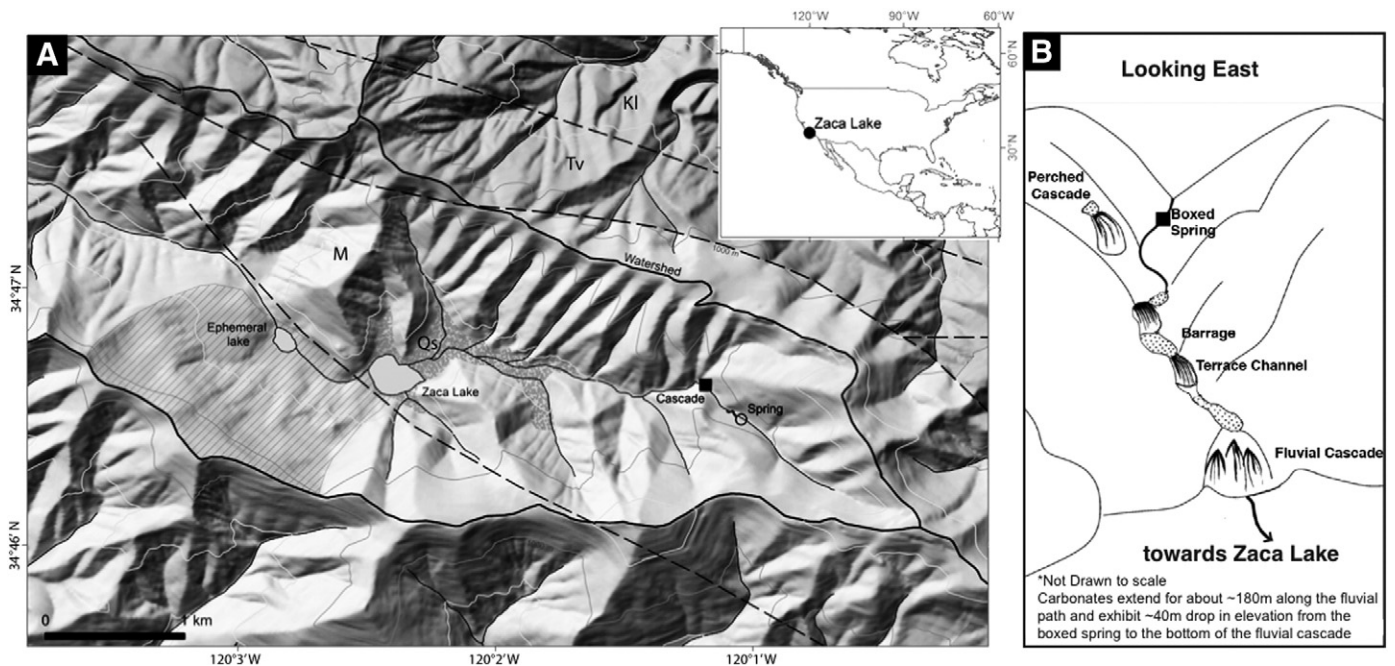
## 3. Methods

### 3.1. Facies descriptions

In our approach, we describe the macro- to micro- characteristics (sensu Shapiro, 2000) of four distinct facies (Fig. 1B) along the spring carbonate transects. Carbonate rock samples were obtained from the topmost (~10–20 cm) part of the four sections where there was good surface exposure and samples were easily accessible. Samples were slabbed, polished, and scanned for mesostructural studies (cm scale). Microstructural observations were carried out via light microscopy of thin sections. Complementary thin-section rock pieces were etched with diluted HCl and examined further using a scanning electron microscope (SEM). Mineralogy was determined via X-ray diffraction (XRD) at the Los Angeles Museum of Natural History. Here, we focus on the microfabric of a particular lamination that is conspicuous in outcrop and hand sample.

### 3.2. Carbonate isotopic analyses

Isotopic analyses of carbonate oxygen and carbon were conducted on an Elementar Americas Inc. (Micromass Ltd) Isoprime stable isotope ratio mass spectrometer (IRMS) with a multi-prep/carbonate device and dual inlet at the Stott Laboratory at the University of Southern California. Samples were drilled from polished hand sample specimens after careful inspection for recrystallization via thin section analyses. Samples are measured relative to CO<sub>2</sub> reference gas calibrated against the NBS-19 ( $\delta^{18}\text{O}$  value +2.20‰,  $\delta^{13}\text{C}$  value +1.95‰) carbonate standard, which allows for normalization to the 2-point VPDB-LVSEC



**Fig. 1.** Geologic setting of the spring carbonates. (A) Geologic map of the Zaca Lake catchment. Abbreviations: M = Monterey; Qs = surface Quaternary; L = landslide; Tv = Tertiary volcanics. Dashed lines indicate fault lines. Contours are at 200 m intervals. (B) Schematic representation of carbonate deposit (imitating Viles et al., 2007) with the labeled location of the boxed spring, fluvial deposit, and perched deposit (the image is not drawn to scale; the approximate distance from the boxed spring to the cascade is ~180 m).

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