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**BASAL TRAVERTINE OF THE BOUSE FORMATION: GEOCHEMISTRY,
DIAGENESIS AND IMPLICATIONS FOR THE INTEGRATION OF THE
COLORADO RIVER**

BY

**CHRISTINA L FERGUSON
BACHELOR OF SCIENCE**

THESIS

Submitted in Partial Fulfillment of the
Requirements for the Degree of

**Master of Science
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Basal travertine of the Bouse Formation: Geochemistry, diagenesis, and implications for integration of the Colorado River

by

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B.S., Earth and Planetary Sciences, University of New Mexico, 2017

M.S., Earth and Planetary Sciences, University of New Mexico, 2020

ABSTRACT

The Pliocene Bouse Formation is discontinuously exposed in the lower Colorado River region and is a record of the first arrival of the Colorado River to the Gulf of California 5 million years ago. It consists broadly of a lower carbonate member (travertine, marl, and bioclastic units) and an upper siliciclastic member (claystone, mudstone, and Colorado River sands). This paper focuses on the basal travertine (synonymous with “tufa”) unit of the lower carbonate member. Because of its basal position and its chemical encrustation of pre-Bouse topography, the travertine can offer insight into the earliest depositional settings and may be a proxy for the composition of the waters that deposited the first Bouse carbonates. Hence the travertine unit, if it can be shown to preserve a primary geochemical signal, offers the potential to discriminate between alternative hypotheses for marine versus non-marine deposition of the Bouse carbonates of the Blythe Basin. This paper examines the geochemistry of the travertine unit using stable isotopes of carbon and oxygen, $^{87}\text{Sr}/^{86}\text{Sr}$, petrographic examinations of thin sections, and microprobe traverses. Testing for diagenesis included subsampling techniques and textural studies using thin section examinations and SEM investigations.

The travertine unit forms an encrustation that drapes and mantles pre-Bouse topography, including volcanic bedrock and fan conglomerates. The travertine unit is generally thin, often less than several meters thick although it can reach thicknesses of tens of meters. It is intermittent but fairly widespread in the Blythe Basin, the southernmost of the Bouse basins, and also is present in scattered locations in the more northern basins. Its facies include: porous tufa, microbialite domes (bioherms), vegetation-casts (charophytes of marsh and probable non-marine origin), and botryoidal travertine, all overlapped by and interfingering with marl and high energy bedforms of

bioclastic sandstone that were deposited before the first arriving Colorado River sands. This Walther's Law relationship suggests that the travertines are broadly coeval with the other facies in the basal carbonate unit of the Bouse Formation. Stable isotope data for travertine reveal a covariation of $\delta^{13}\text{C}$ with $\delta^{18}\text{O}$ and a spread of values between (+4, +2‰) and (-16, -9‰) for the southern Blythe Basin and a regression line with $R^2 = 0.63$. Northern basin travertines have a similar covariation trend ($R^2 = 0.73$). Travertines show multiple carbonate generations in thin section, but stable isotope analyses did not show continuous or regular differences in composition of subsamples. Silica diagenesis was observed in the Buzzard's Peak area where the 4.834 Ma Lawlor Peak tuff is interbedded with carbonates, but this area showed overlapping carbonate chemistry to other areas, although somewhat more positive along the regression line. Compiled and new $^{87}\text{Sr}/^{86}\text{Sr}$ analyses show that the basal Bouse carbonates have non-marine values of ~ 0.711 (as opposed to 0.709 for seawater) in all carbonate facies (marls, bioclastic unit, travertine, and numerous fossil types). Double dissolution tests for $^{87}\text{Sr}/^{86}\text{Sr}$ values were performed in travertine and marl to evaluate potential diagenetic changes: these revealed little change in values (from 0.71051 to 0.71081; from 0.71056 to 0.71074; and from 0.71088 to 0.71088). Plots of $\delta^{18}\text{O}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ and versus latitude show no covariation in $^{87}\text{Sr}/^{86}\text{Sr}$ over a wide range of $\delta^{18}\text{O}$ and facies types.

The combined data are interpreted as showing only limited carbonate diagenesis within the basal travertine of the Bouse Formation such that carbonate geochemistry can be used as a proxy for the waters that deposited them. Two possibilities are examined to explain the covariation of $\delta^{18}\text{O}$ with $\delta^{13}\text{C}$: 1) mixing of sea water (0, 0) and meteoric water (-16, -7); or 2) evaporation of basin water. We favor evaporation as the dominant explanation based on the similarity of travertine variation in northern (lacustrine) and southern (debated marine versus lacustrine) basins, the presence of non-marine charophytes in travertines, and absence of covariation between $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, consistent with evaporation but not mixing. Radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ and the presence of localized zones of large volumes of travertine suggest influences from deeply circulated geothermal groundwaters. We

do not rule out mixing of marine and non-marine waters in an estuarine environment to explain marine fossils and reported sequence stratigraphic and tidal sedimentary evidence, but the geochemical data are more consistent with the interpretation that the initial travertine deposition in multiple Bouse basins (and the travertine-depositing waters) were dominantly non-marine.

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Introduction

The Pliocene Bouse Formation (Metzger, 1978) provides a sedimentary record of the initial integration of the southward-extending Colorado River (Crossey et al., 2005) to the northward-opening Gulf of California (Umhoeffer et al.,

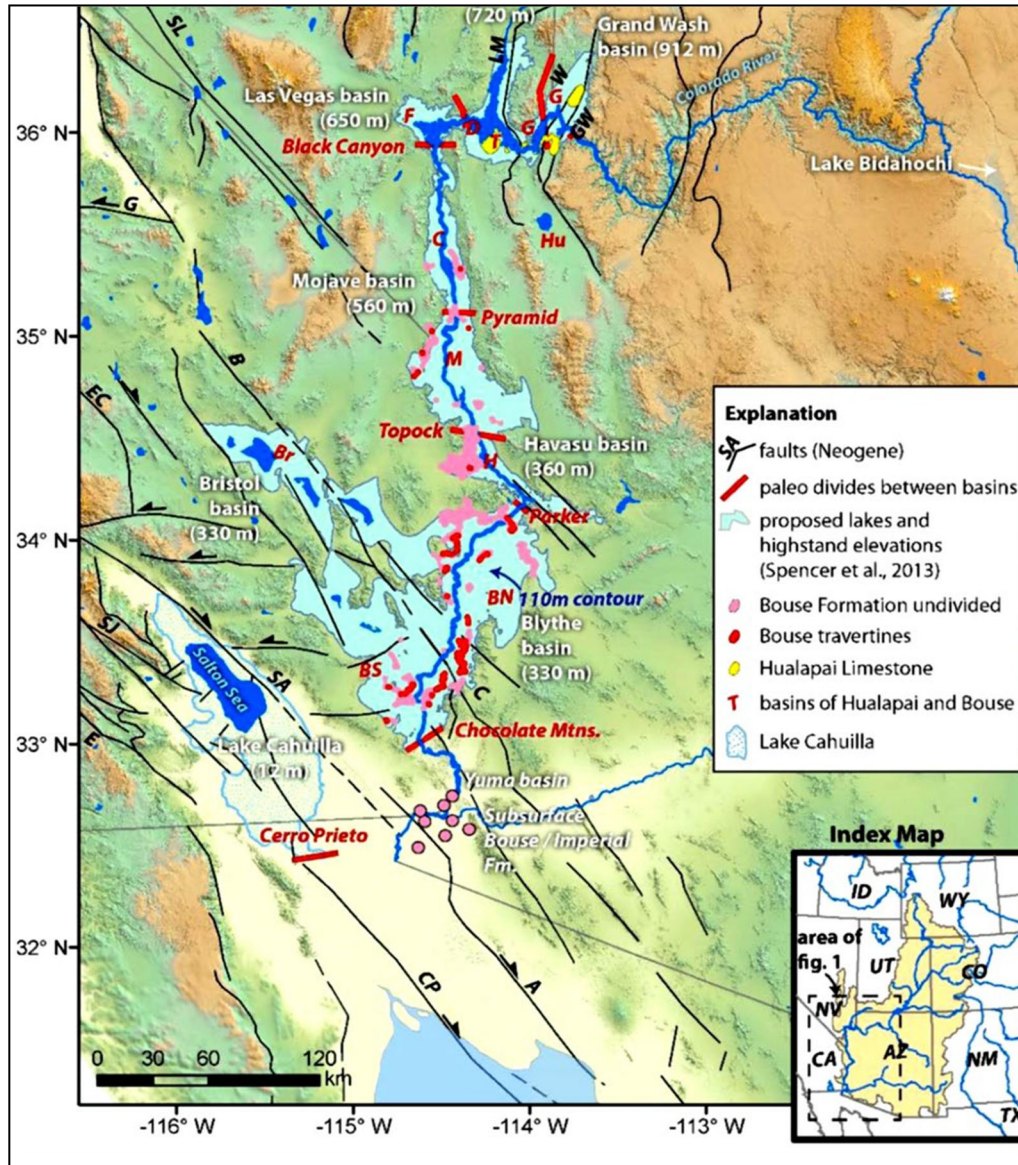


Figure 1: Map of outcrops of the Bouse Formation and the paleo-divides between basins (red lines). Identified faults are shown with black lines and motion is shown with black arrows where known. Red polygons contain travertine. The focus of this work is on the southernmost basin, the Blythe Basin, bound on the north by the Parker Divide and on the south by the Chocolate Divide, but comparisons to travertines of northern basins is also included.

2018) about 5 Ma (Crow et al., 2019). Figure 1 shows the lower Colorado River corridor, from Lake Mead to the Gulf of California. From north to south, the basins that contain the Bouse Formation are the Cottonwood, Mojave, Havasu (Chemehuevi), northern and southern Blythe, and Yuma

basins. In many models, the solid red lines on the map represent bedrock paleo-divides that would have separated lake basins until they filled with Colorado River water and spilled over to the next southerly basin (Spencer and Patchett, 1997; House et al, 2008; Pearthree and House, 2014). The basins decrease in average elevation from north to south with Bouse Formation outcrops found as high as 560 m above sea level (asl) north of Topoc Divide, and 330 m asl in the Blythe basin. This paper focuses on the Blythe Basin where the depositional environment of the Bouse Formation is currently under debate as marine (McDougall and Miranda-Martinez, 2014; Dorsey et al., 2018) versus non-marine (Spencer et al., 2013; Pearthree and House, 2014; Bright et al., 2018). For this work, we focus on the basal carbonate unit in the southernmost portion of the Blythe Basin. The goal is to evaluate its facies associations and use carbonate geochemistry to inform interpretations of depositional environments.

The stratigraphy of the Bouse Formation is shown in Figure 2. The upper Bouse siliciclastic unit (Fig. 2A; also known as the interbedded unit of Metzger (1978) and

basin fill facies of Busing (1990)) contains sands that are texturally like modern Colorado River sand and that contain detrital zircon signatures similar to recent Colorado River samples (Kimbrough et al., 2015). This unit is interpreted by all

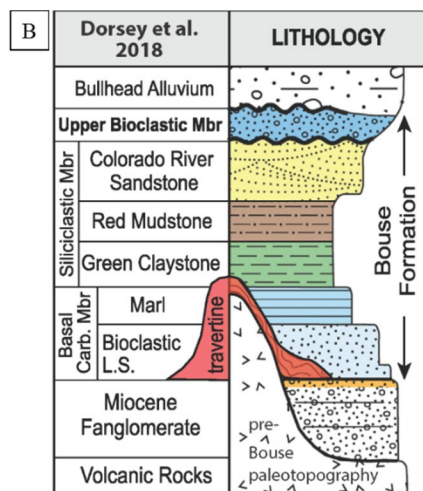
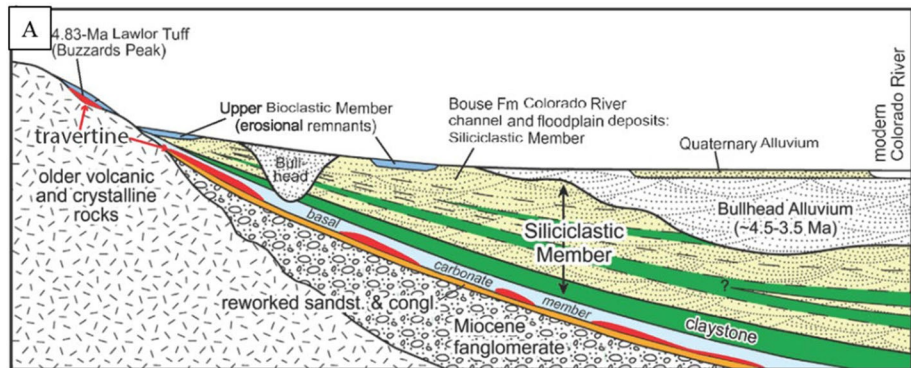


Figure 2: Generalized stratigraphy of the Bouse Formation from Dorsey et al., 2018. The basal travertine unit drapes pre-Bouse topography (A) and is overlain by and also interfingers with the bioclastic and marl units (B). Thickness of the Bouse Formation basal carbonate member is generally meters to tens of meters. The upper bioclastic member (also known as the Trigo Sediments (Gootee et al., 2019)) is currently under debate as either a second marine re-flooding of the basin (Dorsey et al., 2018) or alluvial fan reworking of basal carbonate that occurred as paleo-Lake Blythe waned (Gootee et al., 2019).

current workers to record first arriving Colorado River sediments. In contrast, the thin and discontinuous basal carbonate unit of the Bouse Formation presents persistent research controversies in several subdisciplines. Figure 2A (Dorsey et al., 2018) shows the basal travertine member forms a discontinuous bathtub shape that was deposited as the basin filled and then was blanketed by basin marls and bioclastic carbonates. Figure 2B (Dorsey et al., 2018) shows the travertine as an encrustation that mantles pre-existing topography over vertical distances of tens of meters in individual outcrops and extending hundreds of meters vertically at the basin scale. An upper carbonate unit (Upper Bioclastic Member) is argued to record a second marine flooding of the basin (Dorsey et al., 2018) although Gootee et al. (2018; 2019) interpreted it to be alluvial fans (not part of the Bouse Formation) that rework the lower carbonates.

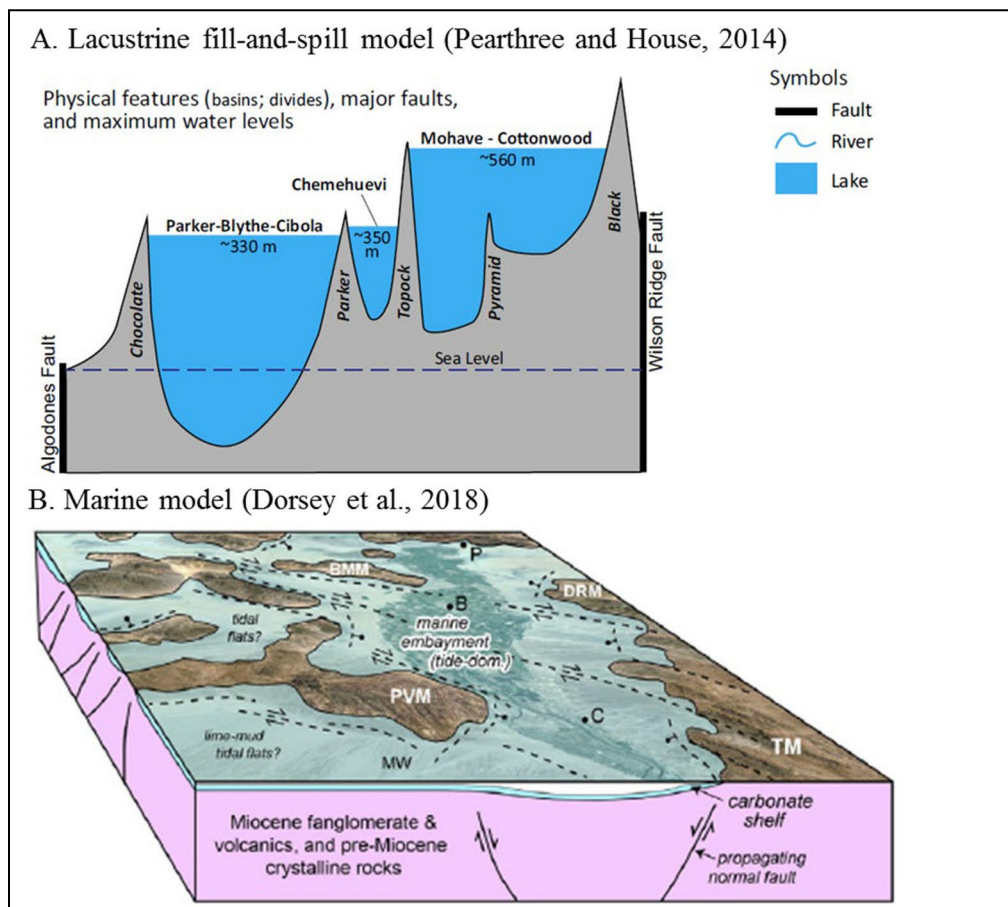


Figure 3: Depositional models for the Bouse Formation. (A) Fill-and-Spill model from Pearthree and House (2014) posits a lacustrine environment created as the Colorado River filled and spilled over sequential basins from north to south. (B) Marine/estuary model proposed by Dorsey et al. (2018) shows that the lower Colorado River corridor was alternatively lacustrine and marine due to topographical changes during the integration of the Colorado River.

Alternative depositional models are shown in Figure 3. Lacustrine models have been favored by Spencer and Patchett (1997), Pearthree and House (2014), Spencer et al. (2013) and Bright (2018). Marine models have been favored by Metzger (1978), Buising (1990), McDougal and Miranda-Martinez (2014), O'Connell et al. (2016), and Dorsey et al. (2018). Hybrid or estuarine models have also been proposed (Crossey et al., 2015; Dorsey et al., 2018). In keeping with these different interpretations, marine fossils found in the Blythe Basin of the Bouse Formation are variably interpreted to be in situ (McDougal and Miranda-Martinez, 2014; Homan, 2014; Dorsey et al., 2018) or transported in by birds and established in coastal saline lakes (Spencer et al., 2013). Previous work has shown that $^{87}\text{Sr}/^{86}\text{Sr}$ values average 0.710860 (Spencer and Patchett, 1997; 2013; Crossey et al., 2015) and are much higher than values for open marine conditions of ~ 0.709 and this has been interpreted to support the non-marine models (Spencer and Patchett, 1997). However, radiogenic carbonate values might also reflect mixing, in a reverse-analog to the San Francisco Bay in which $^{87}\text{Sr}/^{86}\text{Sr}$ in the bay are lowered (in that case) by fluvial inputs (Crossey et al., 2015) whereas in the Blythe Basin case, fluvial inputs would be more radiogenic than seawater. Stable isotopic data have been used to support both marine and non-marine interpretations.

Geochronology constraints on age are also debated within the interval 6.0 Ma (Dorsey et al., 2018) to 4.834 Ma (Spencer et al., 2013). The 4.834 Ma Lawlor Tuff (Harvey, 2014; Sarna-Wojcicki et al., 2011) at Buzzard's Peak is interlayered with and has been interpreted as the age of the Bouse carbonate member (Spencer et al., 2013; this paper). Alternatively, McDougal and Miranda-Martinez (2014) and Dorsey et al. (2018) proposed an age of 6 Ma for the lower Bouse carbonate based on foraminifers' age ranges and correlated the 4.834 Ma age given by the Lawlor Tuff with what they considered to be a younger upper bioclastic carbonate member. The age of the first-arriving Colorado River deposits to the Gulf of California were interpreted as 5.3 Ma by Dorsey et al. (2013). A subsequent dating study, including samples from the same section, suggest first arrival of the Colorado River to the Gulf of California between 4.834 and 4.65 Ma (Crow et al., 2019).

The purpose of this paper is to examine the basal travertine facies of the Bouse Formation as it has received less attention than other facies. The term “travertine” is used synonymously here with “tufa” of other workers (Benson, et al., 1995; Busing, 1990; Metzger, 1978). Because travertine is a chemical precipitate, its geochemistry may be a good proxy for first arriving waters if we can show minimal diagenesis or are able to “look through” diagenetic overprints. In addition to outcrop facies studies, multiple geochemical tracers used here are $^{87}\text{Sr}/^{86}\text{Sr}$ (new and literature values), $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$

(new and literature values), field, thin section and SEM carbonate work on textures, and selected microprobe carbonate analyses. Tubular fossils seen in this unit are also examined as part of the paleo-environmental interpretations.

Methods

Samples were collected in 2016-2018 from the southern Blythe basin in a northeast to southwest transect across the current lower Colorado River

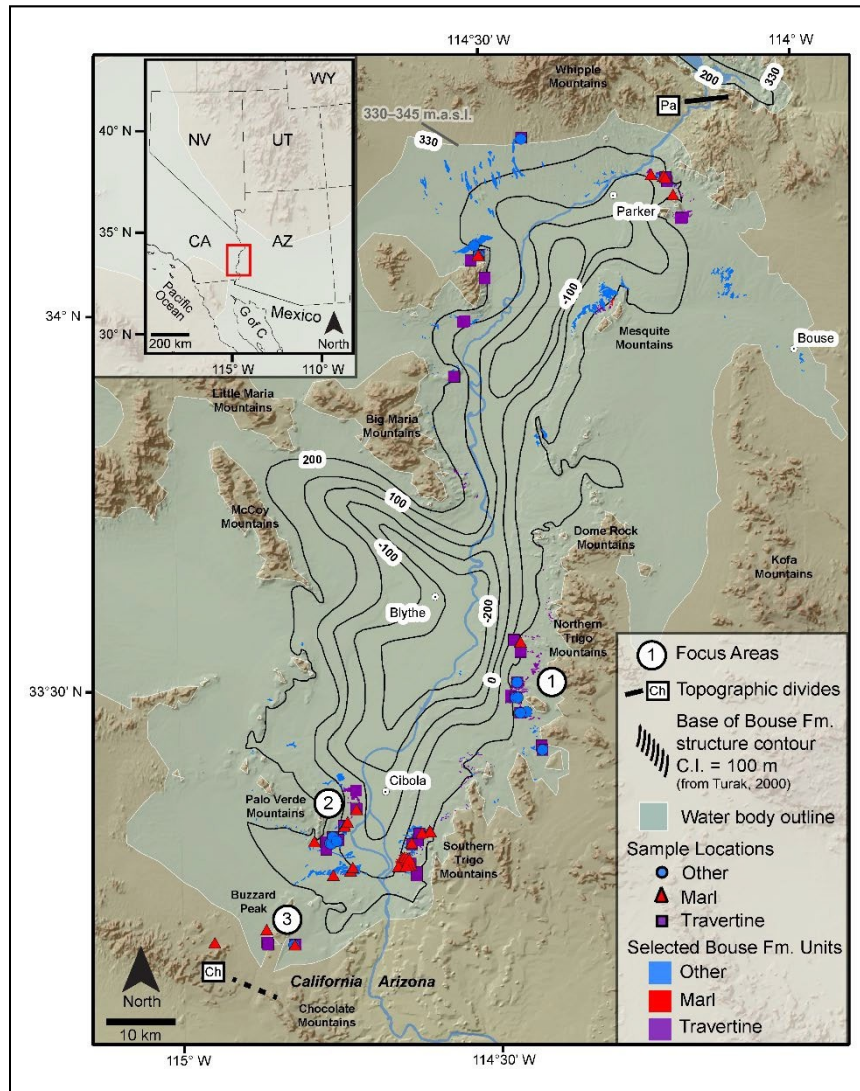


Figure 4: Sample map showing the locations of all the samples analyzed. This includes new samples collected in 2018 and those already in the collection at UNM. Travertines collected in 2018 represent a transect across the lower Colorado River corridor that includes (1) the northern Trigo Mountains, (2) the Palo Verde Mountains, and (3) Buzzard’s Peak.

corridor (Figure 4). Samples were recorded, photographed, and cut. Slabbed sections

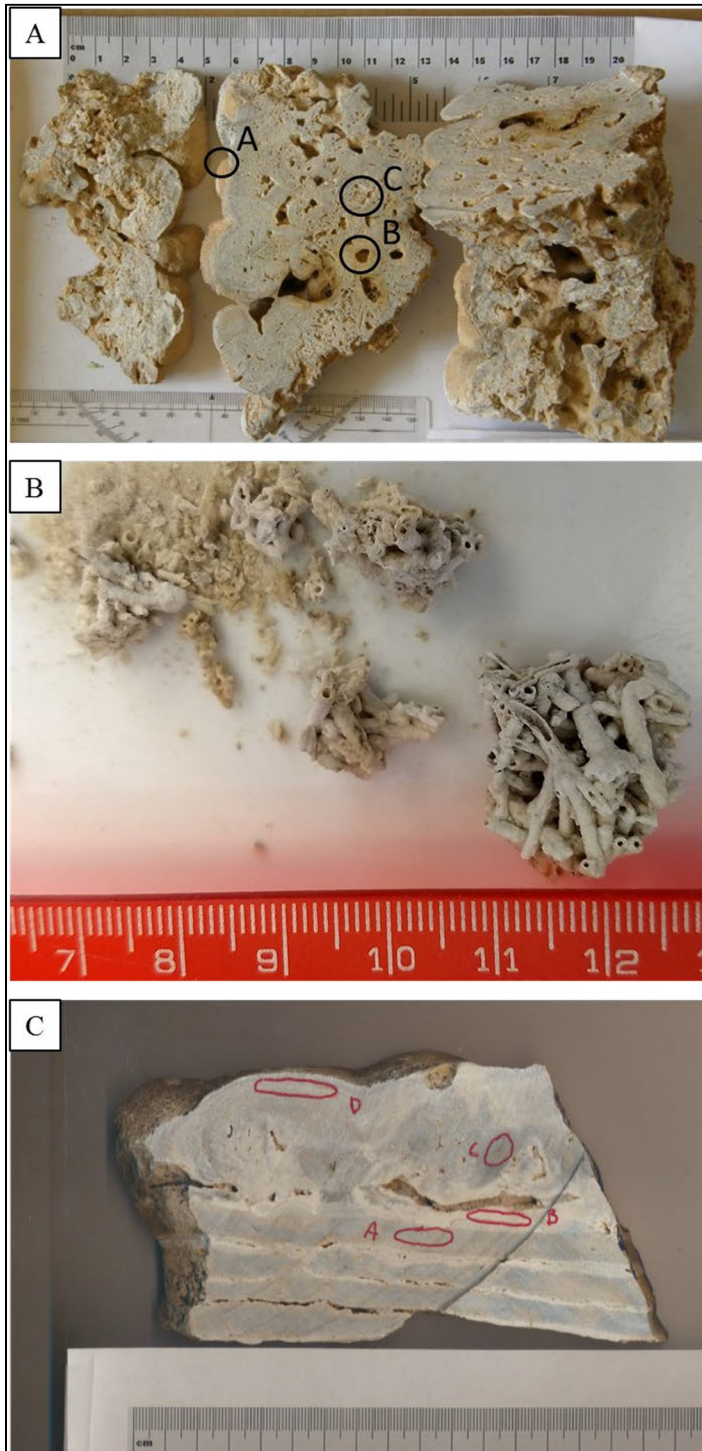


Figure 5: (A) Photo of a single hand sample from the Trigo Mountains (KLC17-8-4) showing slabbed section and subsampling locations. A is the orange “rind” sample, B is the tube sample, and C is the matrix sample. (B) Tubular travertine sample, also from the Trigo Mountains (KLC18-TR1-5) showing complete separation of tubes from the matrix material. (C) A mottled travertine sample from Petroglyph Park in the Palo Verde Mountains (KLC16-PP-11). The same subsampling techniques were applied in an effort to separate textures to determine if there was any difference in isotopic values between portions of the sample.

were visibly inspected for different textures, and these different textures have been selectively sampled for carbon and oxygen isotopic analyses. Remaining portions of the slabs were sent off for thin sections.

Thin sections were inspected with the petrological microscope with a focus on determining crystallization sequences. Select sections were also viewed with the scanning electron microscope (SEM) and spot sampled for chemistry with the microprobe. All instruments are located at UNM in the Earth and Planetary Sciences Department.

Analyses of stable isotopes were performed with a focus on separation of textures within a single sample. Different carbonate textures were analyzed from travertines, including the matrix, outer rind, and tube features within a single

rock (Figure 5). Sub-samples were selected as a test for diagenetic effects. The chosen locations were drilled or chipped out of the rocks and then powdered. The powders were weighed out to between 0.6 and 0.8 milligrams and put into vials as preparation for analysis with the Isotope Ratio Mass Spectrometer. The powders were flushed with He gas and then reacted for 24 hours with phosphoric acid (H_3PO_4) at 50°C (Spotlts and Vennemann, 2003). The CO_2 that evolved from this reaction was measured via continuous-flow isotope ratio mass spectrometry using a Gasbench device coupled to a Finnigan Mat Delta Plus Isotope Ratio Mass Spectrometer at the Center for Stable Isotopes in the Earth and Planetary Sciences department at the University of New Mexico. Oxygen and carbon results are reported in per mil (‰) relative to Peedee belemnite (PDB) with a precision of $\pm 0.3\text{‰}$.

Strontium Isotope Analyses

We analyzed three samples of carbonate from the Bouse Formation for double dissolution treatment following procedures in Li et al. (2011). This process has been shown to extract the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values from carbonate samples. We did not use microdrilling and instead used a rock saw to cut out small pieces that were visually dense and homogeneous; we avoided mottled textures, veins, fractures, or alteration bands. The chips were then washed with tap water then etched with 3% acetic acid. The chips were crushed into a rough powder with a ceramic mortar and pestle. The powders were dissolved in 10 mL of 1N acetic acid on a hot plate at low heat for three hours. Once samples had cooled, two drops of 15 N nitric acid were added to each sample. If a sample reacted with the nitric acid, it was placed back onto the hot plate for one-hour increments until it no longer reacted with newly added nitric acid. This step determined the amount of insoluble residue left over after complete carbonate dissolution. The samples were then centrifuged for four minutes at 2800 rpm. After centrifuging, the remaining liquid was transferred into the beakers and the insoluble residue was left in the centrifuge tubes. The liquid in the beakers was then dried over the hot plate. Once dry, 40 drops of 7N nitric acid was added to the beakers. If any visible residue remained in the solution the sample was dried out again and 40 drops of 6N HCL were added to the beaker. The last step was repeated until the sample was a clear solution. At that point the sample was re-dried and

then 40 drops of 7N nitric were re-added. Half of the solution was extracted and prepared for $^{87}\text{Sr}/^{86}\text{Sr}$ analysis using Sr-spec column chemistry. The rest of the solution was transferred into a cleaned 250 mL bottle and prepared for inductively coupled mass spectrometer (ICPMS) elemental analysis by adding approximately 200 mL of 3% 10ppb nitric acid. The insoluble residue was dried and weighed to determine the amount of carbonate in each sample as well as make dilution calculations used for elemental analyses.

Elemental analyses were done on a Thermo X-series II ICPMS calibrated against concentration standards. Strontium isotopic compositions were measured with a Thermo Neptune multi-collector ICPMS in static mode. Sr standard NBS-987 was run with each batch obtaining the accepted $^{87}\text{Sr}/^{86}\text{Sr}$ values within error of 0.710253 ± 0.000008 (n=28), typical internal errors were about 6 ppm (2σ).

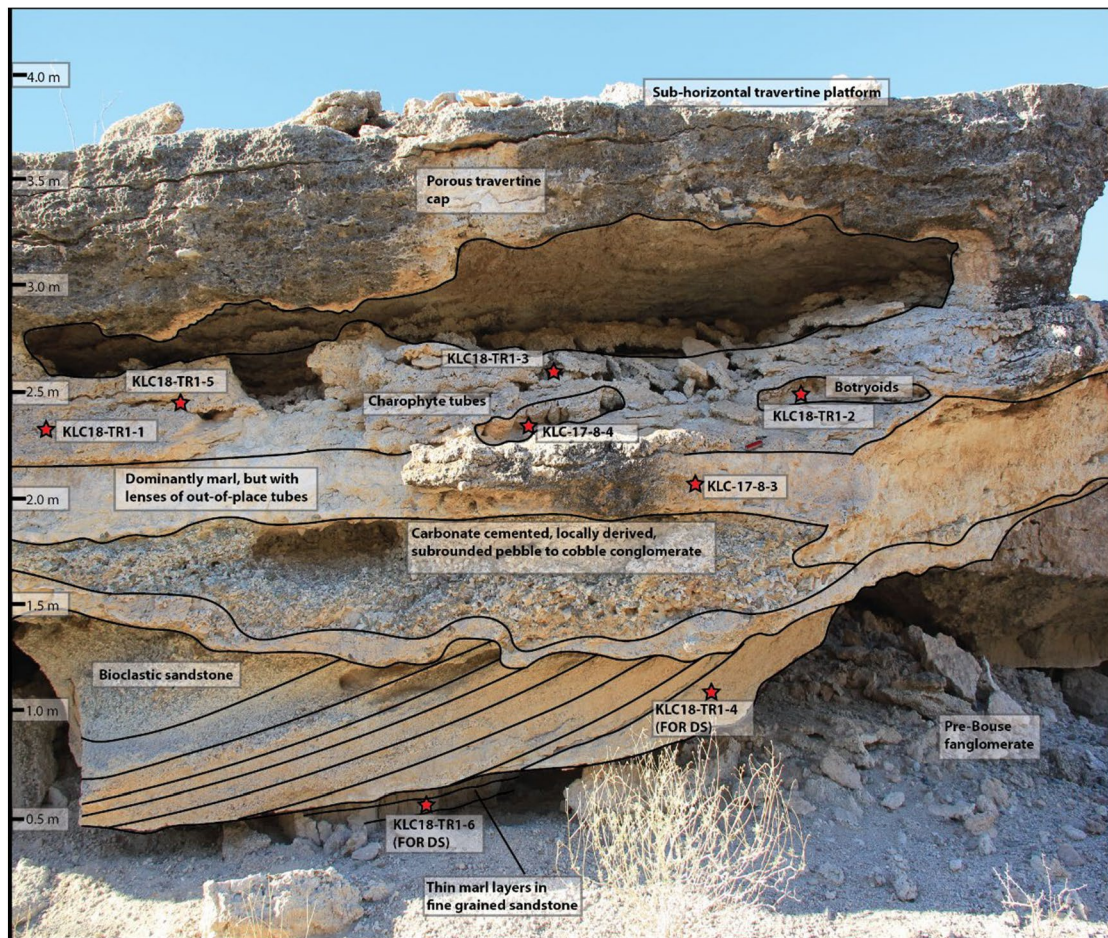


Figure 6: Reference section of the travertine unit from the Trigo Mountains showing a 4 m thick section of interbedded carbonate facies. Facies shown are: pre-Bouse fanglomerates at the base: marl and mudstone, m-scale cross beds of carbonate cemented bioclastic sandstone, carbonate cemented locally derived sub-rounded pebble to cobble conglomerate, marl with lenses of out-of-place tubes, charophyte tube encrustations with open space botryoidal infillings, and tufa/travertine cap and platform.