

Towards a depositional model for travertines of the Bouse Formation: examples from the southern Blythe Basin

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The Bouse Formation provides a sedimentary record of the first arrival of the Colorado River, water and sediment, as it was integrated from the Colorado Plateau to the proto-Gulf of California approximately 4.8-5.3 Ma (House et al., 2008; Spencer et al., 2013). This unit is generally thin (1-100s m) but widespread within basins in the lower Colorado River corridor from Lake Mead to Yuma (Fig. 1). The lower (informal) member of the Bouse Formation is predominantly carbonate; the middle part (the “interbedded unit” of Metzger et al., 1973) consists mainly of siliciclastic deposits, including Colorado River-derived clays, silt, and sand; and the upper member is sandy to gravel-rich bioclastic limestone and locally derived conglomerate that was recently recognized in the upper member of the southern Blythe basin. This paper focuses on basal carbonates of the Blythe basin. Two depositional models for the Bouse in this basin are considered: (1) deposition in a freshwater lake (e.g., Spencer et al., 2008; 2013); and (2) a marine estuary, as proposed for the southern part of the corridor (e.g., Miller et al., 2014; McDougall and Miranda-Martinez, 2014; Crossey et al., 2015; Homan, 2014; O’Connell et al., 2016; 2017).

This paper focuses on the travertine (aka tufa) facies of the Bouse with a goal of understanding the different origins of Bouse carbonates and follows interpretations of Crossey et al. (2016). Dorsey et al. (2016) describe three carbonate facies in the southernmost part of the corridor: (1) lower bioclastic limestone and “tufa” that are interpreted to represent high-energy shallow water (including tidal) environments; (2) a marl succession

that is interpreted to record precipitated carbonate settling below wave base in a large body of water; and (3) an upper unit of fossil-rich calcarenite and conglomerate (Gootee et al., 2016) that overlies the other carbonate facies, mudstone, and cross-bedded Colorado River sandstone,

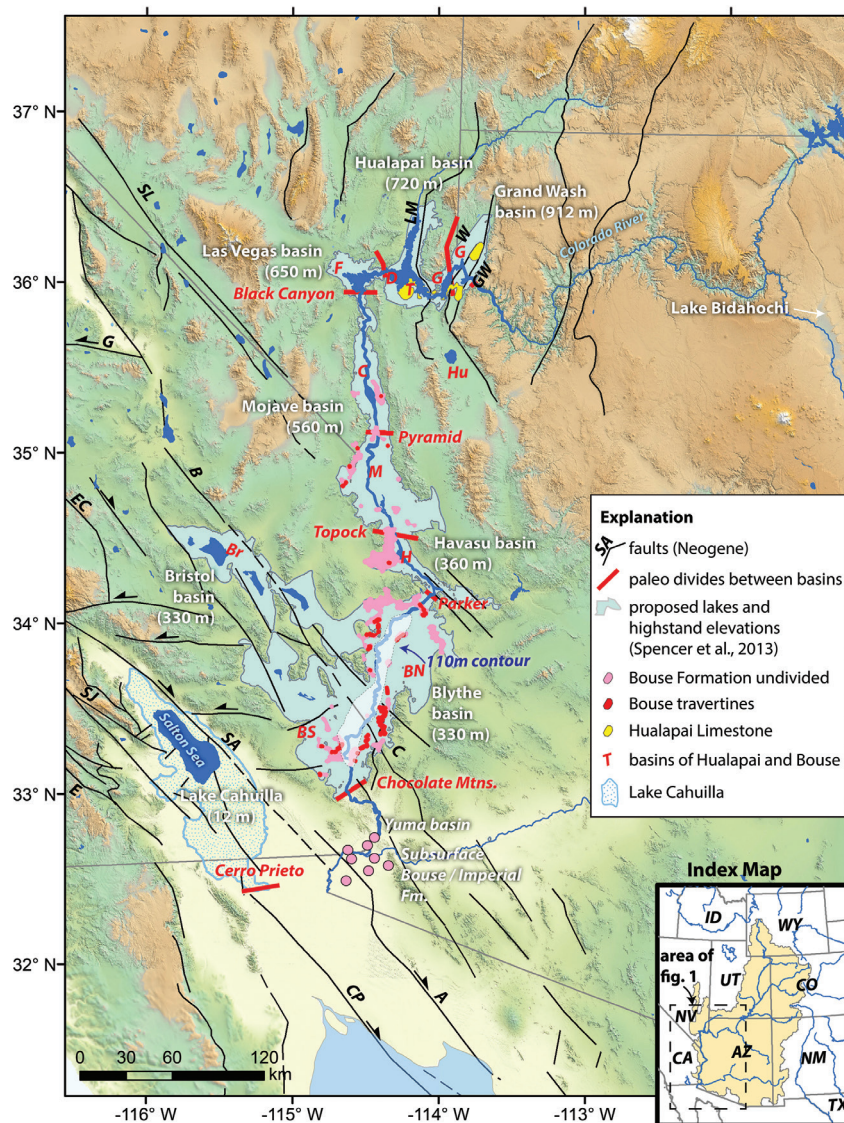


Figure 1. Distribution of the Bouse Formation; Red= Bouse travertine; Pink= Bouse Fm. undivided. This paper focuses on travertines from the Blythe basin; general locations indicated with black stars. The blue arrow indicates the location of the 110m elevation contour, which corresponds to the highest elevation of interpreted marine facies in the Blythe basin. Modified from Crossey et al. (2016).

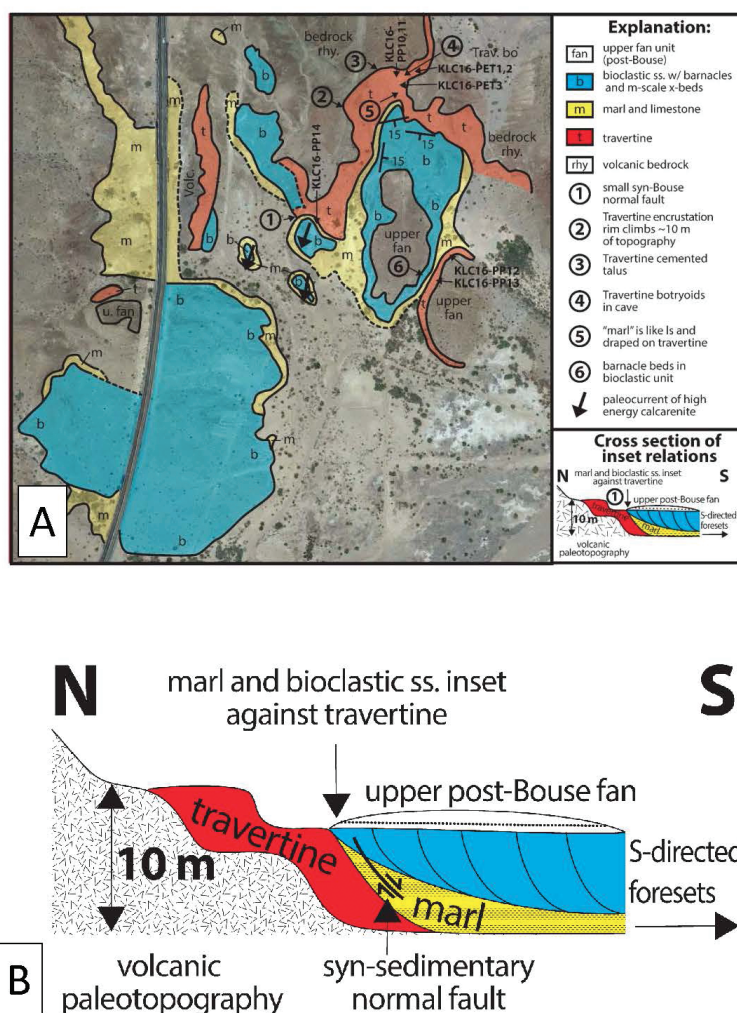


Figure 2. (A) Geologic map of the Bouse Formation at Petroglyph Park; Red= Bouse travertine; Blue=bioclastic sst., Yellow=marl & ls. (B) Schematic cross-section from north to south across the map area illustrating marl onlapping travertine, and high-energy facies inset into both.

and is locally interbedded with mudstone. Here we argue that the travertine deposits constitute a widespread and definable facies as well.

We emphasize that the travertine facies of the Bouse records the first arrival of carbonate- oversaturated waters (the "carbonate factory") that deposited basal Bouse carbonates and hence the need to develop a depositional model for this facies and how it relates to the overlying bioclastic limestone, marl, and calcarenite facies of the Bouse Formation. The term travertine is used here as the more inclusive term and refers to *chemically-precipitated continental limestone that forms as groundwater discharge deposits at spring outlets, and in lakes and streams, via precipitation of calcite from waters that are supersaturated with respect to calcium carbonate* (Ford and Pedley, 1996; Pentecost, 2005). The term "tufa" is sometimes used interchangeably as a mapping term for porous carbonates that occur in spring mounds and "tufa towers" around lakes. However, we prefer the term "travertine" and use it inclusively with no implied interpretation about

temperature of the depositing waters, as this is generally unknown for inactive/fossil systems. The term travertine, in our usage, encompasses a very wide range of freshwater carbonate textures (Fig. 2; see also Crossey et al., 2016).

As also summarized by Crossey et al. (2016), fresh-water carbonates form according to a well-recognized suite of chemical reactions (Pentecost, 2005; Crossey et al., 2006, 2009). For waters to become supersaturated with respect to CO_2 , an "external" CO_2 source (e.g. soil gas and/or magmatically derived volatiles) is needed to make waters aggressive enough to dissolve calcite in regional aquifers. The dissolution reaction is: $\text{extCO}_{2(g)} + \text{H}_2\text{O} + \text{CaCO}_{3(\text{limestone})} \rightarrow \text{Ca}^{2+}_{(\text{aq})} + 2\text{HCO}_3^{-}_{(\text{aq})}$. The precipitation phase of travertine involves degassing of CO_2 due to pressure drop (as artesian waters move upward) and/or turbulence (e.g. due to groundwater discharge or wave action) via the reaction: $\text{Ca}^{2+}_{(\text{aq})} + 2\text{HCO}_3^{-}_{(\text{aq})} \rightarrow \text{CO}_{2(g)} \uparrow + \text{H}_2\text{O} + \text{CaCO}_{3(\text{travertine})}$. When groundwater carries calcium, for example, mixing with an alkaline lake can result in localized supersaturation. Biological influences can also facilitate travertine precipitation of calcite by changing saturation state of waters or by algal trapping of fine grained carbonate. Formation of Bouse travertines is interpreted here as ultimately due to spillover of alkaline waters derived from Lake Hualapai (Crossey et al., 2015), but groundwater mixing and amplification of the degree of carbonate supersaturation by biologic processes as represented by the tube cast facies of the travertine results in the remarkable localized precipitation.

Bouse travertines are most voluminous in the Blythe basin, but they have been found in all Bouse basins (Fig. 1). Interestingly, they occur throughout the Blythe basin on east, center, and west sides of the basins, near the mapped highest elevations of Bouse outcrops (~ 330 m asl), and near the modern Colorado River (~ 100 m asl). Extensive mapping by various workers (Pearthree and House, 2014 and references therein) shows that travertine occurs in conjunction with paleo shoreline deposits and is found in numerous locations draped against (encrusted on in our interpretation) bedrock of a variety of lithologies (Fig. 2A). The transect from lowest to highest elevations imply time transgressive deposition, possibly with components of post-depositional tilting. Encrustations on underlying paleotopography indicate a rough landscape at outcrop scale exceeding 10s of m of relief. Large 'reef' complexes (Fig. 3 & 4; sensu Benson, 1994) and apparent shoreline deposits rimming paleotopography need special

emphasis in more refined depositional models. Field relationships with other Bouse carbonate facies consistently indicate that travertine accumulations (encrustations) are first, or early; travertine generally pre-dates and is occasionally coeval (interbedded) with marl and calcarenite. Where preserved, marl carbonates (deposited from a water column) are typically inset (Fig. 2B). Travertine-coated cobbles and boulders, and clasts of travertine are also found in the lag gravels and fanglomerates below the basal Bouse marl and bioclastic carbonate (Fig. 3, 4). Thus, we infer that Bouse travertines are likely time transgressive (timescale unknown) but were deposited mainly before other Bouse carbonates were deposited at a given locality.

Our depositional model for Bouse travertine relies on a close analog documented in tufa mounds and shoreline tufas of Pyramid Lake and Lake Lahontan (Benson, 1994; 2004), tufa mounds in Mono Lake (Dunn, 1953; Scholl and Taft, 1964), stromatolites in groundwater springs (Wolaver et al., 2013), and shoreline deposits around both marine and lake basins. Remarkably similar travertine morphology is illustrated in figures 3 and 4. Marine examples include Shark Bay and the Coorong delta (Australia).

Using these analogs, the distribution of travertine outcrops suggests two likely controls on deposition: subaqueous groundwater inputs along faults and lake-margin seepage that interact with shoreline wave action. Fault control (or modulation) of deposition of travertine seems likely to provide a source of excess CO_2 , and possibly calcium, and locating springs along fault conduits. Additional mapping of Bouse travertine mounds similar to those observed in the Palo Verde and Trigo Mountains may help define source springs. However, preserved travertine deposits are quite extensive in some areas and encrust complex topography, and few direct fault- travertine associations are yet documented with the exception of several rare carbonate veins. A lake-shore origin similar to Pyramid Lake, Nevada for the travertine is thus our preferred interpretation for the occurrences seen to date as this might provide turbulence needed for degassing, form the concentric geometry of travertine outcrops around paleotopography (aka shorelines), and explain the general association of travertine with basin highstands in terms of a basin transgression. If so, the presence of similar mound complexes at low elevations and encrustations across paleotopography might be ascribed to lacustrine

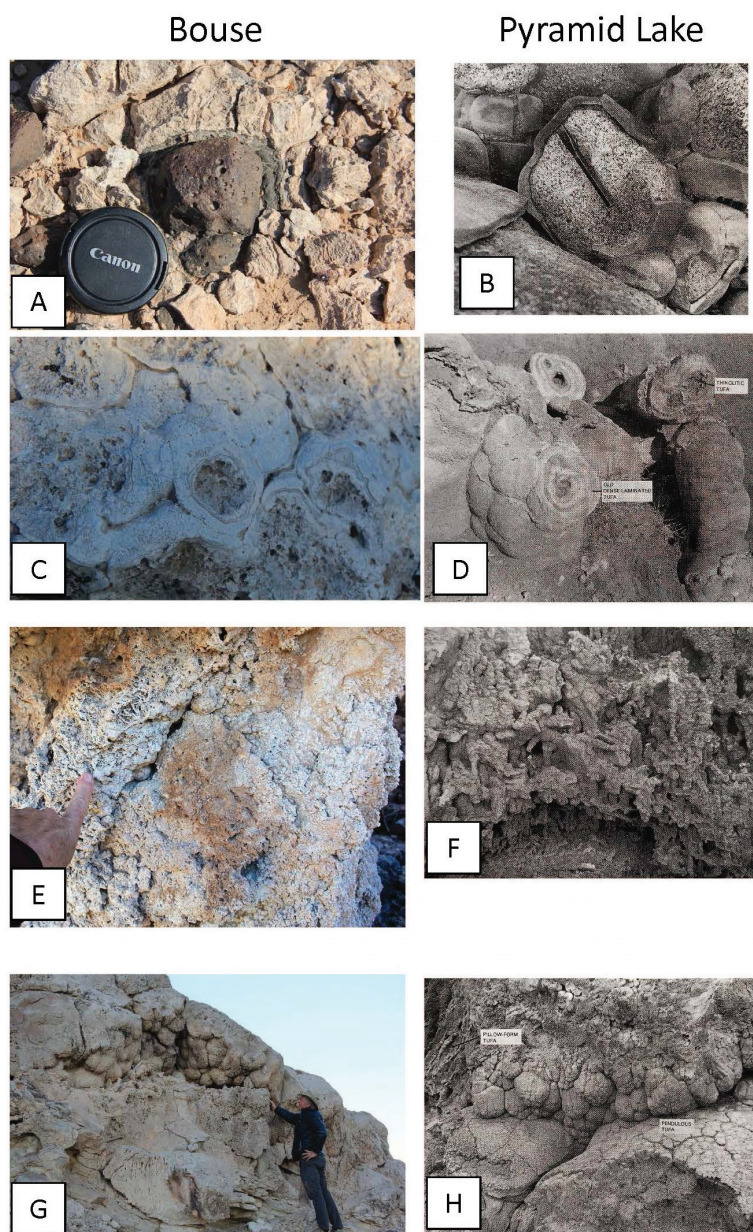


Figure 3. Comparison of Bouse travertine (left photo for each pair) and Pyramid Lake (right, from Benson, 1994) (A, B). Dense carbonate rinds on clasts. (C, D) Concentrically laminated travertine tubes and botryoids (Bouse ~4-10 cm diameter; Pyramid lake up to 50 cm). (E, F) small-diameter tubular 'tufa' (mm- to cm-scale). (G, H) 'Pendulous or mammillary forms 20-50 cm diameter.

transgression in which travertine is older than other carbonate facies at any location.

Geochemical tests for origin of the travertine are underway and include multi-tracer analysis of travertine versus other Bouse carbonate facies. If spring inputs were important sources, the travertine may show higher $^{87}\text{Sr}/^{86}\text{Sr}$ when groundwater flowpaths were through Precambrian granites relative to low $^{87}\text{Sr}/^{86}\text{Sr}$ young volcanic bedrock. The presence of silica diagenesis, local manganese mineralization, and geothermal-associated trace elements like B, Br, Li may help establish any geothermal inputs. A lakeshore origin may show

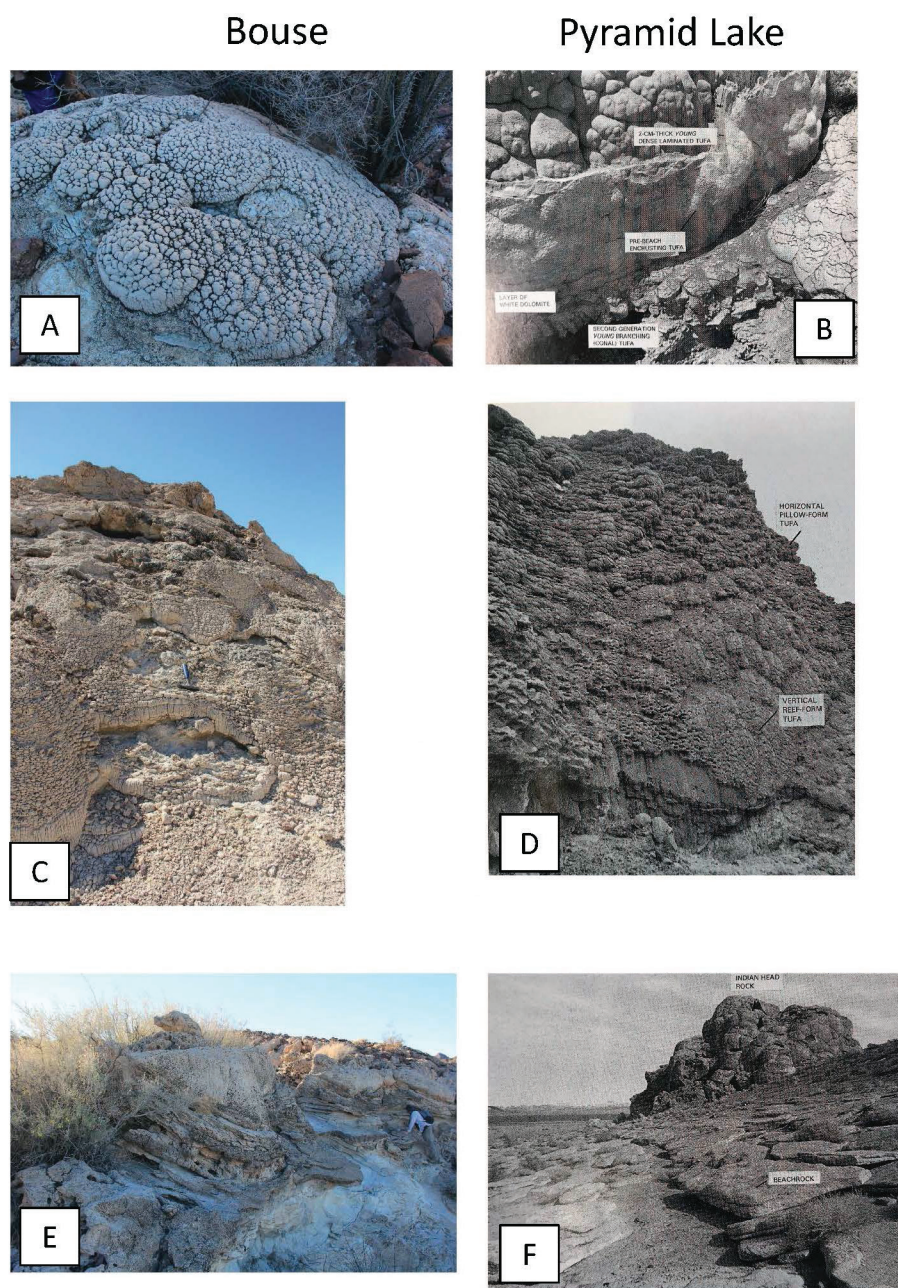


Figure 4. Comparison of Bouse travertine (left photo for each pair) and Pyramid Lake (right, from Benson, 1994) (A, B). Mature branching conal or cauliflower-shaped morphology. (C, D) Reef-form tufa morphology (described by Benson, 1994). Both locations show encrustation of travertine on near-vertical bedrock exposures. (E, F) Onlapping, inset relationships of dipping marl (left, Palo Verde Mountains) and beachrock (right, Pyramid Lake) onto encrusting travertines.

significant degassing and fractionation of stable isotopes. Another important aspect of travertine is that they may be datable using U-Pb dating to help establish the timeframe for Bouse deposition. For example, in the current spill-and-fill model for downward integration of the Colorado River system (Spencer et al., 2013; Pearthree and House, 2014), travertine deposits record rising lake levels in each basin. With progressive filling and spilling of basins, travertine deposits in northern basins travertines would generally be older than southern basins. Depending on how rapidly these postulated lakes filled, it might also

be possible to distinguish the ages of the lowest and highest travertine deposits in each basin, and make inferences about gradual versus sudden filling of the basin.

Geochemical work to date shows wide variation in C and O stable isotopes of Blythe basin travertine, with some studies (Crossey et al., 2015) showing fairly well behaved linear mixing trend between river-like endmembers in ($d^{18}O, d^{13}C$) of (-8,-5) to marine-like endmembers of (0,0) and other studies (Bright et al., 2016) showing reproducible chemostratigraphy in several location and a more scattered C-O plot. A linear isotopic mixing trend observed in travertine is very similar to values from the overlying marls, but both are dramatically different from similar mixing arrays seen in our Pyramid Lake analog whose endmembers are displaced by + 5 in $d^{13}C$. Geochemical studies are ongoing, but at present, evidence for both carbonate and silica diagenesis of carbonates raises caution about interpreting measured values as primary; this alteration may also affect attempts at U-Pb dating (Crow et al., 2014). We envision that subaqueous encrustations of carbonate may have been diagenetically altered during rising and falling water levels and therefore microsampling is needed to reveal any least/unaltered carbonate

geochemistries. Sample analysis methods (microdrilling versus dissolution) may help explain the different isotopic results found by different studies (linear versus more scattered) if biogenic influences produced heavier $d^{13}C$ in the fossil-bearing marls.

Nevertheless, preliminary impressions are as follows. (1) Deposition of the first Bouse carbonate involved precipitation of carbonate encrustations on local paleotopography via degassing of carbonic waters, groundwater-supplied calcium, and biological

influences; this could have happened in a mixed or stratified estuarine or lacustrine environment based on the C-O mixing trend (if this trend is borne out by further analyses and can be shown to be primary). (2) Bouse marls represent carbonate that rained out of the (rising but fairly quiescent) water column as chemical precipitates and fine grained carbonate, likely in a mixed marine- estuary environment in the Blythe basin, based on the paleontology and stable isotopic C-O mixing trend. (3) In the southern Blythe basin, the presence of onlapping bioclastic carbonates with abundant tidal sedimentary facies and tidal rhythmites in the basin axis (O'Connell et al., 2017) suggests the possibility that the basin first filled with lake waters (1 and 2), then the lake drained or lowered substantially, and later a regional marine transgression produced widespread tidal deposits. Lake and marine transgressions separated by a short-lived lowstand might explain the diagenetic alteration documented or suspected in some samples.

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