New directions in research on the Bouse Formation and the origins of the lower Colorado River

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The goal of this paper is to pose research questions that may help resolve controversies about the depositional setting of the ~ 5–6 Ma Bouse Formation and paleohydrology of the earliest Colorado River system. We also summarize and update a recent Geosphere paper (Crossey et a., 2015) that discusses the application of multiple geochemical tracers ($^{87}Sr/^{86}Sr$, [Sr], $\delta^{13}C$, $\delta^{18}O$) for understanding carbonates of the Bouse Formation.

The Bouse Formation, whose age is bracketed regionally between about 6.1 and 4.8 Ma, was deposited at least in part by first-arriving waters of the Colorado River as it was integrated through several previously internally drained basins to the Gulf of California (e.g. House et al., 2008; Pearthree and House, 2014; McDougall and Miranda-Martinez, this volume). The northern basins (C=Cottonwood, M=Mojave on Fig. 1) have Bouse outcrops that reach modern elevations of ~560 m that are interpreted as lake high stands. Downstream basins (Havasu and Blythe) have interpreted high stand carbonate deposits at ~ 360 and 330 m, respectively (Pearthree and House, 2014). Carbonate chemistry, especially $^{87}Sr/^{86}Sr$, has been used to interpret that Bouse deposition took place in a lake isolated from the ocean (Spencer and Patchett, 1997) rather than a marine estuary (Buising, 1990).

Figure 1 shows that the lower Colorado River region is transected by the San Andreas plate boundary, the eastern California shear zone, and the Stateline fault systems (among others). This raises the question of whether neotectonics may have modified outcrops relative to their depositional paleoelevations. Two alternative tectonic hypotheses need to be tested: (1) Highest Bouse carbonate outcrops

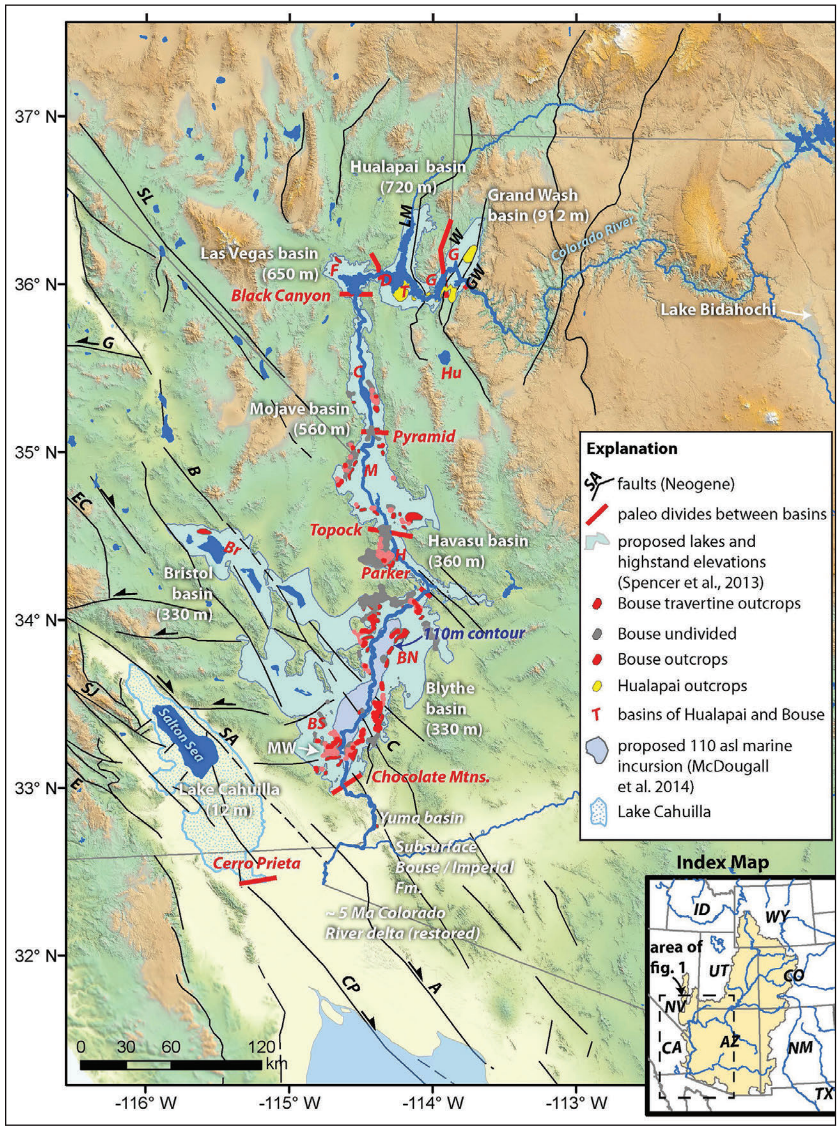

Figure 1. Map of the Grand Canyon and lower Colorado River region with inferred Bidahochi, Hualapai and Bouse paleolakes. Surface exposures of the Hualapai Limestone are yellow; Bouse Formation are red; red dots show drill holes that encountered Bouse Formation. Paleolake maximum elevations are from Spencer et al. (2008; 2013) and Pearthree et al. (2014). SM= Split Mountain Gorge outcrops of Imperial Formation (solid line) restored 230 km to the SE (dashed line).

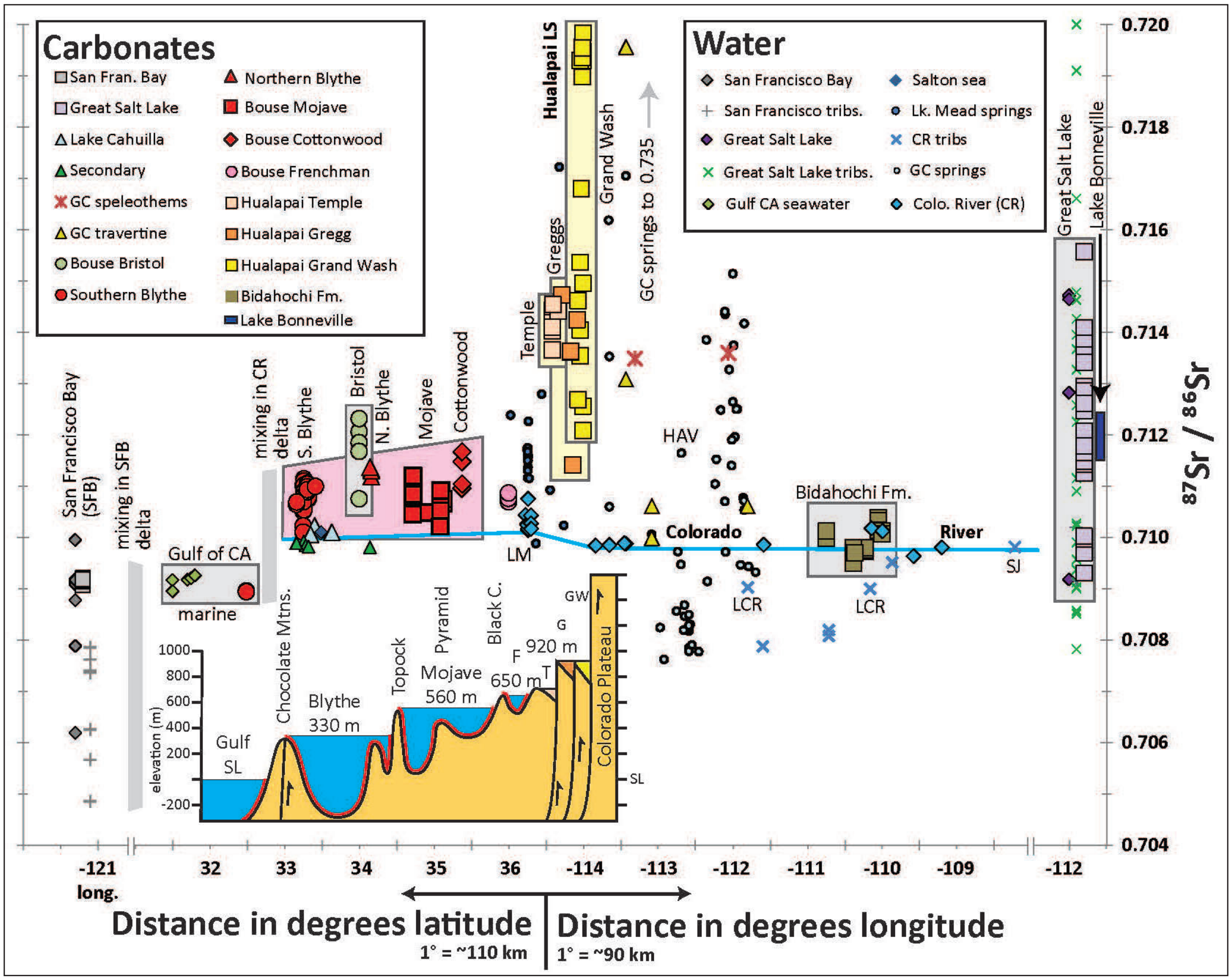

Figure 2. This figure traces the $^{87}Sr/^{86}Sr$ isotopic composition of waters and carbonates of the Colorado River region from upstream to downstream. A main point of this diagram is that Lake Hualapai waters were highly radiogenic because of spring inputs and that Bouse waters were distinctly more radiogenic than Colorado River water because of mixing between Colorado River water and Lake Hualapai waters, plus any additional spring inputs. Mixing between Colorado River water and seawater in the Pliocene Colorado River delta (in Blythe and/or Yuma basins) may have been a “reverse” analog to mixing in the modern San Francisco Bay estuary (Ingram and DePaolo, 1993) in that rivers in the former were more rather than lass radiogenic than seawater. The inset shows the hypothesized series of lakes that filled and spilled during Colorado River integration (Spencer et al., 2013).

reflect undeformed lake highstands (e.g. Pearthree and House, 2014), highest Bullhead (early Colorado River gravel) outcrops represent the degraded tread surface of maximum aggradation, and lowest (subsurface) gravels are a proxy for the ~ 3.5–4.5 Ma pre-Bullhead bedrock strath (Howard et al., 2015; Crow et al., this volume). Alternatively: (2) Post- 5–6 Ma tectonism (faults and differential uplift/subsidence) has modified topography, lake highstands and the tread of Bullhead aggradation represents a complex (unresolved) combination of perhaps subtle deformation and selective preservation. Tests involve better understanding of post- 5–6 Ma deformation via analysis of faults, additional mapping of paleo Colorado River deposits, depositional paleo-environments of shoreline deposits?, and characterization of subsurface Bouse and Bullhead deposits with shallow and deep drilling.

Figure 2 shows the $^{87}Sr/^{86}Sr$ of regional waters and carbonates from upstream areas on the Colorado Plateau west, then south, to the Gulf of California. The modern Colorado River $^{87}Sr/^{86}Sr$, shown in the blue solid line, shows an increase due to mixing with radiogenic spring waters (up to 0.735) in western Grand Canyon. Hualapai Limestone is highly radiogenic and is interpreted to also require similar spring inputs. The springs themselves get their high $^{87}Sr/^{86}Sr$ from deeply circulated geothermal fluids that cause water-rock reactions along the flowpaths that liberate Ca and Sr, especially in areas of radiogenic Precambrian basement rocks of the Mojave province (Crossey et al., 2006). Uppermost Hualapai Limestone

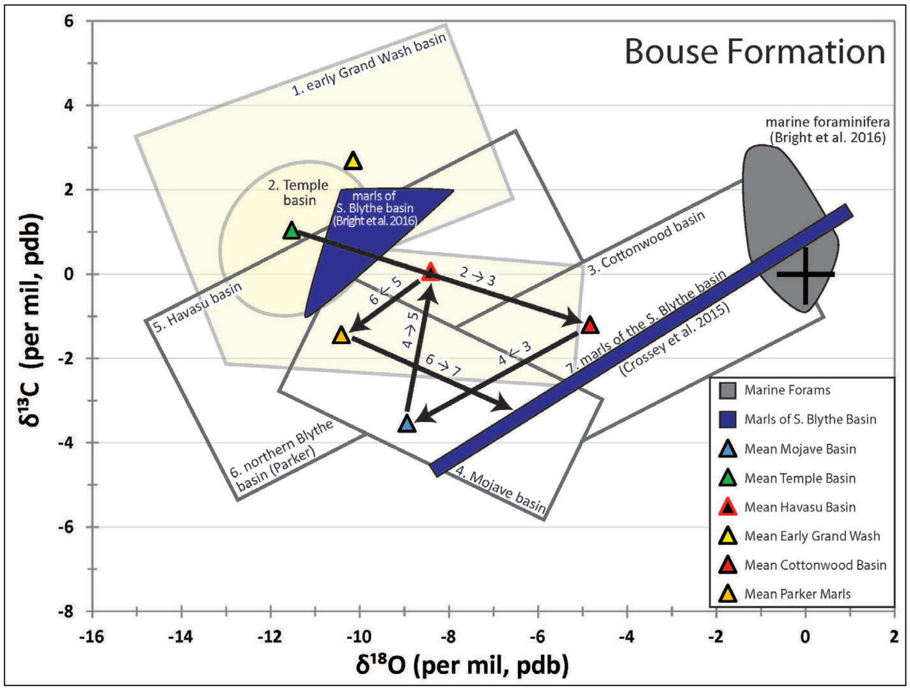

Figure 3. $\delta^{13}C$ versus $\delta^{18}O$ plot of the Bouse Formation carbonates by basin. This diagram also suggests complex mixing for Bouse waters. The main sources for upper Bouse lake waters (2 to 3 arrow) may be a mix of Hualapai Limestone water (light shading) plus first arriving Colorado River water. Additional changes from north to south suggest that each of the Bouse basins had different evolution trends in water/carbonate isotopic composition compatible with evolving open and closed basins and mixing of different waters. Marls of southern Blythe Basin form a mixing line anchored at near-marine values of (0,0).

in Grand Wash basin was deposited in spring-fed lakes and marshes where waters were mainly sourced from Colorado Plateau karst-aquifer groundwater that mixed with high-$^{87}Sr/^{86}Sr$ spring inputs similar to those seen today in springs of western Grand Canyon and Lake Mead. The downstream decrease in $^{87}Sr/^{86}Sr$ in Gregg and Temple, then various Bouse basins, is interpreted to reflect progressive downstream mixing of Hualapai water with increasing Colorado River input as lakes became integrated southward. Thus, the best explanation for the $^{87}Sr/^{86}Sr$ of the Hualapai and Bouse carbonates, both of which are elevated relative to the modern Colorado River water, involves contributions from springs and groundwater. A test of this hypothesis is to identify paleo-spring vent locations using travertine textures coupled with additional $^{87}Sr/^{86}Sr$ analysis.

Figure 3 shows application of stable isotope tracers to each of the Hualapai and Bouse basins. In this plot of C and O stable isotopes, closed basins often produce positive slope covariation due to evaporation and other mechanisms of isotope fractionation, whereas open basins often show negative covariation reflecting mixing during flow-through of input waters (Talbot, 1990). Marine waters plot near (0,0), as do late Miocene–early Pliocene planktonic foraminifera and nannofossils from the Pacific Ocean (Bright et al., 2016). Data from the Bouse Formation show that covariation trends and mean values of $\delta^{13}C$ and $\delta^{18}O$ differ between basins. This may be compatible with existing "fill-and-spill" models for alternating closed and open systems and incomplete mixing during progressive downward integration of internally drained basins, as Lake Hualapai waters flowed to Cottonwood then Mojave and Havasu paleo-lakes at ~5–6 Ma (Spencer et al., 2013; Pearthree et al., 2015). An important current ambiguity shown in Figure 3 is the C–O data from southern Blythe basin where Roskowski et al. (2010) and Crossey et al. (2015) showed that marls fall along a strong co-variation trend anchored at (0,0). In contrast, Bright et al. (2016) showed values for marls from this basin (Hart Mine Wash section) that are much lighter in oxygen than the marls analyzed in previous studies, but are similar to values reported for fossils (Crossey et al., 2015).

The timescales for downward integration remain poorly known, and may range from <100 ka (Spencer et al., 2008) to perhaps 1 Ma. New age constraints will require better geochronology of Bouse Formation in each sub basin. Similarly, the timescales and processes of downstream mixing basin-to-basin of the type suggested in Figure 3 remain poorly resolved. Necessary new geochemical data include new tracers (Mn/Sr, Al/Sr, etc.) placed in better stratigraphic context with a complete understanding of different carbonate lithofacies.

Figure 4 combines multiple tracers and shows that Bouse carbonates display a general southward (downstream) trend toward less radiogenic $^{87}Sr/^{86}Sr$ values and perhaps heavier $\delta^{18}O$. This was interpreted as compatible with the hypothesis for increased proportion of Colorado River water entering the system through time during Colorado River integration and/or increased evaporation in southerly basins. However, the negative $\delta^{18}O$ values of -8 to -12 for fossils and marl

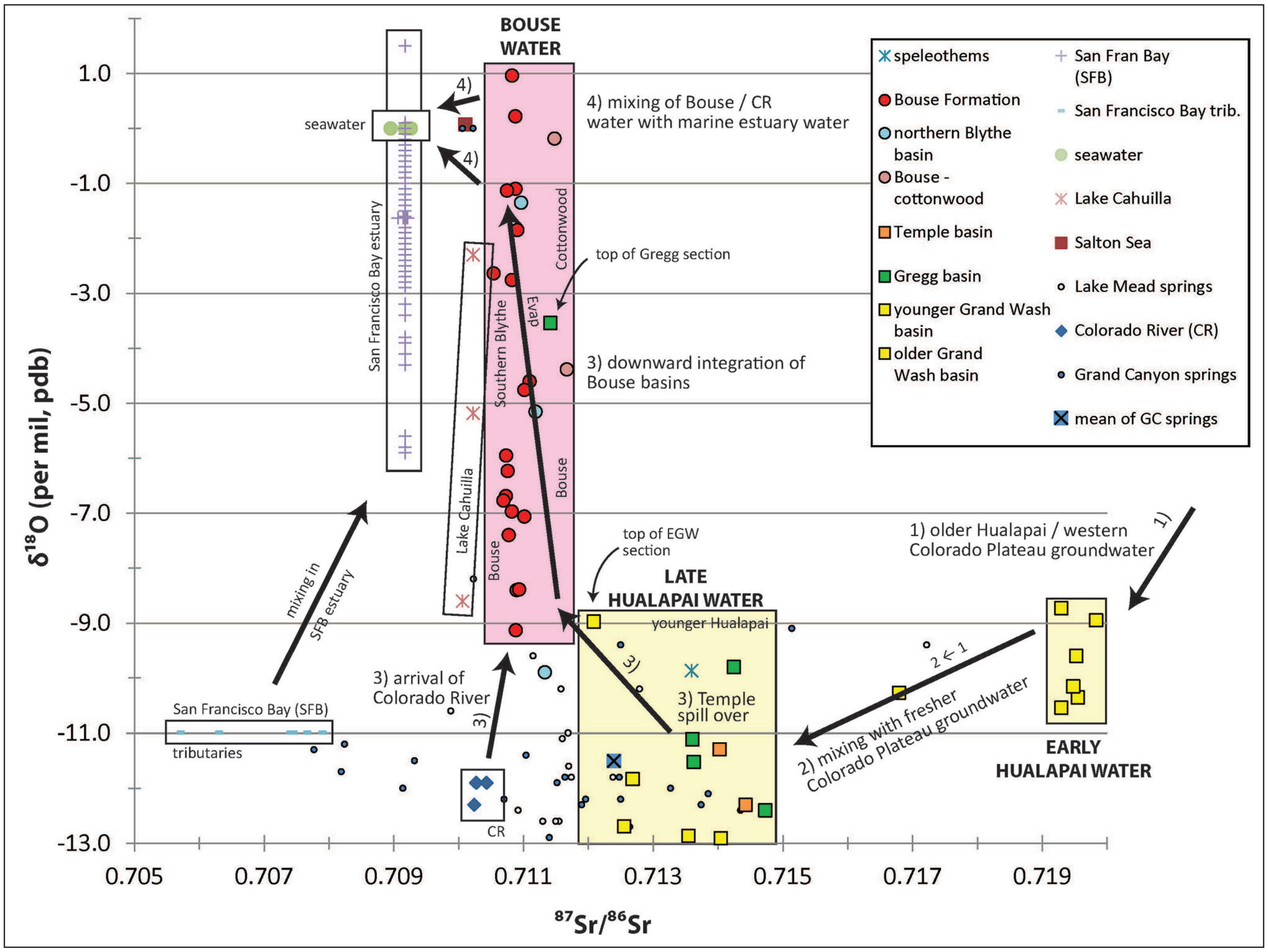

Figure 4. $^{87}Sr/^{86}Sr$ versus $\delta^{18}O$ for the inferred downward integration of Lake Hualapai basins to-and-through different Bouse basins. As with $^{87}Sr/^{86}Sr$ mixing in Figure 2: 1) western Colorado Plateau groundwaters are inferred as the source of the older parts of the Hualapai Limestone in Grand Wash basin. 2) 6-8 Ma input of progressively fresher Colorado Plateau groundwater is inferred to explain the upsection change in Hualapai Limestone observed in the top ~50 m of the section. 3) Arrival of the Colorado River 5-6 Ma is interpreted to have caused spill-over and downward integration of the Hualapai basins to Bouse basins and complex southward change in hydrochemistry with overall trends toward more negative $\delta^{18}O$ values from north to south interpreted as increased proportion of Colorado River water plus evaporation effects.

in the southern Blythe basin (Bright et al., 2016) do not appear to be consistent with this idea, and still need to be reconciled. Bouse and Imperial Formation carbonates in the subsurface of the Yuma Basin have marine $^{87}Sr/^{86}Sr = 0.709$ and are interpreted to have a marine origin, whereas elevated $^{87}Sr/^{86}Sr$ values of 0.710 in the Blythe basin are higher than marine values of 0.709. Nevertheless, it remains debated whether Colorado River water first encountered and mixed with marine waters in the Blythe basin or in the Yuma basin. Bouse Formation of the southernmost Blythe basin may record at least intermittent mixing between marine water and river water in an estuary setting; this is based on $\delta^{13}C$ and $\delta^{18}O$ covariation trends anchored at (0,0), sedimentological evidence consistent with marine sequences (Dorsey, 2012; O'Connell and Dorsey, this volume), and presence of marine fossils (McDougall and Miranda-Martinez, this volume; McDougal et al., 2015), which might alternatively be explained by avian trasport and establishment of marine organisms in saline lakes (Spencer and Patchett, 1997) . If radiogenic Bouse water was mixed with seawater in the southernmost Blythe basin, it may be a "reverse analog" to mixing of non-radiogenic tributary waters with seawater in the San Francisco Bay estuary system depicted at left (Ingram and DePaolo, 1993).

Figure 5 plots the Sr concentration [Sr] versus $^{87}Sr/^{86}Sr$ and shows how mixing of different waters could plausibly explain the observed ranges of $^{87}Sr/^{86}Sr$ in Hualapai and Bouse carbonates. These simple binary mixing models require knowledge of $^{87}Sr/^{86}Sr$ and [Sr] of mixed endmember waters. $^{87}Sr/^{86}Sr$ is "known" because carbonate values are generally equal to values of waters that deposit them. [Sr] is unknown but perhaps

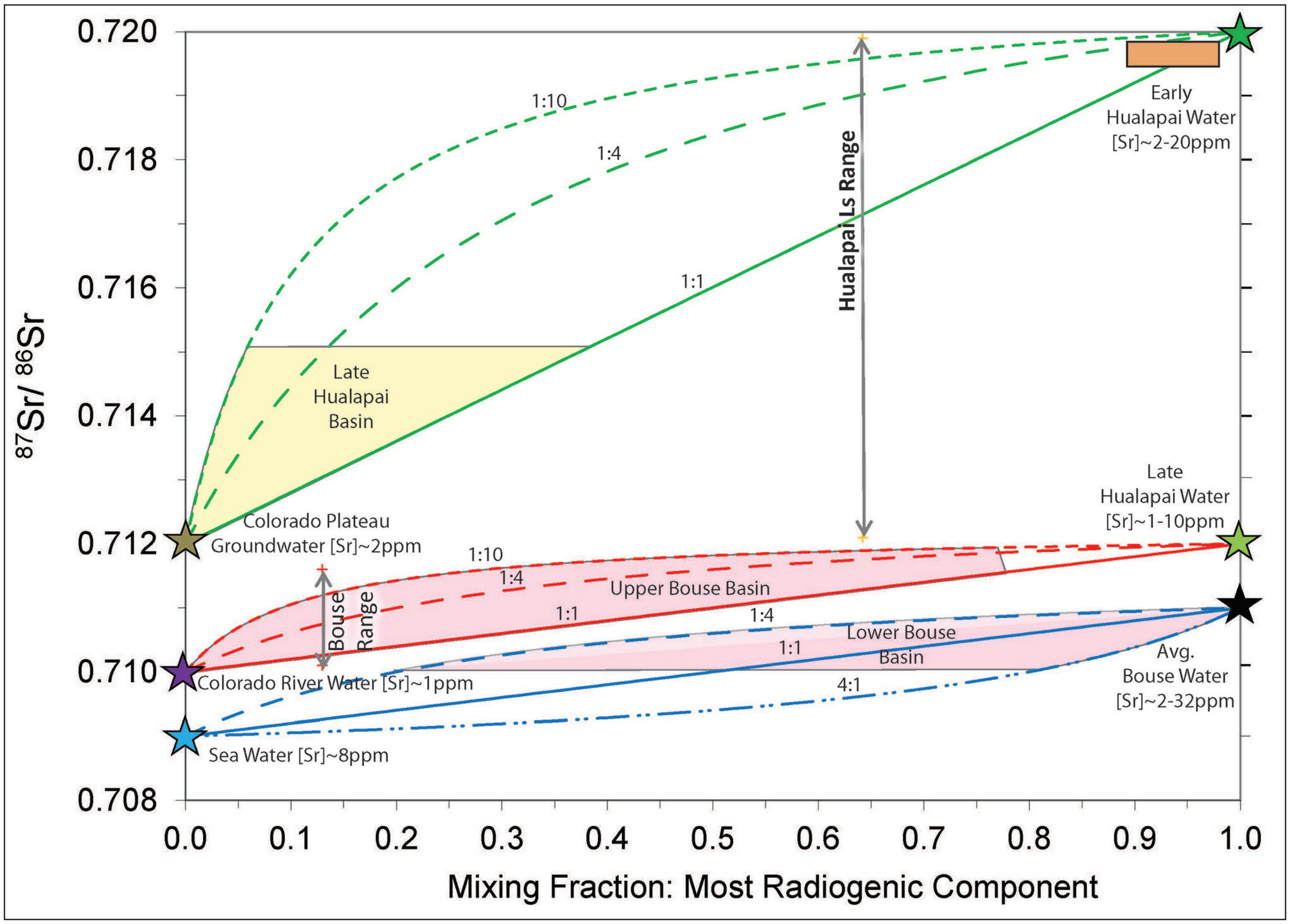

Figure 5. This figure shows how mixing of different waters might explain the observed ranges of $^{87}Sr/^{86}Sr$ in the Hualapai and Bouse carbonates. These are simple binary mixing models that require knowledge of $^{87}Sr/^{86}Sr$ and [Sr] (concentration) of mixed endmember waters. $^{87}Sr/^{86}Sr$ is "known" because carbonate values are generally equal to values of waters that deposit them. [Sr] is unknown but perhaps can be estimated from modern water analogs (boxes). Straight line mixing lines represent equal volumes of end members; others show 4-to-1 or 10-to-1 mixing proportions. These mixing models demonstrate that Bouse carbonate $^{87}Sr/^{86}Sr$ values of 0.710-0.711 could be produced in several ways, for example by a mixture of Lake Hualapai spring water with Colorado Plateau groundwater (CPGW) and Colorado River (CR) water, followed downstream by a mixture of seawater with arriving lake/river water. Additional inputs of radiogenic geothermal waters similar to modern waters at Cerro Prieto could also have had a strong leveraging affect.

can be estimated from modern water analogs (boxes). Straight mixing lines represent equal volumes of end members; curved lines show 4-to-1 or 10-to-1 mixing proportions. These mixing models demonstrate that Bouse carbonate $^{87}Sr/^{86}Sr$ values of 0.710–0.711 could have been produced in several ways, for example by a mixture of late Lake Hualapai water with increasing volumes of Colorado Plateau groundwater (CPGW) and Colorado River (CR) water, followed downstream by a mixture of seawater with arriving Bouse plus Colorado River water. Additional inputs of radiogenic geothermal waters along the flowpath, for example (Fig. 5) similar to western Grand Canyon springs ($^{87}Sr/^{86}Sr$ up to 0.735; [Sr] up to 6 ppm), Lake Mead springs ($^{87}Sr/^{86}Sr$ up to 0.724; [Sr] up to 8 ppm, or modern geothermal waters in the Salton Sea geothermal fields ($^{87}Sr/^{86}Sr$ up to 0.7115; [Sr] in excess of 600 ppm), all of which would have a very strong leveraging affect on mixing models (Crossey et al., 2015). This diagram suggests that southern Blythe $^{87}Sr/^{86}Sr$ values could have been produced by 25–75% sea water mixed with river water in a delta/marine estuary system. These and other hypothetical mixing models can be tested if end member values are better constrained. Analysis of $^{87}Sr/^{86}Sr$ and [Sr] in diverse carbonate facies, fossils, and fluid inclusions should continue to be expanded. Additional analyses of potential modern analog waters will also help show most likely ranges of endmembers values.

In summary, we suggest several refinements to the "lake fill-and-spill" downward integration model for the Colorado River. (1) Overall, hydrochemical mixing is required to explain the multi-tracer geochemical data. (2) Lake Hualapai was fed by western Colorado Plateau groundwater from 12 to 8 Ma. (3) High-elevation

Colorado Plateau groundwater was progressively introduced to Lake Hualapai from ~8 to 6 Ma. (4) Colorado River water arrived across Grand Wash cliffs at ~6 Ma. (5) The combined inputs led to downward integration by a combination of groundwater sapping and sequential lake spillover. (6) The high $^{87}Sr/^{86}Sr$ of Hualapai and Bouse carbonates is best attributed to radiogenic spring inputs that took place in the western Grand Canyon, Grand Wash, Lake Mead regions and possibly also farther down the flowpath. (7) Until [Sr] of mixing endmembers is better known, $^{87}Sr/^{86}Sr$ values alone cannot be used as proof of non-marine deposition of Bouse carbonate. (8) Marine versus non-marine interpretations of the Bouse Formation of Blythe basin require reconciliation of paleontological data (McDougall et al., 2015; Bright et al., 2016) and integration of all other datasets. 9) The effects of post-6 Ma faulting and differential epeirogenic uplift need to be quantified to resolve paleoelevations of basins relative to each other and to sea level during Bouse deposition.

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