A late Miocene-early Pliocene chain of lakes fed by the Colorado River:

Evidence from Sr and Stable Isotopes of the Bouse Formation between Grand Canyon and the Gulf of California

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ABSTRACT

The latest Miocene to early Pliocene Bouse Formation was originally interpreted as a Miocene embayment of the Gulf of California on the basis of paleontology; however, isotopic work has suggested a lacustrine origin for the Bouse Formation. Rather than a single-lake model, elevations of Bouse outcrops suggest a lake-overflow model involving a chain of four separate lake basins for integration of the lower Colorado River including a newly identified upstream lake in the Las Vegas basin. The Hualapai Limestone of the Lake Mead area records a separate lake that existed farther upstream and slightly earlier in time. Prior geochemical data for the Bouse carbonates showed seemingly random variations that some researchers claimed weakened the lacustrine interpretation. In order to evaluate the source of isotopic variation, we conducted a detailed and systematic sampling to obtain Bouse Formation samples with a discernable relationship to one another by collecting the basal 10 cm of marl at various elevations in most paleo-basins. Stable isotope analyses were conducted in conjunction with Sr ratio analyses for samples from the lowest-elevation basin that contains freshwater, brackish, and marine fossils. Strontium isotope data from Bouse Formation carbonates give an average $^{87}Sr/^{86}Sr$ ratio (0.7108) close to the Sr ratio of the present-day Colorado River (0.71075) and well above late Neogene marine strontium (0.7090). $\delta^{18}O$ values range from –13.7 to +0.96 ‰ VPDB, while carbon isotopes for these same samples are between –6.46 to +1.69 ‰ VPDB. Stable isotope trends suggest a continental origin and significant evaporation of Bouse waters. Strontium and stable isotopes in combination argue against diagenetic replacement of marine Sr with later Colorado River strontium and any mixing between seawater and river water. Comparisons are also made with the Miocene Hualapai

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Limestone, located in the Grand Wash Cliffs area. The Hualapai Limestone has a significantly higher $^{87}Sr/^{86}Sr$ ratio (0.7195-0.7137), but systematically decreases towards the time of Colorado River integration, suggesting that the first arrival of Colorado River type water to the Basin and Range occurred just before 6Ma.

INTRODUCTION

The initial development of the Colorado River is the subject of much controversy, and the origin of the Bouse Formation and similar deposits exposed along the lower Colorado River has important implications for this debate. Integration of the upper and lower Colorado River took place between 5 and 6 Ma, but the mechanism for integration remains enigmatic. While on expedition with Lieutenant J.C. Ives, John Strong Newberry (1861) was the first to describe the geology and evolution the lower Colorado River from Grand Canyon south to the Gulf of California. Newberry opined that canyons connecting the large basins along the course of the lower Colorado formed when the basins filled with water and subsequently cut through the surrounding mountain ranges. In 1934, Eliot Blackwelder extrapolated on Newberry's interpretation and proposed a cascading lake-spillover model for the formation of the Colorado River supported by geomorphic observations and by analogy with the Owens River, CA.

During the first half of the twentieth century other researchers interpreted calcareous sediments along the lower Colorado River as both lacustrine and marine, but it was not until 1968 that Metzger mapped and described these same sediments as the Bouse Formation. The upper Miocene to Pliocene Bouse Formation, exposed in several basins along the lower Colorado River and at elevations as high as 500m (Fig. 1), has been interpreted as a marine incursion of the Gulf of California into the lower Colorado

River trough (Metzger, 1968; Smith, 1970; Buising, 1990) coeval with the appearance of proto-Colorado River sediments to the area. Bouse sediments deposited in an estuary would require up to 550m of uplift since Pliocene time, which Lucchitta (1979) considered to represent the edge of the major uplift that created the Colorado Plateau.

Since the advent of modern analytical techniques, some authors have used geochemical data to reinterpret the Bouse Formation as a lacustrine deposit formed by a cascading chain of lakes fed by the Colorado River (Spencer and Patchett, 1997; Poulson and John, 2003). However, controversy surrounds the interpretation due mostly to the strontium isotopic variation inherent in Bouse carbonates and the lack of evidence for more upstream basins (Lucchitta et al., 2001). The purpose of this paper is to present new strontium, carbon, and oxygen isotope data that allow us to examine the nature of Bouse isotopic variability and provide evidence of an interconnecting chain of lakes from Grand Canyon to the Gulf of California.

GEOLOGIC SETTING

Bouse Formation

The Bouse Formation occurs as scattered outcrops along the lower Colorado River from the southern tip of Nevada to south of Cibola, AZ, though it also occurs abundantly in the subsurface near and to the south of Yuma, AZ (Metzger, 1968; House et al, 2005) (Fig. 1, 2). The Bouse Formation was originally divided into three lithologic units by Metzger (1968) and later redivided by Buising (1990) into two interfingering lithofacies groups: basin-margin and basin-fill deposits. The basin-fill deposits consist of tens to hundreds of meters of siltstone and sandstone. The basin-margin unit consists mainly of carbonate material in the form of finely-bedded marl and barnacle coquinas

with sporadic but large patches of tufa adhering to pre-Bouse rocks.   The basal marl is underlain by an erosional contact with Tertiary volcanic rocks and their associated fanglomerates and is generally flat-lying except in the vicinity of mountain ranges where it is draped over the preexisting landscape (Metzger, 1968). Subaerial Bouse outcrops exist at a variety of elevations ranging from 70 – 550 meters, whereas subsurface data place the Bouse as low as 270m below sea level.

Several types of marine, brackish, and freshwater fossils have been identified in the 4-5Ma Bouse marl, though the fossils occur mainly in southern-most exposures of the Blythe basin (Metzger, 1968; Smith, 1970; Winterer, 1975; Todd, 1976; McDougall et al, 1999). The fossil assemblage in the southern Bouse surface outcrops consists of many individuals of only a few species (Metzger, 1968; Buising, 1990; Lucchitta et al, 2001). The outcrop assemblage is dominated by a species of barnacle, *Balanus canabus* (Zullo and Buising, 1989), and by the foraminifer *Ammonia beccarii,* which is very tolerant of changes in salinity; several fresh-water species and many brackish-water species are present in the Blythe-Cibola area including mollusks, gastropods, ostracodes, and charophytes (Metzger, 1968; Smith, 1970). The southern Bouse basin has the thickest, most extensive outcrops of basal marl with the highest diversity of fossils, though significant Bouse marl outcrops occur in the other basins upstream (Fig 1, 2). The Bouse outcrops farther to the north in Havasu and Mohave Basins contain very few fossils, mainly ostracodes and charophytes.

The extent and character of the Bouse marl and its fauna have been used to support a marine origin for the Bouse Formation, as it was originally believed to be a Miocene embayment of the Gulf of California (Metzger, 1968; Smith, 1970; Lucchitta,

1979). Based on its interpretation as an estuarine deposit, the Bouse Formation was used as a means of constraining the uplift of the Colorado Plateau to post-5Ma (Lucchitta 1979). The reasoning was that if the Bouse was marine in origin, then it was deposited at or below sea level and subsequently uplifted to its current elevation of up to 550m. The hypothesized uplift of the Colorado River Trough was viewed as the lower part of the widespread uplift needed to form the Colorado Plateau, therefore constraining the uplift to post 5-Ma time (Lucchitta, 1979). The regression of the inland sea would have provided both the base level fall and the outlet necessary to create the modern course of the modern day lower Colorado River. Lucchitta (1979, 1989) proposed that integration of the upper and lower Colorado river occurred by headward erosion, yet headward erosion is highly unlikely due to the fact that it is a very inefficient process, especially in the arid Southwest (Spencer and Pearthree, 2001). In addition, Karlstrom and others (2007) calculated that the lower Colorado River region has subsided 180m relative to western Grand Canyon since 6Ma, rather than experiencing uplift.

A more recent hypothesis for the formation of the lower Colorado River is that of basin filling and spillover: water from the proto-Colorado river may have filled pre-existing closed basins at high elevations until the inland lake overtopped a restrictive geographic barrier and spilled over into each downstream basin (Blackwelder, 1934; Meek, 1989; Spencer and Patchett, 1997; Meek and Douglass, 2001; Spencer and Pearthree, 2001). By this mechanism the proto-Colorado river would have catastrophically overflowed its topographic barriers, incising the modern course of the lower Colorado and propagating southward to the sea as a chain of lakes that began at the western end of Grand Canyon and ended in the Gulf of California (Fig. 2). It is

significant that the spillover hypothesis eliminates the need for any post-5Ma Colorado Plateau uplift previously imposed by inferred Bouse deposition at sea level.

Hualapai Limestone

An important component of the lake overflow hypothesis and the Colorado River integration debate involves the Hualapai Limestone, which was also originally interpreted as a marine-estuarine deposit based on several factors including fossil assemblage (Blair 1978; Blair and Armstrong, 1979), but has now been firmly identified as lacustrine (Lucchitta, 1979; Faulds et al, 1997, Faulds et al, 2001). The Hualapai is classified variously as the upper member of the Muddy Creek Formation or as its own formation, with outcrops at the western end of Grand Canyon in Grand Wash trough and surrounding areas (Lucchitta 1966, 1972; Blair and Armstrong, 1979). The Hualapai limestone is dated using ^{40}Ar/^{39}Ar and tephrochronologic correlation to a range of 11-6Ma and is one of the youngest documented deposits in the paleowatershed predating the integration of the Colorado River (Faulds et al, 2001; Blair and Armstrong, 1979).

GEOCHEMICAL BACKGROUND

The availability of Bouse and Hualapai carbonate material has inspired several studies investigating both the strontium and stable isotopic character of the basal Bouse marl and related deposits in an attempt to resolve the debate over the mechanism for Colorado River integration (Spencer and Patchett, 1997; Gross et al, 2001; Poulson and John, 2003, Patchett and Spencer, 2001). Authigenic and biogenic calcite are ideal for both strontium and stable isotopic studies because they can capture the isotopic character

of its precipitating waters. Carbon and oxygen are main constituents of calcite, allowing us to obtain both $\delta^{18}O$ and $\delta^{13}C$ values for carbonate samples. Calcite also preferentially incorporates strontium into its crystal structure and excludes rubidium, thus preserving the $^{87}Sr/^{86}Sr$ ratio of the waters that precipitated the carbonate material. As such, strontium isotopic ratios can be used as a geochemical tracer in many systems.

Because the strontium isotopic character of seawater and freshwater differ significantly, the $^{87}Sr/^{86}Sr$ of the Bouse Formation is of utmost importance to the lower Colorado River debate. Though the $^{87}Sr/^{86}Sr$ of seawater is homogeneous at any given time, it changes as a function of time because of the varying nature of Sr inputs from different sources. A rigorous record of the strontium isotopic character of seawater has been compiled (Palmer and Elderfield, 1985; Hodell et al, 1991). The $^{87}Sr/^{86}Sr$ values of seawater for the 4-5Ma time period of Bouse Formation deposition are very near 0.7090 (Hodell et al, 1991). The Sr ratio for fluvial waters, however, varies substantially between rivers as a result of the variable $^{87}Sr/^{86}Sr$ ratio in rocks and soils in of catchment areas (Palmer and Edmond, 1989; Bryant et al 1995). Because of the varied nature of the fluvial strontium isotopes, it was necessary to establish the range of values for components of the Bouse geochemical system.

Spencer and Patchett (1997) undertook a reconnaissance-type study in order to examine the $^{87}Sr/^{86}Sr$ character of the Bouse Formation and related deposits and were able to define an isotopic range for many components of the system. Spencer and Patchett's (1997) study, in conjunction with Gross et al (2001) and Goldstein and Jacobson (1987), provides a broad $^{87}Sr/^{86}Sr$ for the important components of the lower Colorado River system including both outcrop and well-bore Bouse Formation

carbonates, the Hualapai Limestone, the modern Colorado River, regional mobile calcium carbonate from dust and soils, and the late-Miocene Colorado delta deposit known as the Imperial Formation. The Hualapai limestone was reported to have a very radiogenic Sr isotopic signature near 0.7145 derived from groundwater percolating up along faults from Proterozoic basement rocks (Crossey et al, 2006). Bouse Formation marl and fossils have an average strontium ratio (0.7108±0.0006, Spencer and Patchett, 1997) similar to modern Colorado River waters ($^{87}Sr/^{86}Sr$ = 0.71075, Goldstein and Jacobsen, 1987; Gross et al, 2001). Mobile calcite, equivalent to soil carbonate, in the lower Colorado River corridor has an average strontium ratio of 0.7099, and seawater isotopic signatures (0.7090) are reported in the Imperial Formation near the Gulf of California and in Bouse subsurface deposits south of the Chocolate Mountains, the southern-most geographic barrier for deposition of subaerially exposed Bouse carbonates (Spencer and Patchett, 1997). Poulson and John (2003) also investigated the stable isotope and trace element geochemistry of the Bouse Formation marls and fossils in an attempt to resolve the unit's origin. They reported a wide range of both carbon (-3.7 to +1.4 ‰ VPDB) and oxygen (-11.8 to +1.1 ‰ VPDB) isotope ratios and trace element patterns more consistent with a lacustrine rather than estuarine origin.

Despite the success of these original studies in quantifying the strontium isotopic range of the Bouse Formation, significant variation in Bouse $^{87}Sr/^{86}Sr$ ratios presented a serious concern for some researchers (Lucchitta et al., 2001). Furthermore, no absolutely conclusive evidence could be presented in support of Bouse Formation deposition in a chain-of-lakes environment, and the source of the strontium isotopic variation in the Bouse carbonates remained unresolved.

SAMPLES AND SAMPLING STRATEGY

The challenge that remained in ascertaining the origin of the Bouse Formation included both gaining an understanding of the source of strontium isotopic variation inherent in the Bouse carbonates and providing evidence for or against a continuous chain of lakes from Grand Canyon to the Gulf of California. We devised a sampling strategy designed to:

(1) obtain detailed strontium, carbon, and oxygen isotopic evidence in order to examine the source of isotopic variability in the Bouse Formation carbonates, and

(2) obtain strontium isotopic ratios for possible upstream basins with previously undetermined geochemistry and unclear origins.

The sampling strategy for this study was designed to address Bouse carbonate isotopic variation both spatially and stratigraphically (temporally). The marl outcrops are not continuous and have no uniform marker beds, so stratigraphic correlation is very difficult. We have sampled the basal carbonate layers at progressively increasing elevation as a way to derive time-stratigraphic Sr isotope information.

The Bouse marl disconformably to conformably overlies locally-derived fanglomerates with a sharp contact and marks the first arrival to the region of a new hydrologic regime that eventually delivered quartz-rich sands derived from the Colorado Plateau (Spencer and Pearthree, 2001; Buising, 1990). Therefore, we assume that the basal Bouse carbonate represents the first Bouse waters present at each location. When little water fills the basin, carbonate is precipitated only at low elevations. As a basin fills, carbonate begins to precipitate at higher and higher elevations. Thus, as there has not been differential deformation of outcrops within each basin, low-elevation samples

within each basin correspond with early deposition, while high-elevation samples represent deposition at a later time, provided each sample is collected at the base of the Bouse sedimentary sequence.

We sampled the basal 5-10cm of Bouse marl at a variety of elevations in Blythe and Mohave basins, and collected several samples within the marl of Las Vegas basin (Fig 2); the Havasu basin was not sampled. The lowest elevation sample occurred at 70m a.s.l. in the Blythe basin. Samples generally increased in elevation moving northward to an elevation of 546m in the Mohave basin and up to 675m in the Las Vegas basin. Twenty-five samples of Bouse carbonate from the river corridor section of the Blythe basin were analyzed for strontium isotopes. Twenty-one of these Blythe samples were collected from the bottom 10 cm of basal marl, while one was collected from tufa outcropping at a higher elevation than the marl. Three samples are of marl from the Cibola area whose exact stratigraphic context is uncertain, but contained the fish fossil *Colpicthys regis*. These samples were obtained from John M. Harris of the George C. Page Museum and Samuel A. McLeod of the Natural History Museum of Los Angeles County. The specimens were collected in February 1965 by R. Cruzen from location LACM 4090, which is in the NE 1/4 of Section 8, T 2 S, R 23 W on the Cibola 7.5' quadrangle, Yuma County, Arizona, about 2 1/2 miles north of Cibola Lake and about 24 miles south of Blythe, California. Using the 1927 datum, this would be about 33/16/15 N, 114/39/02 W. Samples come from both specimen LACM 33115, consisting of part and counterpart slabs, and from specimen LACM 33116. Samples were taken from the surface with the fish on it. Five samples from near Amboy, CA were collected in an attempt to determine whether the carbonate in that area is Bouse in origin. We also

analyzed twenty samples each from the Mohave Basins, including several previously

unsampled locations towards the northern end of Mohave Basin. Most importantly, we

collected five samples in the Las Vegas Basin from marl deposits with an unclear origin.

An extensive outcrop of marl overlain by algal-textured limestone occurs near

Frenchman Mountain, NV in the Las Vegas Basin and is described in Castor and Faulds

(2001). Castor and Faulds (2001) interpreted this outcrop as lacustrine and dated it to

post-6Ma based on tephrochronology but were unsure about its origins. They surmised

that it may be related to the Hualapai Formation or perhaps to the Bouse. If the outcrops

are indeed correlative with the downstream Bouse Formation rather than the Hualapai

Limestone, they could be viewed as evidence of a probable upstream lake required to

complete the lake chain from Grand Canyon to the Gulf of California.

 We also sampled a stratigraphic sequence through the Hualapai Limestone in the

Hualapai basin near the western end of Grand Canyon. We know from Colorado River

gravel deposits that the early river course west of Grand Canyon flowed over the

Hualapai lakebeds (Howard and Bohannon, 2001). Colorado River integration took place

after Hualapai Limestone deposition, although the strontium isotopic signature of the

Hualapai Limestone should decrease through time if mixing of Hualapai and Colorado

River-type waters was occurring. To examine this possibility, we obtained samples from

several Hualapai outcrops of differing ages. Within each of these outcrop locations, we

collected limestone samples through the stratigraphic section.

 Most samples were analyzed only for strontium isotopes; however samples from

southern-most Blythe basin were analyzed for both strontium and stable isotopes because

continuous and plentiful outcrops allowed for the best stratigraphic control. By obtaining

data from several different isotopic systems, we intended to better constrain the source of strontium isotopic variability. Nearly all Bouse outcrops at different elevations are spatially separated, but in the Blythe basin we were able to achieve stratigraphic control because we could sample the base of the Bouse carbonate along a single wash transect for nearly 50 vertical meters. The southern-most basin is also of special interest in the debate over the origin of the Bouse Formation because of the abundance and diversity of fossil species preserved in the carbonate and because of its proximity to the Gulf of California. By analyzing the same samples from the Blythe basin using several different isotopic systems, we hoped to more rigorously examine possible sources of variation, and thus gain further insight into both the origin of the Bouse Formation and the mechanism for the formation of the lower Colorado River.

ANALYTICAL METHODS

After removing weathered surfaces, all samples were powdered by hand using a Utech MP-65 mortar and pestle. Approximately 0.4g of carbonate material was transferred into 50mL centrifuge tubes and washed with ultrapure 0.8M ammonium acetate (pH=8) to remove loosely-bound cations introduced by normal weathering processes. The carbonate samples were then gently dissolved in ultrapure 1M acetic acid, while the gypsum samples were dissolved in distilled 6M HCl. Insoluble material, consisting mostly of fine-grained silicates, was removed by centrifugation. Sample leachate was then transferred to acid-cleaned Teflon beakers and evaporated on a hotplate. Once dry, the samples were redissolved in distilled 3.0M Nitric acid. Chemical separations were performed using Eichrom Sr-specific resin columns using 3.0M Nitric acid as eluent. Samples were loaded on to oxidized Ta filaments as phosphates, and

analyzed for $^{87}Sr/^{86}Sr$ using a VG Sector 54 thermal ionization mass spectrometer at the University of Arizona. NBS-987 standards were analyzed to give an average $^{87}Sr/^{86}Sr$ value of 0.710231±17 (n=10, 2σ).

$\delta^{18}O$ and $\delta^{13}C$ of carbonates were measured using an automated carbonate preparation device (KIEL-III) coupled to a gas-ratio mass spectrometer (Finnigan MAT 252). Powdered samples were reacted with dehydrated phosphoric acid under vacuum at 70°C. The isotope ratio measurement is calibrated based on repeated measurements of NBS-19 and NBS-18 and precision is ± 0.1 ‰ for $\delta^{18}O$ and ±0.06‰ for $\delta^{13}C$ (1σ).

Sr ISOTOPIC RESULTS

Strontium isotopic results for all Bouse basins are broadly consistent with earlier results (Patchett and Spencer, 1997), but contain several values both below and above this pre-established span as shown in Table 1. Most Bouse carbonate samples have an isotopic value near that of modern day Colorado river water (0.71075) and within an $^{87}Sr/^{86}Sr$ range of 0.7105 to 0.7112; however, we report values as high as 0.7123 for several samples from an isolated arm of the Blythe paleo-basin (Amboy) and lower than 0.7105 for three samples (Fig. 7). One sample with a low Sr ratio appears recrystallized, whereas the other two are heavily weathered. Strontium isotopic ratios for the slab of rock containing the *Colpicthys regis* fish fossil identified by Todd (1976) also show a Bouse isotopic signature with an average value of 0.7108, very near the value of the modern day Colorado River.

Strontium isotopic ratios for samples in the Blythe basin display important trends for understanding the evolution of Bouse waters. The strontium isotopic ratios for the

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wash transect in the Blythe basin (Fig. 3) systematically increase with elevation up to 100m. At low elevations, when the basin had a smaller amount of water, the strontium values were relatively high at 0.7110. As the basin filled with water, the strontium values decreased toward modern Colorado River water values. Once the basin reached about 25 percent of its total capacity, around 400 km^3 (calculation by J. Spencer, personal communication, 2007), the ^{87}Sr/^{86}Sr leveled off to an average value near 0.7109. Strontium values appear to have changed systematically through time in the region with good stratigraphic control, suggesting that seemingly random fluctuations in the ^{87}Sr/^{86}Sr are perhaps a product of the lack of continuous Bouse outcrops.

^{87}Sr/^{86}Sr data for Hualapai samples support values from previous work but extend the range of isotopic values in the Hualapai Limestone to as low as 0.7137 (Table 1). Samples collected by Faulds et al., (2001), showed very radiogenic values (0.7195) low in the Hualapai section near Grand Wash Cliffs, decreasing upsection to 0.7153 in the same location. At a different location but higher stratigraphically, Hualapai strontium ratios continue to become less radiogenic (Spencer and Patchett, 1997). Samples from this Hualapai section near Temple Bar, NV are interbedded with a 6 Ma tephra (Spencer et al, 2001) and the ^{87}Sr/^{86}Sr ratios begin at 0.7145 in the lowest outcrop and decrease to 0.7137 in the highest-elevation outcrop in the area (Table 1, Fig. 7). The strontium isotopic ratios of the Hualapai Limestone indicate that the precipitating waters became less radiogenic and more like that of modern Colorado River water through time.

O AND C ISOTOPIC RESULTS

The carbonate samples from the Blythe basin were also analyzed for both oxygen and carbon isotopes (Table 2, Fig. 4). Our results broadly corroborate those of Poulson and John (2003), although we observed a wider range of variation. For whole rock and whole shell samples, oxygen isotopes have a range of 14 ‰, varying from –13.7 to +0.96 ‰ VPDB. Carbon isotopes for these same samples also show a large range of values, from –6.5 to +1.7 ‰ VPDB. The variation occurs as a trend from more negative carbon and oxygen isotope values towards more positive carbon and oxygen isotope values. The majority of samples with more negative oxygen values have more negative carbon values. A small number of samples, including carbonate from the *Colpicthys regis* fish slab, a bivalve shell cast, and micromilled Barnacle1 had a combination of very negative $\delta^{18}O$ value but extremely positive $\delta^{13}C$ values. The bivalve shell cast had the most negative $\delta^{18}O$, but its values may have been diagenetically derived. Two Bouse barnacles were micromilled along growth axes and analyzed for carbon and oxygen isotopes in addition to the whole rock and shell samples (Table 2, Fig 4). Both barnacles lie within the range of expected C and O isotopic ratios for continental waters and show systematic variations in $\delta^{18}O$ and $\delta^{13}C$ along growth axes. Data for Barnacle1 is shown in Figure 5.

DISCUSSION

Much evidence exists to support the chain-of-lakes hypothesis as the mechanism for integration of the Colorado River, yet a lively debate still surrounds the topic. Support for this uncommon fluvial mechanism includes tectonic, sedimentary, and geochemical evidence. Nevertheless, some authors continue to express doubt over the

fluviolacustrine interpretation because: (1) there is a lack of concrete evidence of a continuous chain of lakes from Grand Wash Cliffs to the Gulf of California; (2) the fossil assemblage of the Blythe basin contains several marine fauna; (3) the Sr isotopic variation inherent in Bouse carbonates could imply alteration and/or replacement of original seawater Sr ratios by modern Colorado River Sr; or (4) there could have been mixing of seawater with continental water during Bouse deposition. Strontium and stable isotope data in the Blythe basin are used to discuss the isotopic indications for the Bouse paleoenvironment, and a combination of carbon, oxygen, and strontium isotopic data help us examine the source of isotopic variation in the Bouse carbonates. Strontium isotope values from previously identified Bouse outcrops as well as new Bouse areas presented in this study from upstream basins provide evidence for a continuous chain of lakes from western Grand Canyon south to the Gulf of California.

Hualapai Limestone

Hualapai carbonate samples were collected from several locations within the Hualapai basin, both within Grand Wash trough and at higher stratigraphic positions to the west (Fig 2). Average Hualapai $^{87}Sr/^{86}Sr$ is considerably more radiogenic than Bouse ratios at 0.716 ± 0.002 but Hualapai samples display an enormous range of values (0.7195 – 0.7137). The oldest Hualapai Limestone sample from Grapevine Wash near an interbedded 11Ma tephra displays the most radiogenic value (0.7195), while Hualapai carbonates interbedded with a 6Ma tephra near Temple Bar, NV exhibit the least radiogenic, and most Bouse-like, strontium ratios. Samples at Temple Bar range from 0.7145 (Spencer and Patchett, 1997) to 0.7137, whereas higher elevation samples have lower $^{87}Sr/^{86}Sr$ values than low elevations. The same pattern is apparent in the older

Hualapai section in Grapevine Wash (Table 1). Strontium ratios decrease with higher stratigraphic position: younger Hualapai samples have systematically lower and lower $^{87}Sr/^{86}Sr$ values. As the time of Colorado River integration approached, Hualapai samples began to have less radiogenic strontium isotopic values. We interpret this trend as evidence of mixing between radiogenic groundwaters that precipitated the early Hualapai carbonates and non-locally derived waters with Bouse isotopic signatures, marking the first appearance of proto-Colorado River water to the west of Grand Canyon.

Extent of Bouse Carbonate Unit

All $^{87}Sr/^{86}Sr$ ratios for Bouse carbonates, regardless of basin, fall well above the Sr value for late Miocene seawater and close to the modern Colorado River. In an attempt to fill in the spatial gaps from the western end of Grand Canyon to the southern end of the Mohave basin, we sampled Bouse-like carbonates in northern Mohave basin, upstream Las Vegas basin, and the Hualapai limestone near the Grand Wash Cliffs in addition to the documented downstream basins.

Las Vegas Basin: Several limestone outcrops similar in appearance to the Bouse basal carbonate and of late Miocene to early Pliocene age occur in the Las Vegas Basin (Fig. 2). An ash bed twenty meters below the base of the limestone has been geochemically correlated with the 5.59Ma Wolverine Creek tuff, providing a maximum age for the carbonate unit (Castor and Faulds, 2001). The outcrops are described in Castor and Faulds (2001) and were tentatively correlated with Hualapai Limestone because field evidence suggested that the deposits may predate integration of the Colorado River. We sampled carbonate material at both Nellis Air Force base and near

Pabco Gypsum Mine for strontium isotopic study expecting to observe $^{87}Sr/^{86}Sr$ ratios similar to that of the Hualapai Limestone. Instead, $^{87}Sr/^{86}Sr$ values for carbonate samples within the Las Vegas basin resemble the strontium ratio of the Bouse Formation, with an average $^{87}Sr/^{86}Sr$ of 0.71079 ± 0.00008. The marl and limestone of Las Vegas basin remarkably shows no influence from the waters that precipitated the Hualapai Limestone farther to the east. We interpret the carbonates of Las Vegas basin as a relict of a hitherto unknown upstream Bouse paleolake that represents the upstream end of the Bouse lake system, indicating Bouse waters as high as 675 meters a.s.l.

Mohave Basin: The Mohave Basin Bouse carbonates exist as a much thinner sequence than in the more southerly basins, yet display the same Bouse strontium isotopic ratio (average $^{87}Sr/^{86}Sr$ =0.7107 ± 0.0003). Previous work has identified the Bouse Formation in only the southern two-thirds of the Mohave basin. We present additional data from carbonates in the more northerly portion of Mohave basin that indicate the presence of Bouse Formation up to 546m and as far north as Cottonwood Valley (Table 1, Fig. 2). Bouse carbonates from southern Mohave Basin also exhibit the typical Bouse strontium isotopic ratio, with an average $^{87}Sr/^{86}Sr$ of 0.7109 ± 0.0002. These data confirm previous work by Spencer and Patchett (1997). Neither part of Mohave Basin shows any influence from Neogene seawater, and both indicate a lacustrine origin for the Bouse Formation.

Blythe Basin: The Blythe basin is the southern-most extent of subaerial Bouse outcrops and contains the only marine fossils associated with the Bouse Formation. In addition to scattered Bouse outcrops in the Blythe basin, samples of basal Bouse carbonate along a single wash transect for nearly 50 vertical meters facilitated a detailed

Sr isotopic record through time for an area with good stratigraphic control. The strontium isotope results for the wash transect in the Blythe basin (Fig. 3) show a systematic variation with increased elevation up to 100m. Initial ^{87}Sr/^{86}Sr values for the Blythe basin were rather high (0.711096±13). As the basin filled with water, the strontium values decreased gradually toward modern Colorado River values at a rate of -0.00001/m (Fig 3). Eventually the strontium ratio began to increase again, and subsequently leveled off to an average value of 0.7109 once the basin reached about 25 percent of its final volume or approximately 400 km^3. It appears that the strontium values were changing systematically through time rather than displaying a random pattern of isotopic variation within the region of good stratigraphic control. The change in isotopic character is most easily explained by changing ^{87}Sr/^{86}Sr of water inputs to the river system through time. Above 100m elevation, when volume of water in the Blythe basin was very large and where we have only scattered outcrops, we see significant variation in the Sr isotopic values but do not have the necessary stratigraphic resolution to determine the nature of this variation. It appears that values remained reasonably constant once the basin contained a significant volume of water. It is likely that the chemical inertia of such a large volume of water allowed only smaller changes in the overall strontium ratio during this time, though the isotopic signature of water inputs may have continued to vary. Regardless of the small-scale variation in the lowest basin, all strontium isotopic ratios support a lacustrine rather than marine origin for the Bouse Formation in the Blythe area.

An outcrop of limestone and tufa near Amboy, CA (Fig. 2) closely resembles the Bouse carbonates found in the central Blythe basin and is at an appropriate elevation to

have been submerged when the Blythe basin was near its total capacity. Strontium isotopic ratios for the Amboy samples suggest at the very least that they were deposited in non-marine conditions. The $^{87}Sr/^{86}Sr$ values range from 0.7108 in a basal tufa mound up to 0.7120 in the overlying marl and to 0.7123 in the highest sample from the area (tufa). The strontium isotopic ratios are well above Neogene seawater and similar to those of the Bouse Formation, though such radiogenic values are atypical of the Bouse deposits nearer the river course. We do not fully understand the significance of the outcrop at Amboy, but suggest that it represents an isolated arm of the Blythe basin where locally derived $^{87}Sr/^{86}Sr$ exerted a large influence. Higher strontium ratios could be related to nearby Precambrian crystalline rocks, either from surface or groundwater contributions analogous to early Hualapai deposition. It is possible that a significant proportion of radiogenic groundwater was added to Bouse-type water in an isolated region of the Blythe basin.

Strontium, Oxygen and Carbon Isotopes in Marine and Fresh waters

Marine and fluvial waters have markedly different geochemical signatures that allow us to distinguish the origin of precipitated carbonates based on their isotopic character (Veizer, 1989; Ingram and DePaolo, 1993; Ingram and Sloan, 1992; Bryant et al., 1995). Neither biologically nor chemically precipitated carbonates fractionate strontium as it is incorporated into the calcite crystal structure, and carbonates precipitated in marginal seas tend to reflect the $^{87}Sr/^{86}Sr$ of marine water (Veizer, 1989; Bryant et al, 1995; Ingram and DePaolo, 1993). The $^{87}Sr/^{86}Sr$ of Neogene seawater is well-known from drill-core analyses and remained at a nearly constant value of 0.7090 during the 3-5Ma interval (Hodell et al., 1991; Palmer and Elderfield, 1985). The

strontium isotopic ratio of river water is defined by the $^{87}Sr/^{86}Sr$ ratio of the rocks and soils exposed in the drainage basin and by the $^{87}Sr/^{86}Sr$ of groundwater inputs to the river system (Goldstein and Jacobsen, 1987; Palmer and Edmond, 1992, English et al., 2000; Gross et al., 2001). The strontium isotope value for modern Colorado River water varies along its course, but below Grand Canyon is 0.7103 or higher (Gross et al., 2001). Goldstein and Jacobsen (1987) measured an isotopic value of 0.71075 and a Sr concentration of 1.16ppm for the Colorado River, about one seventh of the well-known seawater concentration of 8ppm.

Mixing systematics have been used to estimate the proportion of freshwater inflow to estuarine environments based on the differences in both concentration and strontium isotopic ratio of seawater and river water (Ingram and Sloan, 1992; Ingram and DePaolo, 1993; Bryant et al., 1995). Seawater has a fairly low Sr isotopic ratio (0.7090) but a high Sr concentration, whereas fluvial waters usually have a higher Sr isotope value but a low Sr concentration. A mass balance mixing calculation weights the isotopic value of seawater strontium heavily because Sr is much more concentrated in seawater than in river water; thus, a small amount of seawater would greatly influence the $^{87}Sr/^{86}Sr$ of the mixed water towards marine values. Even in estuaries dominated by freshwater inflow, marine $^{87}Sr/^{86}Sr$ predominates with only minor deviations from the global seawater strontium ratio (Bryant et al., 1995). Present-day Colorado River water is among the most saline of fluvial waters (Goldstein and Jacobsen, 1987; Gross, et al., 2001) but still has only about 15% of the seawater Sr concentration. Since Bouse Formation carbonate $^{87}Sr/^{86}Sr$ values do not resemble marine strontium values, we interpret these Sr isotopic ratios to indicate precipitation in a lacustrine environment with no connection to the sea.

Stable isotope compositions of carbonates also replicate the geochemical conditions during precipitation and can be used to distinguish between marine and non-marine source fluids. Because fluvial and ocean waters have such distinct isotopic compositions, oxygen isotopes, like strontium isotopes, can be used to examine the extent of mixing in marginal marine environments (Dettman et al., 2004). Seawater $\delta^{18}O$ and $\delta^{13}C$ values fall near 0‰, while inland waters are much more variable and tend to have $\delta^{18}O$ values between –12 and –7 ‰ (Clark and Fritz, 1997; Dettman et al., 2004). Even in the highly-evaporated modern Gulf of California, Dettman and others (2004) measured the mean $\delta^{18}O$ of seawater to be 0.60±0.16 ‰ (1σ); however, they found the Colorado River had a significantly more negative average $\delta^{18}O$ value of -12‰ that is typical of meteoric waters on continents.

The $\delta^{13}C$ of seawater, near 0‰, is a reflection of the isotopic character of its dissolved inorganic carbon and is insensitive to changes in temperature. Terrestrial carbonates tend to have more negative $\delta^{13}C$ values (-5 to -12‰) due to dissolved carbon from decayed ^{12}C-rich organic matter (-30 to -13‰); however, lacustrine carbonates may also have carbon isotopic values as positive as +4‰ (Sharp, 2007 p. 161-171). Increased photosynthesis by organisms in the water that preferentially remove ^{12}C from the surrounding environment as well as increased exchange with atmospheric CO_2 (-7‰) can lead to these more positive $\delta^{13}C$ values (Sharp, 2007 p. 161-171). Modern Colorado River Total Dissolved Inorganic Carbon $\delta^{13}C$ is near -5‰ (Poulson and John, 2003). The important reference point for carbon isotopes in the Colorado River and any inferred lake is that incoming water will show a negative $\delta^{13}C$ value until it is modified towards more positive values by photosynthesis and equilibration with the atmosphere.

Many factors control the stable isotopic character of water in rivers and lakes, and thus in lacustrine carbonate material, including the source of the water, extent of evaporation and atmospheric exchange, and residence time in the basin. The initial isotopic value of water is controlled by its origin and then evolves through time. Closed lake systems, such as the proposed chain of lakes along the lower Colorado River, tend to have covariant carbon and oxygen isotopic ratios due to long residence time of water in the basins (Talbot, 1990; Li and Ku, 1997). In this type of system, average carbon isotopic character is controlled more by exchange with the atmosphere than by local productivity, and in arid environments temperature is less important in affecting oxygen isotopic ratios than evaporation (Heaton et al., 1995; Cohen, 2003 p.260-270). Loss of ^{12}C-enriched carbon dioxide to the atmosphere causes lake waters to evolve towards more positive δ^{13}C values through time, while preferential evaporation of ^{16}O forces lake water towards more positive δ^{18}O values (Fig 4). We would expect to see a trend from more negative carbon and oxygen isotopes toward more positive carbon and oxygen isotopes through time if the lake were hydrologically closed and experiencing greater evaporation than input.

The wide range of stable isotope results for the Blythe basin suggest a continental origin for the Bouse Formation, supporting the conclusion of Poulson and John (2003), though oxygen and carbon data examined without regard to strontium isotopic ratios are equivocal. The range of oxygen isotope ratios is quite large (-13.7 to +1 ‰ VPDB), and the presence of such negative δ^{18}O values suggests that meteoric waters played a significant role in the composition of Bouse water. Carbon isotopes for the same Blythe basin Bouse samples show a wide range of values, from –6.5 to +3.4 ‰ VBDP. Such a

range of stable isotope values is inconsistent with what we expect for marine carbonates. Correlation between the carbon and oxygen isotope ratios from more negative to more positive values lends further support to an evaporative lacustrine origin.

Isotopic Results for Fossils

Several researchers have proposed a marine origin for the Bouse Formation based on paleontological evidence, including the presence of barnacles and the fish *Colpicthys regis* known to tolerate only very saline conditions. However, geochemical analyses of both the barnacles and the fish specimens reveal isotopic values more indicative of inland water than ocean water. The samples from two fish specimens have an average ^{87}Sr/^{86}Sr of 0.7108 ± 0.0001, nearly identical to modern Colorado River water, and a combination of average δ^{13}C and δ^{18}O values atypical for seawater (+1‰ and –12.4‰ respectively; both 0‰ for seawater). Such negative oxygen isotope ratios in conjunction with a very positive carbon isotope ratio could imply that the fish were occupying a more restricted shallow-water environment where the δ^{13}C of the area may have been increased by exchange with carbon dioxide in the atmosphere (Heaton et al., 1995).

Barnacles also show strontium, carbon, and oxygen isotopic ratios much more like those of modern Colorado River water rather than seawater. Individual barnacle samples were selected on the basis of minimal alteration and spar content using petrography and SEM imaging and have an average ^{87}Sr/^{86}Sr near 0.7110 (Spencer and Patchett, 1997). Two barnacles micromilled along growth axes at 15µm increments show stable isotope ratios indicative of non-marine water (Table 2, Fig.5). Barnacle1 has stable isotope values resembling those of the fish slab marls, and Barnacle2 has values that fall along

the general trend of Bouse carbonate stable isotope data (Fig. 4). The cycles of variation in both carbon and oxygen isotopes along barnacle growth axis are shown in Figure 5. The simplest explanation is that the $\delta^{18}O$ of the water remained constant (-9‰) throughout the year and that the –8.9‰ to –10.3‰ variation can be attributed to temperature fluctuations. The annual amplitude of 1.4‰ implies a temperature range of only 6 to 8°C, a rather large temperature range suggesting that perhaps isotopic variability may be dampened by changing $\delta^{18}O$ inputs. Alternatively, the temperature cycle may have been completely overwhelmed by change in water $\delta^{18}O$ as can happen in hydrologically closed basins. Knowing where summer occurs in the cycle can remove this uncertainty. Carbon isotope values can be a guide to the seasonal progression in these plots. Mid-summer $\delta^{13}C$ values in shallow water carbonates tend to be most positive due to removal of ^{12}C during enhanced productivity and water column stratification (McKenzie, 1985). The most positive $\delta^{13}C$ values occur when $\delta^{18}O$ is most negative, implying that warm temperatures cause both lower shell $\delta^{18}O$ values due to lesser isotope fractionation with warming, and higher $\delta^{13}C$ values due to enhanced productivity and/or greater atmospheric interaction. We interpret the cyclic patterns to represent original seasonal variation.

Although the barnacle and fish species are predominantly found in marine waters, geochemical evidence points toward their existence in saline waters with non-marine isotopic signatures. Extensive evaporation of meteoric waters in a large closed basin like the Blythe could easily lead to quite saline water in an inland environment. Marine species could have been introduced to the saline basin by birds or other natural mechanisms (Spencer and Patchett, 1997; Cohen, 2003).

Replacement of Sr with Modern Colorado Sr

Wholesale replacement of carbonate material has been suggested as a mechanism by which Bouse carbonates could have been deposited in an estuary but now possess Colorado River strontium isotope ratios (Lucchitta et al, 2001). Lucchitta and others (2001) have suggested that marine strontium ratios were replaced by prolonged flushing of Bouse carbonates with later Colorado River water. Replacement of carbonate material should not only alter the fine micritic texture of marls and shells to sparry calcite, but should also produce a correlation between the stable isotopes and the strontium isotopes. Samples with apparent marine stable isotopes should show marine strontium values because unaltered samples should retain all original isotopic character, but this is clearly not so; all samples regardless of stable isotopic composition show non-marine strontium ratios. No correlation exists between the isotopic systems (Fig. 6). Most whole rock marl samples and shells maintain original textures, and though some spar (<5%) is present, it is more likely derived from secondary addition of mobile calcite ($^{87}Sr/^{86}Sr$ = 0.7099, Spencer and Patchett, 1997) from the surface environment. Additional evidence from fossil specimens provides further evidence against replacement and recrystallization. As discussed, the two barnacle specimens from the Bouse Formation micromilled along growth axes display what appears to represent seasonal variation in their oxygen and carbon isotopes (Fig. 5). If replacement had occurred, these signatures would not be preserved today. We interpret this evidence to support evaporative evolution of lacustrine waters rather than isotopic replacement.

It is possible, however, that some of the small-scale variation in the Bouse $^{87}Sr/^{86}Sr$ could be due to the addition of small amounts of mobile calcite to some samples.

Samples with $^{87}Sr/^{86}Sr$ values near or below 0.7105 may suggest contamination with mobile carbonate (0.7099) as stable isotope values for these samples indicate non-marine conditions when data are available. As we noted in our examination of the wash transect strontium ratios, it is also possible that the isotopic variation characteristic of the Bouse carbonates is due to changing $^{87}Sr/^{86}Sr$ inputs through time. Without better stratigraphic control in more areas, it is difficult to ascertain what extent of the $^{87}Sr/^{86}Sr$ variation is due to evolving water inputs to the Colorado River system.

Mixing of marine and freshwater in a Bouse estuary

While evaporation of Colorado River type waters could produce the stable isotope trend we observe, mixing between seawater with $\delta^{18}O$ and $\delta^{13}C$ values near zero and river water with negative values could also lead to a similar mixing line. Stable isotope data alone cannot distinguish between the two, but by combining both strontium and stable isotope data for the same samples we hope to gain further insight. Mixing was dismissed by Spencer and Patchett (1997) on the basis of strontium isotopic evidence, but was revisited by Lucchitta and others (2001). Lucchitta and others (2001) present an argument in which they propose that mixing occurred between seawater (0.7090) and an un-integrated proto-Lower Colorado River with very radiogenic water similar to that of the Hualapai Limestone (>0.7140). If this were the case, samples with a marine stable isotope signature should also bear a marine strontium signal, while samples with freshwater stable isotope character should have more radiogenic strontium values. We would expect to see samples with more positive, seawater-like stable isotopes (near 0‰) have very low strontium ratios near than of seawater (0.7090) and samples with more

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negative, meteoric-type carbon and oxygen isotopes contain higher strontium ratios; however, this is not the case, and there is no evidence for correlation between the stable isotopes and the strontium isotopes (Fig. 6). Strontium isotopic ratios fall near the value for modern day Colorado River water regardless of their stable isotope character, and no samples have either marine strontium ratios or very radiogenic strontium ratios. This observation contradicts the estuarine mixing hypothesis and supports deposition of Bouse carbonates in an evaporative lacustrine environment.

Chain of Lakes

We observe $^{87}Sr/^{86}Sr$ ratios very near those of modern Colorado River water and very similar to other Bouse carbonates in both the northern Mohave and Las Vegas basins suggesting a continuation of the Bouse lake system to the north. The Hualapai Limestone shows a trend of decreasing strontium ratios through time, indicating possible late mixing of radiogenic Hualapai water and proto-Colorado River type water immediately prior to the integration of the entire Colorado River system. Overall, the variation in the Bouse $^{87}Sr/^{86}Sr$ seems extremely small compared with the $^{87}Sr/^{86}Sr$ differences between the other components of the system. The $^{87}Sr/^{86}Sr$ for the Bouse carbonates is distinctly different from that of the Hualapai Limestone, mobile calcite, and Neogene seawater and falls very near the strontium value for modern Colorado River water (Fig 7). We propose that the four paleobasins with Bouse-like $^{87}Sr/^{86}Sr$ (Blythe, Havasu, Mohave, and Las Vegas) represent late-Pliocene to early-Miocene inland lakes fed by the Colorado River, and that the youngest Hualapai Limestone may record the initial influx of proto-Colorado River waters west of Grand Canyon.

CONCLUSIONS

Strontium isotopic data from the 4-5Ma Bouse Formation carbonates and the slightly older Hualapai Limestone are inconsistent with a marine origin and support an interconnecting chain of lakes fed by the Colorado River. Carbon and oxygen isotope data, in conjunction with strontium results, are also inconsistent with Bouse deposition in an estuary. Stable isotopes suggest the waters that precipitated the Bouse carbonates were influenced by evaporation and provide evidence against a seawater-freshwater mixing scenario as well as diagenetic replacement of Bouse strontium signatures.

The Hualapai Limestone may record the first appearance of Colorado River water to the Basin and Range, and inundation of Bouse basins is ascribed to the arrival of Colorado River waters from upstream by an overflow mechanism. As river water arrived in each basin, it began precipitating the Bouse Formation carbonate and filled the basin with water. Once the basin reached its capacity, water spilled over at the lowest elevation outflow, eventually cutting the canyons that connect the basins along the modern course of the lower Colorado River.

A lacustrine, rather than estuarine, origin lends support to the unusual basin filling and overflow mechanism for river integration. Additionally, the new isotopic evidence eliminates the likelihood of deposition at or below sea level implied by a marine origin and does not require any amount of post-5Ma uplift for the Bouse Formation or the Colorado Plateau.

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FIGURE CAPTIONS

Fig. 1. Regional map of Arizona and adjacent areas showing proposed Bouse lake system and other related features.

Fig. 2. Map of the lower Colorado River trough and proposed extent of Bouse paleolake system. Sample locations are plotted with red crosses.

Fig. 3. $^{87}Sr/^{86}Sr$ vs. Elevation (m) for Blythe basin Bouse carbonates and proposed trajectory of strontium isotopic evolution of Bouse waters. Data include all samples for a continuous wash transect as well as higher elevation samples within the Blythe basin. Solid line represents a best fit line for the wash transect (0.00001 unit change in $^{87}Sr/^{86}Sr$ per meter; R^2=0.723) while dashed line shows estimated trend of strontium isotopic change with elevation. Elevation provides a relative time-scale, with low elevations earlier in time than higher elevations.

Fig. 4. $\delta^{13}C$ vs. $\delta^{18}O$ for Blythe basin Bouse carbonate samples including whole rock and micromilled barnacle samples. Arrows denote environmental influences on carbon and oxygen isotopic ratios. $\delta^{13}C$ tend to increase with increasing exchange with atmospheric CO_2 and degassing of ^{12}C-rich CO_2 from lake waters. $\delta^{18}O$ values likely represent initial influx meteoric waters with negative values that were subsequently evaporated to give a much more positive oxygen isotopic ratio. $\delta^{18}O$ and $\delta^{13}C$ display a strong positive correlation, often indicative of hydrologically closed lake systems.

Fig. 5. $\delta^{13}C$ and $\delta^{18}O$ values plotted for each sample along the growth axis of Barnacle1. Increasing sample number corresponds with increasing distance from the growth axis origin and occur in 15µm intervals. Cyclic variations in both carbon and oxygen isotopic ratios suggest the retention of isotopic seasonal variation signals and argue against recrystallization.

Fig. 6. $\delta^{18}O$ vs. $^{87}Sr/^{86}Sr$ in Blythe basin carbonate samples. No correlation exists between oxygen and strontium isotope ratios (R^2=0.0028), eliminating the possibility that replacement or mixing of sea and river water created the stable isotope trend seen in Figure 4. Shaded regions indicate regions of $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ values for Neogene seawater (SW) and modern Colorado River water. The range of $^{87}Sr/^{86}Sr$ values for the Miocene Hualapai Limestone (gray) increases off the graph to 0.7195.

Fig. 7. $^{87}Sr/^{86}Sr$ vs. Position along Colorado River course from western Grand Canyon south to the Gulf of California. Data is shown for seawater (Imperial Formation, Spencer and Patchett, 1997), Blythe, Havasu, Mohave, and Las Vegas basins, and the Hualapai Limestone. Approximate Sr isotopic ranges for Neogene seawater, mobile carbonate, and modern Colorado River water (Spencer and Patchett, 1997) are shown by the shaded regions.

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