Zircon age and oxygen isotopic correlations between Bouse Formation tephra and the Lawlor Tuff

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ABSTRACT

The Bouse Formation in the lower Colorado River trough holds an important record of the onset of the modern drainage patterns in the southwestern United States. It comprises calcareous and clastic infill deposited during flooding of several basins, including the Bristol and Blythe subbasins of Lake Bouse. An intercalated ash bed, which is key to constraining its depositional age, is exposed in two locations, Buzzards Peak and Amboy. Comparative zircon tephrochronology by secondary ion microprobe analysis of U-Pb zircon crystallization ages, U-Th trace element abundances, and oxygen isotopic composition confirm a correlation between the Bouse Formation tephra and the 4.834 ± 0.011 Ma Lawlor Tuff (40Ar/39Ar eruption age). Zircon in a coeval tephra associated with the Heise volcanic complex in the Snake River Plain has distinctly lower (by ~4.8‰, δ18O VSMOW [Vienna standard mean ocean water]) oxygen isotopic compositions than zircon from Bouse tephra, and can be ruled out as a source. The ca. 4.834 Ma depositional age for the Bouse Formation tephra in fine-grained sedimentary beds of the flooded Bristol and Blythe subbasins requires widespread Colorado River inundation in the lower Bouse basins at that time.

INTRODUCTION

Models for the arrival of the modern Colorado River in the lower Colorado River trough range from headward erosion from a marine estuary to top-down basin spillover. Differences between the models reflect variations in the influence on river development of the regional tectonics of much of the southwestern United States, including the uplift and erosional history of the Colorado Plateau and Grand Canyon, and the opening of the Gulf of California. The deposition of the Bouse Formation is a key element in the regional geologic evolution. The first arrival of the Colorado River in the lower Colorado River trough of the Basin and Range province and downstream in the Gulf of California is generally recognized to have occurred after the deposition of the Hualapai Limestone from 11 to 6 Ma in a lacustrine environment that has been reconstructed as and called Hualapai Lake (Fig. 1A) (Spencer et al., 2000; Faulds et al., 2001). There is also agreement that the full integration of the modern lower Colorado River postdated the deposition of the Bouse Formation (House et al., 2008; Metzger, 1968; Lucchitta et al., 2000; Spencer and Pearthree, 2000; Roskowski et al., 2010) and was concurrent with the deposition of Colorado Plateau–derived sediments, at least in the upper marine facies of the Imperial Formation of the early Gulf of California (Dorsey et al., 2007, and references therein). The exact timing of the arrival and organization of a through-going river to the Gulf of California, however, is still debated. An age of 5.33 Ma was assigned to the onset of deposition of Colorado Plateau and presumably Colorado River quartz sands in the lower Imperial group sediments currently exposed in the western Salton Trough at Split Mountain, California (Dorsey et al., 2007, 2011). If the identification of Colorado River–derived sands in early Gulf of California marine deposits and their assigned age of 5.33 Ma are correct, this would predate the inundation of water and fine sediment upstream in the Bouse Formation, currently assigned an age of 4.834 ± 0.011 Ma (Sarna-Wojcicki et al., 2011). This conundrum has directed attention (e.g., Dorsey et al., 2007) to the accuracy of published correlations, based on glass chemistry, between tephra within Bouse Formation deposits in two locations and the Lawlor Tuff (Sarna-Wojcicki et al., 2011). The ages are apparently contradictory, because impounding an early Pliocene Colorado River to a sufficient depth to fill the lower basin ~330 m above the present sea level appears incompatible with a prior throughput of the Colorado River to the Pliocene Gulf of California (e.g., Spencer and Pearthree, 2000).

Accurately constraining the depositional age of these tephra deposits is therefore crucial to resolve the timing for the deposition of the Bouse Formation and Colorado River integration. To this end, new secondary ion mass spectrometer (SIMS) U-Pb zircon age spectra, U-Th trace element abundances, and oxygen isotope compositions for the Bouse ash deposits at Amboy and Buzzards Peak, southern California (Fig. 1C) and candidate tephras (including the proximal Lawlor Tuff from Lawlor ravine, northern California) have been determined.

Accessory mineral geochronology is a promising chronostratigraphic tool to correlate dispersed volcanic rocks through their eruption and cooling ages, especially when applied to zircon in strongly weathered or hydrothermally altered tephra where primary glass chemistry may not be preserved (Lowe, 2011, and references therein, Wilson et al., 2010). In addition, zircon age spectra can be combined with trace element and isotopic compositions to provide a useful weathering-resistant correlation technique (e.g., Aydar et al., 2012). Zircon age and compositional data jointly provide a robust discrimination when comparing distal ash deposits to potential proximal equivalents, which may have similar chronologies, but differ in their melt (and thus zircon) chemistry.

These single-crystal data are the first successful direct radiometric age determinations for tephra in the Bouse Formation, and they provide a solid geochemical correlation that is based on the alteration-resistant mineral zircon. This resolves extant discrepancies between
Figure 1. (A) Western United States showing distribution of known Lawlor Tuff outcrops from Sarna-Wojcicki et al. (2011), Wolverine tuff localities mentioned in the text, and the Heise volcanic center (source of Pre-Kilgore outcrops and eruption). Estimated approximate extent of Hualapai and Bouse Formation paleolakes and topographic base were derived from finished 3-arc-second Shuttle Radar Topography Mission (SRTM) elevations. (B) Study region after slip restoration along the main plate boundary system to ca. 4.7 Ma, showing latitudinal equivalence of Ventura and Los Angeles Basins Lawlor Tuff deposits to the Lake Blythe (Bristol and Blythe basins) outcrops. Hualapai and upper Bouse Formation paleolakes are shown at estimated maximum extents, which likely predate 4.7 Ma. (C) Map of southernmost Bouse Formation paleolake, Lake Blythe, including the Blythe and Bristol subbasins. Extent of Lake Blythe estimated from U.S. Geological Survey SRTM version 2 (http://dds.cr.usgs.gov/srtm/version2_1/) 330 m contour. Bouse Formation outcrops digitized by Jon Spencer after Metzger (1968). Imperial group location is after Dorsey et al. (2011). IF—Imperial fault; IG—Imperial group; SAF—San Andreas fault zone; SJF—San Jacinto fault zone; SBM—south Bristol Mountains.
Bouse tephra age confirmation

chemical tephra correlations (Sarna-Wojcicki et al., 2011) and previous unsuccessful attempts to radiometrically date the distal tephra (Spencer et al., 2000).

GEOLOGIC BACKGROUND

The Bouse Formation in the lower Colorado River trough (Basin and Range province) comprises a series of basal limestone travertine (commonly called Bouse tufa), mudstones, sandstones, and gravel deposits (Metzger, 1968; Buising et al., 1990). These deposits fill a series of four paleobasins (Lakes Las Vegas, Mojave, Havasu, and Blythe) that progressively step down in elevation from north to south (Fig. 1). The deposits are thought to predate the complete integration of the lower Colorado River system into the modern throughgoing river, and overlie exclusively local alluvial deposits (Spencer and Patchett, 1997; House et al., 2008). Models for the arrival of the modern Colorado River in the lower Colorado River trough either advocate headward erosion from a marine estuary (e.g., Lucchitta, 1969) or top-down basin spillover (e.g., Blackwelder, 1934). These models are also intimately related to the regional tectonics of much of the southwestern United States, including the uplift and erosional history of the Colorado Plateau and Grand Canyon, and the opening of the Gulf of California. The deposition of the Bouse Formation is thus a key element in the regional geologic evolution.

There are competing depositional models for the Bouse Formation, i.e., (1) an exclusively marine origin for either the entire basin system, or just the lower southern basin, with subsequent uplift of the Bouse deposits from the early Pliocene sea level to current outcrop elevations ranging to 550 m above present-day sea level in the upper basins, and 330 m in the lower Lake Blythe basin (Lucchitta, 1972, 1969; Lucchitta et al., 2000; Smith, 1970; McDougall, 2005), or (2) an exclusively lacustrine origin in which the preintegration Colorado River was impounded by structural dams in perched lakes, with subsequent lake spillover and downcutting until a throughgoing river to the Pliocene Gulf of California was achieved (Blackwelder, 1934; Spencer and Patchett, 1997; Spencer and Peartree, 2000; Meek and Douglass, 2000; Spencer et al., 2008; House et al., 2008, 2005).

Global sea-level estimates for the early Pliocene have ranged from −48 m to +50 m (Miller et al., 2005), whereas more recent work places the global sea level during the mid-Pliocene at +22 ± 10 m (Miller et al., 2012). Spencer et al. (2013) illustrated that the local sea level in the Colorado River trough region is expected to be within ~5 m of the global mid-Pliocene sea level during the early Pliocene. Even the highest estimates, though, still strand the top of the Bouse Formation in the southern Bristol-Blythe basins (Figs. 1C and 2) ~250 m above the early Pliocene sea level, in the absence of identified regional uplift.

A marine origin of the Bouse Formation is supported by paleontological arguments that salt-water species found in lower southern Bouse Formation strata could only have prospered in marine-estuarine conditions (McDougall, 2008). A lacustrine origin is consistent with basin-wide Sr, C, and O isotopic evidence that continental, rather than marine waters, filled saline lakes in which the fine sediment of the Bouse Formation was deposited (Spencer and Patchett, 1997; Gross et al., 2001; Patchett and Spencer, 2000; Poulson and John, 2003). Moreover, according to the carbonate clumped isotope study of Huntington et al. (2010), uplift of the lower Colorado River trough since ca. 5 Ma is insufficient to restore the Bouse carbonates to sea level. Hybrid models between these two end members exist, but are currently problematic (Spencer and Patchett, 1997; Spencer et al., 2013). A model with marine transgression into the lower trough, combined with lacustrine deposition into the upper lakes, and a later depositional or tectonic impounding of fluvial waters in the lower Bristol-Blythe basin is conceivable, but there is currently neither sedimentologic nor geochemical evidence for successive deposits that would provide support for this hybrid model, and the tectonic reconfiguration necessary to impound the lower basin is not supported.

Figure 2. Estimated geographic settings for Bouse tephra locations, based on modern topography derived from the National Elevation Dataset 3-arc-second data (http://ned.usgs.gov/). (A) Amboy ash bed located offshore of significant modern topography in the south Bristol Mountains. (B) Buzzards Peak ash located offshore of subdued modern topography.
by current observations (Spencer and Pearthree, 2000; Spencer et al., 2013). Spencer et al. (2013) provide further reviews and in-depth looks at these competing models.

Lower Colorado River Chronology

Currently the upper and lower age limits for the arrival of the Colorado River in the lower Colorado River trough are bracketed by tephrachronology on several tephas beds within the Miocene–Pliocene continental sedimentary succession, and the identification of Colorado River sands in the Gulf of California. Underlying the Bouse Formation is an ash correlated with the Wolverine tuff (House et al., 2008). This ash is interbedded with alluvial fans beneath the basal Bouse Formation of Lake Mojave (Fig. 1A; Metzger, 1968; House et al., 2008) and also occurs ~20 m below the basal limestone of paleo–Lake Las Vegas (Fig. 1; Castor and Faulds, 2000; Spencer et al., 2008). There is a discrepancy, however, in the proximal stratigraphic definition and dating of the Wolverine Creek ash. Morgan and McIntosh (2005) defined and dated it with a 40Ar/39Ar age of 5.59 ± 0.05 Ma, and Anders et al. (2009) partially redefined the proximal stratigraphy, reporting a 40Ar/39Ar age of 5.84 ± 0.03 Ma for the Wolverine tuff. Here, in the absence of consensus for the proximal stratigraphy, I follow the established nomenclature and age for the Wolverine tuff by Morgan and McIntosh (2005) and Watts et al. (2011). Stratigraphically above the Bouse Formation are Colorado River gravels that postdate Colorado River incision into the Hualapai Limestone, dated as 4.4 Ma by interbedded basalts (Faulds et al., 2001) at Sandy Point (modern Lake Mead) and as 4.1 ± 0.5 Ma by a lower Nomlaki ash deposit in the upper Bullhead alluvium, Mojave Valley (House et al., 2008). The Bullhead alluvium is recognized as a marker for the integrated Colorado River system (House et al., 2008). Downstream, the appearance of distinctive Colorado Plateau type sediments (C-suite) (Dorsey et al., 2007), including hematite-coated, well-rounded quartz sand grains, in the lower Wind Caves member of the marine Imperial group at Split Mountain Gorge (southern California) between 5.33 and 5.24 Ma has been identified as the first appearance of Colorado Plateau and/or Colorado River sands in the Pliocene Gulf of California (Dorsey et al., 2007, 2011, and references therein). This was followed by the appearance of Cretaceous foraminifera reworked from the Mannos Shale on the Colorado Plateau and carried by the Colorado River into the upper Dequylos formation at the same location (Merriam and Bandy, 1965) after ca. 4.6 Ma (Dorsey et al., 2007). Dates for the Split Mountain Gorge section are derived from a paleomagnetic section sampled at 14 m stratigraphic intervals at Split Mountain Gorge, anchored to the magnetic polarity time scale from micropaleontologic identification of the Miocene–Pliocene boundary in the section, and a 2.3 ± 0.4 Ma U–Pb zircon age for ash in the overlapping Fish Creek–Vallecito transect (Dorsey et al., 2007, 2005).

The key direct age constraint for the deposition of the Bouse Formation is from an ash bed located in the lowest Bouse basin, first identified (Metzger, 1968) at the Buzzards Peak location in the Chocolate Mountains of California (Fig. 1C). This ash bed also occurs above tufa north of Amboy. At both locations, this ash has been correlated based on glass chemistry with the 4.834 ± 0.011 Ma Lawlor Tuff (Fig. 1A) (Sarna-Wojcicki et al., 2011). Direct attempts to date the ash bed in the Chocolate Mountains have been inconclusive. They include a K-Ar glass date of 5.47 ± 0.20 Ma (Shafiqullah et al., 1980), and discordant 40Ar/39Ar geochronology on bulk glass and bulk plagioclase separates (Spencer et al., 2000). Spencer et al. (2000) reported disturbed low-temperature heating steps for 40Ar/39Ar dating of bulk plagioclase separates, and concluded that this resulted from adhering glass or plagioclase alteration, whereas their much older higher temperature heating steps (plateau age = 17.5 ± 0.5 Ma at ~60% total released argon) were interpreted to result from xenocrystic contamination of the bulk plagioclase sample. Two bulk glass separates yielded progressively older ages with increasing heating temperature, interpreted as argon loss, with a preferred age from selected moderate-temperature heating steps of 4.76 ± 0.25 Ma and 5.01 ± 0.09 Ma.

The Lawlor Tuff has been successfully dated at its proximal location. At its type locality (Lawlor Ravine, northern California), 40Ar/39Ar multigrain stepwise heating of plagioclase from 2 samples from the lower pumice fall deposit yielded an average isochron age of 4.834 ± 0.011 Ma (Sarna-Wojcicki et al., 2011). The source for the Lawlor Tuff is within the faulted Napa-Sonoma volcanic field; one potential source complex is the Cup and Saucer eruptive center in the southeastern Sonoma volcanic field (Fig. 1A; Sweetkind et al., 2011), identified by Sweetkind et al. (2011) as the source of the 5.2–5.4 Ma (K/Ar; Everenden et al., 1964) Pinole Tuff, although thicker deposits of the Pinole Tuff are found farther south within the Napa-Sonoma volcanic field (Sarna-Wojcicki et al., 2011). Within the Sonoma volcanic field, proximal to the suggested eruptive center, Plinian fall deposits of the Lawlor Tuff are recognized east of the Cup and Saucer complex (Sarna-Wojcicki, 1976; Sweetkind et al., 2011) and a ~60-m-thick rhyolitic ash-flow tuff with a basal vitrophyre south of Napa is suggested to correlate with the proximal fall deposit and with widespread regional fall and ash-flow deposits (Sweetkind et al., 2011). Distal Lawlor ash has been identified in early Pliocene deposits within the Mojave and Colorado Deserts and in the Los Angeles and Ventura Basins (Sarna-Wojcicki et al., 2011), which restore approximately to the latitude of the southern Bouse outcrops when slip is restored on the San Andreas fault system (Fig. 1B).

Modern delivery of Colorado Plateau sands to the Gulf of California is by the Colorado River through lower Colorado River trough valleys that host Bouse Formation deposits. The identification of Colorado Plateau sediments in the Gulf of California prior to widespread flood- ing of intermediate basins, as required by the glass correlation age for the Bouse Formation, is problematic. This conundrum can be resolved if either the glass correlation age for the Bouse Formation or the lower Wind Caves member stratigraphic age is in error by 0.4–0.5 m.y., or by identification of plausible methods to deliver Colorado Plateau sediment to the early Gulf of California prior to, or concurrent with, impounding of Colorado River water in the Bristol-Blythe basin. The latter could be achieved either by the development of a tectonic or sedimentary dam that could have impounded the Colorado River below the Bristol-Blythe basin, after throughgoing integration of the river to the Miocene Gulf of California (or to a marine incursion within the lower Bristol-Blythe basin), or through an alternative Colorado Plateau sediment route into the lower Imperial group, bypassing the lower Bouse basins. Spencer et al. (2013, p. 452), discussed the feasibility of such a dam, but concluded that such a “complex scenario is highly implausible” due to the necessity that the pace of dam construction would have to exceed the rate of erosion by a river on the scale of the Colorado River, and the lack of sedimentological support for such a dam. Alternatively, a hypothetical late Miocene Gila River route for Colorado Plateau sediments, prior to the integration of the Colorado River through to the Gulf of California (Kimbrough et al., 2011), would bypass the Bouse basins and eliminate the need to dam the Colorado River, but this scenario also lacks independent support (Spencer et al., 2013). The need for an independent age constraint to either confirm or refute the glass correlation age for the Bouse tephra motivated this study, and SIMS dating of the zircon within the Bouse tephra was undertaken to obtain zircon age spectra and chemical compositions that would inform robust correlations with proximal ashes of well-known eruption age.
METHODS

Sample Amboy 1 was collected from an ash bed (elevation ~290 m above sea level; U.S. Geological Survey Shuttle Radar Topography Mission version 2 [SRTM v2; http://dds.cr.usgs.gov/srtm/version2_1/], UTM [Universal Transverse Mercator] Zone 11, NAD [North American datum] 83, 615026 m E, 3828006 m N) draping over the top of a tufa head overlying alluvial gravels north of Amboy (Fig. 1C). It corresponds to the location MO2AM-110B T489–7 (mislabeled Afton Canyon in table 5 of Sarna-Wojcicki et al., 2011; D. Miller, 2011, personal commun.), and is equivalent to the basal ~5 cm of ash described by D. Miller (2013, personal commun.) as overlying sandy beds in a nearshore environment. At the Amboy location, this portion of ash lacks visible bioturbation, and was interpreted as unworked primary fall material. Sample Buzzard was provided by Jon Spencer, collected at Buzzards Peak, California (~306 m above sea level, SRTM elevation, UTM, zone 11, 699088m E, 3670811m E; Spencer et al., 2000, 2003, and corresponds to sample IMP95–03 T526–4 in Sarna-Wojcicki et al. (2011). Buzzards Peak ash contains primary vitreous glass, and appears as largely pure ash. Samples Buzzard, Amboy, Lawlor1, and Lawlor2 (with sufficient size to avoid beam overlap with epoxy) were further analyzed for oxygen isotopes as described in Watts et al. (2011). Proximal Lawlor Tuff samples Lawlor1 and Lawlor2 (with extended pre-eruptive residence, of zircon with extended pre-eruptive residence, or possibly antecrysts recycled from a previous melt) comprise detrital grains with ages between 5.01 ± 0.10 (MSWD = 1.01; n = 44) interpreted to represent the last phase of pre-eruptive zircon crystallization in the Lawlor magma. This average is significantly older than the 4.83 ± 0.01 Ma 40Ar/39Ar age, and is within reversed polarity Chron 3n.3r (Lourens et al., 2005), whereas the proximal Lawlor Tuff has been shown to carry a normal magnetic polarity orientation concordant with the 40Ar/39Ar eruption age (Sarna-Wojcicki et al., 2011). The older 206Pb/238U zircon age thus must reflect pre-eruptive zircon crystallization over time scales of tens of thousands of years typical for many silicic magma systems (e.g., Simon et al., 2008). It is emphasized that the zircon age does not supersede the 40Ar/39Ar age for the eruption age for the Lawlor Tuff. The 40Ar/39Ar eruption and 206Pb/238U zircon crystallization ages are geologically compatible, and their difference is of secondary importance for the purpose of correlation between proximal and distal tephra.

RESULTS

Proximal Lawlor Tuff

Proximal Lawlor Tuff samples Lawlor1 and Lawlor2 have indistinguishable mean U-Pb zircon ages, 4.94 ± 0.08 and 5.04 ± 0.04 Ma (Fig. 3B; Table 1; Supplemental File 1), and yielded a combined weighted mean 206Pb/238U zircon crystallization age (after correction for 230Th disequilibrium) of 5.00 ± 0.04 Ma (mean square of weighted deviates, MSWD = 2.80; n = 52; all uncertainties reported as 2σ and errors scaled by the square-root of the MSWD). Although the data suggest a slight age zonation in the Lawlor magma, the overlapping mean age and probability distribution functions preclude uniquely assigning a distal ash to either the fall or flow phase of the Lawlor ravine deposits, and so the combined age is used for comparison. The elevated MSWD indicates age dispersion outside analytical uncertainties. This is interpreted to result from the presence of zircon with extended pre-eruptive residence, or possibly antecrysts recycled from a previous magma episode. To provide a consistent and objective method of identifying the youngest zircon population, the limits for MSWD values indicating a homogeneous population (Mahon, 1996) were applied to exclude older ages from the weighted mean age until the MSWD is in the acceptable range for a single population. Excluding the eight oldest zircons from both proximal Lawlor samples yields an average 206Pb/238U zircon age of 4.94 ± 0.04 Ma (MSWD = 1.41; n = 44) interpreted to represent the last phase of pre-eruptive zircon crystallization in the Lawlor magma. This average is still significantly older than the 4.83 ± 0.01 Ma 40Ar/39Ar age, and is within reversed polarity Chron 3n.3r (Lourens et al., 2005), whereas the proximal Lawlor Tuff has been shown to carry a normal magnetic polarity orientation concordant with the 40Ar/39Ar eruption age (Sarna-Wojcicki et al., 2011). The older 206Pb/238U zircon age thus must reflect pre-eruptive zircon crystallization over time scales of tens of thousands of years typical for many silicic magma systems (e.g., Simon et al., 2008). It is emphasized that the zircon age does not supersede the 40Ar/39Ar age for the eruption age for the Lawlor Tuff. The 40Ar/39Ar eruption and 206Pb/238U zircon crystallization ages are geologically compatible, and their difference is of secondary importance for the purpose of correlation between proximal and distal tephra.

Kilgore Tuff, Pre-Kilgore Tuff, Neroly Formation

With additional U-Pb zircon data, Kilgore Tuff HS-11 (HS samples from Watts et al., 2011) was quickly ruled out as too young for a potential match. Pre-Kilgore Tuff HS-14, however, yielded a weighted mean zircon crystallization age of 5.01 ± 0.10 (MSWD = 1.01; n = 44) that closely overlaps with the Lawlor zircon ages. By contrast, juvenile Neroly Formation zircons yielded an older average 206Pb/238U age of 11.4 Ma ± 0.3 Ma (MSWD = 1.52; n = 18). The young population in the Neroly Formation composes only ~27% of the zircon population in the sample; the remainder probably comprises detrital grains with ages between ca. 24 Ma and ca. 1.63 Ga (see the Supplemental File [footnote 1]).

Boue Tephra: Amboy and Buzzards Peak Tephra

The Boue tephra samples (Amboy and Buzzards) both have complex but similar zircon age populations comprising juvenile grains and...
detrital or xenocrystic grains (Fig. 4). Combining both samples, the weighted mean zircon crystallization age of the youngest population initially classified as juvenile is 5.26 ± 0.11 (n = 22; MSWD of 3.89). Similar to the proximal Lawlor samples, a high MSWD indicates the presence of zircon age heterogeneity in this population. Applying the method of Mahon (1996) yields a younger average age of 5.05 ± 0.11 Ma (MSWD = 1.56; n = 15). For the Buzzards Peak zircons alone, the younger age population averages 5.06 ± 0.12 Ma (MSWD = 1.87; n = 12). Using Isoplot (Ludwig, 2003) or other unmixing algorithms for a binary population yields slightly different results, but requires an additional assumption that the second age peak within the Bouse tephra constitutes a single population. For the Amboy zircons alone, excluding older crystals defines a younger age peak at 5.19 ± 0.30 Ma (MSWD = 2.2; n = 6), although the sample size results in comparatively large uncertainties. All three combinations of the Bouse tephra weighted mean ages are within error of the average zircon crystallization age for both the proximal Lawlor sample and the Pre-Kilgore Tuff sample HS-14 (Table 1).

Zircon δ¹⁸O and Uranium Abundances

Zircon δ¹⁸O for Lawlor samples averages 6.6‰ (relative to VSMOW) with a standard deviation of 0.6‰ (n = 20). Assuming a zircon-melt fractionation of ~+1.8‰ (Trail et al., 2009), this would correspond to a magmatic composition of ~8.4‰, consistent with the elevated bulk oxygen isotopic compositions of the Sonoma volcanics (Johnson and O’Neil, 1984). The Lawlor zircon value closely overlaps with the average for Bouse zircons (δ¹⁸O = 6.9‰ ± 0.5‰; 1 standard deviation, s.d.; n = 12). Pre-Kilgore zircon δ¹⁸O values, by contrast, are characteristically depleted, and more variable (δ¹⁸O = 2.1‰ ± 1.5‰; 1 s.d.; n = 13) compared to the Bouse and Lawlor zircons. This reflects zircon crystallization in the Heise caldera magmas containing variable but significant amounts of remelted or assimilated hydrothermally altered rock that are typical for large multicycle caldera systems of the Snake River Plain (Watts et al., 2011). U abundances in zircon are highly variable, ranging between 60 and 4600 ppm (Lawlor), 150 and 8800 ppm (Bouse), and 50 and 4600 ppm (Pre-Kilgore Tuff).

DISCUSSION

Buzzards Peak and Amboy ashes, here collectively termed Bouse tephra, show a significant spread in ages compared to their potential proximal equivalents, mainly because in addition to significant age peaks of late Miocene–early Pliocene zircon, they carry a broad detrital zircon population ranging from early Miocene to Proterozoic ages (Fig. 4; Supplemental File [see footnote 1]). These older ages are absent in any of the potential proximal equivalents. Surface exposures within the south Bristol Mountains are typical of the rock types within the Mojave geologic province, including Miocene–Oligocene volcanic rocks, Mesozoic arc rocks, and Mesoproterozoic basement rocks (Harvey et al., 2011; Ingersoll et al., 2013), with minor exposures of variably metamorphosed Paleozoic sedimentary sequences (Brown, 1981). The similarity between the older age populations...
TABLE 1. SUMMARY OF AGES AND δ¹⁸O FOR RELEVANT TEPHRA

<table>
<thead>
<tr>
<th>Sample</th>
<th>40Ar/39Ar 2σ (Ma)</th>
<th>U-Pb age 2σ (Ma)</th>
<th>MSWD</th>
<th>δ¹⁸O (average) 1σ (%)</th>
<th>δ¹⁸O magma†† (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amboy1 + Buzzard</td>
<td>N.D.**</td>
<td>5.26 ± 0.11 (n = 22)</td>
<td>3.89</td>
<td>6.9 ± 0.5 (n = 12) zircon</td>
<td>8.7</td>
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<tr>
<td>Amboy1</td>
<td>N.D.</td>
<td>5.05 ± 0.11 (n = 15)</td>
<td>1.56</td>
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<tr>
<td>Buzzard</td>
<td>N.D.</td>
<td>5.19 ± 0.30 (n = 6)</td>
<td>2.16</td>
<td>6.22 ± 0.11 (n = 2) zircon</td>
<td>8</td>
</tr>
<tr>
<td>Lawlor1 + Lawlor2</td>
<td>4.83 ± 0.011(LAWL2)</td>
<td>5.00 ± 0.04 (n=52)</td>
<td>2.80</td>
<td>6.6 ± 0.6 (n = 20) zircon</td>
<td>8.4</td>
</tr>
<tr>
<td>Lawlor1</td>
<td>N.D.</td>
<td>4.94 ± 0.04 (n = 44)</td>
<td>1.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lawlor 2</td>
<td>4.83 ± 0.011</td>
<td>5.04 ± 0.04 (n = 30)</td>
<td>2.88</td>
<td>6.6 ± 0.6 (n = 20) zircon</td>
<td>8.4</td>
</tr>
<tr>
<td>Pre-Kilgore (HS-14)</td>
<td>N.D.</td>
<td>5.04 ± 0.10 (n = 24)</td>
<td>1.01</td>
<td>2.1 ± 1.5 (n = 13) zircon</td>
<td>3.5†</td>
</tr>
<tr>
<td>Neroly Formation</td>
<td>N.D.</td>
<td>11.4 ± 0.3 (n = 18)</td>
<td>1.52</td>
<td>3.5†</td>
<td></td>
</tr>
<tr>
<td>Wolverine (HS-16)</td>
<td>5.59 ±0.05**</td>
<td>5.45 ± 0.14 (n = 15)</td>
<td>1.57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Data are from this study unless otherwise specified. N.D.—no data; MSWD—mean square of weighted deviates; n—number of samples. HS prefixes are from Watts et al. (2011).
*Data from Watts et al. (2011) and this study.
1Data from Watts et al. (2011).
1Data from Sarna-Wojcicki et al. (2011).
**Data from Morgan and McIntosh (2005).
†† δ¹⁸O magma calculated using an average zircon-melt fractionation of ~+1.8‰ (Trail et al., 2009) unless otherwise specified.

Figure 4. Detrital components in the Bouse tephra; histograms and relative probability curves. (A) Amboy ash zircons. (B) Buzzards Peak ash zircons. Older ages shown in inset panel after later Neoproterozoic through Paleozoic age gap. Probability peaks and histogram frequencies are offset in some age ranges due to the histogram bin size. (C) Comparison zircon age spectra from Ingersoll et al. (2013). Mojave adjacent Miocene–Pliocene sediments from Soledad basin and Lockwood Valley contain the Oligocene–Miocene volcanic zircon ages, the Jurassic–Cretaceous volcanic arc zircon ages, and the Mesoproterozoic age zircon components typical of the Mojave Province. Modern Colorado River sediments, by comparison, have subordinate Oligocene–Miocene and Mesozoic arc peaks, and include later Neoproterozoic through Paleozoic age components.
and the ages of the local Miocene volcanic and plutonic basement rocks implies that these populations are local detrital input, and argues for excluding these ages from statistical comparisons. Kolmogorov-Smirnov statistical analysis is used here because there is no expectation that the geologic variance in the data follows a Gaussian distribution. All probability analyses are done between the bounds of 3.0–7.0 Ma; this excludes the unambiguously detrital zircon population. The probability of the Amboy (n = 6) and Buzzards Peak (n = 16) zircons representing the same population is P = 0.99 (Fig. 3C; Table 2). The dominance of local input in the Amboy ash is likely due to the proximity of the Amboy shoreline to an extensive high of local topography in the south Bristol Mountains, as opposed to the Buzzards Peak location with more subdued or submerged local topography (Fig. 2). In addition, there may have been enhanced local sedimentation concurrent with ash deposition in the northern part of the basin. While the Amboy ash is, in outcrop, a homogeneous, well-sorted, glassy bed, it is not unexpected to find water-lain ashes cryptically reworked (e.g., Schmitt and Hulen, 2008). Lacustrine ashes may include primary fall-out in addition to later pulses of ash redeposited from the environment with possibly only minor evidence of bedding differentiation in the absence of strong currents. Even primary fall-out tephra may be contaminated by local sediment sources because detrital components can be present in suspension in the water column at the time of fall-out deposition, and eolian input coincident with the fall-out is plausible. The Amboy and Buzzards Peak locations are on the northern and southern perimeter of Bouse Lake Blythe (Figs. 1C and 2) with different local sedimentation patterns (nearshore sand and channels at Amboy, carbonate formation at Buzzards Peak). It is thus reasonable to expect that local sedimentary input could have varied between locations, with more local input at Amboy.

Considering only zircons younger than 7 Ma and disregarding the detrital components leaves a zircon population with an age peak of ca. 5 Ma for the Bouse tephra; this is broadly similar to that in proximal tephras that are potential correlatives. For all zircons younger than 7 Ma, there is a probability of equivalence P = 0.05 for proximal Lawlor (n = 52) and combined Bouse tephra (n = 22), and P = 0.56 for proximal Pre-Kilgore (n = 24) and combined Bouse tephra (n = 22). The relatively poor match between proximal Lawlor and Bouse tephra is due to the distinct presence of slightly older (ca. 5.5 Ma) zircon crystals exclusively in the distal samples (Fig. 3). Applying the same objective criteria (Mahon, 1996) to isolate the youngest zircon population leads to the exclusion of a minor ca. 5.5 Ma peak of zircon ages (Table 1) in the distal samples. In the Bouse tephra zircon population, this ca. 5.5 Ma peak occurs in addition to the shoulder of slightly older (recycled or antecryptic) zircons that characterize both proximal Lawlor and distal Bouse tephra deposits (Fig. 3). If the ca. 5.5 Ma population is excluded, the probability of age equivalence between proximal Lawlor and younger Bouse increases to P = 0.88, 0.77, and 0.32, for the combined Bouse (n = 15), Buzzard (n = 12), and Amboy (n = 6) zircons, respectively. A similarly high probability (P = 1.0) also exists for the younger combined Bouse (n = 15) and Pre-Kilgore (n = 24) zircons being drawn from equivalent age populations. There is, however, also a high probability of zircon age equivalence between Pre-Kilgore (n = 24) and Lawlor (n = 52) of P = 0.99. This underscores that age alone may not be a sufficient criterion to uniquely source tephra deposits.

Two-Dimensional Probability Analysis

In addition to the U-Pb crystallization age, zircon δ18O and U compositions are considered. Two-dimensional probability density plots in Figure 5 take into account analytical uncertainties and the non-Gaussian distribution of the data, and are contoured according to increasing probabilities in zircon δ18O and U abundance versus U-Pb age space, respectively. Based on the clearly distinct fields in δ18O versus 206Pb/238U age (Fig. 5A), the Bouse zircons can be discerned from the Pre-Kilgore zircons. The elevated δ18O zircon values of the Bouse tephra lack the extremely low intracontinental oxygen isotopic values that were imparted via hydrothermal alteration of the source rocks from which the Pre-Kilgore magmas derived (Watts et al., 2011), whereas the Lawlor Tuff and Bouse tephra δ18O values are more typical of the elevated composition of continental crustal magmas (e.g., Taylor, 1968). Although the range of U concentration in the Bouse tephra and Lawlor Tuff varies by an order of magnitude, probability contours in U-age space show a higher degree of correspondence between Lawlor and Bouse tephras than between Pre-Kilgore and Bouse tephras.

Combining the age and δ18O probability fields in Figures 5A and 5B reveals a strong overlap between the Bouse samples and the proximal Lawlor Tuff. This lends additional credibility to previous glass chemistry correlations between the Bouse tephra and the Lawlor Tuff (Sarna-Wojcicki et al., 2011), and the statistical correspondence between the Amboy and Buzzards Peak samples independently corroborates the assumption that both outcrops record the same event during a period of widespread concurrent flooding in both subbasins of Lake Blythe.

Although all identified potential source ashes other than the Lawlor Tuff can be ruled out by either the glass chemistry or zircon age and composition, another unknown source for the Bouse tephra cannot be completely dismissed. A potential source in the Snake River Plain (e.g., Kilgore or Pre-Kilgore Tuffs), however, would be inconsistent with glass and zircon age and composition, although a potential match specifically with Pre-Kilgore Tuff glass chemistry had remained untested in previous correlation studies (Sarna-Wojcicki et al., 2011). Combining the zircon age analysis with the electron microprobe data from Sarna-Wojcicki et al. (2011) also allows for a more targeted search for additional potentially correlating tephra. Even when conservatively doubling the ∼200 k.y. lag period between zircon crystallization age and eruption age generalized by Simon et al. (2008), few other potential correlative volcanic sources are identified. A search of the Western North American Volcanic and Intrusive Rock Database (NA VDAT) (Walker et al., 2006) within an ∼300 km radius of the Bouse

| TABLE 2. SUMMARY OF KOLMOGOROV-SMINOV TWO SAMPLE TEST STATISTICS |
|-------------------|-------------------|-------------------|-------------------|
| Probability of correspondence (P) | Bouse tephra combined | Lawlor1 + Lawlor2 | Pre-Kilgore (HS-14)* |
| Sample             | (n = 16)          | (n = 52)          | (n = 24)          |
| Bouse tephra combined |                  |                  |                  |
| all                | n = 22           | N.D.              | 0.05              | 0.56              |
| younger            | n = 15           | N.D.              | 0.88              | 1                 |
| Amboy Buzzards Peak | n = 6            | 0.99              | 0.32              | N.D.              |
| all                | n = 16           | N.D.              | 0.77              | N.D.              |
| younger            | n = 12           | N.D.              | N.D.              | N.D.              |
| Lawlor1 + Lawlor2  | n = 52           | 0.77              | N.D.              | 0.99              |

*Note: Bouse tephra combined comprises samples Amboy and Buzzard from the Amboy and Buzzards Peak outcrops. N.D.—not determined; n—number of zircons.

*HS prefix after Watts et al. (2011).
The ca. 5.5 Ma zircon age peak that is exclusively present in Bouse tephra, but not in the proximal Lawlor (Fig. 3), is intriguing. Assuming that the younger population (with a shoulder representing antecrystic or recycled zircons) is juvenile Lawlor, this would suggest another source of late Miocene zircons in the Bouse Formation catchment. There is also a possibility that the Lawlor eruption was zoned in its zircon age distribution, with the distal tephra representing a phase of the eruption that incorporated juvenile magma or antecrystic material, which differs from the eruption products that are sampled at the proximal location; however, the proximal samples record no evidence of zoning on this scale. Alternatively, the older population in the Bouse tephra could represent a detrital pulse of at least one older ash, such as the Wolverine tuff (Castor and Faulds, 2000; Spencer et al., 2008), introduced or reworked from the surrounding drainage primarily into the Buzzards Peak sample. This would be consistent with the presence of detrital zircon crystals in the Bouse tephra (Fig. 4; Supplemental File [see footnote 1]). Two zircons from the Bouse tephra (5.24 ± 0.12, Buzzards Peak zircon; 5.67 ± 1.02, Amboy zircon) that were excluded from the weighted mean age for the juvenile Bouse tephra have δ¹⁸O values of 6.74‰ ± 0.52‰ and 6.52‰ ± 0.30‰. These values indicate a source magma with a δ¹⁸O value of ~8.3‰, more similar to the Lawlor Tuff than to the published Wolverine tuff magma δ¹⁸O value of 6.5‰ (Watts et al., 2011), although probability analysis cannot unambiguously assign individual crystals to the overlapping peaks (Fig. 3C).

Figure 5. Two-dimensional probability comparison of data for zircon ages younger than 7 Ma. SMOW—standard mean ocean water. (A) δ¹⁸O versus U-Pb age for Pre-Kilgore Tuff (combined data from Watts et al., 2011 and this study). (B) δ¹⁸O versus U-Pb age for proximal Lawlor Tuff. (C) δ¹⁸O versus U-Pb age for the Bouse tephra zircon. Bouse tephra probability fields include the ca. 5.5 Ma age peak excluded from the weighted mean age. Bouse tephra and Lawlor Tuff overlap and are clearly distinguished from the Heise center Pre-Kilgore Tuff. (D) U concentration versus U-Pb age for Pre-Kilgore Tuff. (E) U concentration versus U-Pb age for Lawlor Tuff. (F) U concentration versus U-Pb age for Bouse tephra. Bouse tephra and Lawlor Tuff overlap and have an extended probability range in U concentration not seen in the Pre-Kilgore Tuff.
Older and Detrital Components in Lawlor Tuff and Bouse Tephra

The older shoulder on the juvenile zircon peak present in the proximal Lawlor and Bouse tephra relative probability curves (Fig. 3) overlaps with the K-Ar age for the Pinole Tuff, indicating potential incorporation of zircons of a Pinole age crystallization episode in the younger Lawlor samples. This is consistent with the possible identification of the Cup and Sau- cer eruptive center as common to both (Sarna-Wojcicki et al., 2011).

More than 86% of analyzed zircons from the Bouse tephra samples are interpreted as detrital crystals, based on the absence of equivalent ages in the proximal Lawlor samples (see the Supplementary File [see footnote 1] for full details). The majority of the analyzed detrital grains were contributed by the Amboy sample, which was deposited in a nearshore environment on an allu- vial fan draining the south Bristol Mountains. The pre–late Miocene detrital zircon signature from the Amboy ash largely lacks zircon of Neoproterozoic to Triassic age, and matches the exposed basement rock ages and the xenocrystic and juvenile zircon population from the late Oli- gocene to early Miocene volcanic rocks within the southern Bristol Mountains, which also lack zircons from the Neoproterozoic to Triassic, but contain xenocrystic zircons from outside that window (Harvey et al., 2011). This is similar to regional southern California detrital zircon age populations from Miocene to Pliocene sedi- ments (Fig. 4C) on the perimeter of the Mojave Desert province (Ingersoll et al., 2013). Local zircon could have been introduced via nearshore mixing in the water column or concurrent eolian sediment delivery. Buzzards Peak ash has a much smaller percentage of detrital zircons, but their ages are consistent with selection from the same Mojave-type source. Field observations are that the Amboy deposit macroscopically appears to be a pure ash draped over an algal tufa head with little bioturbation, whereas Buzz- ards Peak ash shows evidence for bioturbation, but primary sedimentary layering within the ash remains intact. This suggests potentially stronger reworking in the Buzzards Peak compared to the Amboy location, yet detrital zircons indi- cate reworking in both, and an even more dominant input to the Amboy deposit. This illustrates that field observations and hand-sample analy- sis may not be sufficient to accurately assess the degree of reworking or detrital contamination of apparently primary subaqueous ash deposits.

The percentage of detrital zircon present cannot easily be translated into detrital abundances of other minerals or glass because the physical and chemical resistance of zircon favors its survival in sediments. Moreover, hand-picking in this study targeted pristine-looking zircons excluding, when possible, rounded or discol- ored zircons, which would represent an obvi- ous older detrital component. However, among the analyzed zircons, juvenile, xenocrystic, or detrital zircons in the Bouse tephra and NEROly sample could not be distinguished by morphol- ogy, grain size, degree of rounding, or color. The preponderance of reworked detrital material in these tephra deposits therefore illustrates the potential pitfalls for eruption dating (and potentially glass chemical correlations) of dis- tal ashes in fluvial or lacustrine settings with- out prescreening of individual grains. During the glass chemistry analysis of the Mojave and Colorado Deserts distal Lawlor samples, replic- ate analyses of 17–20 shards were conducted; some locations yielded 1–3 outliers, but no indi- cations of multiple populations were identified in the Amboy and the Buzzards Peak samples (A. Sarna-Wojcicki, 2012, personal commun.). Thus, if the interpretation of the 5.5 Ma zircon population as representing reworking of an older tuff into the younger ash bed is correct, then the corresponding older glass shards were either obliterated in the intervening ~0.75 m.y. or overlooked in previous studies. In the same context, it appears possible that the bulk plagioclase and glass separates analyzed by Spencer et al. (2000) included detrital plagioclase grains and possibly multiple glass populations that confounded their 40Ar/39Ar age measurements.

This successful correlation between proximal and distal tephras demonstrates the strong potential of zircon as a tephra correlation tool. In this study, the age spectra, U concentration, and δ18O were sufficient to distinguish between the potentially correlated units. Aydar et al. (2012) also used titanium, hafnium, and yttrium concentra- tions in zircon to correlate altered ignimbrites where glass chemistry was unreliable. Although U-Pb zircon ages represent crystallization ages that can significantly predate the eruption (e.g., Simon and Reid, 2005), this does not invalidate the potential of precisely dating the depositional age of zircon-correlated tephra if the eruption age is known from dating elsewhere. Alterna- tively, zircon can directly yield an eruption age via (U-Th)/He dating (e.g., Tagami et al., 2003; Schmitt et al., 2006). If feldspar populations in distal tephra contain a similar mixture of detrital and juvenile grains, zircon (U-Th)/He dating, where target zircon grains can be quickly pre- screened using SIMS, might actually be prefer- able to 40Ar/39Ar dating of feldspar or (U-Th)/He in apatite, if juvenile grains in the target popula- tion cannot be easily distinguished either opti- cally or with similar screening methods. Alter- natively, sufficient single crystal measurements must be made to identify dominant juvenile ages among a detrital population. These results also indicate that zircon tephrochronology may also be successfully applied to other regional ashes within the Colorado River system, particularly to the tephra beds previously correlated with the Wolverine tuff, to provide additional constraints on the chronology of the establishment of the modern drainage regime in the southwestern United States.

CONCLUSION

Zircon tephrochronology corroborates a previous correlation between tephra within the Bouse Formation and the Lawlor Tuff, and thus the 4.834 ± 0.011 Ma age for Bouse Formation deposition in the lower Bouse basin. This result is at variance with a 5.33 Ma minimum age for the Bouse Formation that is seemingly required by the arrival date of Colorado River sands in the Gulf of California (Dorsey et al., 2007) under the assumption that the presence of fine sediment deposition of the Bouse Formation in paleolakes is incompatible with a concurrent or prior Colorado River throughput into the Gulf of Califor- nia. Even if one were to disregard the glass and zircon compositional correlations to the Lawlor Tuff, the 5.05 ± 0.11 Ma zircon crystallization age for the youngest population in the Bouse tephra provides a maximum possible age for the deposition of that Bouse horizon. Because of the seemingly inevitable requirement that Bouse Formation deposition within the Bristol–Blythe basins was ongoing later than 5.33 Ma, a tec- tonic or fluvial compatibility solution is required that could account for Colorado River sediment delivery to the Gulf of California at 5.33 Ma, and subsequent impounding of sufficient water in the lower trough to flood both the Bristol and Blythe basins and deposit the Bouse Formation. Alterna- tively, the 5.33 Ma age for the appearance of Colorado River–derived sands in the Gulf of California needs to be reconsidered.

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