Paleoclimate controls on lithium enrichment in Great Basin
Pliocene-Pleistocene lacustrine clays

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ABSTRACT

Terminal lakes are important archives of continental hydroclimate and in some cases contain important economic resources. Here we present an ~3.6 Myr lacustrine carbonate carbon and oxygen stable isotope record from a Great Basin continental drill core. We pair these measurements with bulk lithium concentrations to reveal a relationship between past climate and lithium enrichment in authigenic lacustrine clays. Further, we explore the possible effects of changing seasonality on the isotope record through the use of paired air mass trajectories and modern isotope data. Our findings show the evolution of the basin’s moisture balance over million-year timescales, which we attribute to variations in precipitation seasonality as well as fluctuations in the amount of evaporation associated with changes in atmospheric moisture convergence and divergence. We observe a positive correlation between the oxygen isotope values of the lake carbonate and the bulk sediment lithium concentrations, which we argue is indicative of evapoconcentration of the lake environment and subsequent enrichment of the authigenic clays. Our results suggest a link between past hydroclimate changes and the formation of lithium rich authigenic clays feeding high lithium concentrations in this modern brine aquifer system.

INTRODUCTION

Evidence from the relatively recent geologic past suggests that the Great Basin region of the western United States experienced enhanced moisture convergence in both warmer and colder climates compared to the modern (Matsubara and Howard, 2009; Salzmann et al., 2011; Pound et al., 2014; Ibarra et al., 2014; 2018; Lee et al., 2021; Fu et al., 2021). For example, the Last Glacial Maximum (LGM) was a vastly different climate state, with global sea level 140 m lower and global
mean annual temperatures ~6 °C cooler than present (Clark et al., 2009; Annan and Hargreaves, 2013; Lora and Ibarra, 2019). During this time, the Great Basin sustained many pluvial lakes whose maximum extents represent a balance between precipitation and evaporative demand and suggest a much wetter environment (Mifflin and Wheat, 1979; Reheis, 1999; Orme, 2008; Kurth et al., 2011; Godsey et al., 2011; Munroe and Laabs, 2013; Ibarra et al., 2014; Reheis et al., 2014; Oster and Ibarra, 2018; Santi et al., 2020). A metric for evaluating the moisture balance of these pluvial lakes is precipitation minus evaporation (P-E), associated with regional atmospheric convergence changes (e.g., Lora and Ibarra, 2019), which we will use hereafter when talking about moisture balance. Similarly, the mid-Pliocene (3-3.3 Ma) experienced wetter-than-modern conditions in the southwestern United States (Pound et al., 2014; Ibarra et al., 2018; Fu et al., 2022). However, and in contrast to the LGM, a combination of proxies and modeling efforts suggest the mid-Pliocene global mean annual temperature was around 3.5°C warmer than today and had atmospheric CO₂ levels greater than pre-industrial (Ravelo et al., 2004; Dowsett and Gill, 2010; Burke et al., 2018; Haywood et al., 2020). There are numerous hypotheses which have been invoked to explain the wet conditions in the mid-Pliocene. Burls and Fedorov (2017) propose that weaker atmospheric circulation in response to the different ocean surface temperature patterns of the Pliocene reduced meridional and zonal temperature gradients. Another recent hypothesis argues for more enhanced convergent monsoonal circulation that develops over late boreal summer due to increased SST in the Pliocene (Fu et al., 2022). Lastly, strengthened southwesterly moisture delivery could have resulted in greater wintertime precipitation that fed the southwest USA lakes (Ibarra et al., 2018).

Lake basins in the Great Basin are important archives of climate, and in some cases, they also host significant economic resources (e.g., Davis and Gleason 1986; Munk et al., 2011; Bradley et al., 2013; Castor and Henry, 2020). Clayton Valley Nevada is a long-lived Pliocene-Pleistocene
lake system and is also the location of the largest lithium brine resource in North America (Coffey et al., 2021). The availability of lithium is critical for the transition to renewable energy and electric vehicles because it is an important component of modern battery technology (e.g., Munk et al., 2016; Manthiram, 2017). In this study, sediment cores from Clayton Valley allow us the opportunity to explore the intersection between Pliocene-Pleistocene hydroclimate change and the formation of this important resource. Additionally, the similarity between the climate state of the mid-Pliocene and today (Burke et al., 2018; Haywood et al., 2020), with minimal changes in continental configuration, orography and paleogeography, make this lake system an excellent case study for how regional hydroclimate in the southwestern United States might evolve in the future.

As such, in this study we address the following two key questions: (1) How has the hydroclimate of Clayton Valley varied from the Pliocene-Pleistocene? (2) What role does climate play in the formation of lithium rich clays in the Clayton Valley Basin?

To answer these questions we present a new carbonate-based stable isotope hydroclimate record for Clayton Valley (CV) a terminal basin in the Great Basin area of the western United States, and demonstrate through additional geochronology (cf. Coffey et al., 2021) that this basin contains lake deposits from the Pliocene to late Pleistocene. We measured, in detail, stable carbon and oxygen isotopes of carbonates from one of the previously described sediment cores (EXP2), and expand on the sedimentological interpretations of Coffey et al. (2021) to include thin section analysis and chemical weathering indices of alteration (CIA) based on bulk elemental analyses, as well as additional higher-resolution bulk lithium concentration measurements. Further, to provide a clear picture of the modern hydroclimate dynamics, we also include air mass back trajectory and analysis of precipitation for Clayton Valley using Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) (Stein et al., 2015; Warner,
We characterize these trajectories with nearby modern precipitation isotope data. Our results demonstrate that the long-term Pliocene to late Pleistocene hydroclimate evolution from wet deep-lake conditions to increasingly desiccated and punctuated pluvial lake conditions greatly influenced lithium accumulation in this lacustrine clay deposit, which are the primary source of lithium to the modern brine aquifer system.

**SETTING**

CV is a topographically closed half-graben basin in Esmeralda County along the western margin of the Basin and Range Province about 80 miles to the northwest of Death Valley (Fig. 1). Basement fault blocks of Late Neoproterozoic to Ordovician North American western passive margin siliciclastic and carbonate units bound the basin on all sides. Surficial deposits consist of Tertiary volcanic and sedimentary rocks. During the late Paleozoic and Mesozoic the region underwent shortening and low grade-metamorphism. Since ~16 Ma the area has undergone continuous extension (Coffey et al., 2021; Oldow et al., 2009; Burrus, 2013).

CV sits on the northernmost extent of the North American Monsoon (NAM) (e.g., Ray et al., 2007; Means, 2013; Bhattacharya et al., 2017). The average annual precipitation the area receives is 13 cm (Munk and Chamberlain, 2011), which is delivered in the summer months via the NAM and wintertime westerlies. The valley floor playa spans 100 km² at an elevation of 1298 m. The entire topographic watershed for Clayton Valley is 1,437 km² (Coffey et al., 2021). Recent groundwater flow modeling has shown a potential contribution of surrounding basins of upwards to 12,610 km² (Brooks et al., 2014; Underdown et al, 2017). Despite the large influence of interbasin flow, the groundwater terminates from all surrounding basins into Clayton Valley
(Rush, 1968; Coffey et al., 2021). Water outflow is therefore limited to playa evaporation and evapotranspiration in the lowland areas of the valley where there is a shallow groundwater table.

**Figure 1.** Map of Clayton Valley (CV), Fish Lake Valley (FLV), Lake Manly (M), Searles Lake (S), and Owens Valley (O) with watershed boundaries, late Pleistocene lake extents and modern playas. Note that the groundwater flow vectors (Brook et al., 2016) surrounding the study site terminate in the CV basin.
Figure 2. (A) Annual average 3-day air mass back trajectories for Las Vegas weighted by precipitation. Colors indicate modern precipitation isotope values (Welker, 2012) recorded in Las Vegas, NV. (B) Average winter (blue) and summer (red) 3-day air mass back trajectories for CV weighted by precipitation. (C) as in (B) zoomed in with elevation.

MATERIALS AND METHODS

The EXP2 core was one of five cores drilled in the CV basin between June 2017 and November 2017 by the Albemarle Corporation. The 3,250 ft (990.6 meter) long core was photographed and logged to the nearest tenth of a foot, with depths herein converted to meters. Coffey et al. (2021) detailed the sedimentology producing the stratigraphic column shown in Figure 3. The dominant sedimentology from 0-47.24 m consists of sands and gravels. From 47.24 m to about 243.54 m the material is composed of silts and finer-grained sands. From 243.54-405.38 m there are predominately greenish gray clays with some thinly-bedded ashes. From 405.38 m-534.92 the clays are interbedded with halite beds up to 8 meters thick. From 534.92-768.10 m the sediments are predominantly greenish gray clay with the occasional thin-bedded ashes. From 768.10 m- 894.59 m the material is silt. The remaining base of the core is angular gravel derived from a partially lithified tuff sitting atop basement rock.
In the following we briefly summarize our methods. We evaluated oriented thin sections under an optical microscope to assess the degree of alteration of lake carbonates. We observed fine-grained micritic texture with little to no overgrowth on the carbonate grains and no large or small crosscutting calcite veins (Fig. 2), suggestive of primary lacustrine clays with little to no secondary precipitation. Whole rock and bulk lithium concentrations were analyzed by SGS Lakefield, as in Coffey et al. (2021). XRF analysis and mineral percentages from XRD (when available) were used to calculate weathering indices (corrected for carbonate content). We constructed a new age model using previously reported and new $^{40}$Ar/$^{39}$Ar ages from volcanic ash sanidine and biotite crystals, and a new U-Pb age on zircon grains. We constructed a Monte-Carlo based age-depth model using six ages and one correlated ash age (Fig. 2) and assigned probable ages to all samples. An apparent change in sedimentation rate or a hiatus is observed near the base of the core at 775.11m and thus sample ages below this depth are assigned based on three possible scenarios (see supplementary material; Figure 3). The hydroclimate interpretations for CV relies heavily on the time evolution of oxygen and carbon isotopes along with the sedimentology of the core. A total of 285 carbonate samples from EXP2 were measured for $\delta^{18}$O and $\delta^{13}$C. The stable isotope measurements were made on one of three instruments—Thermo Finnigan MAT 252 with a Kiel III at Brown University, Thermo Finnigan MAT 253+ with a Kiel IV at Brown University, or a Thermo Finnigan Deltaplus XL with a gasbench at Stanford University (Table 1), with replication across laboratories and mass spectrometers. Carbonate stable isotope ratios are reported using standard $\delta$-notation relative to the VPDB standard. In addition to the isotope timeseries, we used HYSPLIT to create 3-day back-trajectories at 1500 meters above ground level for precipitation events at CV. We used 40 years of modern NARR (1979-2019) meteorological records, and geographically clustered the
precipitation trajectories, weighting them by frequency. Further detailed methods can be found in the supplementary material.

RESULTS AND DISCUSSION

Paleoenvironmental Interpretation of Clayton Valley

The stratigraphic succession of the EXP2 core is typical of an underfilled to balance-filled lake in an extensional basin setting (e.g., Carroll and Bohacs, 1999; Ingersoll, 2012). Assuming no hiatuses the sedimentation rate appears to be highest at the base of the core, where we observe gravel that fines upward into lacustrine clays. As such, we infer that the sedimentation rate is slower from 4,529 to 2,478 ka and is relatively linear, slightly faster, and unvarying from 2,478 to 22 ka to the top of the core.

Depositional System

Based on the sedimentology we describe the depositional system. Starting at ~3.5 Ma, CV sustained a deep lake, evident from the thick green laminated lacustrine muds which persisted intermittently until the late Pleistocene with the youngest lacustrine muds at ~17.6 ka. The thick halite beds that abruptly punctuate the lacustrine deposits likely represent rapid changes in the moisture balance for the CV area which operate on ten to hundred-year timescales, based on our linear age model, between ~1.4 to 1.8 Ma. This change in the moisture budget is also supported by a notable transition in the degree of weathering from high to low, such that we start to see less weathered material in the core above the halite section. At around 35 ka, the sediments coarsen upward in the section, signifying a gradual transition from a long-standing lake to the more arid playa environment, consistent with no significant LGM lake above
the playa being present in this basin (Reheis, 1999). The uppermost coarse-grained sediments in EXP2 are more difficult to interpret, due to the poor core recovery, so it is unclear when the playa lake became permanently desiccated, we infer this to be ~17.6 ka. Further, in the neighboring valley to the west, Fish Lake Valley (FLV), there is minimal evidence for a large LGM (~21 ka) lake (Reheis et al., 1993; Reheis, 1999a).

Figure 3. Age model for Clayton Valley EXP2 core alongside a stratigraphic column detailing the major lithologic units. Age model solid lines indicate mean ages, while dotted lines are 2σ based. Between the last two ages, we calculate (1) the linear interpolation assuming no hiatuses (black), (2) the projection of earlier sedimentation rates (gray), and (3) the average between these two (blue).
Stable Isotope Results

The $\delta^{18}O$ values range from -14.1‰ to +4.6‰. The $\delta^{13}C$ values range from -8.0‰ to +5.4 (Fig. 3). The running correlation coefficient between $\delta^{13}C$ and $\delta^{18}O$ shows a strong positive correlation for much of the timeseries, confirming as expected, that based on the water balance that the basin was closed and terminal throughout its existence (Li et al., 1997; Leng and Marshall, 2004). The running standard deviation of $\delta^{18}O$ from 2 Ma to 17 ka increases by a factor of 2 relative to the pre-2 Ma samples (Fig. S3). This is likely related to the onset of Northern Hemisphere glaciation and the intensification of glacial-interglacial cycles during the Pleistocene. There is also a gradual positive shift of about 10‰ in the oxygen isotopes from the base of the core to around 2 Ma. From 2 Ma to about 17 ka, there is a long-term negative trend in the oxygen isotopes of about 10‰.
Figure 4. Timeseries from the Clayton Valley EXP2 core. From left to right: percent carbonate; bulk sediment lithium concentrations (ppm); carbonate $\delta^{18}$O ($\%$, VPDB); carbonate $\delta^{13}$C ($\%$, VPDB); running correlation coefficient between oxygen and carbon isotopes with a moving window of 10 data points; lake stage for Clayton Valley compared to neighboring valleys adapted after Knott et al. (2019). Solid red lines are a low pass filtered curve on the carbonate $\delta^{18}$O and $\delta^{13}$C records. Blue horizontal line marks the Pliocene-Pleistocene boundary.

There are a few hypotheses that may explain the long-term trend we observe from the mid-Pliocene to present. First, Quaternary uplift in the White Mountains and Sierra Nevada and subsequent blocking of winter moisture derived from the west of CV could have led to further depletion of source $\delta^{18}$O via orographic effects (Lechler and Galewsky, 2013; Mix et al., 2019;
Second, changes in precipitation seasonality from summer precipitation to winter precipitation could drive source water $\delta^{18}O$ towards progressively depleted values. For example, this would entail the addition of moisture from a more northerly source during colder glacial periods rather than the central Pacific (Oster et al., 2020; discussed further below). Both changes in orographic rainout due to topographic changes or changes in seasonality would primarily influence the light endmembers in the observed oxygen isotope timeseries. Lastly, a gradual decrease in temperature through the Pleistocene and subsequent reduction in the effective evaporation could also lead to a more depleted lake water composition (i.e., less overall P-E). This effect would influence the declining average and the range in the observed oxygen isotope timeseries. As such, with existing data, because of the evaporative nature of lacustrine carbonate oxygen isotope records, we cannot necessarily rule out these scenarios. However, as described in the next section, data from adjacent basins with differential evaporation suggests that further orographic rainout can be ruled out (first scenario above associated with Quaternary uplift of the White Mountains and Sierra Nevada). Further, we can rule out an additional alternate scenario that changes in carbonate formation temperature (i.e., lake water temperature) influence our observations. Long term cooling would cause an increase not a decrease in the carbonate $\delta^{18}O$ values towards the present because of a larger fractionation factor between lake water and carbon at decreasing temperatures (Kim and O’Neil, 1997).

Comparison to Regional Records

There are multiple records of pluvial lakes in the region surrounding Clayton Valley ranging in age from the mid-Pliocene to the late Pleistocene which suggest a different regional moisture balance for this area of the Great Basin relative to today. The lake stages shown on
Figure 4, adapted from Knott et al. (2019), shows the interpreted lake stages for Clayton Valley (CV) and nearby lakes. Pluvial lakes in Death Valley (Lake Manly) (Lowenstein et al., 1999; Forester et al., 2005; Knott et al., 2018), to the south in Searles Valley (Smith et al., 1983; Jannik et al., 1991; Knott et al., 2018), and in Eureka Valley (Lake Andrei) began to form ~3.5–3.4 Ma in the late Pliocene during the cooler, wetter, glacial climate of MIS MG5 (Knott et al., 2019). The Death Valley lake persisted until ~3.30 Ma, while Searles lake persisted through the start of Northern Hemisphere glaciation until about 2.5 Ma. Lake Andrei was very short-lived, existing for only around 400,000 years (Knott et al., 2019). Evidence from Fish Lake Valley suggests a lake existed from ca. 3.4 to 2.8 Ma (Reheis et al., 1993; Reheis et al., 2002; Knott et al., 2018). Lakes in these areas also existed intermittently during the Pleistocene. Pluvial lakes in Death Valley formed again ~1.98–1.78 Ma, 1.3–1.0 Ma, and ca. 0.6 Ma, while Searles Lake existed from about 2 Ma to the late Pleistocene. Fish Lake Valley sustained a lake in the middle Pleistocene ~2.2–0.7 Ma. A short-lived lake record also exists for Owens Valley (0.8 Ma to the late Pleistocene) (Smith et al., 1997).
Figure 5. Stable isotopes of Clayton Valley carbonates compared to neighboring Fish Lake Valley (FLV). FLV samples from this study (in blue) were collected in the summer of 2021. Red samples are taken from Mix et al. (2019). Shown in black are values for Clayton Valley.

Stable isotope evidence from Fish Lake Valley (FLV), the adjacent valley to the west of CV, and Clayton Valley lake stages suggest that the basins experienced asynchronous changes, which could potentially be linked to uplift in the White Mountains and Sierra Nevada west of FLV. Blocking of westerly moisture (Mix et al., 2019) could potentially have led to FLV drying prior to CV (Reheis et al., 1993), which is why a shallow lake is observed for Clayton Valley after Fish Lake Valley desiccated (by ~0.6 Ma). However, we would expect to see progressively more depletion in oxygen isotopes as moisture moves eastward encountering subsequent orographic rainout, into Fish Lake Valley, then into Clayton Valley. However, the oxygen isotope record generated for Fish Lake Valley (this study; Mix et al., 2019) discredits this
potential scenario, as the lightest endmember $\delta^{18}O$ of Fish Lake Valley is more depleted than that of Clayton Valley (Fig. 5).

Modern back trajectory analyses for Clayton Valley show the area receiving different sources of water vapor depending on the season (Fig. 2). These different sources, which are characterized by different isotopic compositions, could impact the source water composition of the lake in Clayton Valley directly impacting the light $\delta^{18}O$ endmember of our record. Therefore, we argue that the majority of the variance in the isotope record for Clayton Valley is controlled by changes in seasonality and subsequent evaporative enrichment. Specifically, through the Pliocene there is a shift to more summertime precipitation events likely related to an enhancement of the convergent monsoonal circulation. Through the Pleistocene, we observe a decrease in $\delta^{18}O$ values, which we attribute to the weakening of monsoonal circulation, and strengthened southwesterly moisture delivery of wintertime precipitation.

Hydroclimate controls on lithium enrichment

The lithium concentrations in the clays are one to two orders of magnitude greater than that of the average continental crust (Fig. 3), 35 ± 11 ppm (Teng et al., 2004). There is no statistical correlation between lithium and sediment age, however there is a distinct positive logarithmic correlation ($R^2 = 0.56$) between the paired measurements of lithium concentrations and carbonate $\delta^{18}O$ (Fig. 6A). We generally observe higher $\delta^{18}O$ values in conjunction with higher lithium concentrations.

Coffey et al. (2021) details the conceptual model for lithium brine development in basins like Clayton Valley that we draw from here. Hydrothermal fluids rich in lithium interact with the basin sediment. For example, results from Araoka et al. (2014) indicate that the lithium
concentrated in playas in Nevada was supplied mainly through high-temperature water–rock interaction associated with local hydrothermal activity and not directly by low-temperature weathering of surface materials. Basin sediments adsorb lithium, until groundwater liberates the adsorbed lithium into the shallow subsurface waters and outcropping water table. The lithium then becomes concentrated in the shallow subsurface brines through evapoconcentration. The findings of this study bear on the initial lithium enrichment of the basin sediments and link them to the hydroclimate evolution of the basin and lake system over the Pliocene-Pleistocene.

The covariance between the authigenic carbonate $\delta^{18}O$ in the lacustrine clays and the bulk lithium concentrations are related to the degree of evapoconcentration of the lake during authigenic clay and carbonate precipitation in the lake water (Fig. 6A). Variations in the past surface area to volume ratio of the lake could have an impact on the degree of effective evapoconcentration of the lake water. For example, early in the record (~3.6 to ~1.5 ka), as indicated by the CIA values and sedimentology (Figs. S2 and S3), P-E was relatively large, the lake was deep, and the surface area to volume ratio of the lake was likely smaller. This deep lake existed during this time, until the onset of halite deposition. The climate then transitions at ~1.5 ka to a lower P-E, the lake became smaller and frequently desiccated, due to the higher surface area to volume ratio of the shallower lake, there was highly effective evapoconcentration. These high concentration lithium values in the lake are driven by evaporation, which we propose is then incorporated into the structure and onto the surfaces of the authigenic clays precipitating in the lake water. Additionally, a survey of brine samples (Fig. 6B) demonstrates a similar logarithmic relationship between modern water $\delta^{18}O$ and brine lithium concentrations (This Study; Coffey et al., 2021) compared to the geologic EXP2 samples shown in Figure 5A.
Figure 6. (A) Bulk sediment lithium concentrations (ppm) for EXP2 samples paired with carbonate oxygen isotope values (VPDB). The red line is a logarithmic fit with an R$^2$ value of 0.56. (B) Lithium (ppm) and oxygen isotope values (VSMOW) of natural modern water samples.
There is a question of whether the lithium became incorporated into the clays post deposition due to hydrothermal interactions, or if the clays incorporated the lithium during initial genesis in the lake water (cf. Coffey et al., 2021). The covariance between $\delta^{18}$O and lithium concentrations (Fig. 6) and the thin sections show no evidence for post-depositional alteration (Fig. S4), suggesting that the lithium became incorporated in the clays at the time of formation, and not post-depositionally. Future work analyzing the oxygen, hydrogen and lithium isotopes of clay fractions from EXP2 may demonstrate this link more concretely.

CONCLUSION

Our lacustrine carbonate isotope record for Clayton Valley, NV reveals a rich continuous history of hydroclimate spanning the last ~3.6 Myrs. We argue that while the lake sustains high overall isotope values due to evaporative enrichment, million-year scale variations are driven by changes in the seasonality of precipitation being sourced to the basin as well as changes in P-E. Specifically, we argue that the mid-Pliocene to early Pleistocene saw enhanced convergent monsoonal circulation, and through the Pleistocene, strengthened southwesterly moisture delivery could have resulted in greater wintertime precipitation. We find a covariance between carbonate oxygen isotopes and paired bulk lithium concentrations, which we attribute to the effects of evapoconcentration prior to authigenic clay precipitation in the lake water. This finding suggests that climate may play a key role in the concentration of lithium in authigenic lacustrine clays.

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SUPPLEMENTARY MATERIALS

for

Paleoclimate controls on lithium enrichment in Great Basin

Pliocene-Pleistocene lacustrine clays

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The following is included in this file:

Figure S1. Zircon U-Pb age
Figure S2. CIA ternary diagram
Figure S3. Timeseries of all datasets from EXP2
Figures S4. Thin sections

The following is included in an attached Excel File:

Table S1. EXP2 age constraints
Table S2. EXP2 samples and data table
Table S3. Zircon U-Pb data
Table S4. 40Ar/39Ar data
Table S5. Fish Lake Valley age constraints
Table S6. Fish Lake Valley samples and data table
Table S7. Modern water samples

Precipitation Back-Trajectory Analyses

Back-trajectories were generated using the desktop version of the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model and the North American Regional Reanalysis (NARR) as the HYSPLIT meteorological input. We tracked air parcels backwards for 72 hours every 24 hours at 1500 meters above ground level to gauge the precipitation sources of each of the study sites. Daily 72 hour back-trajectories began at the end of the day and were generated for every day between 1979-2019, which covers the extent of the NARR climate record.
In order to filter trajectories by precipitation events, we used weather station data in the Global Historical Climatology Network-Daily (GHCN-D) database, keeping both geographical location and elevation as close as possible. The station record from Silverpeak NV (within Clayton Valley) records historic snow and rain events throughout 1979-2019, both of which are considered in our precipitation analyses. For each site, trajectories were matched with the corresponding day in the meteorological record and filtered based on whether there was any rain or snow for that day. Days that were missing both a rain and snow record were not included in the analyses. The resulting precipitation trajectories were then filtered by summer (April-September) and winter (October-March) half year months.

Once the precipitation-carrying trajectories were filtered, a cluster analysis was completed for each site’s summer, and winter trajectories using HYSPLIT’s built-in clustering program. The number of clusters in each analysis was determined by the change in Total Spatial Variance (TSV) curve generated as clusters were combined. The point at which the fewest number of clusters had a change in TSV less than about 15% was selected for the analysis. The trajectories in each cluster were then averaged and plotted on a map with a topographic overlay. Finally, we weighted the cluster means by total precipitation delivered. The thickness of the lines on Figure 1 are scaled to this weighting.

A similar set of HYSPLIT analyses (without clustering) was conducted for weekly precipitation samples from the NV00 site at Red Rock Canyon (36.13483 °N, -115.422 °W, 1,137 m) from the USNIP network (Welker, 2012), the closest site to CV. Shown on Figure 2A are daily trajectories for all days with precipitation colored by the oxygen isotope value of the weekly aggregated rainfall. This station contains data spanning May 1989 to December 1994, with 29 total weeks of isotope data.
Dating Methods, Age Model and Sample Age Assignment

In previous work Coffey et al. (2021) dated six ashes from the EXP cores using $^{40}\text{Ar}/^{39}\text{Ar}$ methods on sanidine. In this work we presented two additional $^{40}\text{Ar}/^{39}\text{Ar}$ age and one zircon U-Pb ages to refine the age model for EXP2.

For the new $^{40}\text{Ar}/^{39}\text{Ar}$ ages at 336.35 m and 774.8 m, sanidine and plagioclase (respectively) were isolated from the tephras via magnetic and density sorting techniques, and their composition was verified using a variable pressure scanning electron microscope. Separates were wrapped in aluminum foil, placed in 2.5 cm aluminum disks, and irradiated along with the 1.1864 Ma Alder Creek sanidine standard (Jicha et al., 2016) at the Oregon State University TRIGA reactor in the Cadmium-Lined In-Core Irradiation Tube (CLICIT). Single crystal fusion experiments were performed with a 50 W CO$_2$ laser in the WiscAr laboratory at the University of Wisconsin-Madison. Gas was analyzed using a Noblesse multi-collector mass spectrometer using the procedures in Jicha et al. (2016). Weighted mean ages are calculated using the decay constants of Min et al. (2000), and are reported with analytical uncertainties at the 95% confidence level. Atmospheric argon value used is that of Lee et al. (2006).

One volcanic ash sample (EXP2_3277) was collected from Albemarle Corporation EXP2 drill core for zircon U-Pb crystallization age at 998.8 m. Zircon grains were isolated by traditional physical and chemical mineral separation methods, including crushing, grinding, and hydraulic, heavy-liquid, and magnetic separation. Zircon grains were then poured onto double-sided tape on epoxy resin mounts and 33 inclusion-free zircons were selected for U-Pb analysis by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) at the University of Texas at Austin. Mounts were transferred to a large-volume Helex sample cell and analyzed by a magnetic sector, single collector Element2 HR-ICP-MS with an attached PhotonMachine.
Analyte G.2 Excimer Laser ablation system. Data reduction was performed in the Iolite software (Paton et al., 2011). A weighted mean average age (6.134 ± 0.095 Ma) was calculated from a unimodal population of 16 zircon ages, with an MSWD of 0.78. Ages with discordance >30% were excluded from the age calculation. Weight Mean Average plot and Whetherill Concordia were constructed using IsoplotR (Fig. S1; Vermeesch, 2018). See Table S3 for zircon U-Pb analytical results.

Figure S1. Weighted Mean Average age plot (left) showing 16/33 zircon ages used to calculate volcanic ash age for sample EXP2_3277, and Whetherill Concordia plots (right) showing (top) 16/33 ages used to calculate volcanic ash age and (bottom) all 33 zircon ages for sample.
In the following we describe our age model constraints from top to bottom. First, we assumed that the top of the core to be Holocene (5±5 ka). The first age used in our core comes from a relatively thick ash at 184.4 m which we have correlated in other regional cores to be the Lava Creek B Yellowstone eruption. The main ash aquifer in Clayton Valley is the Bishop Tuff (Long Valley Caldera), this thick ash unit appears in all 5 Clayton Valley cores (Coffey et al., 2021) at only slightly offset depths. This ash was verified in EXP1 by Coffey et al. (2021) to be the Bishop Tuff. The next four dates used were constrained with $^{40}\text{Ar}/^{39}\text{Ar}$, including our new ages of 1,145.7±10.8 ka (at 336.35 m), and 2,476 ± 68 ka (at 774.8 m), while the last age was determined by zircon U-Pb of the basal lithic tuff unit (6,134 ± 95 ka). Because of an apparent change (increase) in sedimentation rate at the base of the core, the relatively few number of ages, and the otherwise linear nature of our age-depth relationship, we construct a simple age model using a Monte-Carlo based age-depth model using and assigned probable ages to all samples. The three probable scenarios at the base of the core shown in Figure 2 include: 1) extrapolation of the above sedimentation rate, 2) a maximum sedimentation rate assuming no hiatuses, and 3) an average of 1) and 2). For the purposes of plotting our measurements vs. age in Figure 4 and Figure S3 we use scenario three. However, we note that the interpretation of our dataset in this paper is not influenced by these assumptions.
**FLV Outcrop Samples and Age Model**

The FLV samples used to generate the carbonate stable isotope values in this study were outcrop samples collected in the summer 2021 field season. We visited the southeast playa and rimrock sections (Reheis et al., 1991, their Figures 2 & 4) as well as the northeast 179-EP section (Reheis et al., 1993; their Figure 7). We attributed depths/heights to the outcrop samples relative to boundaries of units described by Reheis (1991, 1993). We then used a combination of previously dated ashes (Knott et al., 2018; 2019) and previously correlated magnetostratigraphy (Sarna-Wojcicki et al., 2005; their figure 15) following Mix et al. (2019) (Tables S5 and S6).

**Carbonate Stable Isotope Analyses**

The samples that were analyzed at Brown University were first dried overnight at 60 °C, then homogenized via mortar and pestle. Of the sample, 500 µg were weighed out and reacted with 70 degree C phosphoric acid using a Thermo Finnigan Kiel III or Kiel IV carbonate device. This measured weight is based on a typical 10% sample carbonate content and a required 50 micrograms of CaCO₃ for the desired range of measurement voltage (3 to 6 V). The evolved CO₂ was measured on either a Thermo Finnigan MAT 252 gas-ratio mass spectrometer or Thermo Finnigan MAT 253+ (Table 1, Table S1). External precision (1σ) of oxygen and carbon isotope data is <0.1‰, based upon repeated measurements of two internal laboratory standards, BYM63150 and Carrara63150, calibrated against NBS 18, NBS 19, and IAEA 603.

The samples that were analyzed at Stanford University in 2018 were homogenized via mortar and pestle. Stable carbon and oxygen isotope values of carbonates were obtained at the Stable Isotope Biogeochemistry Laboratory, Stanford University, using a Thermo Finnigan Gasbench and measured on a Finnigan MAT Delta+ XL mass spectrometer using a Thermo
Finnigan ConFlo III unit. Approximately 300 μg of sample powder was weighed into sealed vials that were flushed with He gas and reacted with ca. 0.25 ml of phosphoric acid (H₃PO₄) for 1 hour at 72°C. External precision (1σ) of oxygen and carbon isotope data is <0.1‰, based upon repeated measurements of two internal laboratory standards calibrated against NBS 18, NBS 19, and LSVEC. δ¹³C and δ¹⁸O values are reported relative to VPDB for datasets from both laboratories.

Whole Rock Elemental Analyses and Lithium Concentrations

As in Coffey et al. (2021) whole rock samples were analyzed by SGS Environmental Services for whole rock geochemistry by X-ray fluorescence and Inductively Coupled Plasma Emission Spectrometry. Briefly, approximately 1 gram of crushed and pulverized samples were formed into a homogenous glass disk by fusion with a lithium tetraborate/lithium metaborate mixture and then analyzed by wavelength dispersion XRF (WD-XRF). All reporting limits are less than or equal to 0.01%. Calibration checks are performed daily. SGS methods conform to the ISO/IEC/17025. Lithium concentrations on solid samples were performed by ICP-OES by SGS. A 0.1 gram sample of crushed and pulverized sample was fused using Na₂O₂ and digested in HCl, and Li concentrations analyzed on an Agilent ICP-OES.

Weathering Indices

The results of the CIA calculations are summarized in Figure S2 and shown in the timeseries in Figure S3. There does not appear to be a distinction between the lithologies in terms of the CIA values, with most plotting close to the Ca/Na and Al endmembers. There are,
however, distinct shifts in the CIA value time series (Figure S3). From the base of the core, the CIA values stay below 40 until they reach the top of the halite beds where they then increase their weathered CIA value to ~60. The weathering indices stay high until the base of the thick ash at ~750 ka where they drop to below 40. From the base of the ash to the top of the core the CIA values then increase gradually. We also plot Si/Al on Figure S3, which shows similar trends.

Figure S2. Ternary diagram for all clay samples with available data, showing the relative mole fractions of CaO+Na₂O, K₂O, and Al₂O₃.
Figure S3. Timeseries from the Clayton Valley EXP2 core. From left to right: percent carbonate; bulk sediment lithium concentrations (ppm); carbonate $\delta^{18}$O (% VPDB); 5 point running carbonate $\delta^{18}$O standard deviation; carbonate $\delta^{13}$C (% VPDB); correlation coefficient between oxygen and carbon isotopes with a moving window of 10 data points; chemical index of alteration; and Si/Al ratio. Solid red lines are a low pass filtered curve on the carbonate $\delta^{18}$O and $\delta^{13}$C records.
Figure S4. Photomicrographs of select lacustrine carbonate intervals from the EXP2 core in plane polarized light (PPL) and cross-polarized light (XPL) showing rare mixed clastic-carbonate intervals (A,D) and micritic text with limited porosity (B-D). Scale bar (5 mm) is displayed on PPL image and core depth in meters is displayed on XPL image.
Supplemental References


