Reconstructing Past Elevations From Triple Oxygen Isotopes of Lacustrine Chert: Application to the Eocene Nevadaplano, Elko Basin, Nevada, United States

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Triple oxygen isotope measurements are an emerging tool in paleoclimate reconstructions. In this contribution we develop the application of triple oxygen isotope measurements to lacustrine sediments to reconstruct past elevations. We focus on a well-constrained sample set from the Eocene North American Cordillera (Cherty Limestone Formation, Elko Basin, NV, United States, 42–43.5 Ma) on the east side of the elevated Nevadaplano. We present triple oxygen isotope measurements on freshwater lacustrine chert samples from the Cherty Limestone Formation. Across an evaporation trend spanning 6.5 h in δ18O values we observe a negative correlation with δ17O ranging from −0.066 to −0.111‰ (λRL = 0.528), with an empirical slope (λchert, δ17O vs. δ18O) of 0.5236. Additionally, we present new carbonate clumped isotope (147) temperature results on the overlying fluvial-lacustrine Elko Formation, which indicate an error-weighted mean temperature of 32.5 ± 3.8°C (1σ), and evaporatively enriched lake water spanning δ18O values of −3.7 to +3.5‰ (VSMOW). Paired chert and carbonate δ18O values demonstrate that co-equilbrium among the carbonate and chert phases is unlikely. Thus, as also previously suggested, it is most likely that Elko Basin chert formed during early diagenesis in equilbirium with pore waters that reflect evaporatively 18O-enriched lake water. Using this scenario we apply a model for back-calculating unevaporated water composition to derive a source water of δ18O = −16.1‰ (VSMOW), similar to modern local meteoric waters but lower than previous work on paired δ18O-δD measurements from the same chert samples. Further, this back-calculated unevaporated source water is higher than those derived using δD measurements of Late Eocene hydrated volcanic glass from the Elko Basin (average δ18O equivalent of approximately −18.4‰, VSMOW). This suggests, assuming Eocene meteoric water Δ17O values similar to today (~0.032‰), either that: (1) the hypsometric mean elevation recorded by the lacustrine Cherty Limestone was lower than that derived...
INTRODUCTION AND GEOLOGIC SETTING

Reconstructing the topographic history of mountain belts relies heavily upon the oxygen ($\delta^{18}O$) and hydrogen ($\deltaD$) isotopes of authigenic minerals in paleosols and paleolake sediments (e.g., Chamberlain et al., 1999; Poage and Chamberlain, 2002; Takeuchi and Larson, 2005; Ghosh et al., 2006a; Garzione et al., 2006; Davis et al., 2009; Takeuchi et al., 2010; Mulch et al., 2010, 2015; Gebelin et al., 2013; Schwartz et al., 2019; Pingel et al., 2020; Ingalls et al., 2020a; Quade et al., 2020; San Jose et al., 2020; Kukla et al., 2021). Rainout causes systematic monotonic depletion in $\delta^{18}O$ and $\deltaD$ with elevation (e.g., Rowley et al., 2001), which can be exploited to reconstruct past elevations of ancient mountain belts. However, the interpretation of these isotopic data as signals of past elevation is often complicated by evaporation in soils and lakes that will enrich waters in $^{18}O$ and $^2H$ (e.g., Abruzzese et al., 2005; Davis et al., 2009; Mulch et al., 2015; Mulch, 2016; Ingalls et al., 2020a). These evaporitic effects are particularly problematic in semi-arid to arid settings that often form in the rain shadow of uplifting mountains. Thus, methods to determine the pre-evaporative isotopic composition of meteoric waters are needed to isolate the signal of surface uplift from progressive drying.

One way of assessing evaporative trends is to use combined $\deltaD$ and $\delta^{18}O$ values of chert deposits in the paleolake sediments. Abruzzese et al. (2005) used this approach in their study of the Eocene chert found in foreland lake deposits of the Rocky Mountains. Despite recording strong evaporitic signals, the trends in $\deltaD$ and $\delta^{18}O$ values of chert were used to extrapolate to the isotopic composition of original un-evaporative meteoric waters (Abruzzese et al., 2005). Oxygen isotope ratios of the hydroxyl ions of chert are likely a robust indicator of waters from which they form (Kauth, 1973) since hydroxyl ions appear to resist post-depositional exchange (Michelsen, 1966). However, it is strongly material dependent how resilient hydrogen isotopes are to later diagenesis and exchange particularly given that other minerals (clays and micas) can exhibit some degree of later exchange of hydrogen (O’Neil and Kharaka, 1976; Chamberlain et al., 2020). For this reason, we explore the triple oxygen system ($^{16}O$, $^{17}O$, and $^{18}O$) of chert to determine meteoric water compositions. Complementary to triple oxygen isotopes, carbonate clumped isotope analyses are needed to constrain the effect of evaporation on the $\delta^{18}O$ values of the minerals by assessing the carbonate formation temperatures and the $\delta^{18}O$ values of (evaporatively enriched) lake water from which the carbonate mineral formed.

In this study we present the first lacustrine chert triple oxygen isotope dataset from a Cenozoic basin in western North America and use this data set, with carbonate clumped isotope measurements from overlying strata, to derive an elevation estimate for the Eocene Nevaadaplan. Our study site in the vicinity of Elko, Nevada (United States) hosts well-studied sections from the Eocene eastern Nevaadaplan. We focused on the Eocene sections in the Elko Basin because of the controversy concerning the timing and extent of surface uplift in this region [contrasting Smith et al. (2017) and Cassel et al. (2018) with Mulch et al. (2015) as well as Lund Sneee et al. (2016)]. In essence the controversy revolves around the timing and amount of surface uplift of this region that was first discovered through the stable isotopic studies of Horton et al. (2004). These authors argued that ~2 km of surface uplift occurred between the middle Eocene and the early Oligocene based on oxygen isotope changes in paleosol and lacustrine carbonate. These data are important as they are one of the few basins with somewhat continuous Cenozoic sedimentation providing a key datum on the progressive north to south topographic response associated with the removal of the Farallon slab or piecemeal removal of the mantle lithosphere (Carroll et al., 2008; Mix et al., 2011; Chamberlain et al., 2012). However, at the time of the Horton et al. (2004) paper there was insufficient age control to know with any certainty when this uplift occurred. New ages and stable isotope data provided by Mulch et al. (2015) suggested that the surface uplift of 2 km occurred in the late Eocene between 43 and 38 Ma. Yet, this has recently been challenged by Smith et al. (2017) who argues that the Mulch et al. (2015) data for pre-uplift isotope values are from lacustrine samples that have been strongly affected by evaporation and they argue that surface uplift likely occurred after the formation of the Eocene lakes, possibly during the Oligocene (Cassel et al., 2018). However, very low $\delta^{18}O$ values in the full isotopic record are consistent with high elevations occurring during the Eocene (Mulch et al., 2015). To place new constraints on this issue we focused on the Eocene lacustrine cherts because the triple oxygen isotopes allow us to quantitatively assess evaporative effects and previous work demonstrated significant spread in the $\delta^{18}O$ of the chert samples from the Elko Formation (Abruzzese et al., 2005).

Our findings suggest that paleoelevation estimates using volcanic glass $\deltaD$ values (Smith et al., 2017; Cassel et al., 2018) give higher elevations than the data derived here from the basin depocenter indicating lower hypsometric mean elevations. Nonetheless, the findings presented below suggest a >2.5 km elevation in the Elko Basin region during the middle Eocene and surface uplift of about 1–1.5 km between deposition of the Cherty Limestone at 42–43.5 Ma and the late Eocene, ~38–40 Ma.

ISOTOPE NOTATION AND SYSTEMATICS

We summarize the isotope notation used in this study and define the nomenclature and fractionation factors used for the
triple oxygen and carbonate clumped isotope measurements as well as the subsequent calculations. Isotopic abundance ratio is reported here in both standard and linear notation. The standard δ-notation is defined as (McKinney et al., 1950):

\[ \delta^Y = \left( \frac{x_{\text{Sample}}}{x_{\text{Standard}}} - 1 \right) \times 1000 \]  

where \( x \) is the heavier mass of interest, \( Y \) is oxygen (O), carbon (C) and R is the ratio of interest (i.e., \( ^{18}\text{O}/^{16}\text{O}, ^{17}\text{O}/^{16}\text{O}, ^{13}\text{C}/^{12}\text{C} \)). We report chert oxygen isotopes (\( \delta^{18}\text{O} \) and \( \delta^{17}\text{O} \)) relative to the VSMOW2-SLAP2 scale via primary standards (Wostbrock et al., 2020; see section “Materials and Methods”), and the carbonate oxygen and carbon isotopes (\( \delta^{18}\text{O} \) and \( \delta^{13}\text{C} \)) relative to the VSMOW and VPDB standards, respectively, normalized via carbonate standards. Equilibrium fractionation (\( \alpha \)) between two phases (A and B) is:

\[ \alpha_{A-B} \equiv \frac{R_A}{R_B} = \frac{\delta_A - 1000}{\delta_B - 1000} \]  

We are interested in oxygen isotope fractionation between water and minerals (\( \text{CaCO}_3 \cdot \text{H}_2\text{O} \) and \( \text{SiO}_2 \cdot \text{H}_2\text{O} \)), as well as oxygen isotope fractionation between liquid and vapor water during lake water evaporation.

Following the recent triple oxygen isotope literature (e.g., Pack and Herwartz, 2014; Passey et al., 2014; Sharp et al., 2018; Barkan et al., 2019; Passey and Ji, 2019; Liljestrand et al., 2020; Bindeman, 2021; Herwartz, 2021; Xiang et al., 2021), we report our oxygen isotope data using linear notation, which removes curvature when comparing \( \delta^{18}\text{O} \) and \( \delta^{17}\text{O} \) variations (Hulston and Thode, 1965; Miller, 2002):

\[ \delta^{18}\text{O} = 1000\ln \left( \frac{\delta^{18}\text{O}}{1000} + 1 \right) \]  

where \( x \) is either 17 or 18 (as in \( ^{17}\text{O} \) or \( ^{18}\text{O} \)). In linearized notation the equilibrium fractionation equation between two phases (A and B) is:

\[ 1000\ln (\alpha_{A-B}) = \delta^{18}\text{O}_A - \delta^{18}\text{O}_B \]  

The fractionation of \( ^{17}\text{O} \) relative to \( ^{18}\text{O} \) is given by the following equations [standard (eq. 5) and linearized (eq. 6) forms]:

\[ \alpha^{17}\text{O}_A-B = (\alpha^{18}\text{O}_{A-B})^{\theta} \]  

\[ \ln (\alpha^{17}\text{O}_{A-B}) = 0 \times \ln (\alpha^{18}\text{O}_{A-B}) \]  

where \( \theta \) is ~0.5 and is defined, for the triple oxygen isotopes, as:

\[ \theta_{A-B} = \frac{\delta^{17}\text{O}_A - \delta^{17}\text{O}_B}{\delta^{18}\text{O}_A - \delta^{18}\text{O}_B} \]  

representing the mass law associated with physical processes (e.g., mineral precipitation, evaporation, etc.). Originally, variations in \( \theta \) were observed to be close to ~0.5, and thus it was thought that the measurement of \( ^{17}\text{O} \) provided no new additional information (Craig, 1957). Recent high-precision work and theory demonstrates measurable (10 s of ppm level) variations in \( \theta \) for Earth-surface processes like the temperature dependence of equilibrium fractionation during mineral precipitation (\( \theta = 0.5237-0.5255 \) for \( \text{SiO}_2 \cdot \text{H}_2\text{O} \) fractionation from 0 to 100°C; Cao and Liu, 2011; Sharp et al., 2016; Hayles et al., 2017; Wostbrock et al., 2018), equilibrium condensation and evaporation of water vapor (\( \theta = 0.529 \); Barkan and Luz, 2005), and water vapor diffusion (\( \theta = 0.5185 \); Barkan and Luz, 2007; \( \theta = 0.5194 \); Yeung et al., 2018), all of which are lower than the theoretical infinite-temperature end-member (\( \theta = 0.5305 \); Matsuhsaha et al., 1978; Young et al., 2002). To visualize variations graphically and normalize to a specific process (Meijer and Li, 2006; Passey et al., 2014; Sharp et al., 2016, 2018; Barkan et al., 2019; Passey and Ji, 2019; Sha et al., 2020; Bindeman, 2021; Herwartz, 2021; Miller and Pack, 2021; Zakharov et al., 2021) we define a reference slope \( \lambda_{RL} \) to look at small deviations in \( \delta^{17}\text{O} \) relative to \( \delta^{18}\text{O} \) using \( \Delta^{17}\text{O} \) notation (sometimes also denoted \( ^{17}\text{O}-\text{excess} \)):
defined as (Ghosh et al., 2006b; Huntington et al., 2009):

\[ \Delta_{47} = \left[ \frac{47R}{47R^*} - 1 \right] - \left( \frac{46R}{46R^*} - 1 \right) - \left( \frac{45R}{45R^*} - 1 \right) \times 1000 \] (9)

where \(^3R\) is for CO\(_2\) relative to mass 44 (i.e., \(47R = [^{17}\text{CO}_2]/[^{14}\text{CO}_2]\)), and the superscript * is the R value for a system with a stochastic distribution (i.e., high-temperature) for the same bulk composition calculated from the abundance of \(^{13}\text{C}\) and \(^{18}\text{O}\) in the sample.

Lastly, combinations of temperatures derived from \(\Delta_{47}\) values along with the \(\delta^{18}\text{O}\) values of carbonates allow the \(\delta^{18}\text{O}\) of the formation fluid, in this case lake water, to be calculated (e.g., Came et al., 2007; Huntington et al., 2010; Lechler et al., 2013). For the calculations carried out here we use the temperature-dependent equilibrium oxygen isotope fractionation of Kim and O’Neil (1997) (and updated by Kim et al., 2007) for inorganic calcite and the temperature calibration of Petersen et al. (2019).

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**MATERIALS AND METHODS**

**Chert Triple Oxygen Isotope Measurements**

Chert samples analyzed in this study were 2–4 mg chips of hand samples from Horton et al. (2004) and Abruzzese et al. (2005). Chips were tested for carbonate with HCl, and only those without carbonate were analyzed. We performed triple oxygen isotope measurements using a Thermo Scientific™ 253 Plus 10kV Isotope Ratio Mass Spectrometer (IRMS) on chert samples at Stanford University with O\(_2\) as the analyte. We generated O\(_2\) gas from silicates using the laser fluorination method after Sharp (1990), on the setup described in Chamberlain et al. (2020) (see also Sharp et al., 2016; Wostbrock et al., 2018, 2020; Lowe et al., 2020; Kukla et al., 2021). This setup is similar to recent studies from other labs producing triple oxygen isotope measurements of chert and silica (Pack and Herwartz, 2014; Levin et al., 2014; Liljestrand et al., 2020; Sengupta et al., 2020; Zakharov et al., 2021). Two to four micrograms of samples are loaded into the vacuum line sample chamber. For a given set of analyses, we generally load 2–3 standards and 3–4 samples. Following loading, samples were pumped down to <10 mbar using a turbopump and then pre-fluorinated with 30 Torr BrF\(_5\) in order to remove absorbed water before analysis. This pre-fluorination step is repeated until it generates <2 mbar of non-condensible gas in a liquid nitrogen trap. When possible, the samples and standards were loaded and vacuumed by turbopump overnight or over several days prior to pre-fluorination.

Following pre-fluorinations, we add 130 mbar BrF\(_5\) to the sample chamber and heat the sample using a 50 W CO\(_2\) infrared laser (Elemental Scientific Lasers/New Wave Research MIR10-25). Consistent with the results of Sharp (1990), we found that we achieve better reproducibility for isotopic measurements and sample yields if the laser fluorination of samples is completed within 5 min. Following laser fluorination, excess BrF\(_5\) is frozen into a liquid nitrogen trap and the evolved O\(_2\) gas is passed over a heated NaCl trap to remove produced waste gases (such as F\(_2\)).

and then frozen onto a 5 Å mol sieve immersed in liquid nitrogen. The sample is then thawed at room temperature, entrained in a high purity He stream, and passed through a through a GC column to remove NF\(_3\) and other contaminants and refrozen in another 5 Å mol sieve trap immersed in liquid nitrogen. Helium is then pumped away (with the trap still immersed in liquid nitrogen) and the 5 Å mol sieve is heated using heat tape and a heat gun to release the trapped O\(_2\). This purified O\(_2\) is then introduced to and equilibrated with the IRMS sample-side bellow for 6 min. During this equilibration step, the bellow is cycled from 25 and 75% compression ~6 times.

Samples are measured against an O\(_2\) reference tank (\(\delta^{18}\text{O} = 24.067\)) with an oxygen isotope composition similar to air and chert samples analyzed in this study. Mass 32, 33, and 34 ion beams are collected on faraday cups, slit widths of 4.5, 1.5, and 4.5 mm, respectively, with a \(3 \times 10^{13} \Omega\) amplifier for mass 33. Samples are measured at a mass 32 ion-beam intensity of 5–7 volts in blocks that consistent of 10 sample-standard brackets with 36 second integrations and 30 s of equilibration. Between 4 and 7 acquisitions are measured per sample (1.5–3 h) until \(\Delta^{17}\text{O}\) precision is <0.01% (SE) for an individual dual inlet measurement on gas from a single fluorination. We applied a pressure baseline correction following methods similar to Yeung et al. (2018) to account for \(\Delta^{17}\text{O}\) variations due to mass spectrometer and source conditions (see also Yeung and Hayles, 2021). Specifically, we measured the negative voltage to the left of the mass 33 peak and calibrated this baseline correction (additional or missing voltage) against the mass 32\(^{18}\text{O}\) intensity every session (2 weeks to 1 month). All of our reported sample and standard analyses are relative to the mean published high-precision L1/UNM\(_Q\) (\(\delta^{18}\text{O} = 18.070; \Delta^{17}\text{O} = 0.076\)) values reported in Wostbrock et al. (2020) on the VSMOW2-SLAP2 scale adjusted for a new calibration of SCO, UWG-2, and NBS 28 (Sharp and Wostbrock, 2020), which are also measured regularly in our laboratory (Chamberlain et al., 2020; Lowe et al., 2020). Both \(\delta^{18}\text{O}\) and \(\Delta^{17}\text{O}\) values are measured here relative to L1/UNM\(_Q\). For \(\delta^{18}\text{O}\) measurements, we correct the data to the measured standards from a given day’s batch of measured samples. For \(\Delta^{17}\text{O}\) values, values were standardized based on the average values of standards measured in a given session. In this case all samples were measured during one session over several weeks in 2019 that amounted to 10 total analysis days. Two samples were measured in replicate and we report the number of acquisitions measured as well as the (SE) for each individual dual inlet measurement on gas from a single fluorination.

During the session of analyses presented here, we also measured two secondary SiO\(_2\) standards. One of these is a low \(\delta^{18}\text{O}\) quartz (Sandia quartz; \(\delta^{18}\text{O} = 0.72 ± 0.05, n = 3\)) also used as an internal standard at University of New Mexico, and the other secondary standard is an in-house chert standard (CH-1; \(\delta^{18}\text{O} = 22.87 ± 0.04, n = 2\)) previously analyzed in the Stanford laboratory (e.g., Abruzzese et al., 2005; Hren et al., 2009). CH-1 has not been previous measured for \(\Delta^{17}\text{O}\). The Sandia quartz has previously been measured at the University of New Mexico (\(\delta^{18}\text{O} = 0.78\) and \(\Delta^{17}\text{O} = -0.016\); Personal Communication, Wostbrock et al., 2018), within error of our measurements (\(\Delta^{17}\text{O} = -0.012 ± 0.022, n = 3\); Table 1).

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Frontiers in Earth Science | www.frontiersin.org 4 March 2021 | Volume 9 | Article 628868
### TABLE 1 | Lacustrine chert triple oxygen isotope measurements.

| Sample ID | Height (m from top) | Chert $\delta^{18}$O (VSMOW2-SLAP2) | Chert $\delta^{18}$O (VSMOW2-SLAP2) | Chert $\Delta^{17}$O ($RF = 0.528$) | Chert $\Delta^{17}$O SE | No. of acquisitions | Lake water $\delta^{18}$O (32°C; scenario 1) | Lake water $\Delta^{17}$O (32°C; scenario 1) | Lake water $\delta^{18}$O (60°C; scenario 2) | Lake water $\Delta^{17}$O (60°C; scenario 2) |
|-----------|---------------------|------------------------------------|------------------------------------|-----------------------------------|------------------------|-------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| CL03      | 10                  | 20.137                             | 19.937                             | 10.441                            | −0.088                 | 0.007             | 5                           | −14.224                     | 0.035                       | −7.999                      | −0.001                      |
| CL04      | 30                  | 21.602                             | 21.372                             | 11.173                            | −0.111                 | 0.006             | 7                           | −12.789                     | 0.010                       | −6.565                      | −0.026                      |
| CL05      | 50                  | 22.901                             | 22.643                             | 11.870                            | −0.085                 | 0.007             | 5                           | −11.518                     | 0.036                       | −5.293                      | 0.000                       |
| CL05 rep  | 50                  | 23.328                             | 23.060                             | 12.075                            | −0.101                 | 0.007             | 5                           | −11.100                     | 0.020                       | −4.876                      | −0.016                      |
| CL06      | 80                  | 20.583                             | 20.374                             | 10.649                            | −0.108                 | 0.008             | 5                           | −13.786                     | 0.013                       | −7.562                      | −0.023                      |
| CL09      | 120                 | 18.911                             | 18.735                             | 9.810                             | −0.082                 | 0.008             | 5                           | −15.426                     | 0.040                       | −9.201                      | 0.003                       |
| CL10      | 125                 | n.m.                               |                                    |                                   |                        |                   |                             |                             |                             |                             |                             |
| CL11      | 140                 | 16.987                             | 16.844                             | 8.823                             | −0.070                 | 0.006             | 7                           | −17.316                     | 0.051                       | −11.092                     | 0.015                       |
| CL12      | 155                 | 23.414                             | 23.145                             | 12.119                            | −0.102                 | 0.007             | 5                           | −11.016                     | 0.020                       | −4.792                      | −0.016                      |
| CL13      | 170                 | 17.617                             | 17.464                             | 9.139                             | −0.082                 | 0.007             | 5                           | −16.697                     | 0.039                       | −10.472                     | 0.003                       |
| CL14      | 180                 | n.m.                               |                                    |                                   |                        |                   |                             |                             |                             |                             |                             |
| CL15      | 200                 | n.m.                               |                                    |                                   |                        |                   |                             |                             |                             |                             |                             |
| CL17      | 210                 | 22.146                             | 21.904                             | 11.456                            | −0.109                 | 0.007             | 5                           | −12.256                     | 0.012                       | −6.032                      | −0.024                      |
| CL18      | 220                 | n.m.                               |                                    |                                   |                        |                   |                             |                             |                             |                             |                             |
| CL19      | 250                 | 18.677                             | 18.505                             | 9.689                             | −0.082                 | 0.008             | 5                           | −15.656                     | 0.040                       | −9.431                      | 0.003                       |
| CL21      | 255                 | n.m.                               |                                    |                                   |                        |                   |                             |                             |                             |                             |                             |
| CL22      | 270                 | 22.779                             | 22.523                             | 11.788                            | −0.104                 | 0.009             | 4                           | −11.638                     | 0.017                       | −5.413                      | −0.019                      |
| CL23      | 290                 | 17.861                             | 17.704                             | 9.250                             | −0.097                 | 0.007             | 6                           | −16.457                     | 0.024                       | −10.232                     | −0.012                      |
| CL23 rep  | 290                 | 16.909                             | 16.768                             | 8.878                             | −0.066                 | 0.006             | 7                           | −17.393                     | 0.055                       | −11.168                     | 0.019                       |
| CL24      | 295                 | n.m.                               |                                    |                                   |                        |                   |                             |                             |                             |                             |                             |

### Sample ID | Age (Ma) | Chert $\delta^{18}$O (VSMOW) | Carbonate $\delta^{18}$O (VSMOW) | Carbonate $\delta^{13}$C (VPDB) | Carbonate $\delta^{18}$O (VSMOW) | Carbonate $\delta^{13}$C (VPDB) |
|--------------|----------|-------------------------------|-----------------------------------|---------------------------------|-------------------------------|---------------------------------|
| CL03         | 42.0     | 18.9                          | 19.2                              | −4.4                             |                               |                                |
| CL04         | 42.1     | 21.8                          | 20                                | −3.9                             |                               |                                |
| CL05         | 42.2     | 23.0                          | 20.1                              | −2.0                             |                               |                                |
| CL05 rep     | 42.2     |                               |                                   |                                  |                               |                                |
| CL06         | 42.5     | 18.0                          | 23.0                              | −3.8                             |                               |                                |
| CL09         | 42.6     | 19.5                          | 17.8                              | −3.4                             |                               |                                |
| CL10         | 42.8     | 15.6                          | 21.2                              | −2.8                             | 21.8                          | −2.1                           |
| CL11         | 42.8     | 15.6                          | 18.3                              | −2.5                             | 18.9                          | −2.5                           |
| CL12         | 42.9     | 21.5                          | 19.2                              | −2.0                             |                               |                                |
| CL13         | 42.9     | 18.4                          | 20.3                              | −4.1                             |                               |                                |
| CL14         | 42.9     | 15.6                          | 16.9                              |                                 |                               |                                |
| CL15         | 42.9     | 14.9                          | 17.2                              | −2.7                             | 21.1                          | −4.4                           |
| CL18         | 43.2     | 20.9                          |                                   |                                 |                               |                                |
| CL19         | 15.9     | 29.9                          | −3.0                             |                                   |                               |                                |

(Continued)
TABLE 1  

| Sample ID | Age (Ma) | Carbonate δ₁³C (VPDB) M2015 | Carbonate δ₁⁸O (VPDB) M2015 | Carbonate δ₁⁴C (VPDB) M2015 | δ₁⁴O (VPDB) M2015 | CL1 | CL2 | CL23 | CL24 | CL24 rep | Quartz standards n | δ₁⁸O SD (VSMOW2-SLAP2) | δ₁₇O SD (VSMOW2-SCQ) |
|-----------|----------|----------------------------|-----------------------------|-----------------------------|-------------------|-----|-----|------|------|---------|------------------|----------------------|----------------------|
| H2004     | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004/A2005 | 48.4     | 18.1                       | 19.2                        | 17.4                        |                   | 0.067 | 0.073| 0.390 |      |         | 0.067            | 0.073                | 0.390                |
| H2004/A2005 | 48.4     | 18.1                       | 19.2                        | 17.4                        |                   | 0.067 | 0.073| 0.390 |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |
| H2004      | 48.3     | 2.31                       | 18.1                        | 19.2                        | 17.4              |      |     |      |      |         | 0.067            | 0.073                | 0.390                |

**Carbonate Clumped Isotope Measurements**

Carbonate clumped ($\Delta_{47}$) and stable ($\delta^{13}C$, $\delta^{18}O$) isotope measurements from the Elko Formation were performed on three lake carbonate samples originally reported in Mulch et al. (2015). Carbonate clumped isotope analyses were conducted at the Goethe University-Senckenberg BiK-F Stable Isotope Facility Frankfurt, Germany, following methods outlined in detail in Wacker et al. (2013) and Fiebig et al. (2016). Carbonate powder (8–12 mg) was digested in >106% phosphoric acid at 90°C ± 0.1°C for 30 min in a common acid bath. In brief, the evolved CO$_2$ gas was purified through cryogenic traps before and after passing through a Porapak Q-packed gas chromatography column with He carrier gas. Measurements of the cleaned CO$_2$ gas were made in dual inlet on a Thermo Scientific™ MAT 253 IRMS for 10 acquisitions consisting of 10 cycles with an ion integration time of 20 s per cycle. CO$_2$ gases equilibrated at 1,000 and 25°C were measured along with the samples to establish the empirical transfer function and the $\Delta_{47}$ values reported here are in the “absolute reference frame” (ARF) (Dennis et al., 2011), also referred to in the literature as the “carbon dioxide equilibrated scale” (CDES). All data was processed using the IUPAC parameters (Daëron et al., 2016). We applied the 25–90°C acid fractionation factor of 0.088% and the temperatures calibration of Petersen et al. (2019).

One or two carbonate reference materials were analyzed each measurement day, including Carrara marble, *Arctica islandica* (also referred to as MuStd, a well-homogenized shell material of an aragonitic cold water bivalve), ETH-1, and ETH-3. During the measurement period, we obtained a mean $\Delta_{47}$ value of 0.205% ± 0.004% (SE, $n = 6$) for ETH-1 and of 0.614% ± 0.005% (SE, $n = 7$) ETH-3, which are similar to the long-term values reported in Bajnai et al. (2020). We use the Gonfiantini parameters and apply a 25–90°C acid fractionation factor of 0.069% to the $\Delta_{47}$ measurements of Carrara marble and *Arctica islandica* in order to compare them to previously reported $\Delta_{47}$ values of these carbonates. The mean $\Delta_{47}$ value of Carrara marble is 0.390% ± 0.005% (SE, $n = 6$), which is just greater than the long-term in-house mean $\Delta_{47}$ value of Carrara marble of 0.376% ± 0.002% (SE, $n = 58$) (Methner et al., 2020). The mean $\Delta_{47}$ value of *Arctica islandica* is 0.722% ± 0.007% (SE, $n = 7$), which is indistinguishable from the 0.724% ± 0.004% (SE, $n = 28$) reported by Wacker et al. (2013). All carbonate clumped data are provided in a comprehensive clumped isotope results and calculations *Supplementary Material*.

In addition to the new carbonate clumped isotope data we report the complete $\delta^{13}C$ values associated with the legacy $\delta^{18}O$ measurements ($n = 15$) originally made by Abruzzese et al. (2005) (see their Table 1 and “Materials and Methods” section for details), some of which ($n = 6$) were also remeasured in the dataset reported in Mulch et al. (2015).

**Back-Calculation of Unevaporated Waters and Paleoaltimetry Calculations**

In this study we follow the approach of Passey and Ji (2019) to back-calculate the unevaporated source water $\delta^{18}O$
value. Passey and Ji (2019) use a simple steady state model for throughflow and closed basin (terminal) lakes first developed by Criss (1999) modified for triple oxygen isotopes (e.g., Herwartz et al., 2017; Gázquez et al., 2018; Surma et al., 2018; Aron et al., 2020) to describe the isotopic composition of the lake water ($R_W$):

$$ R_W = \frac{\alpha_{eq} a_{diff} (1 - h) R_I h X_E R_A}{X_E + \alpha_{eq} a_{diff} (1 - h) (1 - X_R)} $$

where $R_I$ and $R_A$ are the isotope ratios of inflowing river water and ambient atmospheric water, respectively, $h$ is the relative humidity, $\alpha_{eq}$ and $a_{diff}$ are the equilibrium and kinetic fraction factors associated with lake water evaporation, and $X_E$ is the volumetric fraction of inflowing water lost to evaporation. Applying this model to triple oxygen isotopes, and calibrating is the volumetric fraction of inflowing water lost to evaporation.

RESULTS

Chert Oxygen Isotopes

Our triple oxygen isotope external reproducibility (1σ) during the session of analyses based on the standard primary used to correct $\delta^{18}$O and $\Delta^{17}$O data (hydrothermal quartz standard L1/UNM_Q) is ±0.073‰ for $\delta^{18}$O and ±0.016‰ for $\Delta^{17}$O (± 1σ; $n = 13$). Replicates of two samples (CL05 and CL23) indicate similar reproducibility for $\Delta^{17}$O (±0.011 and ±0.022‰, respectively) but larger $\delta^{18}$O variation (±0.295 and ±0.662‰). Comparison to previous measurements made on powders from Horton et al. (2004) and Abruzzese et al. (2005) indicate good agreement [±$\delta^{18}$O difference between the datasets of -0.1 ± 1.3‰ ($n = 14$)] though we note that we analyzed chips from the same hand samples, not the same sample powders as in the original studies.

Our dataset span 6.5‰ in $\delta^{18}$O (16.9–23.4‰) and we observe a negative correlation with $\Delta^{17}$O ranging from −0.066 to −0.111‰ (Figure 1A and Table 1). We calculate an empirical slope ($\lambda_{chert}$, $\delta^{17}$O vs. $\delta^{18}$O) of 0.5236, a value between the slopes expected for processes related to meteoric water and SiO2 precipitation (0.528–0.524), and kinetic fractionation associated with evaporating water (>0.5185) (see section “Isotope Notation and Systematics”).

Carbonate Oxygen, Carbon, and Clumped Isotopes

New carbonate clumped isotope measurements from the Elko Formation yielded $\Delta_{T}$ values of 0.680–0.710‰, corresponding to temperatures (following Petersen et al., 2019) of 17.8 ± 8.8 °C to 39.9 ± 3.4°C (1σ, Table 2). The Elko Formation carbonates are younger than the Cherty Limestone chert. However, as described below, given the existing age constraints, and the overlap in carbonate $\delta^{18}$O and $\delta^{13}$C values, the Elko Formation measurements provide a useful constraint on the triple oxygen isotope chert dataset. We calculate an error weighted mean temperature of 32.5 ± 3.8°C (MSWD = 3.9; Table 2). The error of this mean temperature is propagated in our subsequent calculations (see Scenario 1 in the section “Discussion”). Our calculated MSWD value for the error weighted mean temperature greater than 1 indicates over-dispersion of the dataset unrelated to analytical precision, which is likely a result of geologic scatter. These values are similar to the average temperatures (28.5 and 35°C) to Early Eocene stromatolites from the Rife Bed, Tipton Shale Member of the Green River Formation reported by Frantz et al. (2014). Similar to carbonate clumped isotope datasets from Quaternary lake systems (e.g., Hudson et al., 2017; Santi et al., 2020) this spread is indicative of
FIGURE 1 | Cross plots of isotope datasets from the Elko Basin. (A) $\delta^{18}$O and $\Delta^{17}$O of chert from the Cherty Limestone (This Study). The $\lambda_{	ext{chert}}$ slope of 0.5236 was calculated in $\delta^{18}$O vs. $\delta^{17}$O space (not shown). $\Delta^{17}$O error bars are 1 SE of the analytical measurements (see section “Materials and Methods”). (B) Stratigraphic sections simplified from Lund Snee et al. (2016) and modified from Mulch et al. (2015) summarizing the Elko Basin stratigraphy and sample locations (vs. stratigraphic height) within the Cherty Limestone and Elko Formations. Ages are from $^{40}$Ar/$^{39}$Ar geochronology (Mulch et al., 2015). The reader is referred to Lund Snee et al. (2016) for sampling localities (see their Figure 1B). (C) $\delta^{18}$O of chert vs. carbonate in the Cherty Limestone Formation [This Study, Horton et al. (2004) and Abruzzese et al. (2005)]. Contours are for assumed co-equilibrium at 32.5°C [carbonate formation temperature ($\Delta_{C}$) weighted mean = 32.5 ± 3.8°C (1σ, MSWD = 3.9)] and 30°C carbonate paired with 60°C chert using the fractionation factors of Kim and O’Neil (1997) and Sharp et al. (2016) (following Abruzzese et al., 2005). (D) Carbonate $\delta^{18}$O and $\delta^{13}$C in both the Cherty Limestone and Elko Formations [This Study ($n = 3 \times \Delta_{C}$ measurements), Horton et al. (2004), Abruzzese et al. (2005), Chamberlain et al. (2012) and Mulch et al. (2015)]. The linear regression and confidence intervals are calculated through all data from both formations. As shown in the legend triangles are new measurements from this study, circles are previous measurements of paired carbonate and chert samples from the Cherty Limestone Fm. and squares are previous carbonate measurements from the Elko Fm.

a seasonally evaporitic lake system forming carbonates year around, though the climate system (e.g., the seasonality of temperature, precipitation and humidity) was likely quite different in the Eocene (e.g., Hyland et al., 2018). Based on modern lapse rates (Huntington et al., 2010) these temperatures would put our lake basin and the Green River Formation in Wyoming (Frantz et al., 2014) at <500 m, much lower than the oxygen and hydrogen isotope-based methods would suggest (see section “Discussion”). We propose that these temperatures are likely biased toward seasonal summer/warm month carbonate formation, evidenced by a reduced range in the carbonate $\delta^{18}$O values relative to the chert $\delta^{18}$O values (Figure 1C). Given the hotter mean annual temperature, and a proposed similar seasonality in temperature in the continental interior during the Eocene (Hyland et al., 2018), the temperature range and magnitude are reasonable, though clearly further work is necessary to better constrain temperatures via clumped isotopes in the Elko Basin and possibly, in combination with
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$^{18}$O and $^{13}$C) and clumped isotope ($^{18}$O).

| Age (Ma) | $\delta^{18}$O Replicates | $\delta^{13}$C Replicates |
|----------|------------------------|-------------------------|
|          | Water                  | Water                   |
|          | (VSMOW)                | (VPDB)                  |
|          | Temperature C          | Temperature C           |
|          | SD                     | SE                      |
|          | $\Delta T$ (C)         | $\Delta T$ (%)          |
|          | $\Delta T$ (C)         | $\Delta T$ (%)          |
|          | Error (C)              | Weighted average (C)    |
|          | SD                     | MSWD                    |
|          | Height (m)             |                         |
|          | M2015                  |                         |
|          | Replicates             |                         |
|          | NVEF-06                | 8                       |
|          | M2015                  | 31.5                    |
|          | 2015                   | 31.5                    |
|          | NVEF-06                | 42.5                    |
|          | M2015                  | 6.6                     |
|          | 2015                   | 6.6                     |
|          | NVEF-06                | 42.0                    |
|          | M2015                  | 11.1                    |
|          | 2015                   | 11.1                    |
|          | NVEF-05                | 42.5                    |
|          | M2015                  | 26.4                    |
|          | 2015                   | 26.4                    |
|          | NVEF-24                | 39.9                    |
|          | M2015                  | 26.4                    |
|          | 2015                   | 26.4                    |

The $^{18}$O and $^{13}$C values ($^{18}$O of 26.4–31.5‰ VSMOW, $^{13}$C of 6.3–11.1‰ VPDB) of the three clumped isotope measurements from the Elko Formation reflect evaporatively enriched values relative to the $^{18}$O and $^{13}$C values of incoming source water and dissolved inorganic carbon. These values are relatively high for Cenozoic lake basins in the western US, which range from approximately 10 to 32‰ VSMOW in $^{18}$O and approximately −6 to +12‰ VPDB in $^{13}$C values [see lacustrine samples in compilations by Davis et al. (2009) and Chamberlain et al. (2012)]. Further, these measurements are comparable to previous measurements from the Elko and Cherty Limestone Formations compiled in the box and whisker plots in Figure 2B (Horton et al., 2004; Abruzzese et al., 2005; Chamberlain et al., 2012; Mulch et al., 2015; with legacy $^{13}$C data reported for the first time in Table 1). Lake water $^{18}$O values derived from the three lacustrine carbonate clumped isotope measurements range from −3.7 to +3.5‰ VSMOW (Table 1 and Figure 2). Applying the weighted mean formation temperature (32.5°C) to all samples from the Elko Formation and the Cherty Limestone Formation yields formation water $^{18}$O of approximately −13 to +5‰ VSMOW. In the $^{13}$C-$^{18}$O crossplot shown in Figure 1C the stable isotope data of the two formations define a robust positive correlation, typical of evaporation trends for lacustrine systems (Li and Ku, 1997; Davis et al., 2009; Horton and Oze, 2012; Chamberlain et al., 2013; Ibarra et al., 2014; Ibarra and Chamberlain, 2015; Horton et al., 2016; Ingalls et al., 2020b). We note that in this limited carbonate dataset we do not see a systematic relationship between the enrichment of $^{18}$O and $^{13}$C in the positive evaporation trend and the carbonate clumped isotope derived temperatures.

**DISCUSSION**

**Comparison of Oxygen Isotopes of Chert and Associated Carbonate**

In the original work of Abruzzese et al. (2005) the oxygen isotope data of the chert nodules, the same samples as those re-measured here for $^{18}$O and $^{17}$O, and their associated carbonate (carbonate and chert < 2 cm apart in hand sample) indicated a positive correlation. We pair our measurements...
FIGURE 2 | Scenarios for interpreting chert triple oxygen isotope data. (A) In the upper panel we show the individual $\Delta_Ar$-derived lake water $\delta^{18}O$ values (Table 1) from this study, as well as all data from the Elko (green) and Cherty Limestone (orange) Formations shown in Figure 1 as box and whisker plots (Horton et al., 2004; Abruzzese et al., 2005; Chamberlain et al., 2012; Mulch et al., 2015). Yellow box and whisker plots are all Eocene volcanic glass $\delta D$ data from the Elko Basin region measured by Cassel et al. (2014, 2018) assuming the glass-water fractionation factor determined by Friedman et al. (1993) and conversion to $\delta^{18}O$ using the global meteoric water line. The bottom panel shows the calculations assuming cherts formed at average carbonate formation temperature of 32.5°C (based on $\Delta_Ar$ measurements). Blue triangles are measurements, gray triangles are reconstructed lake water values (Table 1) and using the model equations of Passey and Ji (2019) with the reconstructed average meteoric source water value shown as a yellow star. The thick black line is the regional meteoric water ($\lambda_mwl = 0.528$, intercept = $0.032 \pm 0.015$) determined by Passey and Ji (2019), with the gray hashed horizontal lines representing the error. (B) As in (A) but using a chert formation temperature of 60°C, assumed to be in equilibrium with lake pore waters during early diagenesis.

with the associated carbonate measurements, as well as plot all data from the original study, and find the resulting trend is relatively unchanged (Figure 1B), though Abruzzese et al. (2005) did report some lower chert $\delta^{18}O$ values not measured here. Additionally, we rederive the temperature contours shown in Abruzzese et al. (2005) (see their Figure 6) by equating the fractionation factors from Kim and O’Neil (1997) and Sharp et al. (2016) assuming the samples formed from the same formation water (i.e., exhibiting identical $\delta^{18}O$ values) and in isotopic equilibrium. Importantly, the original fractionation factor for SiO$_2$-H$_2$O used by Abruzzese et al. (2005) from Knauth and Epstein (1976) has changed substantially at low (Earth surface) temperatures (see Sharp et al., 2016 for details), leading to a greater temperature sensitivity of chert $\delta^{18}O$ (a greater 1,000 ln$a$ value). The 32.5°C contour (average $\Delta_Ar$-temperature) does not pass through the samples shown on Figure 1B (lower right long dashed contour in the corner of Figure 1B). Assuming a ~30°C carbonate formation temperature, the best fit through our new data suggests a chert formation temperature of ~60°C (see dashed contour on Figure 1B), likely during early burial diagenesis, as originally suggested by Abruzzese et al. (2005). The total maximum overburden in the basin is less than 3,250 m; whereas the Eocene overburden is likely less than 1,250 m (Smith and Ketner, 1976; Abruzzese et al., 2005). The latter of which, given regional heat flow estimates (~65 mW/m$^2$) and thermal conductivities of similar sediments implemented in basin-scale modeling (e.g., Tong et al., 2017), makes 60°C a reasonable temperature estimate during early burial diagenesis. Using the old SiO$_2$-H$_2$O fractionation factors from Knauth and Epstein (1976) described above the paired $\delta^{18}O$-δD measurements of Abruzzese et al. (2005) originate from an equilibrium chert line of 40°C (see their Figure 7). As such, the new fractionation...
First (Scenario 1), we evaluate the possibility that the Cherty Limestone carbonate vs. the chert (smaller vs. larger range, respectively in Figure 1C), it may be the case that the carbonates are warm season biased and chert formation is more annually distributed. Using the weighted mean clumped isotope derived temperature of 32.5°C and applying the SiO₂·H₂O triple oxygen isotope fractionation factor of Sharp et al. (2016) and Wostbrock et al. (2018) (θ = 0.5244 and α = 1.0348), we calculate from our chert samples water Δ¹⁷O values of 0.010–0.055‰ and an average source water value of 8¹⁸O of −14.1 ± 2.4‰ VSMOW (Figure 2A). These datapoints (gray triangles on Figure 2A) overlap the range of the meteoric water line for the western United States (Li et al., 2015; Passey and Ji, 2019), suggesting negligible evaporation of lake waters since evaporation leads to lower Δ¹⁷O values. Further, these δ¹⁸O values are significantly lower than those from coeval carbonate of the Cherty Limestone (shown as an orange box and whisker plot; Figure 2A). Thus, in this scenario we estimate a source δ¹⁸O of −14.1 ± 2.4‰ assuming that source and lake waters are isotopically indistinguishable.

Applying one single formation temperature is highly unlikely, given that we observe a spread of 6.5‰ in chert δ¹⁸O values, and a negative correlation with Δ¹⁷O ranging from −0.066 to −0.111‰ with an empirical slope (λ₉₉) of 0.5236 (Figure 1A). As such, the negative correlation and spread would have to be explained by temperatures (assuming the mean value of 32.5°C) ranging from 21 to 47°C, a range comparable but larger than the range measured by the individual carbonate clumped isotope samples (note that this range is asymmetric because 1,000h₀ is a function of 1/T with the largest fractionation factor at the coldest temperatures). However, the empirical slope of 0.5236 of our data set (λ₉₉) is lower than the theoretical slopes for SiO₂·H₂O fractionation at this

Estimates for Unevaporated Source Water δ¹⁸O From Three Chert Formation Scenarios

First (Scenario 1), we evaluate the possibility that the Cherty Limestone Formation cherts precipitated at (Earth surface) temperatures similar to those suggested by Δ₄₇ results from the overlying Elko Formation (Figure 2). This scenario is plausible given that the carbonate in the Cherty Limestone associated with the chert samples do overlap in δ¹⁸O composition with some of the carbonate samples from the Elko Formation. This assumes that the climatic and hydrologic conditions were similar (i.e., a balance filled to overfilled lake system; Davis et al., 2009), though as described in the Results above, based on the absolute range of δ¹⁸O values in the co-occurring Cherty Limestone carbonate vs. the chert (smaller vs. larger range, respectively in Figure 1C), it may be the case that the carbonates are warm season biased and chert formation is more annually distributed. Using the weighted mean clumped isotope derived temperature of 32.5°C and applying the SiO₂·H₂O triple oxygen isotope fractionation factor of Sharp et al. (2016) and Wostbrock et al. (2018) (θ = 0.5244 and α = 1.0348), we calculate from our chert samples water Δ¹⁷O values of 0.010–0.055‰ and an average source water value of 8¹⁸O of −14.1 ± 2.4‰ VSMOW (Figure 2A). These datapoints (gray triangles on Figure 2A) overlap the range of the meteoric water line for the western United States (Li et al., 2015; Passey and Ji, 2019), suggesting negligible evaporation of lake waters since evaporation leads to lower Δ¹⁷O values. Further, these δ¹⁸O values are significantly lower than those from coeval carbonate of the Cherty Limestone (shown as an orange box and whisker plot; Figure 2A). Thus, in this scenario we estimate a source δ¹⁸O of −14.1 ± 2.4‰ assuming that source and lake waters are isotopically indistinguishable.

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Factors drive home the original interpretation that chert nodules and chert laminations of this type, with silica sourced from the weathering of volcanic glass and/or diatom blooms, commonly form from early burial diagenesis and/or dehydration of Opal A to microquartz. In marine settings the Opal A to microquartz transition has been found to occur between 50 and 70°C (Yanchilina et al., 2020), consistent with our estimate of Elko Basin chert formation at ~60°C. However, given the freshwater nature of this system and the limited δ¹³C-δ¹⁸O spread within the Cherty Limestone Formation, it also remains possible that the chert and coeval/associated carbonate did not form from waters of the same δ¹⁸O value. To account for these alternative interpretations of our dataset, we propose two scenarios for deriving the δ¹⁸O value of the basin source water. Both, however, allow for similar interpretations with respect to Eocene meteoric source water feeding the Elko Basin.

Estimates for Unevaporated Source Water δ¹⁸O From Three Chert Formation Scenarios

First (Scenario 1), we evaluate the possibility that the Cherty Limestone Formation cherts precipitated at (Earth surface) temperatures similar to those suggested by Δ₄₇ results from the overlying Elko Formation (Figure 2). This scenario is plausible given that the carbonate in the Cherty Limestone associated with the chert samples do overlap in δ¹⁸O composition with some of the carbonate samples from the Elko Formation. This assumes that the climatic and hydrologic conditions were similar (i.e., a balance filled to overfilled lake system; Davis et al., 2009), though as described in the Results above, based on the absolute range of δ¹⁸O values in the co-occurring Cherty Limestone carbonate vs. the chert (smaller vs. larger range, respectively in Figure 1C), it may be the case that the carbonates are warm season biased and chert formation is more annually distributed. Using the weighted mean clumped isotope derived temperature of 32.5°C and applying the SiO₂·H₂O triple oxygen isotope fractionation factor of Sharp et al. (2016) and Wostbrock et al. (2018) (θ = 0.5244 and α = 1.0348), we calculate from our chert samples water Δ¹⁷O values of 0.010–0.055‰ and an average source water value of 8¹⁸O of −14.1 ± 2.4‰ VSMOW (Figure 2A). These datapoints (gray triangles on Figure 2A) overlap the range of the meteoric water line for the western United States (Li et al., 2015; Passey and Ji, 2019), suggesting negligible evaporation of lake waters since evaporation leads to lower Δ¹⁷O values. Further, these δ¹⁸O values are significantly lower than those from coeval carbonate of the Cherty Limestone (shown as an orange box and whisker plot; Figure 2A). Thus, in this scenario we estimate a source δ¹⁸O of −14.1 ± 2.4‰ assuming that source and lake waters are isotopically indistinguishable.

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FIGURE 4 | Paleoelevations for this study and previous datasets (Horton et al., 2004; Mix et al., 2011; Chamberlain et al., 2012; Cassel et al., 2014, 2018; Mulch et al., 2015; Smith et al., 2017) as tabulated and calculated in Table 3 using the model of Rowley et al. (2001). The volcanic glass samples include all samples east of the Eocene drainage divide to the west of the Elko Basin (Henry, 2008). Error bars are the 95% confidence (see Table 3).

temperature range (0.5242–0.5247), suggestive that evaporative processes must still influence a portion of the samples (lower $\Delta^{17}$O and higher $\delta^{18}$O) if this scenario was correct. Additionally, new measurements of carbonates presented by Passey and Ji (2019) from Quaternary lake systems, including the nearby Great Salt Lake, gave $\lambda_{\text{lake}}$ ranging from 0.5219 to 0.5239, similar to that of the Cherty Limestone Formation chert samples analyzed here.

Thus, the alternative (Scenario 2) is that the chert formed during early diagenesis at higher temperatures from waters of a similar oxygen isotopic composition to the carbonates (Figure 2), as originally suggested by Abruzzese et al. (2005). Assuming 60 ± 10°C as the formation temperature places the primary (lake) water $\delta^{18}$O recorded by the cherts in the range of expected values based on the carbonate clumped isotope constraints (blue vertical bar in Figure 2B), and with $\Delta^{17}$O values lower than the meteoric water line (as expected for evaporative systems). Thus, we take this population of data points (gray triangles) and calculate the unevaporated source water for the Cherty Limestone Formation chert samples using the equations present and derived by Passey and Ji (2019) (see also section “Back-Calculation of Unevaporated Waters and Paleoaltimetry Calculations”), accounting for the measurement uncertainty and the meteoric water line uncertainty. Doing so, and fully propagating errors via a distribution-based Monte Carlo sampling routine following that outlined in the original Matlab code of Passey and Ji (2019), we calculate a source water $\delta^{18}$O of −16.3 ± 3.5‰ VSMOW (Figure 2B), lower but within error of that that derived above in scenario 1.

This result is non-unique because the precise temperature of chert formation is (still) unknown despite the added constraint of carbonate clumped isotope temperatures and the third isotope of oxygen. In a sensitivity test we assume chert formation under a wide range of temperatures. Following the same methodology as scenario 2 (Figure 2B), we carried out Monte Carlo simulations at temperatures ranging from 17.5 to 75°C, with the full range of the clumped isotope measurements, the error-weighted mean carbonate clumped temperature and the scenario 2 range shown as gray bars (Figure 3A). Because the SiO$_2$-H$_2$O fractionation factor is greater at lower temperatures, the derived source water values are lower at lower temperatures (Figure 3A). Source water $\delta^{18}$O values across this broad temperature range span −18 to −15‰. In addition, in Figure 3B we show the sensitivity of
our calculations to the intercept of the meteoric water line (i.e., the \( \Delta^{17}\text{O}_{\text{MWL}} \) intercept), a key uncertainty given the paucity of triple oxygen isotope data from modern settings and the question of whether the Eocene intercept was within the range used from Passey and Ji (2019) in our calculations. This sensitivity test shows that the source water \( \delta^{18}\text{O} \) value decreases with increasing \( \Delta^{17}\text{O}_{\text{MWL}} \) intercept (Figure 3B), a relationship that should be expected given that a higher \( \Delta^{17}\text{O}_{\text{MWL}} \) intercept places the reconstructed lake water \( \delta^{18}\text{O} \) and \( \Delta^{17}\text{O} \) points (gray points in Figure 2) further from the meteoric water line (i.e., a greater spacing between the MWL and the data points in the \( y \)-axis). In the next section we discuss the implications of this for the paleoelevation reconstruction if the \( \Delta^{17}\text{O}_{\text{MWL}} \) intercept was in fact higher.

Previously presented sedimentological data suggested that the chert nodules formed during early diagenesis at higher temperatures (Abruzzese et al., 2005; Davis et al., 2009), which likely lead to the shallow \( \delta^{18}\text{O}-\delta^{2} \) slope of 2.7 for these samples (balance to underfilled evaporatively influenced lake systems typically have \( \delta^{18}\text{O}-\delta^{2} \) slopes that fall between \( \sim 4 \) and \( \sim 7 \); Gonfiantini, 1986). As such, given the systematics explored above, including the empirical negative relationship of the chert data following a plausible evaporation trend, we prefer the results of scenario 2 as the most realistic and parsimonious. This includes the assumption that chert formed at temperatures greater than those recorded by the carbonate clumped isotope measurements of the overlying Elko Formation from lake water incorporated into the sediment pore water of a similar \( \delta^{18}\text{O} \) composition range (light blue band in Figure 2) as both the coeval carbonate in the Cherty Limestone and the overlying Elko Formation.

**Implications for Eocene Nevdaplanino Paleoaltimetry and Comparison to Other Datasets**

To determine the paleoelevation of the deposits in the Elko Basin we use the model of Rowley et al. (2001). This model assumes Rayleigh distillation whereby water parcel rainout is proportional to lifting due to orography producing a monotonic relationship between elevation and \( \Delta^{18}\text{O} \) or \( \Delta^{2} \) (defined as coastal precipitation \( \delta^{18}\text{O} \) value minus the inland \( \delta^{18}\text{O} \) value). Assuming a shoreline (i.e., zero elevation) \( \delta^{18}\text{O} \) value and that the air-mass lifting is proportional to the elevation difference between the coast and basin’s hypsometric mean elevation, meteoric (source) \( \delta^{18}\text{O} \) estimates can be converted to elevations (e.g., Rowley et al., 2001; Mulch et al., 2006). In Figure 3 and Table 3 we do so assuming the mean estimates for our new data accounting only for uncertainty in the Rayleigh distillation model of Rowley et al. (2001). A key limitation of this assumption is that upstream rainout due to orography higher than the study area of interest or due to continentality, which both lead to lower \( \delta^{18}\text{O} \) values (Kukla et al., 2019), is negligible. Recent regional mapping work by Lund Snee et al. (2016) supports this assumption. Lund Snee et al. (2016) inferred that the Cretaceous to Eocene deposits in the Elko Basin represents a lake basin covered with volcanic rocks situated in relatively subdued topography, with regional rugged Basin and Range style topography only forming in the Miocene. However, upstream rainout could be due to either Eocene topography and associated rainout through the Sierra Nevada further west inferred by hydrogen and oxygen paleoaltimetry (Mulch et al., 2006; Cassel et al., 2009; Hren et al., 2010; Mix et al., 2016), or a drainage divide just west of the Elko Basin inferred from ash-flow tuffs (Henry, 2008), which are both likely and thus this possibility cannot be ruled out.

Assuming a coastal Eocene precipitation \( \delta^{18}\text{O} \) value of \(-7.1\%\) equivalent to previous studies (e.g., Mulch et al., 2006; Cassel et al., 2009; Hren et al., 2010; Mix et al., 2016), we calculate paleoelevation using the thermodynamic model of Rowley et al. (2001). The \( \Delta^{18}\text{O} \) for scenario 1 is \(-7.0\%\), which for Eocene model results for the western United States give a mean elevation of 2.75 +0.55/−0.42 km (95% confidence). Alternatively, for scenario 2, the \( \Delta^{18}\text{O} \) value is \(-9.2\%\), giving a mean elevation of 3.29 +0.69/−0.68 km. These estimates, not accounting for uncertainty in the meteoric water line shown in Figure 3 are within error, indicating elevations of \( \sim 3 \) km. In Figure 3C we show the sensitivity of our assumed coastal Eocene precipitation \( \delta^{18}\text{O} \) value of \(-7.1\%\), over a range of \(-4 \) to \(-10\%\). Previous work in the Pacific Northwest and Idaho Batholith has suggested shoreline Eocene precipitation values of \(-6\%\) (Methner et al., 2016; Chamberlain et al., 2020), which for scenario 2 would increase our elevation estimate to \(-2.9\)–\(-4.2 \) km.

These estimates are within error of those derived by previous volcanic glass \( \delta^{2} \) measurements made by Cassel et al. (2014, 2018) and Smith et al. (2017) (see Cassel et al., 2018; their Figure 2). However, putting the \( \delta^{2} \) glass data into equivalent \( \delta^{18}\text{O} \) values indicates a discrepancy. In Figures 2A,B we show a box and whisker plot (yellow) of all glass \( \delta^{2} \) data from the Late Eocene sediments in and near the Elko Basin previously reported and converted to \( \delta^{18}\text{O} \) using the fractionation factor of Friedman et al. (1993) to convert to environmental water values and the assumption that waters fall along the global meteoric water line. This approach is similar to assumptions relating \( \delta^{2} \) and \( \delta^{18}\text{O} \) data in clays (e.g., Poage and Chamberlain, 2002; Sjostrom et al., 2006; Mix and Chamberlain, 2014; Mix et al., 2016). The average \( \delta^{18}\text{O} \) of the unevaporatively enriched samples reported by volcanic glass \( \delta^{2} \) studies (Cassel et al., 2014, 2018; Smith et al., 2017), converted to \( \delta^{18}\text{O} \), is \(-18.4 \pm 1.0\%\). This mean value is significantly (Student’s t-test \( p < 0.05 \)) lower than both estimates presented above in scenarios 1 and 2. We note however, that based on our sensitivity tests in Figure 3, associated with both formation temperature and the \( \Delta^{17}\text{O}_{\text{MWL}} \) intercept, it remains possible that the \( \delta^{2} \) glass data and the chert-carbonate derived values presented here are actually in close agreement. For the latter, it would require that the mean value of the \( \Delta^{17}\text{O}_{\text{MWL}} \) intercept be higher, by 0.01–0.02\% (i.e., approximately +1\sigma of the current modern water data), than the modern data from the western United States (Li et al., 2015; Passey and Ji, 2019).

An alternative possible reason for this discrepancy is hydrogen exchange in volcanic glass (noted previously by Chamberlain et al. (2020) for hydrothermally altered granite). Alternatively, and perhaps most parsimoniously, there are true differences in the depositional setting and thus elevation between the lower elevation lacustrine depocenter, where the thick Chery Limestone Formation (Figure 1B) was deposited, and the syn- and/or
### TABLE 3 | Paleoelevation calculations for Scenarios 1 and 2 based on the Rowley et al. (2001) model and previous estimates recalculated.

| Formation | Temperature (°C) | Method for calculating source water | Source water δ¹⁸O | Source water δ¹⁸O SD | Source water Δ¹⁷O (λRF = 0.528) | Source water Δ¹⁷O SD | Δ¹⁸O (−7.1‰ shoreline value) | Mean elevation (km) | 95% confidence (±) |
|-----------|-----------------|-------------------------------------|--------------------|----------------------|---------------------------------|----------------------|-------------------------------|-------------------|-----------------|
| Cherty limestone scenario 1 | 32.5 ± 3.8°C (this study) | Average of all data (Figure 2A) | −14.09 | 2.39 | 0.029 | 0.015 | −7.0 | 2.75 | +0.55/−0.42 |
| Cherty limestone scenario 2 | 60 ± 10°C in Figure 2 (17.5–75°C in Figure 3A) | Passey and Ji (2019) back-trajectory method (Figure 2B) | −16.09 | 3.50 | 0.032 | 0.015 | −9.2 | 3.29 | +0.69/−0.68 |

| Formation | Temperature (°C) | Δ¹⁸O (−7.1‰ shoreline value) | Mean elevation (km) | 95% confidence (±) | Data source |
|-----------|-----------------|-----------------------------|-------------------|-----------------|-------------|
| Indian Wells Fm. paleosol carbonate (lowest δ¹⁸O) | 13°C (Chase et al., 1998) | −11.6 ± 2.2 | 3.76 | +0.80/−0.77 | H2004; C2012; M2015 |
| Humboldt Fm. paleosol carbonate (average δ¹⁸O) | 13°C (Chase et al., 1998) | −11.5 ± 1.0 | 3.74 | +0.84/−0.77 | H2004; C2012; M2015 |
| Hydrated volcanic glass data | | | | | |
| Volcanic glass—eocene, non-lacustrine samples | n/a | −11.2 ± 1.0 | 3.68 | +0.81/−0.66 | C2014; C2018 |
| Volcanic glass—early oligocene | n/a | −10.3 ± 1.0 | 3.52 | +0.81/−0.66 | C2014; C2018 |
| Volcanic glass—late oligocene | n/a | −12.7 ± 1.2 | 3.94 | +0.85/−0.70 | C2014; C2018 |

Note that recent work (Lund Snee et al., 2016) recommends combining the Indian Wells Fm. with the Humboldt Fm. H2004—Horton et al. (2004); M2015—Mulch et al. (2015); C2012—Chamberlain et al. (2012); C2014—Cassel et al. (2014); C2018—Cassel et al. (2018). Note that the formation temperature used in Scenario 1 is the weighted average of the lacustrine carbonates (Table 2) from the Elko Fm.
post-deposition Eocene fluvial sites of volcanic ash deposition associated with higher elevations. We note that Cassel et al. (2018) explicitly removed samples from their regional dataset from basin depocenters in lacustrine settings because they recorded δD values higher than other (nearby) samples from the same age and fluvial depositional settings. Further work to disentangle and systematically document the depositional settings, paleoelevations and geochronologic control of the individual localities for all of the proxies in the Elko Basin and regionally in northeastern Nevada is clearly necessary. One additional line of evidence is the δ18O data of four chert samples from the Miocene Humboldt Formation ranging from 17.2 to 23.7‰ (Knauth and Epstein, 1976), thus, exhibiting a similar range to those of the Eocene Cherty Limestone Fm. (15.6–23.1‰) (Table 1; Horton et al., 2004; Abruzzese et al., 2005). Assuming similar formation temperatures, the Humboldt Formation chert data from Knauth and Epstein (1976) would yield similar paleoelevations to the Cherty Limestone Fm., but lower than nearby time equivalent (Miocene) volcanic glass data from Cassel et al. (2018), similar to our observations for the Eocene.

In Figure 3 we summarize the paleoelevation estimates based on this work on triple oxygen isotopes of chert and those from other studies on younger rocks based on carbonates from paleolakes and paleosols and volcanic glasses of the Elko Basin. These data suggest a relatively simple uplift history of the Elko Basin with high elevations (≈3 km) in the mid to late Eocene in the oldest lake unit in the Elko Basin. Surface uplift of this region occurred at some point during the late Eocene to early Oligocene to elevations around 4 km and remained high throughout the Miocene. We do not think that the elevation estimates for the late Eocene Elko Formation reflect true low elevations as even the lowest δ18O of carbonate have most likely been influenced by evaporation, as pointed out by Smith et al. (2017), and observed here in the positive correlation of δ18O and δ13C among even the lowest δ18O samples (green squares in Figure 1C; see also discussion in Mulch et al., 2015). In addition, we see no evidence for the more complicated surface uplift history given in Cassel et al. (2018) who suggest high elevation in the Late Eocene to lower elevations in the Early Oligocene to the highest elevation in the Late Oligocene. However, this elevation history is largely based on rocks exposed just west of the Elko Basin as there are few to no substantial Oligocene sedimentary rocks exposed in the Elko Basin that allow paleoelevation constraints, based on the most recent mapping that indicates an angular unconformity (spanning ~31–24 Ma) between the units mapped previously as the Indian Well Fm. and the Miocene Humboldt Fm (Lund Snee et al., 2016).

**CONCLUSION**

In this study we presented the first lacustrine chert triple oxygen isotope dataset from a Cenozoic basin in western North America and used this data, in conjunction with carbonate clumped isotope measurements to derive an elevation estimate for the eastern Eocene Nevadaplano. Future measurements on carbonates (e.g., Passey et al., 2014; Bergel et al., 2020; Fosu et al., 2020; Voarintsoa et al., 2020; Wostbrock et al., 2020) from the Elko Basin, specifically on the Elko Formation, would benefit from paired measurement of the carbonates from the Eocene to Miocene strata for both triple oxygen isotopes and carbonate clumped isotopes, allowing for issues for formation temperature associated with chert formation to be overcome. Nevertheless, state-of-the-art data sets presented here indicate that:

1. The empirical negative relationship in triple oxygen isotopes among the dataset is suggestive of evaporative enrichment of δ18O values spanning 6.5‰.
2. Cherts in the Cherty Limestone Formation likely formed during early diagenesis at temperatures hotter than those recorded by coeval carbonate and carbonates in the overlying lacustrine portion of the Elko Formation as recorded by our new carbonate clumped isotope dataset.
3. Comparison to δD datasets (converted to water δ18O values) from volcanic glass of similar age from the Elko Basin demonstrate that either the lacustrine carbonates and chert represent a lower hypsometric mean elevation of the basin depocenter or there exists later hydrogen exchange in the volcanic glass.
4. We calculate a relatively simple surface uplift history for Elko Basin with original deposition of lake sediments (Cherty Limestone Formation) at ~3 km in the mid-Eocene. When compared to other paleoelevation studies in this area, we suggest that the was surface uplift of ~1 km in the late Eocene to early Oligocene with elevations remaining high into the Miocene.

**DATA AVAILABILITY STATEMENT**

All datasets generated for this study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author/s.

**AUTHOR CONTRIBUTIONS**

DI wrote the initial draft of the manuscript with input from CC. DI made the figures. CC, TK, and DI made the triple oxygen isotope measurements. KM made the carbonate clumped isotope measurements. CC and AM provided the samples. DI and TK constructed the modeling framework. All authors provided input on the dataset interpretation and analysis and contributed to writing the manuscript.

**FUNDING**

This research was funded by NSF EAR-1322084 and Heising Simons grants to CC. KM and AM acknowledge support
through the LOEWE funding program of the Hessen State Ministry of Higher Education, Research, and the Arts as part of the LOEWE VeWa project. DI was supported by the UC Berkeley Miller Institute for Basic Research and UC President's Postdoctoral Fellowships, and KM was supported by the Feodor-Lynen-Fellowship of the Alexander von Humboldt Foundation.

ACKNOWLEDGMENTS

We thank NL and JK for thorough reviews and comments, and MH for handling our manuscript. We thank Peter Blinsniuk for help with the isotope measurements at the Stanford University Stable Isotope Biogeochemistry Laboratory, Kristina Butler for providing feedback on a previous version of this manuscript, Max K. Lloyd with triple oxygen isotope data handling, as well as Yuan Gao, Zachary D. Sharp, Jordan A.G. Westbrock, Max K. Lloyd, and Daniel A. Stolper for detailed discussions. We thank both reviewers of this manuscript for thorough and helpful comments and suggestions.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2021.628868/full#supplementary-material

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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