**Supplemental Text to "Looking upstream with clumped and triple oxygen isotopes of estuarine oyster shells in the early Eocene of California"**

**1. Expanded Methods: sample description, preparation procedures, and analytical methods**

*1.1 Sample preparation of the Goler Formation shells*

For conventional stable isotope measurements, material was milled from two locations in each shell to characterize isotopic variability. The largest oyster shell (Goler7) was cut to reveal a cross section and growth bands were subsampled with a computerized drill made by Merchantek Micromill. For clumped and triple oxygen isotope analyses, sufficient material (about 50 mg total) was milled at the lowest possible speed using a dental drill at a single location away from the shell edges that appeared to be most dense and pristine based on visual inspection. Approximate sample collection location is 35.4787, -117.8302.

*1.2 Modern bivalve-water pairs: description and preparation*

Modern bivalve-water pairs are included primarily to determine the mineral-water fractionation factor for triple oxygen isotopes. We measured four bivalves and the waters from which they were collected. Minerology was determined for Silver Lake, San Simeon, and Scott Creek shells using X-Ray Diffraction with a [Rigaku Ultima IV Diffractometer](http://sites.lsa.umich.edu/emal/wp-content/uploads/sites/553/2017/10/XRD_Rigaku.jpg) at the Electron Microbeam Analysis Lab (EMAL) at the University of Michigan.

*Silver Lake, Michigan:*Silver Lake is a shallow (45 ft) glacial lake. Clam and water samples were collected in September 2020 from the beach at Silver Lake, Michigan (42.416720, -83.961118). The outer organic layer was scraped off, then entire shell was reactive in 5% hydrochloric acid to fully remove the organics. Then the entire shell (1 cm in length) was crushed, powdered, and homogenized. This shell is aragonitic.

*Huron River, Michigan:* An aragonitic unionid mussel, *lampsilis cardium*, was collected alive from the Huron River in Ann Arbor, MI on August 31, 2019 (42.244167, -83.610278) under a 2019 Scientific Collector’s Permit granted by Michigan Department of Natural Resources to R. Mulcrone. A single annual growth band (likely from the mid 2010s based on counting) was milled out for this study (average δ18O = -7.17 ‰ vpdb) (sample ID = LC2-mid-HR). The Huron River water in Ann Arbor, MI was sampled on a weekly basis from June 2018 through February 2020 (Pelletier, 2020); the δ18O of the river varies seasonally with a minimum of -9 ‰ and a maximum of -6 ‰. Based on this variation in δ18O and d-excess, the Huron River water is more evaporated in late summer (Pelletier, 2020). In order to minimize inaccuracies in our λc-w value that could arise from comparing a water sample that is not representative of the mussel's true parent water, we measured the Δ'17O of a river water sample of intermediate δ18O collected in July 2019 (IPL-19W-1087) (δ18O = -8.12, d-excess of 11.38). We do not have clumped isotope temperature measurements for this sample. For estimated growth temperature we use an estimate of mean annual water temperature of 12.7 °C measured at USGS gauge 04174500 in the Huron River.

*Scott Creek and San Simeon, California:* Two marine mussels and adjacent ocean waters were collected in California in December 2019: one on a sandy beach near Scott Creek, Davenport, (37.039659, -122.230172) and one at a rocky beach near San Simeon (35.629184, -121.160569). The San Simeon shell is 63% aragonite and 37% calcite; the Scott Creek shell is 70 % aragonite and 30% calcite. The outer organic material coating the shell was scraped away, then samples were milled at the umbo. The salinity of the waters was measured to be 24 and 27 ppt, respectively. The triple isotopic composition of these ocean waters (-0.008 and -0.007, Table 1) is similar to the average of ocean waters of -0.005 ‰ presented in Luz and Barkan (2010) and used in Wostbrock et al.(2020a) in their calculation of triple oxygen isotope fractionation.

*1.3 Carbonate clumped isotope analytical methods*

Clumped isotope data from the Goler Formation shells were generated at the University of Michigan from 2015-2016. A manual, off-line sample preparation vacuum line was used to react carbonate samples in phosphoric acid held at 75 °C (Defliese et al., 2015). Resulting CO2 was purified with cryogenic water traps and with a Poropak trap held between -10 and -15 °C (Petersen et al., 2015). The purified CO2 was measured on a Thermo MAT 253 mass spectrometer. ∆47 values were placed into the absolute reference frame using heated and equilibrated gasses (Dennis et al., 2011) and were calculated using the 17O correction parameters recommended by IUPAC (Daëron et al., 2016; Schauer et al., 2016; Petersen et al., 2019), and corrected into the 25 °C reference frame using an acid fractionation factor of 0.072 for digestion at 75 °C (Petersen et al., 2019). Carrara marble and ooids (an in-house standard) were run alongside sample carbonates; we observe a standard deviation of <0.022 or better for at least 4 replicate analyses of each standards in the two analytical sessions (February 2016 and December 2015). A SD of 0.022 is used to calculate 1 S.E. of the sample means. These analytical sessions predate widespread adoption of the ETH carbonate standards, and thus cannot be placed into the emerging "Intercarb" reference frame (Bernasconi et al., 2021) Temperatures were calculated from ∆­47 values using equation 1 of Petersen et al. (2019) (∆­47 = 0.0383\*10^6/T2 + 0.258).

Clumped isotopes were measured in three of the four the modern mollusk shells (Silver Lake, San Simeon, and Scott Creek) that were used to determine mineral-water fractionations. These clumped data were generated in January-March 2021 the University of Michigan in the Stable and Clumped Isotopes for Paleoclimate and Paleoceanography (SCIPP) Lab (PI Sierra Petersen). Clumped isotope data were generated on a Nu Perspective dual isotope ratio mass spectrometer coupled to a NuCarb automated, online sample preparation unit. Approximately 3-5 mg of carbonate equivalent was reacted for 20 min in individual glass vessels with 150 microliters of orthophosphoric acid (density of 1.93 g/cm3) held at 70 °C. Evolved sample gas was cryogenically purified and passed through a Poropak trap held at -30 °C using cryogenic pumping (no carrier gas). ∆47 was calculated using previously established methods, including the 17O correction parameters of lambda (0.528) and K (0.01022461) recommended by Brand et al. (2010, IUPAC). The 47-∆47 correction is made using the slope between ETH1 and ETH2 (analogous to a heated gas line). The empirical transfer function is made using the values of the ETH 1-4 from the InterCarb comparison (Bernasconi et al., 2021). A running-mean correction based on in-session drift of the ETH standards is applied (usually less than 0.005 ‰). An acid fractionation factor of 0.066 is applied for reaction at 70 °C (Petersen et al 2019). Heated and equilibrated gases and several in-house carbonate standards are analyzed with the unknown samples (a coral (CORS), a marine snail shell (PICA), ooids (OO), a low temperature bivalve (ICE) and Carrera marble (CM)) in addition to the ETH standards. These are not used in the reference frame correction but are tracked to establish continuity between reference frames. Temperatures are calculated using the ∆47-temperature equation of Petersen et al. (2019). For comparison, using the ∆47-temperature equation of Anderson et al. (2021) results in temperatures that are ~ 2 °C lower for each sample.

Clumped isotope data for samples and standards, and ancillary reference frame information, has been submitted to the EarthChem database and included here as a supplementary excel file (Supplementary Tables S5 and S6).

*1.4 Carbonate triple oxygen isotope analytical methods*

Triple oxygen isotope measurements were made in the IsoPaleoLab at the University of Michigan in 2019-2021 using the reduction-fluorination method described in Passey et al. (2014). The analytical methods have been previously described for a similar system located at Johns Hopkins University (Passey et al., 2014; Li et al., 2015, 2017) and for the system at the University of Michigan (Passey and Levin, 2021; Aron et al., 2021; Beverly et al., 2021). In brief, 5-7 mg of carbonate is first digested in a common acid bath of 100% phosphoric acid (H3PO4) held at 90 °C. The evolved CO2 is purified by being passed through cryogenic water traps (methanol and CO2 dry ice slush at temperatures of about -75 °C) and through a Poropak Q column held at -20 °C with He as a carrier gas. Sample CO2 gas is then reacted with H2 over Fe catalyst held at 560 °C in a circulating loop to produce H2O; sample CO2 is circulated through the loop four times to ensure complete conversion. H2O is fluorinated in a CoF3 reactor (with He as a carrier gas) to produce O2, following the procedure of Barkan and Luz (2005). The O2 is analyzed (m/z = 32, 33, and 34) on a Nu Perspective mass spectrometer at an intensity of 20 nA (m/z 32). Each analysis consists of a total integration time of 2,000 seconds, which is accomplished through 40 cycles of 50 seconds of measurement of each sample and reference gas (17O vSMOW = 10.3 ‰, 18O vSMOW = 20.3 ‰). VSMOW2 and SLAP2 are measured in at least triplicate at the start, middle, and end of each analytical session and form the basis for normalization to the VSMOW-SLAP reference frame (Schoenemann et al., 2013). International carbonate standards (NBS-18, NBS-19, IAEA 603, and IAEA C1) are regularly analyzed along with unknowns and an internal carbonate (102-GC-AZ01). We regularly achieve a standard deviation of < 15 per meg of ∆'17O of multiple analyses of standards through a session.

We correct the carbonate measurements for fractionation during acid digestion using acid fractionation factors that we empirically derived in our laboratory. These were derived using the isotopic composition of IAEA-603 mineral determined by Wostbrock et al. (2020b) via direct fluorination (18O = 28.470 ‰, 17O = 14.831 ‰, ∆'17O = -0.100 ‰), along with our long term average value for CO2 of IAEA-603 and IAEA-C1[[1]](#footnote-1)& (measured as O2; 18O = 36.233 ± 0.156 ‰ (1 S.E.) VSMOW-SLAP, ∆'17O = -0.145 ‰ ± 0.0012 (1 S.E.) VSMOW-SLAP, n = 59). This yields α17m-O2 = 0.9957458 and α18m-O2 = 0.9918732. Because of the way these αm-O2 values were determined, they also account for any fractionation that might be induced by the reduction and fluorination steps of our analytical method. Finally, we make session-specific corrections to ∆'17O (usually < 0.015‰) based on the offset from the accepted value (∆'17O = -0.100 ‰; Wostbrock et al., 2020) of co-analyzed IAEA-603 / IAEA-C1. See also a description and code described and available in Huth et al. (2021).

The data reported in this paper were analyzed in five analytical sessions (as established by CoF3 reactors number 13, 14, 15, 16, and 17 at IPL) from December 2019 to April 2021. Each CoF3 reactor lasts for ~200-300 individual measurements (of carbonate, water, or phosphate), which translates to ~ 2-4 months; additional breaks in analytical sessions are identified based on drift in standards and/or maintenance events (i.e., power outages or changing the filament). Mollusk sample analyses are replicated 3-4 times; water sample analyses are replicated 2-3 times. The individual replicate data for the samples and the standards for each analytical session and the value of the offset correction for each session can be found as a .csv file in Supplemental Table S4.

In our analysis of the modern mollusks (ie., calculating the α18 of mineral-water), we use the δ18O measured as CO2 via traditional methods (digestion in phosphoric acid, analysis on a mass spectrometer). For waters, we use the δ18O value measured via traditional methods, either on a Picarro Cavity Ring-Down Spectroscopy (CRDS) (Silver Lake and Huron River waters) or through equilibration with CO2 and measurement on a Thermo 253 Mass Spectrometer (the saline San Simeon and Scott Creek waters). The traditionally-derived estimates of δ18O are more precise and accurate than the δ18O measurements made in O2 and can be combined with the O2-based measurements of Δ'17O (Barkan et al., 2019; Wostbrock et al., 2020b).

For the Goler formation shells, we use the δ18O measured as O2 (O2/CaCO3) and the ∆'17O measured as O­2 in our subsequent calculations (i.e., calculating δ18Ofw, described below). δ18O derived via O2  and via CO2 are reported in Table 1 of the main text. For the Goler shells, we opt to use the less-precise O2 derived values because of known heterogeneity in the sampled powder. The CO2 and O2 analyses were made on different aliquots that were milled out separately (in this case, years apart, and by different workers). Since we observe δ18O variability of up to 3 ‰ within a single shell (Supplemental Figure S3 and S4), it is more accurate to not combine CO2 and O2 derived values in this case.

**2. Evaluating the potential for vital effects in the isotopic composition of mollusk shells**

Mollusk shells are generally thought to be faithful records of the temperature (via ∆47) and oxygen isotopic composition of their parent water (e.g., Wefer and Berger, 1991; Surge et al., 2001, 2003; Henkes et al., 2013; Tynan et al., 2014), with the exception of a single oyster taxon (*Magallana gigas*) that showed measurable offsets in 18O and ∆47 (~ at most -2 ‰ in 18O and -0.03 ‰ in ∆47) in the juvenile (near-umbo) region of the shell (Huyghe et al., 2020, 2022). While there are not yet experimental studies on the reliability of ∆'17O in mollusk shells, a reasonable assumption is that if carbonate 18O and ∆47 do not show any vital or kinetic effects, then ∆'17O should also reliably record paleoenvironment.

Multiple lines of evidence suggest that our fossil and modern samples are free of vital effects in 18O and ∆47. The mineral-water α18 values that we calculate for the modern shells (none of which are oysters) using clumped isotope temperatures or environmental temperatures and measured 18O fall within range of values from accepted empirical relationships (Table S1). There is no correlation between ∆47-derived temperature and 18O in our fossil oyster shells, as would be expected by either CO2 absorption or degassing (Guo, 2020) or progressive re-equilibration of the DIC pool during rapid growth (Huyghe et al., 2022). Reconstructed Eocene temperatures are, if anything, colder than expected, which is opposite the direction in which vital effects biased reconstructed temperatures in juvenile *M. gigas* (Huyghe et al., 2022)*.* Without additional data, it is impossible to disprove the possibility that vital effects impart a small signal in the measured isotopic compositions, but the evidence suggests that vital effects do not dominate the measured values in any of the modern or fossil shells in 18O or ∆47, and therefore likely ∆'17O as well.

**3. Diagnosing diagenesis**

*3.1 Potential for reordering*

Given the relatively shallow burial depths of the samples, solid state reordering of the bonds within the carbonate materials is unlikely. The oyster shells were collected from the top-most member of the Goler Formation (member 4d). We estimate that a conservative maximum burial depth for these samples is 1.7 km, which is the entire thickness of the overlying Ricardo Formation (Cox, 1982; Cox and Diggles, 1986). Burial of < 2 km (~temperatures of <80 °C for less than 50 million years considering a steep geothermal gradient of 34°C/km of the modern Western US (Nathenson and Guffanti, 1987)) is not likely to result in sufficient heat to reorder carbonate bonds (Passey and Henkes, 2012; Stolper and Eiler, 2015; Hemingway and Henkes, 2021). The burial depth varies along the Goler Basin; deeper burial could explain the high T∆47 values of a thin lacustrine deposit reported in Lechler et al. (2013).

*3.2 Potential for Recrystallization*

Recrystallization can affect the isotopic composition of samples regardless of burial depth. To check for the presence secondary material, we examined the oyster shells with a scanning electron microprobe (SEM). The images show slight dissolution in the exterior varnish but no secondary material. Foliated microfabric and pristine laths observed in the SEM are evidence of excellent preservation (Figure S2).

In the oyster shells, we observe a linear correlation between δ18Ogw and δ13C (Figure 3A). Some authors have interpreted such correlations between stable isotope values of shells as indicative of secondary crystallization (e.g., Came et al., 2007; Tobin et al., 2014). However, we think that the correlation that we observe in the oyster shells is primary for several reasons. Foremost, we might expect a correlation in δ18Ogw and δ13C given that these shells were collected near the transition from terrestrial to marine; oyster growth in an estuary where fresh and ocean waters mix readily explains such a relationship (Surge et al., 2003). Second, we also observe a positive correlation in δ13C and δ18O along the growth bands of the single oyster that was large enough for sclerochronology (Supplemental Figure S3**).** It is unlikely that recrystallization could occur in a way that would preserve color and stable isotopic differences in growth bands yet overprint the clumped isotope temperature. Finally, the oyster shells have a stable isotope composition that is distinct from that of soil carbonates from a lower member of the Goler Formation (Torres and Gaines, 2013), and the soil carbonate data does not exhibit a linear correlation between δ13C and δ18O values. This comparison suggests the absence of regionally widespread- fluid flow that recrystallized all the carbonates of the Goler formation along a trend or toward a single value.

**4. Calculation of carbonate-water triple oxygen isotope fractionation**

*4.1 Triple Oxygen Isotope fractionation between carbonate and water: notation*

The triple oxygen isotope fractionation between carbonate and water is needed to calculate the parent water isotope values from geologic samples (unknowns). The equilibrium fractionation between two phases, i.e., carbonate and water, is defined as:

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|  | Equation S1 |

αc-w is calculated for 17O and 18O. The apparent triple oxygen isotope fractionation from mineral-water is defined as θc-w:

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|  | Equation S2 |

Note that we define calcite-water fractionation using the symbol θ to represent a single fractionation process. In the manuscript and in this supplement, we use the mathematically equivalent symbol λ instead of θ because we measured an *apparent* fractionation factor that includes multiple fractionations inherent to the measurement process in addition to the calcite-water fractionation such acid digestion, reduction, and fluorination.

*4.2 Estimate of carbonate-water triple oxygen isotope fractionation & comparison to previous estimates*

We present an estimate of the carbonate-water triple oxygen isotope fractionation (λc-w) based on tiple oxygen isotope measurements of bivalve-water pairs collected in California and Michigan. We determined λc-w for four modern mollusk samples and observed a mean value of 0.5249 ± 0.0002 (1 S.D.) (Supplementary Table S1; see section 2.1 below for detailed information about the samples). We combine these measurements with measurements of synthetic calcite and experiment growth waters, as described in Huth et al. (2021). These measurements were made contemporaneously with the samples described in our study. Combining the biogenic and abiogenic samples increases the number of observations (from n = 4 to n = 8), increasing our confidence in the precision and accuracy of the λc-w  value and its relevancy to our sample unknowns. The combined average λc-w value is 0.5250, with 1 S.D. of 0.00021 and 1 S.E. of 0.00007 (Table S1).

The mineral-water fractionation value (θc-w or λ c-w) has been previously determined for biogenic and abiogenic materials using methanation-fluorination (Passey et al., 2014), Pt-catalyzed CO2-O2 exchange (Bergel et al., 2020; Voarintsoa et al., 2020), and direct fluorination (Wostbrock et al., 2020a). However, there is significant variation in these values (ranging from 0.5231 to 0.5254), which would translate to a ~85 per meg range in ∆'17O of calculated parent water for a typical shell formed at 25 °C with a ∆'17O value of -0.100 ‰. This variation indicates that problems with accuracy in ∆'17O determination persist, despite the excellent analytical precision achieved by the three methods. For this reason, it is essential that laboratory-specific λc-w values are determined using methods that are identical to those used for analyzing unknowns. Our value of 0.5250 differs from the value of 0.5256 or 0.5252 for calcite or biogenic aragonite, respectively, determined by Wostbrock et al. (2020a; calculated for 25 °C using equation 7 and equation 8). It is unclear why this difference exists given that data from both laboratories are normalized to mineral values of IAEA-603 (∆'17O = -0.100 ‰). Some of the difference could be explained by mineralogy; two of our samples are aragonite and two are mixed (70 % aragonite, 30% calcite); the heterogeneity in material will result in different fractionation factors during acid digestion. Another potential source of differences could be that Wostbrock et al. (2020a) included marine mollusks and sediments and assumed a marine water ∆'17O value of -0.005 ‰. Our compilation includes marine and freshwater mollusks, and we measured ∆'17O of the parent waters collected at the time of shell collection. Furthermore, it is unknown from the data reported in Wostbrock et al. (2020a) precisely when the water analyses used to form isotopic reference frames (SMOW/SLAP) were made relative to the carbonate analyses. These uncertainties point to the need for further study of potential causes of analytical discrepancies as well as a standard scheme for reporting sample and standard values.

Another unknown is the extent to which vital effects in triple oxygen isotopes are relevant to the isotope analyses in our study and/or in that of Wostbrock et al. (2020a) and Bergel et al. (2020). As discussed above, we are not aware of empirical studies of vital effects in ∆'17O (or θc-w ) in mollusks. Theoretical calculations of kinetic effects on θHCO3-H2O  predict a depletion of ~0.002 in θc-w  over a 18O depletion of 5 ‰ due to CO2 absorption (Guo and Zhou, 2019). This magnitude difference in θc-w  is ~an order of magnitude greater than the difference observed between our θc-w  value and that of Wostbrock et al. (2020a). While we cannot rule out that vital effects have a minor effect on the measured ∆'17O/ θc-w in either study, this evidence suggests that they are unlikely to dominate the measured θc-w value. A systematic study of vital effects in triple oxygen isotopes in mollusks is merited.

**5. Estimate of δ18Ofw from triple oxygen isotopes in estuarine shells**

We calculate the δ18O of fresh water flowing into the estuary (δ18Ofw) and the fraction of freshwater-derived water in the estuary (ffw­) using isotope mixing models. The measured values are δ18Oew and δ17Oew. We can constrain δ18Oow, δ 17Oow, and ∆'17Ofw (Table S1), as discussed below. Then we describe the mixing model and numerical solving method.

*5.1. Estimating the triple oxygen isotopic composition of an ice-free ocean*

We estimate the δ18O, δ17O, and ∆'17O of the early Eocene ocean assuming that there is no continental ice. We use a simple equation for isotopic mass balance to estimate oxygen isotopic composition of the ice-free ocean:

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|  | Equation S3 |

Where δ refers to the isotope of interest (δ18O and δ17O), m is mass, the subscript t is total ice-free ocean, the subscript o is for the modern ocean, and the subscript i is for modern ice.

The volume of the modern ocean is 1.3324\*10^9 km3 (Charette and Smith, 2010). Using a density of water of 997 kg/m3, the mass of the modern ocean is 1.3284\*10^21 kg. The volume of ice in Antarctica is 2.7\*10^7 km3 (from Bedmap2, (Fretwell et al., 2013)). The volume of is in Greenland is 2.99\*10^6 km3 (from Bedmachine 3, (Morlighem et al., 2017)). Summing these two ice sheets (and ignoring mountain glacier ice), we estimate a total ice volume of 2.999\*10^7 km3. Using a density of 916.7 kg/m3, the mass of modern ice is 2.749\*10^19 kg.

We assume δ18O of modern ocean is 0 ‰ and ∆'17O of the modern ocean is -0.0045 ‰ (mean value from Aron et al. (2021)). We assume δ18O of ice is -45 ‰ and ∆’17O is 0.023 ‰ (mean value of snow and ice from Aron et al. 2021).

Using the values described and Equation S3, we estimate that an ice-free ocean would have a δ18O of -0.912 ‰ and ∆'17O of -0.0085 ‰. This estimate for ice-free δ18O is very close to the canonical -1 ‰ (Zachos et al., 1994; Tindall et al., 2010; Petersen and Schrag, 2015; Zhu et al., 2020). The estimate for ∆'17O is within 1 S.D. of the mean value for modern ocean (-0.0045 ± 0.0043 ‰), suggesting that this value is not particularly sensitive to possible variations in ice sheets.

*5.2 Estimating ∆'17Ofw based on modern meteoric water data*

We have no direct constraints on the triple oxygen isotope composition of precipitation in the Eocene. However, we can use modern distributions of Δ'17O to estimate probable ranges in this parameter (Supplementary Figure S6). The global mean of Δ'17O of unevaporated meteoric waters (i.e., tap, precipitation, springs, groundwater, and rivers with δ18O < 0) is 0.0325 ± 0.014 (1 SD), based on the compilation of Aron et al. (2021). We can consider the subset of global precipitation Δ'17O data with δ18O less than -7 ‰ (the mean δ18O value for Goler Fm estuary water), with the logic that the δ18O of freshwater entering the estuary must be lower than the estuary water itself.  The average Δ'17O of un-evaporated meteoric for waters with δ18O < -7 ‰ is 0.035 ± 0.010 (1 S.D.) (all samples are at latitudes between 50 °N and 38 °S). This compares with a value for the western US of 0.027 ± 0.009 (n = 105), and 0.028 ± 0.009 (n = 69) and 0.025 ± 0.010 (n = 25) for Pacific and Rocky Mountain subsets, respectively (errors are 1 S.D.).  Based on these numbers, we use a value of 0.027 ‰ for ∆'17O of Eocene precipitation in the Western US and assign an uncertainty of 0.005 ‰ in our Monte Carlo error propagation. This uncertainty is larger than the standard error of the measurements for the western US (0.0008‰), but smaller than the standard deviation (0.009‰, n = 105). As in Passey and Ji (2019), we use an error of 0.005 ‰ because this considers uncertainty in addition to 1 SE due to real-world variation in this value. As an example of the sensitivity of reconstructed δ18Ofw, for the estuarine isotope values of sample Goler 4, a change in assumed ∆'17Ofw of ±0.01 ‰ leads to a range in reconstructed δ18Ofw of ± 2.2‰ (range from -12.9 to -8.8 ‰). Future research into the '17Ofw of ancient climates will allow for more certain interpretation of ∆'17O of geologic materials.

*5.3 Mixing model equations and solution*

Estuarine water isotopic composition results from mixing between ocean and fresh waters that have distinct δ18O and ∆'17O values. In this modelled scenario, we have known/good constraints of δ18O and δ17O of the mixed result (estuarine waters, ew) and one of the endmembers (the ocean, ow,), and ∆'17O of the other end member (freshwater, fw) (as described above). With these constraints we can uniquely solve for the unknown δ18O value of freshwater. The unknowns that we are solving for are δ18Ofw and ffw. We use the following system of equations that describe mixing between ocean water and fresh water (terms defined in Table S2):

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|  | Equation S4 |
|  | Equation S5 |
|  | Equation S6 |
|  | Equation S7 |
|  | Equation S8 |
|  | Equation S9 |

Where RST is RSMOW\_18 is 0.0020052 or RSMOW\_17 is 0.00038672 (Assonov and Brenninkmeijer, 2003) and λref is 0.528 (Luz and Barkan, 2010). We are using atom fraction notation instead of delta notation in the mixing calculations (i.e. *F* instead of δ in equations S4 and S5); mass balance is valid for atom fractions (Brenna et al., 1997)). A more familiar version of the same equation is:

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|  | Equation S10 |

Over the range of earth surface waters, including those investigated here, using atom fraction notation vs. δ notation results in a negligible difference in un-mixed δ18Ofw values (<0.1).

Because of the nonlinearity in Equations S8 and S9, we solve the equations numerically with a root-finder (uniroot() in R). We make an initial guess for δ18Ofw. A value of ∆'17Oest is calculated (combining equations S1-S9 and known values) and then compared to the shell-measured value. This process is repeated until the misfit is minimized and the solution is found. The R script used to make these calculations is included as met\_vals.R and met\_vals\_viaR.R.

We characterize the error in the calculated δ18Ofw value using a Monte Carlo approach. We solve for δ18Ofw for each shell 10,000 times. For each parameter, a value from within a normal distribution of the error is chosen and used in the calculations. The values and errors used in the calculations are presented in Supplementary Table S2.

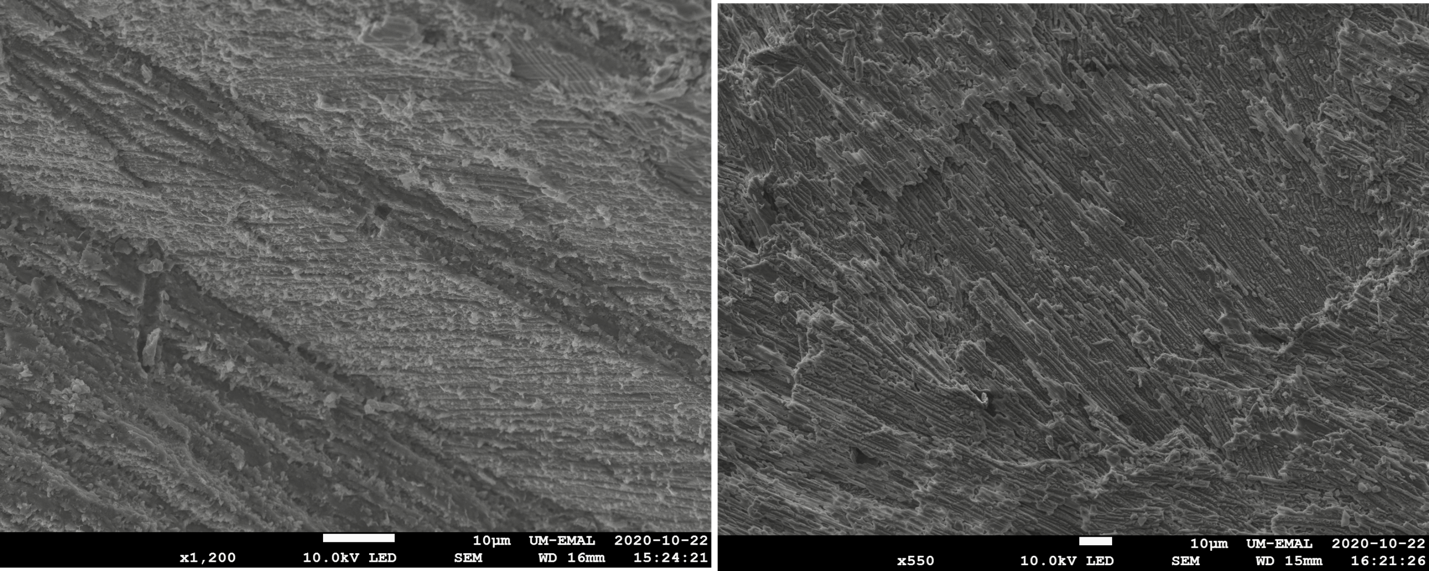
**6. Temperature Data from the Mad River, Arcata, California (USGS gauge No 11481000)**

In the main text, we refer to stream water temperatures from the Mad River in Aracata, California, USA. This gauge is located at an elevation of 3.9 meters above sea level and Latitude 40°54'36", Longitude 124°03'34". It is not a perfect comparison to the inlet in the Goler Formation largely because it is about 4° further north than the Goler Formation. However, we make a comparison with the Mad River because it is un-dammed, drains elevations as high as 1477 meters, and has readily available temperature data. The stream water temperatures vary on an annual basis, with winter temperatures of 4-5 °C and summer temperatures of 25-26 °C. The temperature data and other stream data can be downloaded from the USGS National Water Information System: https://waterdata.usgs.gov/nwis/inventory/?site\_no=11481000 and are shown in Supplemental Figure S9.

A picture containing clip, scissors, indoor, pin

Description automatically generated

**Supplemental Figure S1**. *Acutostrea idriaensis* (oyster) shell fragment from the Goler Formation with safety pin (27 mm) for scale. Sample drill hole is visible in the center-top of shell.



**Supplemental Figure S2:** SEM imagery of select oyster shells from the Goler Fm. Images show pristine foliation (Goler 2, left, oblique view) and laths (Goler 8, right).



**Supplemental Figure S3:** Stable isotope composition along growth bands for a single oyster shell (Goler7).



**Supplemental Figure S4:** Traditional carbon (A) and oxygen (B) stable isotope values for individual oyster shells from member 4d of the Goler Fm. Error bars are ±1 SD and can be smaller than the symbol size. Two spots (large circles) from each shell are two separate powders drilled from two locations. Triangles are δ13C and δ18O generated from re-drilling at one of the two locations, and the values were generated simultaneously with the clumped isotope values (For Goler1, Goler2, Goler3, Goler4, Goler6, and Goler8). Small circles are growth bands from Goler7.



**Supplemental Figure S5:** Stable isotope composition of oyster shells from the Goler Formation. Black dots indicate measurements made with a Kiel device coupled to a MAT 253. Colored dots indicate measurements made with the clumped isotope measurements, where color indicates the calculated clumped isotope temperature (T∆47­). Samples measured for clumped isotopes span nearly the full range of stable isotope values represented in the larger sample set.



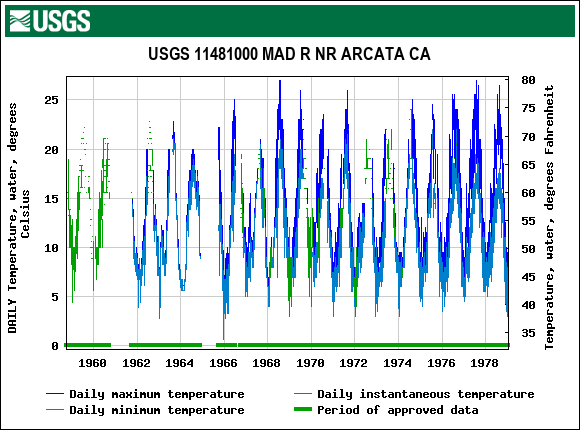
**Supplement Figure S6**: Global meteoric waters (compilation of Aron et al., 2021). Water type as shown, excludes waters with δ18O > 0 ‰. The mean of all shown ∆'17O measurements is 0.0325 ± 0.014 (1 SD). (n = 1557).



**Supplemental Figure S7**: Estimates of δ18Ofw for from the Goler estuarine shells produced using Monte Carlo resampling techniques. Assumed values and errors are reported in Table S2.

****

**Supplemental Figure S8: Histogram and kernel density of the elevation for a stated range of δ18O** **values of modern rivers and streams.** Isotope data are from USA and Canada, excluding data from latitudes of > 50 °N (n = 11509 measurements), as reported in the Waterisotopes Database ((http://waterisotopesDB.org. Accessed 08/20/2020 Query: West Longitude = -160.56868, East Longitude = -104.7202778, North Latitude = 59.96233, South Latitude = 36.24589, Type=River\_Or\_Stream, Snow\_Pit, Spring). Elevations are from the Global Digital Elevation Model (ASTGTM, version 3, 30m resolution) (doi: 10.5067/ASTER/ASTGTM.003). Citations for each source is included as an excel file.



**Supplemental Figure S9: Stream water temperatures for the Mad River in Arcata, California (elevation of 3.9 meters above sea level).** The graph and data are generated through the US Geological Survey National Water Information System https://waterdata.usgs.gov/nwis/inventory/?site\_no=11481000**.**

****

**Supplemental Table S2:** Description of parameters in Monte-Carlo error propagation & triple oxygen isotope estuarine mixing model

|  |  |  |  |
| --- | --- | --- | --- |
| Name | Description | Value/equation/Monte-Carlo error | Comment/Reference |
| δ18Oc | δ18O of oyster shell carbonate | see Table 1; error of 0.1 | Measured value (samples Goler 3, Goler 4, Goler 8) (values from CO2-based measurement) |
| ∆'17Oc | ∆'17O of oyster shell carbonate | see Table 1; error of 1 S.E. | Measured value (samples Goler 3, Goler 4, Goler 8) |
| δ17Oc | δ17O of oyster shell carbonate | see Table 1 | Calculated from measured value of δ18Oc and ∆'17Oc using Equations 1 and 2 |
| T | Temperature of the water in which shells grew | see Table 1;  ∆47 = 0.0383\*(106/T2)+0.258 | Clumped isotope measurement in Goler3, Goler4, and Goler 8 estuarine shells; equation of Petersen et al. (2019) |
| λc-w | Triple oxygen fractionation exponent for fractionation between carbonate and water and fractionation during preparation of analyte O2 | 0.5250 ± 0.00007 | Measured in modern bivalves at UM IPL, error is 1 S.E. (see supplemental text) |
|  | 18O/16O fractionation between carbonate and water |  | Calculated from measured values of δ18Oc (via O2 ) and T∆47; equation of Kim and O'Neil (1997) |
|  | 17O/16O fractionation between carbonate and water |  |  |
| δ18Oew | δ18O value of estuarine water | see Table 1 | Calculated from δ18Oc and : |
| δ17Oew | δ17O value of estuarine water | see Table 1 | Calculated from δ17Oc and : |
| ∆'17Oew | ∆'17O of estuarine water | see Table 1 | Calculated from δ18Oew and δ17Oew |
| δ18Oow | δ18O value of Eocene ocean water | -0.912 ± 0.1 ‰ | Estimate for an ice free ocean assuming ice volumes and isotope values (Supplement) |
| ∆'17Oow | ∆'17O of Eocene ocean water | -0.0086 ± 0.0007 ‰ | Estimate for an ice free ocean assuming ice volumes and isotope values, error is 1 S.E. of n = 39 modern observations (Supplement) |
| δ17Oow | δ17O value of Eocene ocean water | -0.490 ‰ | Calculated from ∆'17Oow and δ18Oow (Equations S8 and S9); error estimated with Monte Carlo resampling |
| ∆'17Ofw | Mean ∆'17O value of modern meteoric waters in the Western US | 0.027 ± 0.005 ‰ | Aron et al., (2020); Bershaw et al., (2020); Li et al., (2015); Passey and Ji (2019) (n = 95 observations) |
| ffw | fractional proportion of fresh water in the estuary | range from 0-1 | Solved for using system of Equations S4-S9, error estimated through Monte Carlo resampling |
| δ18Ofw | δ18O value of fresh water input into the Eocene estuary | see Table 1 | Solved for using system of Equations S4-S9, error estimated through Monte Carlo resampling |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Supplemental Table S3:** Stable Isotope Data (δ18O and δ13C) for Oyster Shells from the Goler Fm | | | | |  |
|  |  |  |  |  |  |
| Sample ID | Spot ID | δ13C (vpdb) | S.D. | δ18O (vpdb) | S.D. |
| Goler1 | G1 | -1.14 | 0.03 | -6.78 | 0.05 |
|  | G1b | -2.02 | 0.15 | -7.64 | 0.16 |
|  |  |  |  |  |  |
| Goler2 | G2 | -1.17 | 0.02 | -7.3 | 0.06 |
|  | G2b | -0.75 | 0.07 | -6.87 | 0.04 |
|  |  |  |  |  |  |
| Goler3 | G3 | -4.59 | 0.03 | -8.14 | 0.03 |
|  | G3b | -4.5 | 0.42 | -7.52 | 0.39 |
|  |  |  |  |  |  |
| Goler4 | G4 | -0.43 | 0.05 | -4.65 | 0.09 |
|  | G4b | -0.27 | 0.06 | -5.86 | 0.08 |
|  |  |  |  |  |  |
| Goler5 | G5a | 0.46 | 0.28 | -4.67 | 0.25 |
|  | G5b | -1.42 | 0.02 | -5.87 | 0.05 |
|  |  |  |  |  |  |
| Goler6 | G6a | -3.67 | 0.04 | -8.69 | 0.24 |
|  | G6b | -3.63 | 0.09 | -8.74 | 0.03 |
|  |  |  |  |  |  |
| Goler7 | G7a | -0.1 | 0.42 | -7.69 | 0.67 |
|  | G7b | -2.41 | 0.02 | -7.71 | 0.03 |
|  | G7-growth band1 | -3.31 | 0.007 | -8.70 | 0.014 |
|  | G7-growth band2 | -1.48 | 0.002 | -7.64 | 0.013 |
|  | G7-growth band3 | -1.48 | 0.010 | -7.54 | 0.008 |
|  | G7-growth band4 | -1.01 | 0.006 | -6.86 | 0.011 |
|  | G7-growth band5 | -3.38 | 0.005 | -8.08 | 0.009 |
|  | G7-growth band6 | -1.14 | 0.003 | -5.98 | 0.010 |
|  |  |  |  |  |  |
| Goler8 | G8a | -5.39 | 0.12 | -9.23 | 0.03 |
|  | G8b | -6.03 | 0.14 | -9.49 | 0.17 |
|  |  |  |  |  |  |
| Goler9 | G9 | -1.17 | 0.02 | -7.3 | 0.06 |
|  |  |  |  |  |  |
| Goler10 | G10a | -0.33 | 0.23 | -4.95 | 0.34 |
|  | G10b | -4.74 | 0.05 | -8.83 | 0.16 |

#met\_vals.R

#code calculates meteoric water d18O/d17O from a mix

#basic assumptions: mix between ocean + fresh water

#knowns:

#ocean water d18O, D17O

#brackish water d18O, D17O (measured in a carbonate shell, for example, water-calculated values)

#meteoric water D17O (assume something reasonable from the GMWL)

#all values are in permille (NOT per meg)

#wants:

#meteoric water d18O

#strategy: guess at met water d18O that will minimize misfit between D17Obrack\_calculated and D17O\_measured, using basic mixing models for d18O and d17O

#governing equation:

#d\_brackish = f\_ocean\*d\_ocean + (1-f\_ocean)\*d\_met

#D17O = dp17O-0.528\*d-18O

########EXAMPLE of how to use function is at end, copy and paste to different script to call

#############################first define a bunch of useful functions

#FYI the last line of the function is what is returned, in some functions return() is used for clarity

met\_vals <-function(d18\_brack,D17\_brack, D17\_met, d18\_ocean, D17\_ocean){

#define function that mixes small deltas with a given frac

little\_d\_brack <- function(d\_ocean, d\_met, f\_ocean) {

d\_brack = f\_ocean\*d\_ocean + (1 - f\_ocean)\*d\_met }

#this function 'primes' a little delta

prime\_d <- function(little\_d) {

prime\_d <- log(little\_d/1000 + 1) \* 1000 }

#this function 'unprimes' a little delta

unprime\_d <- function(litte\_dp) {

(exp(litte\_dp/1000)-1)\*1000 }

#expression to solve for frac\_ocean given d\_brack, d\_met, d\_ocean

#rearrangement of little\_d\_brack

calc\_frac\_ocean <- function(d\_brack, d\_met, d\_ocean) {

frac\_ocean <- (d\_brack-d\_met)/(d\_ocean - d\_met)

return(frac\_ocean) }

#calculates d17O given D'17O and d18O of any water

calc\_d17 <- function(d18, D17) {

dp18 <- prime\_d(d18)

dp17 <- D17+0.528\*dp18 #definition of D17O

d17<- unprime\_d(dp17)

return(d17) }

#calculates D17O\_brack given d18/D17 of ocean, d18/D17 of met, & frac\_ocean

#calculate it then will compare to input/measured D17Obrack\_measured in next function

D17\_brack\_calc <- function(d18\_brack, d18\_met, D17\_met, d18\_ocean, D17\_ocean) {

frac\_ocean <- calc\_frac\_ocean(d18\_brack,d18\_met,d18\_ocean)

d17\_met <- calc\_d17(d18\_met,D17\_met)

d17\_ocean <- calc\_d17(d18\_ocean,D17\_ocean)

D17\_brack\_v2 <- prime\_d(little\_d\_brack(d17\_ocean, d17\_met, frac\_ocean))- 0.528 \* prime\_d(little\_d\_brack(d18\_ocean, d18\_met, frac\_ocean))

return(D17\_brack\_v2) }

#guesses at a d18)\_met value, calculates misfit in D17O\_brack\_measured

get\_D17 <- function(d18\_brack,D17\_brack\_measured,D17\_met, d18\_ocean,D17\_ocean) {

optimize\_this <- function(d18\_met){

D17\_brack\_calc(d18\_brack, d18\_met, D17\_met, d18\_ocean, D17\_ocean) - D17\_brack\_measured

}

return(optimize\_this) #retuns a function that we want to be zero

}

#this finds the root

met\_vals\_root <- function(d18\_brack,D17\_brack\_measured, D17\_met, d18\_ocean,D17\_ocean){

#optimize\_this is the function for which the zero is found

optimize\_this <- get\_D17(d18\_brack,D17\_brack\_measured,D17\_met,d18\_ocean,D17\_ocean)

interval\_guess = c(-40,d18\_ocean-0.5) #min and max guesses

sol <- uniroot(optimize\_this, interval\_guess, tol = 1.0e-8) #uniroot finds the root

return(sol)

}

solution <- met\_vals\_root(d18\_brack,D17\_brack, D17\_met, d18\_ocean, D17\_ocean)

d18\_met <- solution$root

f\_ocean <- calc\_frac\_ocean(d18\_brack, d18\_met,d18\_ocean)

df <- data.frame(d18\_met, f\_ocean)

colnames(df) <- c("d18\_met","f\_ocean")

return(df)

}

########################

#EXAMPLE OF HOW TO CALL (in a different script)

#copy and paste all of this into a different script

#set the path to functions & source the function

#path.to.functions <-"/Users/juliakelson/Documents/Goler/Goler\_R/" #for example

#source(paste(path.to.functions, "met\_vals.R", sep = ""))

##inputs for Goler4 for example, uncomment in order to use

#d18\_brack <- -5.982 #calculated water value from carbonate

#D17\_brack <- 5.978723819/1000 #in permille

#D17\_met <- 27/1000 #in permille

#d18\_ocean <- -0.912

#D17\_ocean <- -8.59/1000 #in permille

#sol\_Goler4 <- met\_vals(d18\_brack,D17\_brack, D17\_met, d18\_ocean, D17\_ocean)

##output is a data frame with d18\_met and f\_ocean

#met\_vals\_viaR.R

#code calculates meteoric water d18O/d17O from a mix

#uses atom fraction notation instead of delta notation

#basic assumptions: mix between ocean + fresh water

#knowns:

#ocean water d18O, D17O

#brackish water d18O, D17O (measured in a carbonate shell, for example, water-calculated values)

#meteoric water D17O (assume something reasonable from the GMWL)

#all values are in permille (NOT per meg)

#wants:

#meteoric water d18O

#strategy: guess at met water d18O that will minimize misfit between D17Obrack\_calculated and D17O\_measured, using basic mixing models for d18O and d17O

#governing equation:

#F\_brackish = f\_ocean\*F\_ocean + (1-f\_ocean)\*F\_met

#D17O = dp17O-0.528\*d-18O

#where F is atom fraction, F = (R/1+R) and delta = (R/Rst-1)\*1000

########EXAMPLE of how to use function is at end, copy and paste to different script to call

#############################first define a bunch of useful functions

#FYI the last line of the function is what is returned, in some functions return() is used for clarity

met\_vals\_viaR <-function(d18\_brack,D17\_brack, D17\_met, d18\_ocean, D17\_ocean){

RSMOW18 <- 0.0020052 #via Baertschi 1976

RSMOW17 <- 0.000386720 #via Assonov 2003

calc\_R18\_sa <- function(d18O) {

R18\_sa =(d18O/1000+1)\*RSMOW18

}

calc\_R17\_sa <- function(d17O) {

R17\_sa =(d17O/1000+1)\*RSMOW17

}

calc\_atom\_frac <- function(R\_sa) {

Fx <- R\_sa/(1+R\_sa)

}

#define function that mixes in atom fraction notation (F) with a given frac

find\_F\_brack <- function(F\_ocean, F\_met, f\_ocean) {

F\_brack = F\_ocean\*f\_ocean + (1 - f\_ocean)\*F\_met }

d17\_from\_F <- function(Fx) {

R =-Fx/(Fx-1)

d17 =(R/RSMOW17-1)\*1000

}

d18\_from\_F <- function(Fx) {

R =-Fx/(Fx-1)

d18 =(R/RSMOW18-1)\*1000

}

#this function 'primes' a little delta

prime\_d <- function(little\_d) {

prime\_d <- log(little\_d/1000 + 1) \* 1000 }

#this function 'unprimes' a little delta

unprime\_d <- function(litte\_dp) {

(exp(litte\_dp/1000)-1)\*1000 }

#expression to solve for frac\_ocean given F\_brack, F\_met, F\_ocean

#rearrangement of find\_F\_brack

calc\_frac\_ocean <- function(F\_brack, F\_met, F\_ocean) {

frac\_ocean <- (F\_brack-F\_met)/(F\_ocean - F\_met)

return(frac\_ocean) }

#calculates d17O given D'17O and d18O of any water

calc\_d17 <- function(d18, D17) {

dp18 <- prime\_d(d18)

dp17 <- D17+0.528\*dp18 #definition of D17O

d17<- unprime\_d(dp17)

return(d17) }

#calculates D17O\_brack given d18/D17 of ocean, d18/D17 of met, & frac\_ocean

#calculate it then will compare to input/measured D17Obrack\_measured in next function

D17\_brack\_calc <- function(d18\_brack, d18\_met, D17\_met, d18\_ocean, D17\_ocean) {

F18brack <- calc\_atom\_frac(calc\_R18\_sa(d18\_brack))

F18met <- calc\_atom\_frac(calc\_R18\_sa(d18\_met))

F18ocean <- calc\_atom\_frac(calc\_R18\_sa(d18\_ocean))

frac\_ocean <- calc\_frac\_ocean(F18brack,F18met,F18ocean)

d17\_met <- calc\_d17(d18\_met,D17\_met)

d17\_ocean <- calc\_d17(d18\_ocean,D17\_ocean)

F17\_met <- calc\_atom\_frac(calc\_R17\_sa(d17\_met))

F17\_ocean <- calc\_atom\_frac(calc\_R17\_sa(d17\_ocean))

D17\_brack\_v2 <- prime\_d(d17\_from\_F(find\_F\_brack(F17\_ocean, F17\_met, frac\_ocean)))- 0.528 \* prime\_d(d18\_from\_F(find\_F\_brack(F18ocean, F18met, frac\_ocean)))

return(D17\_brack\_v2) }

#guesses at a d18)\_met value, calculates misfit in D17O\_brack\_measured

get\_D17 <- function(d18\_brack,D17\_brack\_measured,D17\_met, d18\_ocean,D17\_ocean) {

optimize\_this <- function(d18\_met){

D17\_brack\_calc(d18\_brack, d18\_met, D17\_met, d18\_ocean, D17\_ocean) - D17\_brack\_measured

}

return(optimize\_this) #retuns a function that we want to be zero

}

#this finds the root

met\_vals\_root <- function(d18\_brack,D17\_brack\_measured, D17\_met, d18\_ocean,D17\_ocean){

#optimize\_this is the function for which the zero is found

optimize\_this <- get\_D17(d18\_brack,D17\_brack\_measured,D17\_met,d18\_ocean,D17\_ocean)

interval\_guess = c(-40,d18\_ocean-0.5) #min and max guesses

sol <- uniroot(optimize\_this, interval\_guess, tol = 1.0e-8) #uniroot finds the root

return(sol)

}

solution <- met\_vals\_root(d18\_brack,D17\_brack, D17\_met, d18\_ocean, D17\_ocean)

d18\_met <- solution$root

f\_ocean <- calc\_frac\_ocean(d18\_brack, d18\_met,d18\_ocean)

df <- data.frame(d18\_met, f\_ocean)

colnames(df) <- c("d18\_met","f\_ocean")

return(df)

}

########################

#EXAMPLE OF HOW TO CALL (in a different script)

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#source(paste(path.to.functions, "met\_vals.R", sep = ""))

##inputs for Goler4 for example

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#D17\_brack <- 5.978723819/1000 #in permille

#D17\_met <- 27/1000 #in permille

#d18\_ocean <- -0.912

#D17\_ocean <- -8.59/1000 #in permille

#sol\_Goler4\_viaR <- met\_vals\_viaR(d18\_brack,D17\_brack, D17\_met, d18\_ocean, D17\_ocean)

##output is a data frame with d18\_met and f\_ocean

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1. & We have found that IAEA-C1 is isotopically indistinguishable from IAEA-603. The long-term average values of IAEA-603 are as follows: 18O = 36.67 ± 1.45 (1.S.D.); ∆'17O = -0.147 ± 0.010 ‰ (1.S.D) (n = 17) . The long-term average values of IAEA-C1 are as follows: 18O = 37.00 ± 1.098 (1.S.D), ∆'17O = -0.145 ± 0.010 (1. S.D.) (n = 42). Therefore, we pool the data from these two standards. [↑](#footnote-ref-1)